

Isolation of cationic cyclopentadienyl iron complexes containing phosphinite and formation of metallaphosphineoxide complexes by the Arbuzov-like dealkylation reaction *

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Abstract

Reaction of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCl}$ with $\text{PPh}_2(\text{OR})$ yields an isolable cationic complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{PPh}_2(\text{OR}))]\text{Cl}$ ($\text{R} = \text{Et}$, **Ia**; Me , **Ib**), which reacts with NaOMe to give $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{COOMe})(\text{PPh}_2(\text{OR}))]$ and with $\text{PPh}_2(\text{OR})$ to afford $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{PPh}_2(\text{OR}))_2]\text{Cl}$ ($\text{R} = \text{Et}$, **IVa**; Me , **IVb**). Complexes **Ib** and **IVb** undergo the Arbuzov-like dealkylation reaction in benzene at room temperature to give metallaphosphineoxide complexes, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\text{P}(\text{O})\text{Ph}_2)]$ and $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\text{Fe}(\text{PPh}_2(\text{OMe}))(\text{P}(\text{O})\text{Ph}_2)]$, respectively, whereas **Ia** and **IVa** do not undergo the reaction. This difference in reactivity is discussed from electronic and steric points of view.

Introduction

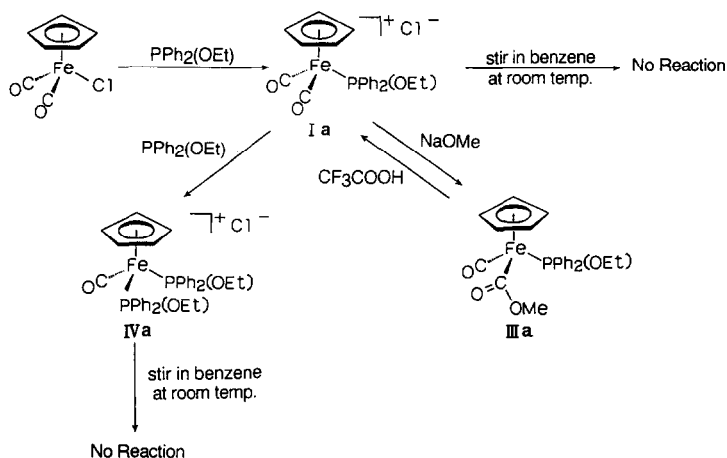
Transition-metal phosphonate complexes have received considerable attention recently [1]. Interest in these complexes is derived, in part, from the presence of a pentavalent phosphorus ligand covalently bonded to the transition-metal centre. Most transition-metal phosphonate complexes have been prepared according to Arbuzov-like dealkylation reaction [1a], which are the reactions of transition-metal complexes (L_nMX) containing a labile nucleophilic ligand such as a halogen atom (X) with trialkyl phosphites ($\text{P}(\text{OR})_3$) to give phosphonate complexes (eq. 1). Most proceed by an ionic mechanism, where the halide in L_nMX is replaced by a

$$\text{L}_n\text{MX} + \text{P}(\text{OR})_3 \rightarrow \text{L}_n\text{M}-\text{P}(\text{O})(\text{OR})_2 + \text{RX} \quad (1)$$

phosphite to give the cationic complex $[\text{L}_n\text{M}\{\text{P}(\text{OR})_3\}]^+$ which is then subjected to nucleophilic attack by the released halide anion at the α -carbon of the coordinated

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* Dedicated to Professor Akio Yamamoto upon his retirement from Tokyo Institute of Technology and in honour of his contributions to organometallic chemistry.



Scheme 1

phosphite, affording the final phosphonate complex. Therefore, in principle, a reaction of L_nMX with a phosphorus compound having at least one OR group can yield an Arbuzov-like dealkylation product. If L_nMX is treated with a phosphinite $\text{PR}_2(\text{OR})$, a metallaphosphineoxide $\text{L}_n\text{M}-\text{P}(\text{O})\text{R}_2$ would be formed. However, reports concerning the preparation of metallaphosphineoxide are quite limited.

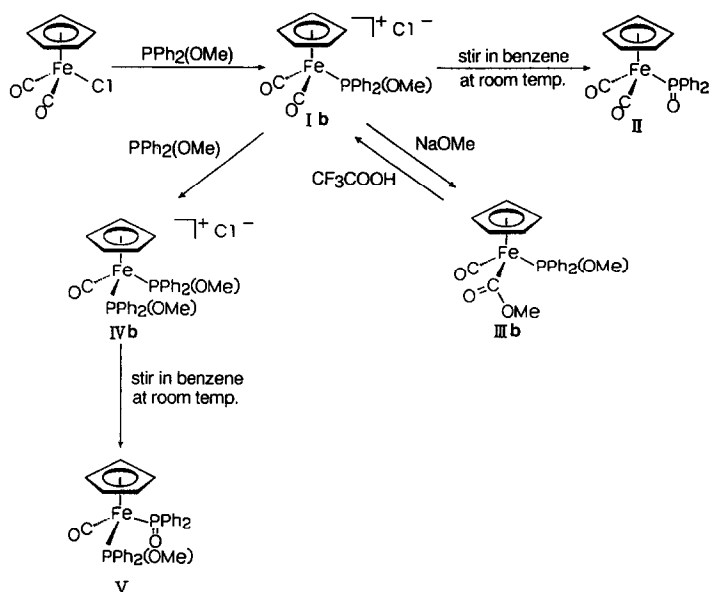
We have been studying cyclopentadienyl iron phosphonate complexes and have reported the structural features, the reaction mechanism, and the reactivity [2]. Here we report the Arbuzov-like dealkylation reactions of $\text{Cp}(\text{CO})_2\text{FeCl}$, where Cp stands for $\eta^5\text{-C}_5\text{H}_5$, with $\text{PPh}_2(\text{OEt})$ and $\text{PPh}_2(\text{OMe})$ to give cyclopentadienyl ironphosphineoxide complexes.

Results and discussion

The reaction sequences mentioned here are summarized in Schemes 1 and 2, and the spectroscopic data for the complexes obtained here are given in Table 1.

Formation of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OEt})\}]\text{Cl}$ (**Ia**) and $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OMe})\}]\text{Cl}$ (**Ib**)

Treatment of $\text{Cp}(\text{CO})_2\text{Cl}$ with equimolar amounts of $\text{PPh}_2(\text{OEt})$ or $\text{PPh}_2(\text{OMe})$ in benzene at room temperature for about 0.5 h yielded a greenish yellow powder. The two absorptions of the each product due to $\nu(\text{CO})$ in the infrared spectra were observed at a frequency higher than 2000 cm^{-1} . The chemical shift due to Cp protons in the ^1H NMR spectrum was observed at a field lower than 5.3 ppm. These two observations indicate that the products are cationic. In the ^{31}P NMR spectra, one singlet was observed at about 160 ppm. The spectroscopic data, together with elemental analyses, confirm the formation of $\text{Cl}/\text{PPh}_2(\text{OR})$ exchange products, $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OEt})\}]\text{Cl}$ (**Ia**) and $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OMe})\}]\text{Cl}$ (**Ib**).



Scheme 2

Formation of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})\text{Ph}_2\}]$ (**II**)

Although most of the Arbuzov-like dealkylation reactions have been found to proceed by an ionic mechanism, cationic complexes $[\text{L}_n\text{M}\{\text{P}(\text{OR})_3\}]\text{X}$ are usually too reactive to be isolated. Recently we found that the ionic intermediates $[\text{Cp}(\text{CO})_2\text{FeL}]\text{Cl}$ are isolable when monoamino- and diamino-substituted phosphites, $\text{P}(\text{NR}_2)_n(\text{OR})_{3-n}$ ($n = 1, 2$), were used as L in place of $\text{P}(\text{OR})_3$ [3,4]. Since the complexes **Ia** and **Ib** isolated above correspond to the intermediates of the Arbuzov-like dealkylation, we examined whether **Ia** and **Ib** can be converted into a metallaphosphineoxide complex.

Complexes **Ia** and **Ib** were suspended separately in benzene and stirred for a few days at room temperature. Complex **Ia** remained unchanged, while **Ib** was converted into $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})\text{Ph}_2\}$ (**II**). The reason why **Ia** does not undergo the Arbuzov-like dealkylation reaction whereas **Ib** does, will be discussed later. Complex **II** can be directly prepared from $\text{Cp}(\text{CO})_2\text{FeCl}$ and $\text{PPh}_2(\text{OMe})$ without the isolation of **Ib**. In this case, there are two important conditions to obtain **II**. The quantity of $\text{PPh}_2(\text{OMe})$ should be used less than that of $\text{Cp}(\text{CO})_2\text{FeCl}$, and the reaction should be carried out in a dilute solution. If either of the two conditions is not satisfied, another complex (**IVb**; see below) becomes a main product.

Reactivity of **Ia** and **Ib** toward NaOMe

Since the reactivity difference between **Ia** and **Ib** towards Cl^- was apparent, we next examined the reactivity towards OMe^- , a stronger Lewis base than Cl^- . The complexes **Ia** and **Ib** were treated with NaOMe in methanol to give **IIIa** and **IIIb** respectively, as a hygroscopic powder. The IR spectra of the products showed patterns characteristic of a methoxycarbonyl ligand ($\nu(\text{CO}) = 1585 \text{ cm}^{-1}$ for **IIIa** and 1584 cm^{-1} for **IIIb**) and of a terminal carbonyl ligand ($\nu(\text{CO}) = 1954 \text{ cm}^{-1}$ both for **IIIa** and **IIIb**). From the IR data, supplemented with ^1H and ^{31}P NMR

Table 1

Spectroscopic data

	IR ^a ($\nu(\text{CO})$ cm^{-1})	¹ H NMR ^b (δ (ppm))	³¹ P NMR ^a (δ (ppm))
[Cp(CO) ₂ Fe(PPh ₂ (OEt))Cl] Ia	2058 2016	7.85–7.33 (m, 10H, C ₆ H ₅) 5.27 (s, 5H, C ₅ H ₅) 3.90 (qui, $J = 7.0$ Hz, 2H, CH ₂) 1.28 (t, $J = 7.0$ Hz, 3H, CH ₃)	159.9 (s)
[Cp(CO) ₂ Fe(PPh ₂ (OMe))Cl] Ib	2060 2018	7.63–7.33 (m, 10H, C ₆ H ₅) 5.32 (s, 5H, C ₅ H ₅) 3.50 (d, $J = 12.5$ Hz, 3H, CH ₃)	163.5 (s)
[Cp(CO) ₂ Fe{P(O)Ph ₂ }] II	2028 1978	7.77–7.17 (m, 10H, C ₆ H ₅) 5.02 (s, 5H, C ₅ H ₅)	89.1 (s)
[Cp(CO)Fe(COOMe)(PPh ₂ (OEt))] IIIa	1954 1585	7.69–7.22 (m, 10H, C ₆ H ₅) ^c 4.52 (s, 5H, C ₅ H ₅) 3.58 (qui, $J = 7.0$ Hz, 2H, CH ₂) 1.20 (t, $J = 7.0$ Hz, 3H, CH ₃)	174.2 (s)
[Cp(CO)Fe(COOMe)(PPh ₂ (OMe))] IIIb	1954 1584	7.60–7.18 (m, 10H, C ₆ H ₅) ^c 4.45 (s, 5H, C ₅ H ₅) 3.48 (d, $J = 12.2$ Hz, 3H, POCH ₃) 3.28 (s, 3H, COOCH ₃)	177.5 (s)
[Cp(CO)Fe{PPh ₂ (OEt)} ₂]Cl IVa	1985	7.60–7.43 (m, 20H, C ₆ H ₅) 4.97 (s, 5H, C ₅ H ₅) 3.47 (m, 4H, CH ₂) 1.08 (td, $J = 6.8, 1.8$ Hz, 6H, CH ₃)	162.3 (s)
[Cp(CO)Fe{PPh ₂ (OMe)} ₂]Cl IVb	1985	7.58–7.30 (m, 20H, C ₆ H ₅) 4.98 (s, 5H, C ₅ H ₅) 3.25 (d, $J = 12.0$ Hz, 6H, CH ₃)	165.9 (s)
[Cp(CO)Fe{PPh ₂ (OMe)}{P(O)Ph ₂ }] V	1938	7.78–6.93 (m, 20H, C ₆ H ₅) 4.41 (s, 5H, C ₅ H ₅) 2.98 (d, $J = 11.4$ Hz, 3H, CH ₃)	170.5 (d, $J = 73.5$ Hz, PPh ₂ (OMe)) 91.6 (d, $J = 73.5$ Hz, P(O)Ph ₂)

^a In CH₂Cl₂. ^b In acetone-*d*₆ unless otherwise noted. ^c In CDCl₃

data, the products were identified as methoxycarbonyl complexes. Therefore, it was found that the OMe[−] anion selectively attacks the carbonyl carbon instead of the α -carbon in the coordinated PPh₂(OR). A similar reactivity has been reported for [Cp(CO)₂Fe{P(NEt₂)₂(OMe)}]Cl [3]. Complexes IIIa and IIIb readily reacted with acids such as CF₃COOH to regenerate Ia and Ib, respectively.

Formation of [Cp(CO)Fe{PPh₂(OEt)}₂]Cl (IVa) and [Cp(CO)Fe{PPh₂(OMe)}₂]Cl (IVb)

The reactions of Ia with PPh₂(OEt) and of Ib with PPh₂(OMe) were examined. Complex Ia was suspended in benzene and equimolar amounts of PPh₂(OEt) were

added. After 1 h of refluxing, the greenish yellow powder of Ia changed to a yellow powder IVa. The complex has only one $\nu(\text{CO})$ absorption at 1985 cm^{-1} and only one singlet at 162.3 ppm in its ^{31}P NMR spectrum. The ^1H NMR showed that the iron has two $\text{PPh}_2(\text{OEt})$ ligands. Therefore, IVa was identified as a $\text{CO}/\text{PPh}_2(\text{OEt})$ exchange product of Ia, i.e., $[\text{Cp}(\text{CO})\text{Fe}(\text{PPh}_2(\text{OEt}))_2]\text{Cl}$. The product was synthesized also by refluxing Ia only in benzene, though the yield was low. Decomposition and disproportionation are presumably responsible for the low yield. The best way to prepare IVa was found to be the treatment of $\text{Cp}(\text{CO})_2\text{FeCl}$ with 2 equiv. of $\text{PPh}_2(\text{OEt})$ without the isolation of Ia. The yield amounted to 83% based on $\text{Cp}(\text{CO})_2\text{FeCl}$.

Complex Ib reacted with $\text{PPh}_2(\text{OMe})$ to give $[\text{Cp}(\text{CO})\text{Fe}(\text{PPh}_2(\text{OMe}))_2]\text{Cl}$ (IVb), which was prepared by thermolysis of Ib, though in low yield, and was also synthesized from $\text{Cp}(\text{CO})_2\text{FeCl}$ and 2 equiv. of $\text{PPh}_2(\text{OMe})$ in a 66% yield.

Reactivity of IVa and IVb

The carbonyl ligands of Ia and Ib were the reaction sites towards OMe^- and a phosphinite. The reactivities toward OMe^- and a phosphinite were examined for IVa and IVb both being cationic complexes and having a CO ligand like Ia and Ib. Complex IVa was dissolved in MeOH and 3 equiv. of NaOMe added and no change was observed. The solution was refluxed for several hours but the methoxycarbonyl complex $[\text{CpFe}(\text{COOMe})(\text{PPh}_2(\text{OEt}))_2]$ was not detected. Complex IVa was treated with $\text{PPh}_2(\text{OEt})$ but no $[\text{CpFe}(\text{PPh}_2(\text{OEt}))_3]\text{Cl}$ was obtained. Complex IVb showed the same reactivity toward OMe^- and $\text{PPh}_2(\text{OMe})$ as IVa. That is, neither $[\text{CpFe}(\text{COOMe})(\text{PPh}_2(\text{OMe}))_2]$ nor $[\text{CpFe}(\text{PPh}_2(\text{OMe}))_3]\text{Cl}$ was obtained.

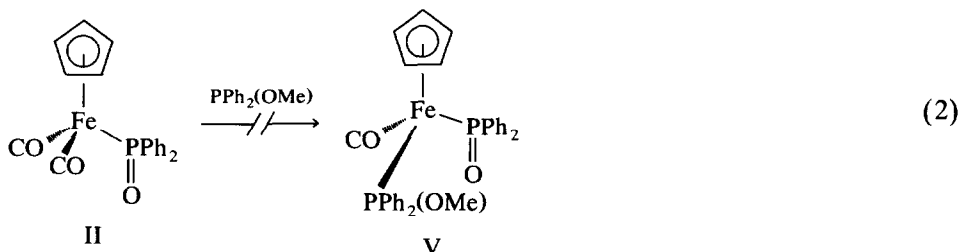
The poor reactivity of the CO ligand in IVa and IVb towards Lewis bases may be explained as follows. The CO in IVa or IVb is the last ligand which strongly accepts π -back donation from the Fe, so the Fe–CO bond is stronger and the π^* orbital of the CO is less electrophilic for IV than I.

Formation of $[\text{Cp}(\text{CO})\text{Fe}\{\text{PPh}_2(\text{OMe})\}\{\text{P}(\text{O})\text{Ph}_2\}]\text{Cl}$ (V)

Complex IVa did not undergo the Arbuzov-like dealkylation reaction, whereas IVb did. Stirring the heterogeneous benzene solution containing IVb for several hours at room temperature yielded a yellow product V. The complex gave rise to only one $\nu(\text{CO})$ at 1938 cm^{-1} in the IR spectrum. The ^{31}P NMR spectrum exhibited two doublets at 170.5 and 91.6 ppm and the coupling constants were both 73.5 Hz. The ^1H NMR spectrum showed that V has one OMe group on the P atom. These data, together with elemental analysis show that the product is $[\text{Cp}(\text{CO})\text{Fe}(\text{PPh}_2(\text{OMe}))\{\text{P}(\text{O})\text{Ph}_2\}]\text{Cl}$. The ^{13}C NMR spectrum was also consistent with this interpretation; 200.51 (dd, $J = 34.2, 30.3\text{ Hz}$, CO), 152.57 (d, $J = 43.5\text{ Hz}$, Ph), 149.45 (d, $J = 45.5\text{ Hz}$, Ph), 139.52 (d, $J = 47.4\text{ Hz}$, Ph), 136.17 (d, $J = 40.6\text{ Hz}$, Ph), 133.32 (d, $J = 11.7\text{ Hz}$, Ph), 131.30 (d, $J = 10.8\text{ Hz}$, Ph), 130.50 (d, $J = 8.8\text{ Hz}$, Ph), 129.85 (d, $J = 9.3\text{ Hz}$, Ph), 86.86 (s, Cp), 53.68 (d, $J = 10.8\text{ Hz}$, CH_3). The complex is of interest because the iron has both a covalently bonded phosphorus ligand ($\text{P}(\text{O})\text{Ph}_2$) and a datively bonded phosphorus ligand ($\text{PPh}_2(\text{OMe})$). In the ^{31}P NMR spectrum, one doublet at 91.6 ppm of V is close in frequency to a singlet of II having a covalently bonded P ligand and the other doublet at 170.5 ppm is close to a singlet of IIIb having a datively bonded P ligand. The singlet at 91.6 ppm is therefore assigned to $\text{P}(\text{O})\text{Ph}_2$ and that at 170.5 ppm to $\text{PPh}_2(\text{OMe})$. In the ^{13}C

NMR spectrum, the carbonyl carbon is coupled with two kinds of phosphorus and it should be noted that the coupling constants are very close (34.2 Hz vs 30.3 Hz), though the bond fashions are different.

The reaction of $\text{Cp}(\text{CO})_2\text{FeCl}$ with 2 equiv. of $\text{PPh}_2(\text{OMe})$ finally yielded II and V. In order to make clear whether V is prepared via II or via IVb, II was treated with $\text{PPh}_2(\text{OMe})$ in benzene reflux condition. It was found that V was not obtained at all, indicating that the CO ligands of II was not replaced by a tervalent phosphorus compound (eq. 2). Similar results have been obtained for $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OEt})_2\}$ [2a].

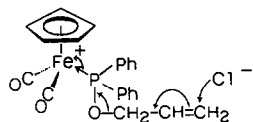


Complex V has a chiral centre at the iron atom and partial optical resolution has been achieved by using a silica gel column with diethyltartrate as a resolving agent [5]. The result indicates that the geometry around the iron is rigid, and the ligands dissociate from V very slowly if at all, and the migration of Me from the $\text{PPh}_2(\text{OMe})$ to the $\text{P}(\text{O})\text{Ph}_2$ is also very slow or non-existent.

Arbuzov-like dealkylation reaction of Ib and IVb

Let us consider the reason why Ib and IVb undergo the Arbuzov-like dealkylation reaction while Ia and IVa do not. The dealkylation reaction is initiated by a nucleophilic attack at an α -carbon of an OR group on a coordinating phosphorus and then an alkyl halide is eliminated with the Walden inversion. Therefore, electronic effects may be one of the reasons. Diminution of the positive charge on the α -carbon will impede the reaction. The α -carbon in Ia and IVa having one electron-donating methyl group and two hydrogens may be less electropositive than that in Ib and IVb having three hydrogens, respectively. Thus, lesser reactivity for Ia and IVa than for Ib and IVb is deduced on electronic grounds. Steric effects may be another reason. At the transition state, the α -carbon takes a trigonal bipyramidal geometry. So, the bulkiness of the substituents on the α -carbon and the groups situated spatially close to the α -carbon, i.e., the substituents on the phosphorus atom should be considered. A phenyl group is bulkier than an OR group. The α -carbon in Ib and IVb having three hydrogens may marginally take the trigonal bipyramidal transition state, whereas the α -carbon in Ia and IVa having one methyl group and two hydrogens may resist sterically taking such a transition state. Therefore, both electronic and steric effects lower the reactivity for Ia and IVa.

Haines reported that $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OCH}_2\text{CH}=\text{CH}_2)\}]\text{Cl}$ undergoes the Arbuzov-like dealkylation to give $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})\text{Ph}_2\}]$ [6]. The experimental results seem to be incompatible with the explanation presented above, because the α -carbon in $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OCH}_2\text{CH}=\text{CH}_2)\}]\text{Cl}$ has a vinyl group which is as bulky as a methyl group. However, if we imagine the pathway for



Scheme 3

$[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OCH}_2\text{CH}=\text{CH}_2)\}]\text{Cl}$ shown in Scheme 3 where Cl^- nucleophilically attacks the γ -carbon in place of the α -carbon to give $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})\text{Ph}_2\}]$ and $\text{CH}_2=\text{CHCH}_2\text{Cl}$, these results would be reasonably explained.

Experimental

General remarks

All reactions were carried out under dry dinitrogen. Benzene was distilled from sodium metal, dichloromethane was distilled from P_2O_5 , acetone was dried with anhydrous CaSO_4 and distilled, and ethanol and methanol were dried over molecular sieve (type 4A) and then distilled. $\text{Cp}(\text{CO})_2\text{FeCl}$ [7], $\text{PPh}_2(\text{OEt})$ and $\text{PPh}_2(\text{OMe})$ [8] were synthesized by published procedures.

IR spectra were recorded on a Shimadzu FTIR-4000 spectrometer. NMR spectra were recorded on a JEOL PMX-60 and GX-270 spectrometers using $\text{Si}(\text{CH}_3)_4$ as an internal standard for ^1H and ^{13}C NMR spectra, respectively, and a JEOL FX-100 spectrometer using 85% H_3PO_4 as an external standard for ^{31}P NMR spectra.

$[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OEt})\}]\text{Cl}$ (Ia)

To a solution of $\text{Cp}(\text{CO})_2\text{FeCl}$ (321 mg, 1.51 mmol) in benzene (5 ml) was added $\text{PPh}_2(\text{OEt})$ (522 mg, 0.49 ml, 2.27 mmol). The reaction mixture was stirred for 0.5 h at room temperature to yield a greenish yellow powder. Prolonged stirring led to the low yield because the product is contaminated by further reaction as mentioned below. After being filtered and washed with benzene, the powder was dissolved in a small amount of CH_2Cl_2 , loaded on a silica gel column, and eluted with CH_2Cl_2 , acetone, and EtOH in that order. The yellow band eluted with EtOH was collected and the solvent was removed under reduced pressure to give Ia as a yellow powder. Yield 588 mg (1.33 mmol, 88%). Found: C, 56.78; H, 4.50. $\text{C}_{21}\text{H}_{20}\text{ClFeO}_3\text{P}$ calc.: C, 56.98; H, 4.55%.

$[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2(\text{OMe})\}]\text{Cl}$ (Ib)

Complex Ib was prepared from $\text{Cp}(\text{CO})_2\text{FeCl}$ and $\text{PPh}_2(\text{OMe})$ in the same manner as that for Ia. Yield 77%. Found: C, 55.91; H, 4.18. $\text{C}_{20}\text{H}_{18}\text{ClFeO}_3\text{P}$ calc.: C, 56.04; H, 4.23%.

$[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})\text{Ph}_2\}]$ (II)

To a solution of $\text{Cp}(\text{CO})_2\text{FeCl}$ (455 mg, 2.14 mmol) in benzene (30 ml) was added $\text{PPh}_2(\text{OMe})$ (474 mg, 0.44 ml, 2.04 mmol). The reaction mixture was stirred for 2 days at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 , loaded on a silica gel column, and then eluted with CH_2Cl_2 , $\text{CH}_2\text{Cl}_2/\text{acetone}$ (1/1), acetone/EtOH (1/1) in that order.

The yellow band eluted with acetone/EtOH (1/1) was collected and the solvents were removed under reduced pressure to give II. Yield 382 mg (1.01 mmol, 47%). Found: C, 60.22; H, 3.92. $C_{19}H_{15}FeO_3P$ calc.: C, 60.35; H, 4.00%.

[Cp(CO)Fe(COOMe){PPh₂(OEt)}] (IIIa)

To a solution of Ia (243 mg, 0.55 mmol) in MeOH (10 ml) was added NaOMe (60 mg, 1.11 mmol). After being stirred for several minutes, the solution was filtered to remove NaCl. The solvent was removed from the filtrate under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and insoluble materials (NaOMe) were removed by filtration. Then, the solvent was removed from the filtrate under reduced pressure to give IIIa. Yield 175 mg (0.40 mmol, 72%). The complex was so hygroscopic that correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

[Cp(CO)Fe(COOMe){PPh₂(OMe)}] (IIIb)

Complex IIIb was obtained from Ib and NaOMe in the same manner as IIIa. Yield 68%. The complex was also so hygroscopic that correct elemental analysis data could not be obtained.

[Cp(CO)Fe{PPh₂(OEt)}₂]Cl (IVa)

To a solution of $Cp(CO)_2FeCl$ (218 mg, 1.02 mmol) in benzene (3 ml) was added $PPh_2(OEt)$ (469 mg, 0.44 ml, 2.04 mmol). The reaction mixture was stirred at room temperature. A greenish yellow powder (Ia) was formed after about 0.5 h. Continuing stirring for further 0.5 h caused the formation of a yellow powder with the yield of the greenish yellow powder diminished. After being filtered and washed with benzene, the yellow powder was dissolved in a small amount of CH_2Cl_2 , loaded on a silica gel column, and eluted with CH_2Cl_2 , acetone, and EtOH in that order. The yellow band eluted with EtOH was collected and the solvent was removed under reduced pressure to give IVa as a yellow powder. Yield 546 mg (0.85 mmol, 83%). Found: C, 63.10; H, 5.49. $C_{34}H_{35}ClFeO_3P_2$ calc.: C, 63.32; H, 5.47%.

[Cp(CO)Fe{PPh₂(OMe)}₂]Cl (IVb)

Complex IVb was prepared from $Cp(CO)_2FeCl$ and $PPh_2(OMe)$ in the same manner as that for IVa. Yield 66%. Found: C, 62.40; H, 4.98. $C_{32}H_{31}ClFeO_3P_2$ calc.: C, 62.31; H, 5.07%.

[Cp(CO)Fe{PPh₂(OMe)}{P(O)Ph₂}] (V)

Complex IVb (194 mg, 0.31 mmol) was suspended in benzene (5 ml) and stirred for several hours at room temperature to give a homogeneous solution. The volatile materials were removed under reduced pressure to give V. Yield 156 mg (0.28 mmol, 87%), Found: C, 65.70; H, 4.89. $C_{31}H_{28}FeO_3P_2$ calc.: C, 65.74; H, 4.98%.

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