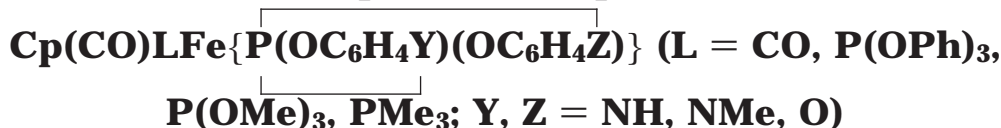


Novel Synthesis, X-ray Crystal Structures, and Spectroscopic Properties of Metalated Hypervalent Phosphorus Compounds,



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Iron phosphorane complexes, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})_2\}$ (**1a**, Y = NH; **1b**, Y = NMe; **3**, Y = O), have been prepared from $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{PF}_6$, *o*- $\text{HOC}_6\text{H}_4\text{YH}$, and a Lewis base. $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{NR})\}$ (**2a**, R = H; **2b**, R = Me) having two different chelates

on the phosphorus has been prepared from $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OPh})\}]\text{PF}_6$, *o*- $\text{HOC}_6\text{H}_4\text{NRH}$, and a Lewis base. These reactions involve nucleophilic attacks of an organic nucleophile at a trivalent phosphorus coordinated to an iron and substitution on the

phosphorus. During the course of preparation of **1b**, $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NMe})(\text{OC}_6\text{H}_4\text{NMeH})\}]\text{PF}_6$ (**4**) was isolated, which corresponds to one of the intermediates on the reaction pathways to give **1–3**. **4** reacts with a Lewis base to give **1b**. The reaction of

hydridophosphorane $\text{HP}(\text{OC}_6\text{H}_4\text{NH})_2$ with *n*-BuLi leads to NH proton abstraction to give the amide $\text{HP}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{N}^-)$, which then reacts with $\text{Cp}(\text{CO})\text{LFeCl}$ to yield $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ (**5**, L = P(OPh)₃; **6**, L = P(OMe)₃; **7**, L = PMe₃) by an apparent 1,2-

proton migration. The X-ray structures of **1b**, **2b**, and **4** were determined. **1b** and **2b** have slightly distorted trigonal-bipyramidal geometries around the phosphorus with the iron fragment in the equatorial position and have P–O_{eq} bonds longer than those of organophosphoranes, indicating that the $\text{Cp}(\text{CO})_2\text{Fe}$ fragment serves as a strong π donor. The Fe–P(phosphorane) bond rotates freely in solution even at -50°C . A Berry pseudorotation around the phosphorane phosphorus does not occur for **1a,b**, **2a,b**, and **5–7**, whereas it does for **3**.

Introduction

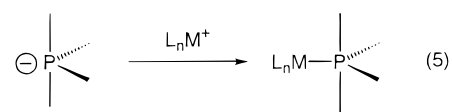
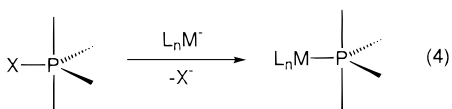
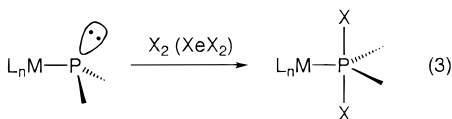
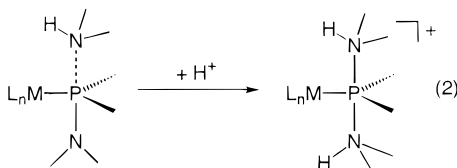
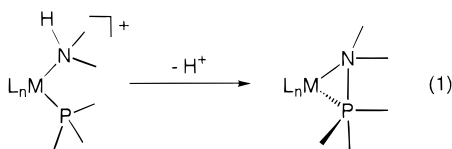
Pentacoordinate phosphorus compounds (phosphoranes) are one class of hypervalent compounds violating the octet rule and have attracted considerable attention in theoretical and experimental studies. In contrast to the widely explored chemistry of organic phosphoranes, a limited number of examples have been known to date for metallaphosphoranes, though they are also considered to be an important class of hypervalent phosphorus compounds.

The preparative methods for metallaphosphoranes which have been developed are roughly classified as follows: (1) deprotonation¹ and (2) protonation² at a nitrogen in polycyclic species with phosphine- and/or amine-metal bonds, (3) oxidative addition of halogen to transition-metal phosphide complexes³ (Sb and As⁴), (4) nucleophilic substitution at a phosphorane phosphorus atom by a transition-metal anion,⁵ and (5) electro-

philic attack of an electron-deficient transition-metal fragment at a phosphoranide⁶ (Sb⁷) (eqs 1–5). Some other preparative methods⁸ and review articles⁹ have been reported.

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We herein report an unprecedented synthetic method for metallaphosphoranes, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; Y, Z = NH, NMe, O; although the complex should be described as $\text{Cp}(\text{CO})_2\text{Fe}\{\overline{\text{P}}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$, the tie bars are omitted in this paper for simplicity), involving the nucleophilic attack of an organic nucleophile at a trivalent phosphorus coordinated to a transition metal. Also reported is the synthesis of $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ ($\text{L} = \text{P}(\text{OPh})_3$, $\text{P}(\text{OMe})_3$, PMe_3) by the reaction of $\text{Cp}(\text{CO})\text{LFeCl}$ with $[\text{HP}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{N}^-)]$ involving an apparent 1,2-proton migration from P to N. On the basis of the structural and spectroscopic data for a series of iron-phosphorane complexes formulated as $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$, we discuss the effect of substituents on both the iron and the phosphorus atoms on

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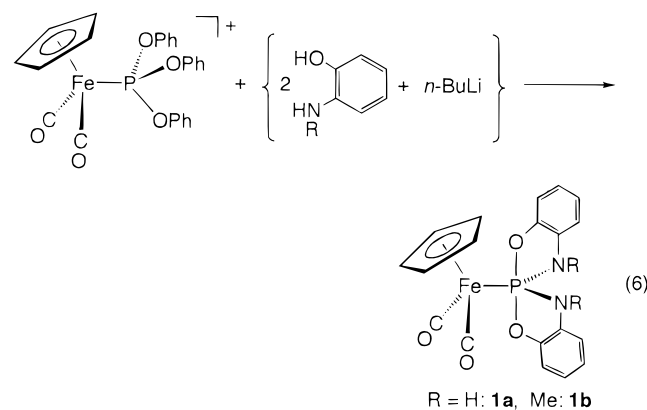
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the nature of the Fe-phosphorane P bond. A part of this work has been previously communicated.¹⁰

Results and Discussion

Formation of $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$. The synthesis and characterization of the metallaphosphoranes are described with $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ (**1a**) as an example. $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{PF}_6$ was treated with a reaction mixture of 2 equiv of *o*- $\text{HOC}_6\text{H}_4\text{NH}_2$ and 1 equiv of *n*-BuLi to give a yellow powder of **1a** in considerable yield (56%) (eq 6).



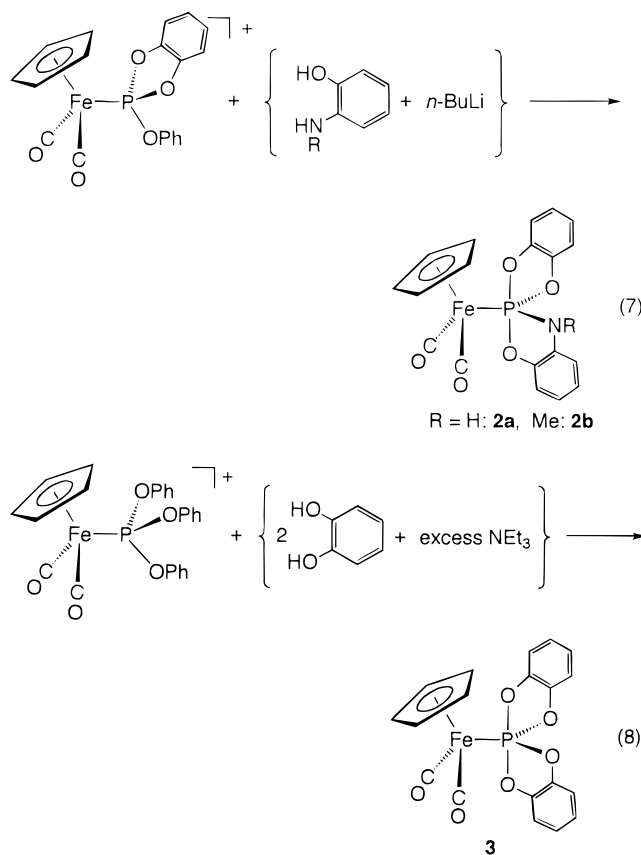
The formation of **1a** was verified by the following spectroscopic data. (i) In the IR spectrum, two absorption bands due to ν_{CO} were observed at 2026 and 1977 cm^{-1} , indicating that the product is electrically neutral. (ii) The presence of a $\text{P}(\text{OC}_6\text{H}_4\text{NH})_2$ group in the product was supported by the observation of a singlet at 24.18 ppm in the proton-decoupled ^{31}P NMR spectrum. The resonance is at a higher field by ca. 136 ppm than that of the starting material, indicating that the phosphorus in the product has a higher valency, and it became a triplet ($J_{\text{PH}} = 19.9$ Hz) in the proton-nondecoupled spectrum, showing the presence of two NH groups on the phosphorus. (iii) A broad doublet at 5.20 ppm ($J_{\text{PH}} = 17.2$ Hz) assigned to NH was observed in the ^1H NMR spectrum together with Cp and substituted phenyl ring signals, as expected.

With some modifications, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NMe})_2\}$ (**1b**; 87% yield) (eq 6) and $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})_2\}$ (**3**; 66% yield) (eq 8) were similarly prepared from $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{PF}_6$. Treatment of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OPh})\}]\text{PF}_6$ with 1 equiv of *o*- $\text{HOC}_6\text{H}_4\text{NRH}$ in the presence of *n*-BuLi gave $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{NR})\}$ ($\text{R} = \text{H}$, **2a**, 87% yield; $\text{R} = \text{Me}$, **2b**, 47% yield) (eq 7). Table 1 summarizes the IR (ν_{CO}) and ^1H , ^{31}P , and ^{13}C NMR data for metallaphosphoranes **1a, b**, **2a, b**, and **3**.

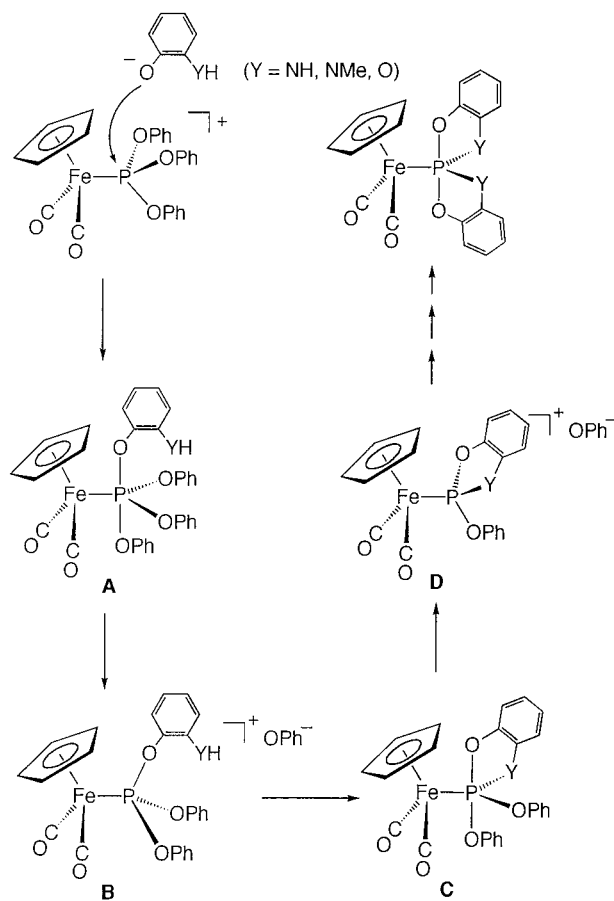
It should be noted in these reactions that the valence of the phosphorus is formally expanded from III to V presumably without Fe-P bond cleavage; that is, the nature of the Fe-P bond changes formally from dative to covalent.

The reaction mechanism is proposed in Scheme 1. $[\text{o-OC}_6\text{H}_4\text{YH}]^-$, produced from *o*- $\text{HOC}_6\text{H}_4\text{YH}$ and a base, nucleophilically attacks the phosphorus atom of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]^+$ to give a metallaphosphorane (**A**),

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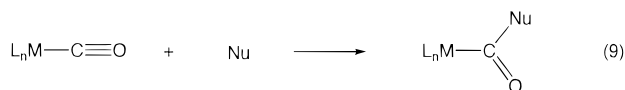


Scheme 1



followed by release of OPh^- to yield a cationic iron complex (**B**). The released OPh^- abstracts the YH proton of **B** to yield the Y^- group, which then nucleophilically attacks the P atom to give **C**, followed by release of OPh^- to obtain **D**. This OPh^- reacts with the remaining unreacted $o\text{-HOC}_6\text{H}_4\text{YH}$ to give $[o\text{-OC}_6\text{H}_4\text{YH}]^-$, which undergoes similar reactions leading finally to the formation of $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})_2\}$. In eq 6, 2 equiv of $o\text{-HOC}_6\text{H}_4\text{YH}$ was necessary, but 1 equiv of a base based on the cationic iron complex was sufficient, which is consistent with the mechanism. The proposed intermediates **A–D** have not been observed even spectroscopically, presumably due to their high reactivity.

It is well-known for cationic transition-metal carbonyl complexes that a Lewis base nucleophilically attacks a coordinated carbonyl carbon (eq 9). For example, the



reactions with OR^- ,^{11,12} NR_2^- ,¹² OH^- ,^{11,13} and R^- ¹⁴ anions give alkoxy-carbonyl, carbamoyl, metalcarboxylic acid, and acyl (aroyl) complexes, respectively. However, in our case, the reaction site is not a carbonyl carbon but a phosphite phosphorus.¹⁵ Nucleophilic attack of F^- ,¹⁶ H^- ,¹⁷ or OH^- ¹⁸ anion at a trivalent phosphorus atom coordinated to a transition metal has been proposed. However, the expected pentavalent

phosphorus species has not been observed. Our results in this paper point to the possibility of such a reaction.

In the reaction of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{PF}_6$, $o\text{-HO-C}_6\text{H}_4\text{NMeH}$, and $n\text{-BuLi}$ in the hope of **1b** formation, we encountered the isolation of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NMe})(\text{OC}_6\text{H}_4\text{NMeH})\}]\text{PF}_6$ (**4**), which has a trivalent phosphorus ligand with a dangling NMeH group. The IR and ^{31}P NMR spectra of the reaction mixture show the formation of **1b**. However, removal of volatile components from the mixture and then addition of ether to the residue caused the formation of **4** as a yellow powder (67% yield). The IR spectrum exhibits two CO stretching bands at 2076 and 2033 cm^{-1} , indicating the formation of a cationic complex. The ^{31}P NMR spectrum shows a singlet at 173.56 ppm, which is at 157 ppm

(15) The ^{31}P NMR spectrum measured after stirring of the reaction mixture of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OPh})_3\}]\text{PF}_6$ and $[o\text{-OC}_6\text{H}_4\text{NH}_2]^-$ at room temperature for 1 h showed a strong singlet at 175.34 ppm together with singlets for the starting complex and the final product (**1a**), and the ratio was approximately 7:1:1. The complex may be an aryloxy carbonyl complex, $\text{Cp}(\text{CO})\text{Fe}\{\text{C}(\text{O})\text{OC}_6\text{H}_4\text{NH}_2\}\{\text{P}(\text{OPh})_3\}$, on the basis of reactions of similar complexes with other anions.^{11–14} The IR spectrum of the reaction mixture also supports the formation of the aryloxy carbonyl complex: ν_{CO} 1953 cm^{-1} for the terminal CO (ν_{CO} for the $\text{FeC}(\text{O})\text{OC}_6\text{H}_4\text{NH}_2$ fragment was not identified due to the complexity in the region). The aryloxy carbonyl complex disappeared after stirring overnight at room temperature, and the amount of **1a** increased instead. Therefore, it is highly likely that the reaction pathway to the aryloxy carbonyl complex is reversible; i.e., it equilibrates with the starting complex, whereas the reaction pathway to **1a** is irreversible. In our case, an aryloxy carbonyl complex may be a kinetic product and a metallaphosphorane is a thermodynamic product.

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Table 1. Spectroscopic Data

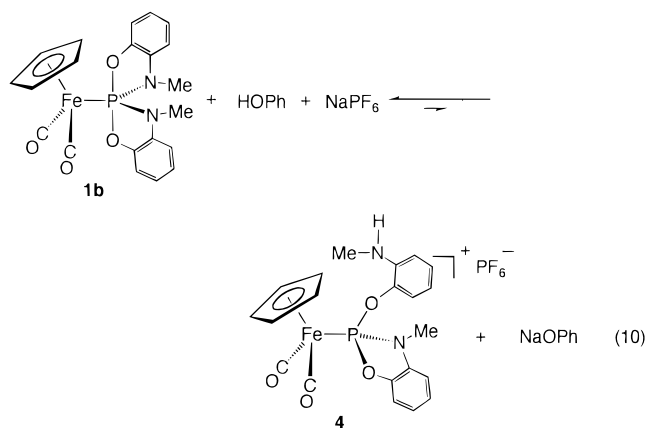
complex	IR ν_{CO} , cm^{-1} (in THF)	^1H NMR, ppm (in CDCl_3)	^{31}P NMR, ppm (in THF)	^{13}C NMR, ppm (in CDCl_3)
1a	2026	4.94 (d, $J_{\text{PH}} = 1.1$ Hz, 5H, C_5H_5)	24.18 (t, $J_{\text{PH}} = 19.9$ Hz)	85.31 (s, C_5H_5)
	1977	5.20 (d, $J_{\text{PH}} = 17.2$ Hz, 2H, NH) 6.60–6.66 (m, 8H, $\text{OC}_6\text{H}_4\text{N}$)		108.55 (d, $J_{\text{PC}} = 12.9$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 108.69 (s, $\text{OC}_6\text{H}_4\text{N}$) 118.73 (s, $\text{OC}_6\text{H}_4\text{N}$) 119.27 (s, $\text{OC}_6\text{H}_4\text{N}$) 132.46 (d, $J_{\text{PC}} = 11.0$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 149.55 (d, $J_{\text{PC}} = 5.5$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 210.96 (d, $J_{\text{PC}} = 42.3$ Hz, CO) 212.62 (d, $J_{\text{PC}} = 44.1$ Hz, CO)
1b	2024	3.20 (d, $J_{\text{PH}} = 7.7$ Hz, 6H, NCH_3)	16.29 (sep, $J_{\text{PH}} = 7.6$ Hz)	32.96 (d, $J_{\text{PC}} = 3.8$ Hz, NCH_3)
	1975	4.86 (d, $J_{\text{PH}} = 0.7$ Hz, 5H, C_5H_5) 6.51–6.77 (m, 8H, $\text{OC}_6\text{H}_4\text{N}$)		84.67 (s, C_5H_5) 107.48 (s, $\text{OC}_6\text{H}_4\text{N}$) 107.60 (d, $J_{\text{PC}} = 8.7$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 118.14 (s, $\text{OC}_6\text{H}_4\text{N}$) 119.05 (s, $\text{OC}_6\text{H}_4\text{N}$) 136.75 (d, $J_{\text{PC}} = 16.1$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 149.44 (d, $J_{\text{PC}} = 9.4$ Hz, $\text{OC}_6\text{H}_4\text{N}$) 210.99 (d, $J_{\text{PC}} = 44.1$ Hz, CO) 213.09 (d, $J_{\text{PC}} = 46.6$ Hz, CO)
2a	2034	5.01 (s, 5H, C_5H_5)	48.50 (d, $J_{\text{PH}} = 21.3$ Hz)	85.19 (s, C_5H_5)
	1988	5.52 (d, $J_{\text{PH}} = 17.1$ Hz, 1H, NH) 6.66–6.99 (m, 8H, $\text{OC}_6\text{H}_4\text{O}$ and $\text{OC}_6\text{H}_4\text{N}$)		108.74 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 108.85 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 109.41 (d, $J_{\text{PC}} = 5.0$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 111.14 (d, $J_{\text{PC}} = 11.0$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 118.60 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 118.98 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 119.84 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 122.24 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 131.33 (d, $J_{\text{PC}} = 11.0$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 143.74 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 148.41 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 149.36 (d, $J_{\text{PC}} = 7.4$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 210.28 (d, $J_{\text{PC}} = 44.1$ Hz, CO) 211.43 (d, $J_{\text{PC}} = 44.1$ Hz, CO)
2b	2033	3.28 (d, $J_{\text{PH}} = 8.1$ Hz, 3H, NCH_3)	45.39 (qua, $J_{\text{PH}} = 6.1$ Hz)	32.59 (d, $J_{\text{PC}} = 4.4$ Hz, NCH_3)
	1985	4.96 (s, 5H, C_5H_5) 6.59–6.97 (m, 8H, $\text{OC}_6\text{H}_4\text{O}$ and $\text{OC}_6\text{H}_4\text{N}$)		84.94 (s, C_5H_5) 107.89 (d, $J_{\text{PC}} = 1.9$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 108.25 (d, $J_{\text{PC}} = 9.3$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 108.99 (d, $J_{\text{PC}} = 1.8$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 110.80 (d, $J_{\text{PC}} = 11.2$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 118.83 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 119.07 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 119.19 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 121.81 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 135.60 (d, $J_{\text{PC}} = 17.4$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 143.79 (s, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 148.20 (d, $J_{\text{PC}} = 3.1$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 149.34 (d, $J_{\text{PC}} = 9.4$ Hz, $\text{OC}_6\text{H}_4\text{O}$ or $\text{OC}_6\text{H}_4\text{N}$) 210.07 (d, $J_{\text{PC}} = 44.1$ Hz, CO) 211.89 (d, $J_{\text{PC}} = 45.3$ Hz, CO)
3	2042	5.04 (s, 5H, C_5H_5)	73.51 (s)	85.17 (s, C_5H_5)
	1996	6.81 (s, 4H, $\text{OC}_6\text{H}_4\text{O}$) 6.91 (s, 4H, $\text{OC}_6\text{H}_4\text{O}$)		110.18 (d, $J_{\text{PC}} = 9.2$ Hz, $\text{OC}_6\text{H}_4\text{O}$) 120.81 (s, $\text{OC}_6\text{H}_4\text{O}$) 145.30 (s, $\text{OC}_6\text{H}_4\text{O}$) 209.83 (d, $J_{\text{PC}} = 45.9$ Hz, CO)

lower field than that of **1b**, suggesting that the phosphorus adopts a lower valency. In the ^1H NMR spectrum, two methyl proton signals are observed; one is a doublet due to coupling with phosphorus, and the other is a singlet. The structure of **4** is confirmed by its X-ray analysis (vide infra).

The isolated complex **4** corresponds to one of the intermediates, which is, however, omitted in Scheme 1 for brevity. In a THF solution, **1b** may be in equilibrium with **4** but the equilibrium is considerably shifted toward **1b** (eq 10). Complex **4** is sparingly soluble in ether, which results in the isolation of **4** in considerable yield. If the H–N(1) proton in **4** is expected to be more acidic than an H–O proton in HOPh, **4** would react with

NaOPh to give **1b** together with HOPh and NaPF_6 . Actually, the reaction of **4** with NaOPh in THF was confirmed to give **1b**. In the cases of **1a**, **2a**, **2b**, and **3**, the corresponding cationic complex was not obtained even in an ether solution. The reason may be the high solubility in ether of the cationic complex to be formed and/or lower basicity of N or O atom(s) on the phosphorus of these complexes compared with the N basicity in **1b**.

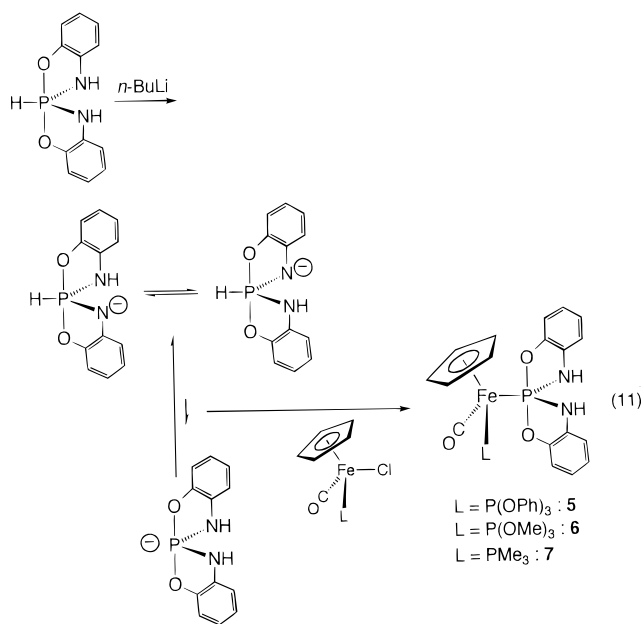
Formation of $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$. Systematic change in the substituents from electron-withdrawing groups to electron-donating groups on the transition metal as well as on the phosphorane phosphorus may help in understanding the nature of the



Fe–P(phosphorane) bond. Thus, we attempted to prepare Cp(CO)LFe{P(OC₆H₄NH)₂} (L = phosphine, phosphite).

The reaction of [Cp(CO)LFe{P(OPh)₃}]PF₆ (L = P(OPh)₃, P(OMe)₃, PMe₃) with *o*-HOC₆H₄NH₂ in the presence of *n*-BuLi was first examined. Monitoring of the reaction mixture by the ³¹P NMR spectra revealed that several reactions take place simultaneously, but the desired iron phosphorane complex was not obtained. The replacement of CO (a good π acceptor) by L (an electron-donating ligand compared with CO) makes the P atom in a P(OPh)₃ ligand electron-rich, which may result in its resisting the nucleophilic attack of [o-OC₆H₄NH₂]⁻.

We sought another preparative method and found that the reaction of HP(OC₆H₄NH)₂ with *n*-BuLi and then Cp(CO)LFeCl leads to the formation of Cp(CO)LFe{P(OC₆H₄NH)₂} (eq 11). In the reaction of HP-



(OC₆H₄NH)₂ with *n*-BuLi, the product is not the phosphoranide ⁻P(OC₆H₄NH)₂ but the amide HP(OC₆H₄NH)(OC₆H₄N⁻), which was deduced from the ³¹P NMR spectra. The product shows a broad singlet at -27.30 ppm, which becomes a doublet with *J*_{PH} = 726 Hz without proton irradiation. The large coupling constant indicates the presence of a P–H bond: for example, HP(OC₆H₄NH)₂ shows a doublet of triplets at -46.14 ppm

Table 2. ³¹P NMR Data^a

complex	NMR, ppm
1a	24.18 (t, <i>J</i> _{PH} = 19.9 Hz)
5	27.09 (dt, <i>J</i> _{PP} = 149.5 Hz, <i>J</i> _{PH} = 18.3 Hz, P(V)) 169.31 (d, <i>J</i> _{PP} = 149.6 Hz, P(III))
5'	30.00 (dt, <i>J</i> _{PP} = 158.7 Hz, <i>J</i> _{PH} = 18.3 Hz, P(V)) 170.41 (d, <i>J</i> _{PP} = 158.7 Hz, P(III))
6	33.89 (dt, <i>J</i> _{PP} = 150.9 Hz, <i>J</i> _{PH} = 18.2 Hz, P(V)) 180.65 (d, <i>J</i> _{PP} = 150.9 Hz, P(III))
6'	35.34 (dt, <i>J</i> _{PP} = 165.5 Hz, <i>J</i> _{PH} = 18.9 Hz, P(V)) 182.96 (d, <i>J</i> _{PP} = 164.2 Hz, P(III))
7	37.78 (d, <i>J</i> _{PP} = 104.6 Hz, P(III))
7'	39.41 (dt, <i>J</i> _{PP} = 104.6 Hz, <i>J</i> _{PH} = 15.2 Hz, P(V)) 38.11 (d, <i>J</i> _{PP} = 104.6 Hz, P(III)) 42.73 (dt, <i>J</i> _{PP} = 104.6 Hz, <i>J</i> _{PH} = 15.8 Hz, P(V))

^a In THF.

(*J*_{PH} = 814.8 and 21.3 Hz). Therefore, it can be said in the reaction of HP(OC₆H₄NH)₂ with a Lewis base that the P–H bond remains intact and an amino proton is selectively abstracted to give the amide HP(OC₆H₄NH)(OC₆H₄N⁻), where the remaining amino proton is shuttling rapidly between the two N atoms.

The amide thus formed reacts with Cp(CO)LFeCl in THF to give Cp(CO)LFe{P(OC₆H₄NH)₂} (L = P(OPh)₃ (**5**), P(OMe)₃ (**6**), PMe₃ (**7**)). The phosphorane complex is the main product, but some unidentified compounds are also produced. Although several attempts to isolate **5** and **6** in a pure form failed, due to the difficulty of purification without decomposition, the formation is strongly supported by the ³¹P NMR data shown in Table 2. **7** could be isolated and the spectroscopic data were obtained, though satisfactory elemental analysis data could not be obtained due to its high reactivity. These metallaphosphoranes show two doublets in the penta-coordinate phosphorus region and two doublets in the coordinating phosphite or phosphine region. The observation is rationalized by diastereomer formation due to the Fe and P chiral centers. In the ³¹P NMR spectra without proton irradiation, the two doublets in the phosphorane region become two doublets of triplets, which is consistent with the presence of an Fe–P(OC₆H₄NH)₂ moiety.

In the reaction of HP(OC₆H₄NH)(OC₆H₄N⁻) with Cp(CO)LFeCl, if a nucleophilic attack of the amido nitrogen on the iron takes place, the iron amido complex HP(OC₆H₄NH)(OC₆H₄N{FeL(CO)Cp}) would be formed. This is not the case. Two explanations seem to be possible. (i) HP(OC₆H₄NH)(OC₆H₄N{FeL(CO)Cp}) is first formed, and then an H on the phosphorus and an FeL(CO)Cp moiety exchange positions in some way. (ii) Although only HP(OC₆H₄NH)(OC₆H₄N⁻) is observed in the ³¹P NMR spectrum, a phosphoranide, ⁻P(OC₆H₄NH)₂, exists in solution as an equilibrium species with the amide, and the equilibrium lies on the side of the amide. If the phosphoranide is much more reactive than the amide toward Cp(CO)LFeCl, then the phosphoranide selectively reacts to give an iron phosphorane complex eventually as the main product. It is not clear now which route is correct. However, route ii seems appropriate because of our following observations. (a) HP(OC₆H₄NH)(OC₆H₄N⁻) reacts with MeI to give MeP(OC₆H₄NH)₂ selectively. (b) For HP(OC₆H₄NMe)₂, an exchange reaction between an H on the phosphorus and an Me on the nitrogen has not been observed.

X-ray Structures of 1b, 2b, and 4. The structures of **1b**, **2b**, and **4** were determined by X-ray diffraction

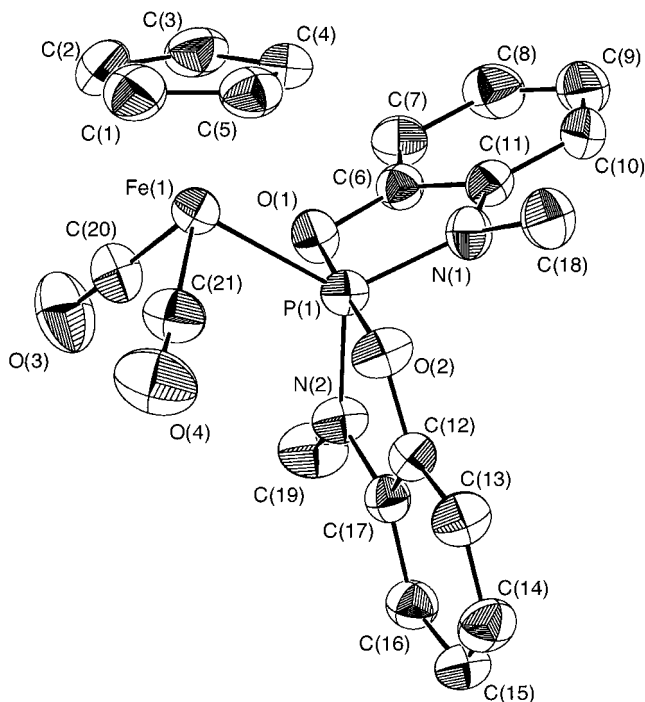


Figure 1. ORTEP drawing of **1b** (50% probability ellipsoids), showing the numbering system. All hydrogen atoms are omitted for clarity.

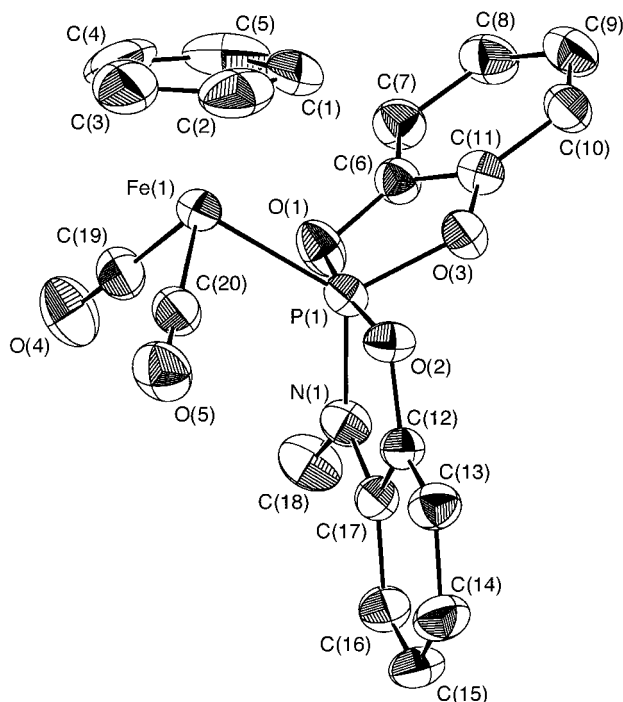


Figure 2. ORTEP drawing of **2b** (50% probability ellipsoids), showing the numbering system. All hydrogen atoms are omitted for clarity.

analyses, and the ORTEP drawings are displayed in Figures 1, 2, and 3, respectively. The crystal data and the selected bond lengths and angles are listed in Tables 3–6.

These complexes have normal piano-stool configurations; the iron has a cyclopentadienyl ligand bonded in an η^5 fashion, two terminal CO ligands, and a phosphorus ligand.

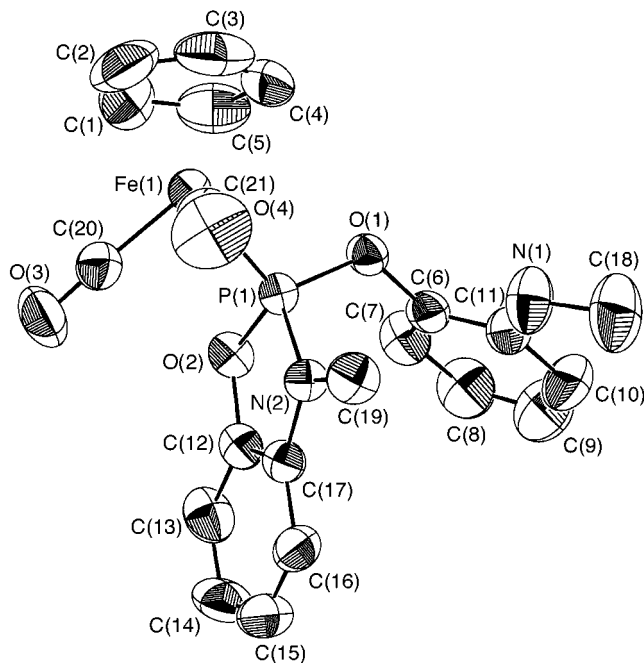


Figure 3. ORTEP drawing of **4** (50% probability ellipsoids), showing the numbering system. All hydrogen atoms and the PF_6^- counterion are omitted for clarity.

For both metallaphosphoranes **1b** and **2b**, the five-coordinate phosphorus adopts a trigonal-bipyramidal (tbp) geometry with two oxygen atoms in the apical positions and with the iron atom in one equatorial position. The tbp geometry is slightly distorted: the two apical bonds bend away from the iron fragment (the $\text{O}_{\text{ap}}-\text{P}-\text{O}_{\text{ap}}$ angle is 176.0° for **1b** and 171.6° for **2b**), and in the equatorial plane, the angles of $\text{Fe}-\text{P}-\text{N}_{\text{eq}}$ and $\text{Fe}-\text{P}-\text{O}_{\text{eq}}$ (121.4 – 124.1°) are slightly greater than the ideal angle (120°), though the sum of the equatorial angles is 359.9° for **1b** and 360.0° for **2b**. The distortion may arise from the apical–equatorial five-membered-ring strain and/or a steric demand of the iron fragment.

The geometry around nitrogen (N1 and N2 for **1b** and N1 for **2b**) is planar. The $\text{O}1-\text{P}1-\text{O}2$ bond is in the same plane as the nitrogens and the three atoms directly bonded to the nitrogens. Therefore, the nitrogen undergoes sp^2 hybridization and the lone-pair electrons are located on the equatorial plane, implying π donation of the lone-pair electrons to equatorial σ^* orbitals on the phosphorus.^{19–22} The observed $\text{Fe}-\text{P}$ bond lengths (2.291 \AA for **1b** and 2.272 \AA for **2b**) are close to that of the only precedent of iron phosphorane (2.300 \AA).⁶

The X-ray structure of $\text{HP}(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{NMe})$ was reported by Holmes.²³ Because this hydridophosphorane corresponds to the nonmetalated version of **2b**, the comparison of these two structures should be informative when we consider the effect of a transition-metal

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Table 3. Summary of Crystal Data for 1b, 2b, and 4

	1b	2b	4
formula	C ₂₁ H ₁₉ O ₄ N ₂ FeP	C ₂₀ H ₁₆ O ₅ NFeP	C ₂₁ H ₂₀ O ₄ N ₂ F ₆ FeP ₂
fw	450.21	437.17	596.20
cryst syst	monoclinic	triclinic	triclinic
space group	<i>P2/a</i>	<i>P1</i>	<i>P1</i>
<i>a</i> , Å	20.829(6)	9.963(3)	10.378 (6)
<i>b</i> , Å	7.280(3)	10.124(3)	11.483 (5)
<i>c</i> , Å	13.056(4)	10.495(4)	12.219 (5)
α, deg		83.86(3)	114.51 (3)
β, deg	91.39(2)	61.87(3)	106.64 (4)
γ, deg		78.76(2)	94.74 (4)
<i>V</i> , Å ³	1979.2(10)	915.5(5)	1235.1 (10)
<i>Z</i>	4	2	2
<i>D</i> _{calcd} , g m ⁻³	1.511	1.586	1.603
μ, cm ⁻¹	8.689	9.392	8.104
cryst size, mm	0.48 × 0.30 × 0.20	0.38 × 0.35 × 0.25	0.43 × 0.33 × 0.25
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
scan technique	ω-2θ	ω-2θ	ω-2θ
scan range, deg	3 < 2θ < 55	3 < 2θ < 55	3 < 2θ < 55
no. of unique data	4554	4210	5411
no. of unique data with <i>F</i> _o > 3σ(<i>F</i> _o)	3705	3649	4235
<i>R</i> ^a	0.037	0.044	0.070
<i>R</i> _w ^b	0.048	0.054	0.064
<i>F</i> _A , <i>F</i> _B ^b	10.0, 0.00030	10.0, 0.00030	3.0, 0

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$ and $w = \exp(F_A(\sin^2 \theta) / \lambda^2) / (\sigma^2(F_o) + F_B F_o^2)$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for 1b

Bond Lengths			
Fe(1)–P(1)	2.291(1)	Fe(1)–C(20)	1.770(2)
Fe(1)–C(21)	1.764(2)	P(1)–O(1)	1.774(1)
P(1)–O(2)	1.757(1)	P(1)–N(1)	1.721(1)
P(1)–N(2)	1.722(1)	O(1)–C(6)	1.352(2)
O(2)–C(12)	1.355(2)	O(3)–C(20)	1.134(2)
O(4)–C(21)	1.143(2)	N(1)–C(11)	1.392(2)
N(1)–C(18)	1.462(2)	N(2)–C(17)	1.395(2)
N(2)–C(19)	1.453(2)	C(6)–C(11)	1.396(2)
C(12)–C(17)	1.397(2)		
Bond Angles			
P(1)–Fe(1)–C(20)	88.8(1)	P(1)–Fe(1)–C(21)	92.8(1)
C(20)–Fe(1)–C(21)	93.4(1)	Fe(1)–P(1)–O(1)	90.1(1)
Fe(1)–P(1)–O(2)	93.8(1)	Fe(1)–P(1)–N(1)	124.1(1)
Fe(1)–P(1)–N(2)	122.1(1)	O(1)–P(1)–O(2)	176.0(1)
O(1)–P(1)–N(1)	87.4(1)	O(1)–P(1)–N(2)	90.4(1)
O(2)–P(1)–N(1)	90.3(1)	O(2)–P(1)–N(2)	87.6(1)
N(1)–P(1)–N(2)	113.7(1)	P(1)–O(1)–C(6)	113.8(1)
P(1)–O(2)–C(12)	113.3(1)	P(1)–N(1)–C(11)	114.7(1)
P(1)–N(1)–C(18)	127.5(1)	C(11)–N(1)–C(18)	117.4(1)
P(1)–N(2)–C(17)	113.7(1)	P(1)–N(2)–C(19)	127.9(1)
C(17)–N(2)–C(19)	117.2(1)	O(1)–C(6)–C(11)	112.5(1)
N(1)–C(11)–C(6)	111.1(1)	O(2)–C(12)–C(17)	112.3(1)
N(2)–C(17)–C(12)	110.8(1)	Fe(1)–C(20)–O(3)	178.8(2)
Fe(1)–C(21)–O(4)	176.9(2)		

fragment on a phosphorane. As we go from the hydriphosphorane to the iron phosphorane (**2b**), although every bond around the phosphorus is lengthened, the remarkable elongation of P–O_{ap} is notable (0.122 Å elongation for two P–O_{ap} bonds vs 0.070 Å elongation for the P–O_{eq} and P–N_{eq} bonds). It has been reported^{6,8} that the π-donating ability of a transition-metal substituent in an equatorial site of a phosphorane may be responsible for apical bond elongation. In our cases of **1b** and **2b**, the orientation of the Cp(CO)₂Fe fragment strongly supports its π back-donation. According to the calculation by Hoffmann,²⁴ the HOMO of the Cp(CO)₂-Fe⁺ fragment has π symmetry, as illustrated in Figure 4. If a phosphorane fragment accepts π-electron density into the σ* orbital of the P–O_{ap} bond, the σ* orbital

Table 5. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for 2b

Bond Lengths			
Fe(1)–P(1)	2.272(1)	Fe(1)–C(19)	1.772(1)
Fe(1)–C(20)	1.775(1)	P(1)–O(1)	1.799(1)
P(1)–O(2)	1.745(1)	P(1)–O(3)	1.675(1)
P(1)–N(1)	1.703(1)	O(1)–C(6)	1.344(1)
O(2)–C(12)	1.352(1)	O(3)–C(11)	1.371(1)
O(4)–C(19)	1.139(2)	O(5)–C(20)	1.129(1)
N(1)–C(17)	1.388(1)	N(1)–C(18)	1.463(1)
C(6)–C(11)	1.388(1)	C(12)–C(17)	1.403(1)
Bond Angles			
P(1)–Fe(1)–C(19)	89.5(1)	P(1)–Fe(1)–C(20)	92.0(1)
C(19)–Fe(1)–C(20)	94.5(1)	Fe(1)–P(1)–O(1)	92.0(1)
Fe(1)–P(1)–O(2)	95.7(1)	Fe(1)–P(1)–O(3)	121.4(1)
Fe(1)–P(1)–N(1)	123.8(1)	O(1)–P(1)–O(2)	171.6(1)
O(1)–P(1)–O(3)	88.3(1)	O(1)–P(1)–N(1)	90.1(1)
O(2)–P(1)–O(3)	84.7(1)	O(2)–P(1)–N(1)	88.6(1)
O(3)–P(1)–N(1)	114.8(1)	P(1)–O(1)–C(6)	111.7(1)
P(1)–O(2)–C(12)	113.8(1)	P(1)–O(3)–C(11)	114.6(1)
P(1)–N(1)–C(17)	114.5(1)	P(1)–N(1)–C(18)	127.9(1)
C(17)–N(1)–C(18)	117.4(1)	O(1)–C(6)–C(11)	112.3(1)
O(3)–C(11)–C(6)	112.4(1)	O(2)–C(12)–C(17)	112.3(1)
N(1)–C(17)–C(12)	110.8(1)	Fe(1)–C(19)–O(4)	178.3(1)
Fe(1)–C(20)–O(5)	176.8(1)		

should overlap with the HOMO orbital shown in Figure 4. This is the case observed in the X-ray structures of **1b** and **2b**.

It can be considered that the Fe–P bond in an iron phosphorane complex consists of σ donation from P to Fe and π back-donation from Fe to P. The substituents on the phosphorus in **1b** are two amino and two aryloxy groups, whereas those in **2b** are one amino and three aryloxy groups. Therefore, supposing that the σ donation is a dominant factor concerning the Fe–P bond, the bond would be shorter for **1b** than for **2b**, and oppositely, if the π back-donation is dominant, the bond would be shorter for **2b** than for **1b**. The X-ray analyses revealed that the Fe–P bond is ca. 0.02 Å shorter for **2b** than for **1b**, indicating that the π back-donation is more important in the Fe–P bond. This is also supported by the IR data. The ν_{CO} stretching bands of **2b** (2033 and 1985 cm⁻¹) are at a higher frequency than those of **1b** (2024 and 1975 cm⁻¹).

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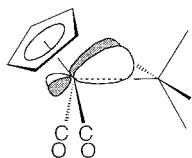


Figure 4. HOMO of the Cp(CO)₂Fe fragment.

Table 6. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for **4**

Bond Lengths			
Fe(1)–P(1)	2.161(1)	Fe(1)–C(20)	1.771(3)
Fe(1)–C(21)	1.789(3)	P(1)–O(1)	1.602(2)
P(1)–O(2)	1.625(2)	P(1)–N(2)	1.651(2)
O(1)–C(6)	1.430(3)	O(2)–C(12)	1.405(3)
O(3)–C(20)	1.143(3)	O(4)–C(21)	1.119(4)
N(2)–C(17)	1.395(3)	N(2)–C(19)	1.462(3)
C(12)–C(17)	1.365(3)		
Bond Angles			
P(1)–Fe(1)–C(20)	88.5(1)	P(1)–Fe(1)–C(21)	94.3(1)
C(20)–Fe(1)–C(21)	94.1(2)	Fe(1)–P(1)–O(1)	112.6(1)
Fe(1)–P(1)–O(2)	111.3(1)	Fe(1)–P(1)–N(2)	122.4(1)
O(1)–P(1)–O(2)	106.1(1)	O(1)–P(1)–N(2)	108.4(1)
O(2)–P(1)–N(2)	93.5(1)	P(1)–O(1)–C(6)	120.7(2)
P(1)–O(2)–C(12)	111.3(2)	C(11)–N(1)–C(18)	121.8(3)
P(1)–N(2)–C(17)	112.2(2)	P(1)–N(2)–C(19)	126.7(2)
C(17)–N(2)–C(19)	121.0(2)	O(2)–C(12)–C(17)	112.5(2)
N(2)–C(17)–C(12)	110.3(2)	Fe(1)–C(20)–O(3)	177.3(3)
Fe(1)–C(21)–O(4)	176.5(3)		

The X-ray structure of **4** (Figure 3) revealed that **4** is a normal iron complex containing an amino-substituted phosphite. It should be noted here that no transannular interaction between N(1) and P(1) is observed. The phosphorus atom adopts a distorted-tetrahedral geometry, in which the O(2)–P(1)–N(2) angle is reduced to 93.5°, probably due to the five-membered ring. The C(18)–N(1)–C(11) angle is 121.8°, and the C(18)–N(1)–C(11)–C(10) torsion angle is 4.9°, indicating that N(1) undergoes sp² hybridization and the lone-pair electrons are delocalized into the attached phenyl ring.

Rotation along the Fe–P(phosphorane) Bond. With phosphoranes, a π-electron-donating substituent favors assuming an equatorial position. In an equatorial position, two types of π interactions are conceivable: (i) π donation to the σ* orbital of an equatorial bond and (ii) that of an apical bond. Theoretical studies^{19–22} suggest that an amino group energetically favors the type i interaction. In addition, in the cases of **1b** and **2b**, the five-membered ring connecting apical and equatorial positions sterically allows the amino substituent to have only a type i interaction. The restriction may make the iron fragment undergo a type ii interaction in the solid state, although a transition-metal fragment would basically favor the type i interaction. Therefore, the difference between types i and ii in energy with respect to the iron fragment is expected to be small. In solution, the free rotation of the Fe–P bond is deduced from NMR measurements. For example, the ¹H NMR spectrum of **1b** showed only one doublet due to NMe (Table 1). If **1b** in solution retains the structure observed in the solid state, the two NMe groups should not be magnetically equivalent. The Fe–P rotation did not cease even at –50 °C.

Rearrangement at Phosphorane Phosphorus. It is well-known for pentacoordinate phosphorus that apical–equatorial rearrangement takes place readily.²⁵ The widely accepted mechanism for the polytopal rear-

angement is a Berry pseudorotation. Experimental and theoretical investigations have been reported for organophosphoranes, but little has been done for metalated phosphoranes. Iron phosphorane complexes in this study have two five-membered rings involving the phosphorus, resulting in the creation of a chiral center at the phosphorus in principle. Therefore, the polytopal rearrangement corresponds to the racemization.

The ¹³C NMR spectra of **1a**, **1b**, **2a**, and **2b** at room temperature exhibit two doublets in the CO region. These observations indicate that the two carbonyl ligands are diastereotopic; in other words, racemization at the phosphorus does not occur on the NMR time scale. The racemization was not observed even at 100 °C. In contrast, the ¹³C NMR spectrum for **3** shows one doublet assignable to CO even at –50 °C, showing that **3** undergoes rapid racemization.

It is highly likely that the racemization takes place by Berry pseudorotation. Complexes **1a** and **1b** require five transformation pathways, and **2a** and **2b** require two pathways to complete the racemization. During the interconversion, some tpb configurations have to have an amino and/or an iron group in apical position(s), though these groups prefer an equatorial position to an apical position and, in addition, have to have a five-membered chelate ring connecting two equatorial positions. Therefore, when the rings contain two different atoms bonded to phosphorus, high-energy intermediates are encountered during racemization by an intramolecular process. In contrast, the racemization of **3** is attained by only one transformation pathway, where the iron fragment retains an equatorial position as a pivotal group. This may be the reason for the fact that **3** racemizes even at –50 °C, whereas **1a,b** and **2a,b** do not even at 100 °C.

Complexes **5–7** have two chiral centers at phosphorus and iron, and so the formation of diastereomers is expected. According to the ³¹P NMR spectra, two diastereoisomers are separately detected at room temperature. Therefore, it can be concluded that racemization occurs at neither phosphorus nor iron for **5–7**.

Spectroscopic Features of Iron Phosphoranes. Let us examine the spectroscopic data which the iron phosphoranes exhibit in this study. As one goes from **1** to **2** and **3**, the number of amino substituents on the phosphorus decreases. The ν_{CO} values in the IR spectra increase in frequency in this order. This trend is considered to be due to the decrease in σ-donicity and/or the increase in π-acceptability of a phosphorane fragment in this order.

Comparison of ν_{CO} values of **1–3** with those of Cp(CO)₂FeX (X = electron-withdrawing ligands) may help the estimation of π-acidity of a phosphorane ligand. Values of ν_{CO} for Cp(CO)₂FeX are as follows: 2011, 1965 cm^{–1} (in CH₂Cl₂) for X = Ph;²⁶ 2022, 1963 cm^{–1} (in CH₂Cl₂) for X = C(O)Me;²⁷ 2040, 1990 cm^{–1} (in CH₂Cl₂) for X = P(O)(OMe)₂;¹⁷ 2053, 2003 cm^{–1} (Nujol mull) for X = CF₃.²⁸ Therefore, it can be roughly said that the

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acidity of a $P(OC_6H_4Y)(OC_6H_4Z)$ ligand ($Y, Z = NH, NMe, O$) is greater than that of Ph or $C(O)Me$ but less than that of CF_3 and is comparable to that of $P(O)(OMe)_2$.

With ^{31}P NMR data, the chemical shift moves upfield on going from **3** to **2** and **1**. This is parallel to the increase in the number of electron-donating amino groups. In a series of $Cp(CO)LFe\{P(OC_6H_4NH)_2\}$ compounds where the ligand on the iron varies, the basicity of L increases from **1a** to **5**, **6**, and **7**, which may cause greater π back-donation of a $Cp(CO)LFe$ fragment to the phosphorus in this order. Thus, an upfield shift in the ^{31}P NMR spectra is expected in this order. However, the opposite tendency was observed. Although factors affecting NMR chemical shifts are sometimes very complicated, one plausible explanation which rationalizes our observations is the following. The apical $O-P-O$ hypervalent $3c-4e$ bond is polarized as $O^{\delta-}-P^{\delta+}-O^{\delta-}$ intrinsically. Because the electron density on the iron atom flows into the antibonding orbital of the $3c-4e$ bond, the π donation makes the $3c-4e$ bond longer, which would cause an increase in the polarization. If so, the π back-donation accumulates a positive charge on the phosphorus, leading to the downfield shift in the ^{31}P NMR.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl, and CH_2Cl_2 and $CHCl_3$ were distilled from P_2O_5 and then stored under dry nitrogen. Sodium amide, *n*-butyllithium (1.6 M in hexane), acetone, triethylamine, catechol, and ammonium hexafluorophosphate were obtained from common commercial sources and used without further purification. *N*-methyl-*o*-aminophenol²⁹ and $HP(OC_6H_4NH_2)_2$ and $Cp(CO)LFeCl$ ($L = P(OMe)_3, PMe_3$)³⁰ were prepared according to the literature procedures. $Cp(CO)\{P(OPh)_3\}FeCl$ ³⁰ and $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ and $[Cp(CO)_2Fe\{P(OC_6H_4O)(OPh)\}]PF_6$ ³¹ were prepared by the published methods with some modifications. NMR spectra were recorded on JEOL LA-300, EX-400, and EX-270 spectrometers. 1H resonances were measured relative to residual proton solvent peaks and referenced to TMS. ^{13}C resonances were measured relative to solvent peaks and referenced to TMS. ^{31}P resonances were measured relative to 85% H_3PO_4 as an external reference. Either a Shimadzu FTIR-8100A or a FTIR-4000 spectrometer was used to obtain IR spectra. EI mass spectra (70 eV) were recorded on a Shimadzu QP-2000 mass spectrometer. Elemental analysis data were obtained on a Perkin-Elmer 2400 CHN elemental analyzer.

Preparation of $Cp(CO)_2Fe\{P(OC_6H_4NH)_2\}$ (1a**).** A solution of *o*- $HOC_6H_4NH_2$ (351 mg, 3.22 mmol) in THF (10 mL) was cooled to $-78^\circ C$, and then *n*-BuLi (1.1 mL of a 1.60 M hexane solution, 1.76 mmol) was added. After the cooling bath was removed, the mixture was stirred for 20 min. The solution was added dropwise to the suspension of $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ (1.02 g, 1.61 mmol) in THF (5 mL) at $-78^\circ C$. The reaction mixture was stirred at room temperature overnight, which led to a homogeneous solution. The solvents were removed under reduced pressure, and the residue was extracted with ether repeatedly until the ether solution became almost colorless. The ether extract was collected, and the solvent was removed

under vacuum. The residual dark red oil was washed repeatedly with a small amount of ether. Finally, a yellow powder was formed, which was dried under reduced pressure to give $Cp(CO)_2Fe\{P(OC_6H_4NH)_2\}$ (**1a**; 396 mg, 0.90 mmol, 56% yield). Anal. Calcd for $C_{19}H_{15}FeN_2O_4P$: C, 54.06; H, 3.58; N, 6.64. Found: C, 53.84; H, 3.38; N, 6.44. MS (EI, 70 eV; m/z (relative intensity)): 422 (2, M^+), 394 (10, $M^+ - CO$), 366 (24, $M^+ - 2CO$), 299 (100), 163 (59), 138 (49).

Preparation of $[Cp(CO)_2Fe\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]PF_6$ (4**).** A solution of *o*- HOC_6H_4NHMe (971 mg, 7.88 mmol) in THF (25 mL) was cooled to $-78^\circ C$, and then *n*-BuLi (2.4 mL of a 1.60 M hexane solution, 3.84 mmol) was added. After the cooling bath was removed, the mixture was stirred for 20 min and then recooled to $-78^\circ C$. Then $[Cp(CO)_2Fe\{P(OPh)_3\}]PF_6$ (2.28 g, 3.61 mmol) was added to the solution. The reaction mixture was stirred at room temperature overnight to give a homogeneous solution. The IR spectrum of the solution showed two ν_{CO} absorption bands at 2024 and 1975 cm^{-1} , indicating the formation of the metallaphosphorane $Cp(CO)_2Fe\{P(OC_6H_4NMe)_2\}$. After NH_4PF_6 (540 mg, 3.31 mmol) was added to the solution, the volatile components were removed under vacuum. The residual yellow oil was dissolved in ether, and the solution was stirred for a few minutes to form a yellow precipitate. The supernatant was decanted off, and the precipitate was dried in vacuo. After addition of a small amount of acetone to the product, the solution was filtered and the solvent was removed quickly under reduced pressure. Finally, the yellow residue was washed with ether until the supernatant became almost colorless and was dried under vacuum to give $[Cp(CO)_2Fe\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]PF_6$ (**4**) as a yellow powder (1.44 g, 2.41 mmol, 67% yield). Anal. Calcd for $C_{21}H_{20}F_6FeN_2O_4P_2$: C, 42.31; H, 3.38; N, 4.70. Found: C, 42.35; H, 3.18; N, 4.42. IR (cm^{-1} ; ν_{CO} , in acetone): 2076, 2033. ^{31}P NMR (δ , in acetone): 173.56 (quartet, $J_{PH} = 10.2$ Hz). 1H NMR (δ , in acetone- d_6): 2.82 (s, 3H, $N(H)CH_3$), 3.42 (d, $J_{PH} = 11.2$ Hz, 3H, $PNCH_3$), 4.72 (bs, 1H, NH), 5.87 (d, $J_{PH} = 1.3$ Hz, 5H, C_5H_5), 6.34–7.19 (m, 8H, OC_6H_4N). ^{13}C NMR (δ , in acetone- d_6): 29.06 (d, $J_{PC} = 9.9$ Hz, $PNCH_3$), 30.37 (s, $N(H)CH_3$), 89.40 (s, C_5H_5), 109.56 (d, $J_{PC} = 6.3$ Hz, OC_6H_4N), 112.15 (d, $J_{PC} = 6.2$ Hz, OC_6H_4N), 112.66 (d, $J_{PC} = 1.9$ Hz, OC_6H_4N), 116.99 (d, $J_{PC} = 1.9$ Hz, OC_6H_4N), 121.41 (d, $J_{PC} = 3.7$ Hz, OC_6H_4N), 121.43 (s, OC_6H_4N), 124.76 (s, OC_6H_4N), 128.12 (d, $J_{PC} = 1.8$ Hz, OC_6H_4N), 136.63 (d, $J_{PC} = 5.6$ Hz, OC_6H_4N), 139.47 (d, $J_{PC} = 14.3$ Hz, OC_6H_4N), 141.97 (d, $J_{PC} = 3.1$ Hz, OC_6H_4N), 148.90 (d, $J_{PC} = 10.0$ Hz, OC_6H_4N), 207.38 (d, $J_{PC} = 36.7$ Hz, CO), 207.63 (d, $J_{PC} = 35.4$ Hz, CO).

Preparation of $Cp(CO)_2Fe\{P(OC_6H_4NMe)_2\}$ (1b**).** $[Cp(CO)_2Fe\{P(OC_6H_4NMe)(OC_6H_4NHMe)\}]PF_6$ (**4**; 951 mg, 1.60 mmol) was suspended in THF (15 mL) and then $NaNH_2$ (81 mg, 2.08 mmol) was added. While the mixture was stirred at room temperature for a few minutes, the suspension of **1b** disappeared. After excess $NaNH_2$ was filtered off, the solvent was removed from the filtrate in vacuo to give a yellow oil, and then the oil was dissolved in $CHCl_3$ followed by filtration. Finally, the solvent of the filtrate was removed under reduced pressure, giving a yellow powder of $Cp(CO)_2Fe\{P(OC_6H_4NMe)_2\}$ (**1b**; 628 mg, 1.39 mmol, 87% yield). Anal. Calcd for $C_{21}H_{19}FeN_2O_4P$: C, 56.03; H, 4.25; N, 6.22. Found: C, 55.79; H, 4.16; N, 6.03. MS (EI, 70 eV; m/z (relative intensity)): 422 (1, $M^+ - CO$), 394 (4, $M^+ - 2CO$), 273 (46), 152 (100), 137 (11).

Preparation of $Cp(CO)_2Fe\{P(OC_6H_4O)(OC_6H_4NH)\}$ (2a**) and $Cp(CO)_2Fe\{P(OC_6H_4O)(OC_6H_4NMe)\}$ (**2b**).** A solution of *o*- $HOC_6H_4NH_2$ (60 mg, 0.55 mmol) in THF (2 mL) was cooled to $-78^\circ C$, and then *n*-BuLi (0.28 mL of a 1.6 M hexane solution, 0.45 mmol) was added. The solution was stirred at room temperature for 20 min. The reaction mixture was added to a THF solution (2 mL) of $[Cp(CO)_2Fe\{P(OC_6H_4O)(OPh)\}]PF_6$ (243 mg, 0.44 mmol) at $-78^\circ C$, and the solution was warmed to room temperature. After the volatile components

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were removed under vacuum, the residue was dissolved in ether followed by filtration. The solvent of the filtrate was removed in vacuo, and the residue was washed with a small amount of ether until the color of the supernatant changed from dark red to yellow. Finally, the remaining yellow powder was dried under reduced pressure to give $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{NH})\}$ (**2a**; 132 mg, 0.31 mmol, 87% yield). Anal. Calcd for $\text{C}_{19}\text{H}_{14}\text{FeNO}_5\text{P}$: C, 53.93; H, 3.33; N, 3.31. Found: C, 53.44; H, 3.33; N, 3.15. MS (EI, 70 eV; m/z (relative intensity)): 423 (1, M^+), 395 (11, $\text{M}^+ - \text{CO}$), 367 (58, $\text{M}^+ - 2\text{CO}$), 258 (24), 230 (75), 164 (41), 138 (100), 121 (34).

Under similar conditions, $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{NMe})\}$ (**2b**) was obtained as a yellow powder (47% yield). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{FeNO}_5\text{P}$: C, 54.95; H, 3.69; N, 3.20. Found: C, 55.07; H, 3.57; N, 3.06. MS (EI, 70 eV; m/z (relative intensity)): 409 (4, $\text{M}^+ - \text{CO}$), 381 (16, $\text{M}^+ - 2\text{CO}$), 152 (100), 137 (11).

Preparation of $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})_2\}$ (3**).** To a suspension of $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O}^i\text{Pr})_3\}]\text{PF}_6$ (989 mg, 1.56 mmol) were added *o*- $\text{HOC}_6\text{H}_4\text{OH}$ (350 mg, 3.18 mmol) and $\text{N}(\text{Et})_3$ (0.44 mL, 3.16 mmol); the solution was then stirred at room temperature overnight. Volatile components were removed under vacuum, and the residue was extracted with ether followed by filtration. The solvent of the filtrate was removed under reduced pressure. After the extraction was repeated again, the residue was washed with a small amount of ether until the color of the supernatant changed from deep purple to yellow and was then dried under vacuum to give a yellow powder of $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{O})_2\}$ (**3**; 441 mg, 66% yield). Anal. Calcd for $\text{C}_{19}\text{H}_{13}\text{FeO}_6\text{P}$: C, 53.81; H, 3.09. Found: C, 53.82; H, 3.18. MS (EI, 70 eV; m/z (relative intensity)): 424 (2, M^+), 396 (8, $\text{M}^+ - \text{CO}$), 368 (100, $\text{M}^+ - 2\text{CO}$), 303 (23), 229 (23), 139 (94), 121 (33).

Preparation of $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ (L** = **P(O}^i\text{Pr})_3** (**5**), **P(OMe)}_3** (**6**)).** $\text{Cp}(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}\text{FeCl}$ (270 mg, 0.55 mmol) was treated with the reaction mixture of $\text{HP}(\text{OC}_6\text{H}_4\text{NH})_2$ (134 mg, 0.54 mmol) and *n*-BuLi (0.5 mL of a 1.6 M hexane solution, 0.80 mmol) in THF (5 mL) at -78°C . The reaction mixture was then stirred at room temperature overnight. Although the formation of the metallaphosphorane $\text{Cp}(\text{CO})\{\text{P}(\text{O}^i\text{Pr})_3\}\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ (**5**) was confirmed by the ^{31}P NMR spectrum, the product could not be isolated in a pure form, because unknown byproducts and the unreacted starting materials were not removed. Complex **6** was prepared under similar conditions.

Preparation of $\text{Cp}(\text{CO})(\text{PMe}_3)\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$ (7**).** $\text{Cp}(\text{CO})(\text{PMe}_3)\text{FeCl}$ (535 mg, 2.05 mmol) was treated with the reaction mixture of $\text{HP}(\text{OC}_6\text{H}_4\text{NH})_2$ (491 mg, 1.99 mmol) and *n*-BuLi (1.5 mL of a 1.6 M hexane solution, 2.4 mmol) in THF (10 mL) at -78°C , and the solution was stirred at room temperature overnight. After NH_4PF_6 (500 mg, 3.07 mmol) was added to the solution, the volatile components were removed under reduced pressure. The residual reddish oil was washed with ether until the supernatant became almost colorless and was dried in vacuo. The product is a pair of diastereomers of $[\text{Cp}(\text{CO})(\text{PMe}_3)\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{NH}_2)\}]\text{PF}_6$, according to its spectroscopic data. IR (cm^{-1} , in THF): ν_{CO} 1985. ^{31}P NMR (δ , in THF): 31.97 (d, $J_{\text{PP}} = 85.2$ Hz), 32.14 (d, $J_{\text{PP}} = 88.8$ Hz), 179.46 (dd, $J_{\text{PP}} = 88.8$ Hz, $J_{\text{PH}} = 28.6$ Hz), 182.40 (dd, $J_{\text{PP}} = 86.4$ Hz, $J_{\text{PH}} = 29.2$ Hz). The product was

dissolved in THF (10 mL), NaNH_2 (111 mg, 2.85 mmol) was added, and the mixture was stirred overnight at room temperature. The volatile components were removed in vacuo, and the product was extracted with ether. The solvent was removed under reduced pressure, and the product was then extracted with ether/pentane (1/1). Finally, the solvents were removed under reduced pressure to give a yellow powder of **7** (228 mg, 0.49 mmol, 24% yield). Complex **7** also consists of a pair of diastereomers in the ratio of ca. 1:1.2. IR (cm^{-1} , in THF): ν_{CO} 1942. ^1H NMR (δ , in C_6D_6): 1.04 (d, $J_{\text{PH}} = 9.7$ Hz, 9H, PCH_3), 4.19 (m, 5H, C_5H_5), 4.62 (d, $J_{\text{PH}} = 13.7$ Hz, 2H, NH), 6.44–6.91 (m, 8H, $\text{OC}_6\text{H}_4\text{N}$), 0.87 (d, $J_{\text{PH}} = 9.6$ Hz, 9H, PCH_3), 4.23 (m, 5H, C_5H_5), 4.79 (d, $J_{\text{PH}} = 13.7$ Hz, 2H, NH), 6.30–6.91 (m, 8H, $\text{OC}_6\text{H}_4\text{N}$). ^{31}P NMR (δ , in THF): 38.11 (d, $J_{\text{PP}} = 104.6$ Hz, P(III)), 42.73 (dt, $J_{\text{PP}} = 104.6$ Hz, $J_{\text{PH}} = 15.8$ Hz, P(V)), 37.78 (d, $J_{\text{PP}} = 104.6$ Hz, P(III)), 39.41 (dt, $J_{\text{PP}} = 104.6$ Hz, $J_{\text{PH}} = 15.2$ Hz, P(V)). ^{13}C NMR (δ , in C_6D_6): 19.91 (d, $J_{\text{CP}} = 29.2$ Hz, PCH_3), 20.42 (d, $J_{\text{CP}} = 29.2$ Hz, PCH_3), 83.09 (s, C_5H_5), 83.15 (s, C_5H_5), 108.49 (s, $\text{OC}_6\text{H}_4\text{N}$), 108.65 (s, $\text{OC}_6\text{H}_4\text{N}$), 108.67 (d, $J_{\text{CP}} = 10.5$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 108.87 (d, $J_{\text{CP}} = 10.0$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 118.25 (s, $\text{OC}_6\text{H}_4\text{N}$), 118.42 (s, $\text{OC}_6\text{H}_4\text{N}$), 118.92 (s, $\text{OC}_6\text{H}_4\text{N}$), 119.05 (s, $\text{OC}_6\text{H}_4\text{N}$), 133.96 (d, $J_{\text{CP}} = 6.2$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 134.03 (d, $J_{\text{CP}} = 4.4$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 151.00 (d, $J_{\text{CP}} = 6.2$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 151.16 (d, $J_{\text{CP}} = 8.1$ Hz, $\text{OC}_6\text{H}_4\text{N}$), 217.03 (dd, $J_{\text{CP}} = 34.2$, 50.4 Hz, CO), 219.02 (dd, $J_{\text{CP}} = 34.5$, 50.0 Hz, CO). MS (EI, 70 eV; m/z (relative intensity)): 470 (5, M^+), 442 (17, $\text{M}^+ - \text{CO}$), 229 (100), 197 (84), 163 (59), 137 (80), 109 (92), 61 (83), 59 (60).

X-ray Structure Determinations. Suitable crystals of **1b** and **2b** were obtained through recrystallization from hot toluene, and that of **4** was obtained similarly from hot 1,2-dichloroethane. The crystals were mounted on a Mac Science MXC κ diffractometer and irradiated with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Unit-cell dimensions were obtained by least squares from the angular settings of 29 accurately centered reflections with $31^\circ < 2\theta < 35^\circ$ for **1b** and **2b** and from that of 20 such reflections with $32^\circ < 2\theta < 35^\circ$ for **4**. $P2_1/a$, $P\bar{1}$, and $P\bar{1}$ were selected as the space groups for **1b**, **2b**, and **4**, respectively, which led to successful refinements. Reflection intensities were collected in the usual manner at 25°C , and 3 reflections checked after every 200 reflections showed no decrease in intensity.

The structures were solved by a direct method with the program SIR92.³² The positions of hydrogen atoms were determined from subsequent difference Fourier maps for **1b** and **2b**, and those for **4** were calculated by assuming idealized geometries. For **4**, the counteranion, PF_6^- , was refined as a disordered molecule. Absorption and extinction corrections were then applied, and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms led to final values of $R = 0.037$ and $R_w = 0.048$ for **1b**, $R = 0.044$ and $R_w = 0.054$ for **2b**, and $R = 0.070$ and $R_w = 0.064$ for **4**. All calculations were performed on an SGI Indy R5000 computer using the program system CRYSTAN-GM³³ with neutral atom scattering factors from Cromer and Waber.³⁴

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and angles for **1b**, **2b**, and **4** (17 pages). Ordering information is given on any current masthead page.

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