Conversion of cationic phosphite complexes into phosphonate complexes with selective deamination on the coordinating phosphorus. Reaction of $[(\eta^5\text{-}C_5H_5)L_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ (L = CO, PMe$_3$) with KOH to afford $(\eta^5\text{-}C_5H_5)L_2Fe\text{-}\{P(O)(NC_4H_8)_{n-1}(OMe)_{3-n}\}$

Hiroshi Nakazawa*,†, Kazuyuki Kubo, Ken Tanisaki, Kazumori Kawamura and Katsuhiko Miyoshi*

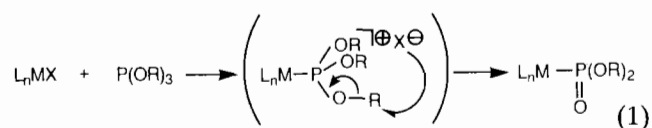*Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 724 (Japan)*

Abstract

Amino-substituted phosphite iron complexes, $[Cp(CO)_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ ($n = 1\text{–}3$), react with KOH in H_2O at room temperature to give phosphonate complexes, $Cp(CO)_2Fe\{P(O)(NC_4H_8)_{n-1}(OMe)_{3-n}\}$ with selective deamination. The reactions with KOH of phosphite complexes $[Cp(PMe_3)_2Fe\{(P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ which have no carbonyl ligands yield deaminated phosphonate complexes $Cp(PMe_3)_2Fe\{P(O)(NC_4H_8)_{n-1}(OMe)_{3-n}\}$, indicating the carbonyl ligand is not essential for the phosphite–phosphonate conversion with selective deamination. A reaction mechanism is proposed in which an OH^- nucleophilically attacks the coordinating phosphite phosphorus to afford a pentavalent phosphorus intermediate (metallaphosphorane).

Key words: Iron complexes; Carbonyl complexes; Phosphite complexes; Phosphonate complexes

Introduction

Transition-metal complexes having a phosphonate group as a ligand, $L_nM\{P(O)(OR)_2\}$, are of interest because the phosphorus atom covalently bonds to the transition metal. This type of compound can be obtained by 'Arbuzov-like dealkylation reaction'. Most of the Arbuzov-like dealkylation reactions have been found to proceed by an ionic mechanism. That is, a transition-metal halide, L_nMX, reacts with a phosphite to give a cationic complex, $[L_nM\{P(OR)_3\}]^+$, which is generally too reactive to be detected even spectroscopically. The cationic complex is then subjected to nucleophilic attack by the released halide ion at the α-carbon of coordinated phosphite, yielding the final transition-metal phosphonate complex (eqn. (1)) [1].

$$L_nMX + P(OR)_3 \longrightarrow \left(L_nM-P\overset{\displaystyle OR}{\underset{\displaystyle O-R}{\overbrace{}}} \right)^{\oplus} X^{\ominus} \longrightarrow L_nM-P(OR)_2 \underset{\displaystyle O}{\overset{\displaystyle \|}{}} \quad (1)$$

We have recently succeeded in isolating the cationic iron phosphite complexes in the reaction of $Cp(CO)_2FeCl$ (Cp stands for $\eta^5\text{-}C_5H_5$) with phosphite having one or two amino or phenyl groups [2–4]. The dealkylation reaction of a cationic phosphite complex takes place by a nucleophilic attack of a halide anion at an α-carbon on a coordinating phosphorus where the α-carbon takes a trigonal-bipyramidal geometry. The introduction of one or two amino groups or phenyl groups on a phosphite phosphorus makes it difficult to take the transition state at the α-carbon in OR group(s) for electronic and/or steric reasons leading to the isolation of a cationic phosphite complex. Refluxing a benzene solution of the chloride salt of the cationic iron phosphite complex generates the corresponding phosphonate complex with dealkylation, showing that the cationic complex is an intermediate of the Arbuzov-like dealkylation reaction.

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*Authors to whom correspondence should be addressed.
†Present address: Coordination Chemistry Laboratory, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

In 1988, Gibson et al. found an interesting way to form phosphonate complexes, $(\eta^5\text{-}C_5R_5)(CO)_2\text{-}Fe\{P(O)(OR')_2\}$ (R = H, Me; R' = Ph, p-tolyl) from $[(\eta^5\text{-}C_5R_5)(CO)_2Fe\{P(OR')_3\}]BF_4$ and KOH in acctonc/water via a pathway other than the Arbuzov-like dealkylation reaction [5]. The reaction has been proposed to proceed by nucleophilic attack of OH^- at the coordinating carbonyl carbon of the cationic complex to give a metallacarboxylic acid complex, followed by deprotonation to generate a metallacarboxylate complex, and then by intramolecular oxygen transfer to yield the final phosphonate complex (eqn. (2)).

$$(2)$$
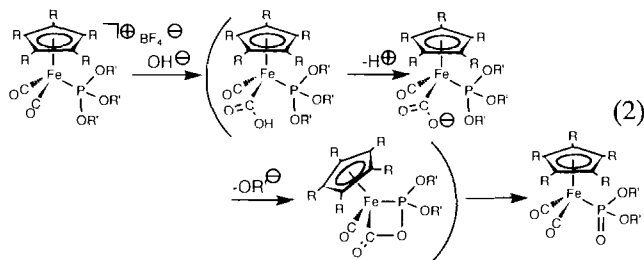
This report stimulated us to start a systematic investigation of the reactions, with OH^- as a Lewis base, of cationic phosphite or amino-substituted phosphite complexes $[Cp(CO)_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ ($n = 0$–3) and their derivatives. We here report that an amino-substituted phosphite complex is converted into a phosphonate complex by an OH^- with selective deamination, and propose a reaction mechanism involving a nucleophilic attack of an OH^- at a coordinating phosphite phosphorus.

Results and discussion

Cationic amino-substituted phosphite complexes of iron, $[Cp(CO)_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ ($n = 1$–3), were prepared by a nucleophilic substitution reaction of $Cp(CO)_2FeCl$ with $P(NC_4H_8)_n(OMe)_{3-n}$ in a benzene solution. This preparative method could not be applied to the trimethylphosphite complex ($n = 0$) because the desired complex quickly underwent the Arbuzov-like dealkylation reaction. Therefore, the complex was obtained by the reaction of $[Cp(CO)_2Fe(THF)]PF_6$ with $P(OMe)_3$ in CH_2Cl_2.

The reaction of a cationic phosphite iron complex with KOH was carried out in water at room temperature. The product was extracted with CH_2Cl_2, and characterized by IR, ^1H NMR and ^{31}P NMR spectra.

The results are summarized in eqns. (3)–(6). In the reaction of 1a with KOH in water at room temperature, no reaction took place. Under reflux conditions for 1 h, 42% of the starting complex was recovered and some unidentified compounds were formed. The lower reactivity of 1a may be due to its lower solubility in water.

$$(3)$$

$$(4)$$

$$(5)$$

$$(6)$$
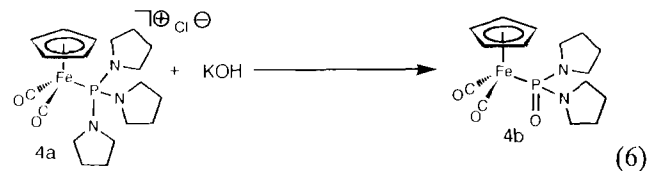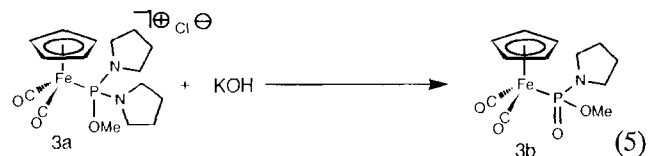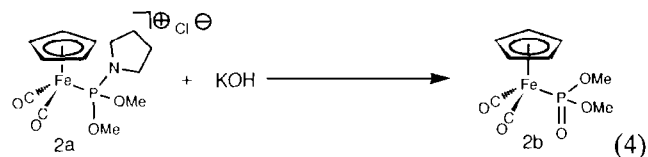
The monoaminophosphite complex 2a reacted with KOH at ambient temperature to afford the dimethylphosphonate complex 2b in 80% yield. The characterization of the product was done by comparison of its spectroscopic data with those of the authentic sample. It is very interesting that 2b is the only product in this reaction and is different from the product expected from the Arbuzov-like dealkylation reaction. There is no evidence for the formation of either the metallacarboxylic acid complex or the metallacarboxylate complex which would be formed by a nucleophilic attack of an OH^- on the carbonyl carbon. Since two OR groups on the phosphorus atom remained intact, the phosphoryl oxygen in the product would be derived from an OH^-.

Similar reactions were observed for 3a and 4a. In both reactions, phosphonate complexes were formed with the elimination of one amino group and with the acquisition of a phosphoryl oxygen from an OH^-.

These reaction products mentioned above are not explained in terms of the Arbuzov-like rearrangement. The most plausible reaction mechanism is shown in eqn. (7). An OH^- group attacks directly the phosphorus atom, but neither the α-carbon of an OR group on a coordinating phosphite nor the carbonyl carbon, to form a metallaphosphorane intermediate. Then the second OH^- eliminates a proton from the OH group on the phosphorus to give A having a $P-O^-$ moiety, followed by the formation of a phosphoryl group releasing an amino group as an anion to give a phosphonate complex. An equimolar amount of KOH toward the phosphite complex is enough in principle though two OH^-s are apparently required, because the released NR_2^- reacts with H_2O to regenerate an OH^-.

(7)
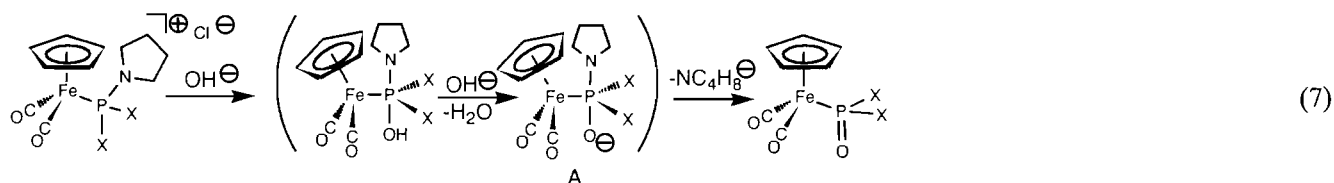
A phosphorus–nitrogen bond is generally demonstrated to have bond character explained by a $2p(N)–3d(P)$ π-system [6]. Therefore most reactions leave the P–N bond intact. However, in the intermediate A in eqn. (7), the P–N π-character might be appreciably weakened by strong $O^- \to P$ π-donation. This may be the main reason for the selective deamination. The mechanism shown in eqn. (7) is different from that proposed by Gibson (eqn. (2)) with respect to whether the carbonyl ligand would participate directly in this reaction or not.

In order to clarify the reaction mechanism, we examined the reaction of cationic phosphite complexes having no carbonyl ligand with KOH. The complexes chosen were $[Cp(PMe_3)_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]^+$ ($n = 0$–2). They were synthesized from $[Cp(PMe_3)_2Fe(CO)]PF_6$ and $P(NC_4H_8)_n(OMe)_{3-n}$. $[Cp(PMe_3)_2Fe\{P(NC_4H_8)_3\}]^+$ corresponding to $n = 3$ could not be obtained presumably due to the steric crowding.

The monoaminophosphite complex ($n = 1$) was treated with KOH in water, water/acetone and water/dioxane individually, but no reactions occurred even at reflux temperature. This resistance of the complex against nucleophilic attack could be caused by the great electron-donating ability of PMe_3 ligands which decreases the positive charge on the phosphite phosphorus. Various solvents were tested and it was finally found that benzene was the best for the reaction, though both the complexes and KOH were less soluble in benzene. In order to increase the solubility of KOH, dibenzo-18-crown-6 was added to the reaction mixture, resulting in a good yield in a short period. Equations (8)–(10) summarize the results of reactions with excess of fine powdered KOH and two times the equivalent of dibenzo-18-crown-6 toward an iron complex at reflux temperature.

(8)

(9)

(10)
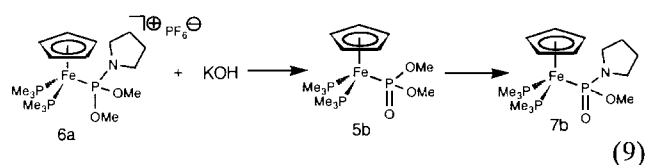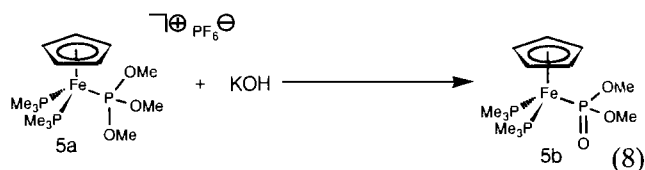
With the trimethylphosphite complex 5a, some insoluble compounds were filtered off after refluxing for 10 h, and then the product was purified by column chromatography to give a yellow powder in 92% yield. This product showed a doublet at 34.5 ppm and a triplet at 144.2 ppm in the ^{31}P NMR spectrum. The chemical shift of the doublet is in the region of a coordinating PMe_3, and thus it is assigned to PMe_3. The triplet is 36.9 ppm higher in magnetic field than that due to the phosphite of the starting cationic complex. The triplet is assignable to a dimethylphosphonate ligand, $P(O)(OMe)_2$. ^1H NMR and elemental analysis data also suggest that the product 5b is formulated as $Cp(PMe_3)_2Fe\{P(O)(OMe)_2\}$. The result shows that a cationic phosphite complex having no carbonyl ligand can be converted into a phosphonate complex in the reaction with KOH.

The next point to be clarified is which atom in the starting complex the OH^- initially attacks; an α-carbon atom of an OR group or a phosphorus atom in the coordinating phosphite. Therefore, the reaction of amino-substituted phosphite complexes having no carbonyl ligands with KOH was examined. A benzene solution containing the monoaminophosphite complex 6a, KOH and dibenzo-18-crown-6 was refluxed for 10 h. The ^{31}P NMR spectrum of the product showed two triplets at 136.1 and 144.2 ppm in the phosphonate region, and complicated signals consisting of a strong doublet at 34.5 ppm and eight signals in the coordinating phosphine region. The triplet at 144.2 ppm and the doublet at 34.5 ppm can be assigned to the dimethylphosphonate complex 5b by comparison with the chemical shifts of the authentic sample. When the same reaction was carried out for 22 h, the reaction mixture showed one triplet at 136.1 ppm and eight signals around 33 ppm. In this case, no signals due to the dimethylphosphonate complex 5b were observed. This reaction mixture was filtered and the solvent was removed under reduced pressure, followed by extraction with ether. The ether solution was worked up to obtain a yellow powder. The ^1H NMR spectrum indicates that the product is the monoaminophosphonate complex 7b (99% crude yield). The coupling pattern in the ^{31}P

NMR spectrum can be explained as follows. The two PMe_3 ligands in this complex are diastereotopic because the phosphonate phosphorus is chiral. Therefore, the two PMe_3 ligands may show different chemical shifts and couple with each other, resulting in the appearance of two doublets of doublet (eight resonances apparently with the same intensity). This is what was observed.

Thus the reaction of **6a** with an OH^- is proposed to proceed as follows. First, the phosphite–phosphonate conversion takes place for **6a** to give **5b** with release of $(NC_4H_8)^-$, and then the OMe/NC_4H_8 substitution reaction occurs on **5b** to give **7b**. The results propose that an OH^- nucleophilically attacks the phosphite phosphorus in **6a** rather than the α-carbon of the OMe group.

The reaction of the diaminophosphite complex **7a** with KOH and dibenzo-18-crown-6 was examined for 10 h at reflux temperature, and the formation of a small amount of the monoaminophosphonate complex **7b** was detected in the ^{31}P NMR spectrum. This reaction was extremely sluggish. The reason may be the electron donation from two PMe_3 ligands and two amino groups on the phosphite phosphorus, as well as from steric crowding around the phosphorane phosphorus in the intermediate.

These results mentioned above strongly suggest that an OH^- nucleophilically attacks the phosphite phosphorus atom in a cationic iron complex to form a metallaphosphorane intermediate. Generally, a phosphorus atom coordinating to a transition metal is not a reaction site so that phosphorus ligands have been used widely as supporting ligands to control the reactivity of the metal center. So our reaction shows a very unusual type of reaction for transition-metal complexes containing phosphorus ligands. The driving force of this reaction may be due to the formation of a very stable phosphoryl group. The rate determining step may be nucleophilic attack of an OH^- on the phosphite phosphorus because the phosphorane intermediate cannot be detected even spectroscopically.

Our results may not directly rule out Gibson's mechanism proposed for phosphite complexes containing carbonyl ligands, but it is highly likely that carbonyl ligands are not essential in this reaction either though they contribute by making the phosphorus atom more positive and therefore more reactive against nucleophiles. Metallacarboxylate complexes could be formed in the reaction of the phosphite complexes having carbonyl ligands with an OH^-, but as the kinetic product, not the intermediate, and be in equilibrium with the starting cationic complex.

There are a few reports suggesting that a trivalent phosphorus ligand may be nucleophilically attacked to form pentavalent phosphorus (phosphorane) intermediates [7, 8]. Recently, we succeeded in isolating

metallaphosphorane complexes in the reaction of triphenylphosphite complex with aminophenoxide, shown in eqn. (11) [9]. These reports also support our reaction mechanism shown in eqn. (7).

$$(11)$$
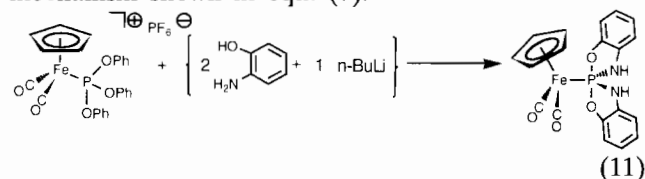
All spectroscopic data are given in Table 1.

Experimental

General remarks

All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. Column chromatography was done quickly in the air. THF, hexane, benzene and ether were purified by distillation from sodium metal, and stored under a nitrogen atmosphere. Other organic solvents and $P(OMe)_3$ were obtained from common commercial sources and used without further purification. Water was purified by passing through an ion exchange column, and degassed under reduced pressure and stored under nitrogen.

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. JEOL PMX-60 and EX-400 spectrometers were used to obtain ^1H NMR and ^{31}P NMR spectra. ^1H NMR data were referenced to $(CH_3)_4Si$ as an internal standard and ^{31}P NMR data were referenced to 85% H_3PO_4 as an external standard.

Preparation of amino-substituted phosphites, $P(NC_4H_8)_n(OMe)_{3-n}$ (n=1–3)

$P(NC_4H_8)_n(OMe)_{3-n}$ were obtained from the reaction of $P(NC_4H_8)_nCl_{3-n}$ which were prepared from PCl_3 and HNC_4H_8, with an appropriate equiv. of MeOH in the presence of NEt_3 followed by distillation [3]. $P(NC_4H_8)_3$ (n=3) was prepared in a manner similar to that for $P(NMe_2)_3$ [10].
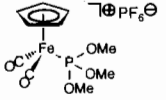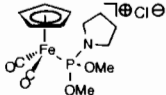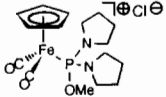
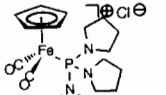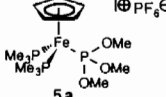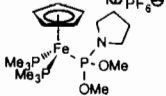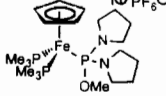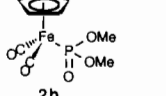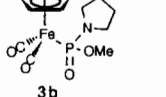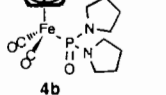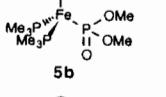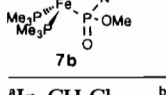### Preparation of $[Cp(CO)_2Fe\{P(OMe)_3\}]PF_6$ (**1a**)

1a was prepared from $[Cp(CO)_2Fe(THF)]PF_6$ and $P(OMe)_3$ in a manner similar to that for $[(\eta^5-C_5Me_5)(CO)_2Fe\{P(OPh)_3\}]PF_6$ [11]. The complex was purified by alumina column chromatography using CH_2Cl_2 as an eluent to give yellow crystals (yield 72%). *Anal.* Calc. for $C_{10}H_{14}F_6FeO_5P_2$: C, 26.93; H, 3.16. Found: C, 26.69; H, 3.15%.

Preparation of $[Cp(CO)_2Fe\{P(NC_4H_8)_n(OMe)_{3-n}\}]Cl$ (n=1–3) (**2a–4a**)

$[Cp(CO)_2Fe\{P(NC_4H_8)(OMe)_2\}]Cl$ (**2a**) and $[Cp(CO)_2Fe\{P(NC_4H_8)_2(OMe)\}]Cl$ (**3a**) were prepared

127

TABLE 1. Spectroscopic data

Complex	IR, ν(CO)[a] (cm^{-1})	^{1}H NMR[b] (δ (ppm))	^{31}P NMR[a] (δ (ppm))
1a	2071 2027	4.01 (d, J=12.4 Hz, 9H, OCH$_3$) 5.82 (d, J=1.4 Hz, 5H, C$_5$H$_5$)	159.8 (s, P(OMe)$_3$) −144.0 (sep, J=710.1 Hz, PF$_6$)
2a	2062 2017	1.97 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.30 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.73 (d, J=12.0 Hz 6H, OCH$_3$) 5.57 (s, 5H, C$_5$H$_5$)	157.2 (s)
3a	2051 2005	1.87 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.05 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.50 (d, J=12.0 Hz, 3H, OCH$_3$) 5.13 (s, 5H, C$_5$H$_5$)	140.4 (s)
4a	2044 2000	1.95 (m, 12H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.31 (m, 12H, CH$_2$CH$_2$CH$_2$CH$_2$) 5.54 (s, 5H, C$_5$H$_5$)	116.5 (s)
5a		1.45 (m, 18H, PCH$_3$) 3.75 (d, J=10.8 Hz, 9H, OCH$_3$) 4.41 (m, 5H, C$_5$H$_5$)	31.0 (d, J=100.7 Hz, PMe$_3$) 181.1 (t, J=103.7 Hz, P(OMe)$_3$) −143.6 (sep, J=710.3 Hz, PF$_6$)
6a		1.44 (m, 18H, PCH$_3$) 1.97 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.20 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.70 (d, J=10.7 Hz, 3H, OCH$_3$) 4.33 (m 5H, C$_5$H$_5$)	28.0 (d, J=97.6 Hz, PMe$_3$) 178.5 (t, J=97.6 Hz, P(NC$_4$H$_8$)(OMe)$_2$) −143.5 (sep, J=711.1 Hz, PF$_6$)
7a		1.43 (m, 18H, PCH$_3$) 1.92 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.17 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.49 (d, J=10.2 Hz, 3H, OCH$_3$) 4.32 (m, 5H, C$_5$H$_5$)	25.2 (d, J=88.5 Hz, PMe$_3$) 165.9 (t, J=88.5 Hz, P(NC$_4$H$_8$)$_2$(OMe)) −144.0 (sep, J=711.1 Hz, PF$_6$)
2b	2040 1990	3.63 (d, J=11.0 Hz, 6H, OCH$_3$) 5.08 (d, J=1.8 Hz, 5H, C$_5$H$_5$)	109.2 (s)
3b	2032 1981	1.82 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.18 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.50 (d, J=11.6 Hz, 3H, OCH$_3$) 4.93 (s, 5H, C$_5$H$_5$)	101.3 (s)
4b	2020 1967	1.78 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.15 (m, 8H, CH$_2$CH$_2$CH$_2$CH$_2$) 5.00 (s, 5H, C$_5$H$_5$)	87.4 (s)
5b		1.42 (m, 18H, PCH$_3$) 3.56 (d, J=10.3 Hz, 6H, OCH$_3$) 4.17 (s, 5H, C$_5$H$_5$)	34.5 (d, J=113.2 Hz, PMe$_3$) 144.2 (t, J=113.2 Hz, P(O)(OMe)$_2$)
7b		1.41 (d, J=8.0 Hz, 18H, PCH$_3$) 1.78 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 3.27 (m, 4H, CH$_2$CH$_2$CH$_2$CH$_2$) 4.14 (m, 5H, C$_5$H$_5$)	32.5 (dd, J=109.9, 61.1 Hz, PMe$_3$) 35.5 (dd, J=109.9, 61.1 Hz, PMe$_3$) 136.1 (t, J=109.9 Hz, P(O)(NC$_4$H$_8$)(OMe))

[a] In CH$_2$Cl$_2$. [b] In CDCl$_3$.

from $Cp(CO)_2FeCl$ and $P(NC_4H_8)_n((OMe)_{3-n}$ ($n = 1$, 2) in benzene according to the published method [3]. $[Cp(CO)_2Fe\{P(NC_4H_8)_3\}]Cl$ (**4a**) was prepared in a manner similar to that for **2a** (yield 92%). The complex is so hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

Preparation of $Cp(CO)(PMe_3)FeCl$

This complex was prepared according to the literature method with some modification [12]. $NaK_{2.8}$ (1.68 g, 2 ml, 12.7 mmol) was added to a solution of $[Cp(CO)_2Fe]_2$ (2.0 g, 5.7 mmol) in 100 ml of THF. Stirring the solution for 40 min at ambient temperature caused a color change from dark red to red. The solution was filtered to give a homogeneous solution containing $K[Cp(CO)_2Fe]$. A hexane solution (20 ml) containing CH_3COOH (1.05 g, 1 ml, 17.5 mmol) was added to the THF solution and the mixture was stirred for 10 min to form a white precipitate. This supernatant contained $Cp(CO)_2FeH$ showing $\nu(CO)$ at 1954, 2012 cm^{-1} in the IR spectrum. After filtration, PMe_3 (15 ml of 1 M ether solution, 15 mmol) was added to the filtrate, and vigorous formation of CO gas was observed. The solution was stirred for 1 h to form $Cp(CO)(PMe_3)FeH$ showing $\nu(CO)$ at 1916 cm^{-1}. Then 40 ml of CCl_4 were added to the mixture, rapidly changing the color from yellow to dark green, and the $\nu(CO)$ shifted to 1950 cm^{-1}. After volatile components were removed under reduced pressure, the residue was dissolved in a small amount of benzene, and charged on an alumina column, and eluted with benzene followed by benzene/CH_2Cl_2. The green band eluted with benzene/CH_2Cl_2 was collected and worked up. $Cp(CO)(PMe_3)FeCl$ was obtained as a dark green powder (1.2 g, 4.8 mmol, 84%).

Preparation of $[Cp(PMe_3)_2Fe(CO)]PF_6$

$Cp(CO)(PMe_3)FeCl$ (802 mg, 3.08 mmol) was dissolved in 80 ml of benzene. Then $AlCl_3$ (821 mg, 6.16 mmol) and PMe_3 (9.2 ml of 1 M ether solution, 9.2 mmol) were added to the solution and the mixture was stirred for 1 h at room temperature to form a yellow oil. The supernatant was decanted off, and 100 ml of water were added to the oil at 0 °C. Then NH_4PF_6 (650 mg, 4.00 mmol) was added to the mixture to form a large amount of pale yellow precipitates. After the precipitates were extracted with CH_2Cl_2 until the CH_2Cl_2 became almost colorless, the CH_2Cl_2 solution was passed through a short $MgSO_4$ column, and worked up to give $[Cp(PMe_3)_2Fe(CO)]PF_6$ as a yellow powder (914 mg, 2.05 mmol, 67%).

Preparation of $[Cp(PMe_3)_2Fe\{P(OMe)_3\}]PF_6$ (5a)

This complex was prepared according to the published method for $[Cp(PMe_3)_2Fe(PPh_3)]PF_6$ with some modification [13]. $[Cp(PMe_3)_2Fe(CO)]PF_6$ (258 mg, 0.58 mmol) was dissolved in 80 ml of MeCN and irradiated with a medium pressure Hg arc lamp for 1 h at the reflux temperature. The color of the mixture turned from yellow to red and the $\nu(CO)$ in the IR spectrum disappeared during the irradiation. The solvent was removed under reduced pressure and the residue containing $[Cp(PMe_3)_2Fe(NCMe)]PF_6$ was dissolved in 30 ml of THF. $P(OMe)_3$ (95 mg, 0.09 ml, 0.77 mmol) was added to the solution and the mixture was refluxed for 1 h causing the color change of the solution from red to yellow. After concentration under reduced pressure until a small amount of precipitate formed, 50 ml of ether were added to form a yellow powder. The supernatant was decanted off and the precipitate was washed with ether several times and dried under reduced pressure to obtain **5a** as a yellow powder (283 mg, 0.52 mmol, 90%). *Anal.* Calc. for $C_{14}H_{32}F_6FeO_3P_4$: C, 31.01; H, 5.95. Found: C, 30.74; H, 6.02%.

Preparation of $[Cp(PMe_3)_2Fe\{P(NC_4H_8)(OMe)_2\}]PF_6$ (6a)

6a was obtained from $[Cp(PMe_3)_2Fe(CO)]PF_6$ (299 mg, 0.67 mmol) and $P(NC_4H_8)(OMe)_2$ (110 mg, 0.11 ml, 0.67 mmol) in a similar manner to that for **5a** as a yellow powder (348 mg, 0.60 mmol, 90%). *Anal.* Calc. for $C_{17}H_{37}NF_6FeO_2P_4$: C, 35.13; H, 6.42; N, 2.41. Found: C, 35.35; H, 6.53; N, 2.51%.

Preparation of $[Cp(PMe_3)_2Fe\{P(NC_4H_8)_2(OMe)\}]PF_6$ (7a)

7a was prepared from $[Cp(PMe_3)_2Fe(CO)]PF_6$ (1382 mg, 3.1 mmol) and $P(NC_4H_8)_2(OMe)$ (800 mg, 0.8 ml, 4.0 mmol) in a similar manner to that for **5a**. The product was purified on a silica gel column using CH_2Cl_2 as eluent to give a yellow powder (1456 mg, 2.4 mmol, 76%). *Anal.* Calc. for $C_{20}H_{42}N_2F_6FeOP_4$: C, 38.72; H, 6.83; N, 4.52. Found: C, 38.46; H, 6.89; N, 3.92%.

Reaction of $[Cp(CO)_2Fe\{P(NC_4H_8)(OMe)_2\}]Cl$ (2a) with KOH

2a (314 mg, 0.92 mmol) was dissolved in 5 ml of water and KOH ($\sim$100 mg, 1.8 mmol) was added to the solution. The mixture was stirred for 1 h, and the product was extracted with CH_2Cl_2 until the CH_2Cl_2 became almost colorless. The CH_2Cl_2 solution was passed through a short $MgSO_4$ column and stirred for 10 h with Na_2SO_4. After filtration, the filtrate was worked up under reduced pressure and spectroscopically pure **2b** was obtained as a yellow oil (209 mg, 0.73 mmol, 80%). This product was identified by comparison of its spectroscopic data with those of the authentic

sample. This product could be obtained as a yellow powder by silica gel column chromatography using acetone/ethanol as eluent but with a lower yield.

Reaction of [Cp(CO)₂Fe{P(NC₄H₈)₂(OMe)}]Cl (3a) with KOH

A 0.1 N KOH aqueous solution (6.3 ml, 0.63 mmol) containing 3a (262.2 mg, 0.63 mmol) was stirred for 1 h. Spectroscopically pure 3b was obtained as a yellow oil (119 mg, 0.37 mmol, 58%) by following the same procedure as that for 2b.

Reaction of [Cp(CO)₂Fe{P(NC₄H₈)₃}]Cl (4a) with KOH

A 0.1 N KOH aqueous solution (33 ml) containing 4a (302 mg, 0.67 mmol) was stirred for 5 h. Spectroscopically pure 4b was obtained as a yellow oil (25.6 mg, 0.079 mmol, 12%) by following the same procedure as that for 2a.

Reaction of [Cp(PMe₃)₂Fe{P(OMe)₃}]PF₆ (5a) with KOH

To 50 ml of benzene solution in which 5a (104 mg, 0.19 mmol) was suspended, fine powdered KOH (~90 mg, 1.6 mmol) and dibenzo-18-crown-6 (138 mg, 0.38 mmol) were added. Refluxing the mixture for 10 h caused a color change of the supernatant from almost colorless to yellow. After filtration, the filtrate was loaded on a silica gel column and eluted with CH₂Cl₂, acetone and acetone/ethanol in this order. The yellow band eluted with acetone/ethanol was collected and worked up. 5b was obtained as a yellow powder (67.2 mg, 0.18 mmol, 92%). *Anal.* Calc. for C₁₃H₂₉FeO₃P₃: C, 40.86; H, 7.65. Found: C, 40.93; H, 7.71%.

Reaction of [Cp(PMe₃)₂Fe{P(NC₄H₈)(OMe)₂}]PF₆ (6a) with KOH

To 30 ml of benzene in which 6a (89 mg, 0.15 mmol) was suspended, fine powdered KOH (~120 mg, 2.1 mmol) and dibenzo-18-crown-6 (133 mg, 0.37 mmol) were added. The mixture was refluxed for 22 h and filtered. The filtrate was worked up and the product was extracted with ether. Removal of the solvent yielded crude 7b as a yellow powder (63 mg, 0.15 mmol, 99%). It was found that the product was contaminated by a small amount of the crown ether used but 7b was too unstable to be purified by column chromatography.

Reaction of [Cp(PMe₃)₂Fe{P(NC₄H₈)₂(OMe)}]PF₆ (7a) with KOH

7a (114 mg, 0.18 mmol) was suspended in 50 ml of benzene, and fine powdered KOH (~100 mg, 1.8 mmol) and dibenzo-18-crown-6 (132 mg, 0.37 mmol) were added to the suspension. After refluxing for 10 h, the mixture was filtered and the filtrate was worked up.

It was found from the ³¹P NMR spectrum that the residue consisted of a small amount of 7b and other unidentified products. We could not isolate 7b from this mixture.

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