

Migration Reaction of a Hypervalent Fragment: Base-Induced Migration of a Phosphorane Fragment from Iron to the Cyclopentadienyl Ring in  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$  (Y, Z = NMe, NH, O)

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Received January 13, 1998

**Abstract:** Iron phosphorane complexes,  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$  (Y, Z = NMe, O), react with lithium diisopropylamide (LDA) and then MeI to give  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}(\text{CO})_2\text{FeMe}$ , showing the first example of migration of a hypervalent phosphorus fragment. The structure of one of the migration products,  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe})_2\}(\text{CO})_2\text{FeCH}_2\text{Ph}$ , was determined by X-ray analysis. Spectroscopic monitoring of the migration reaction suggests that the reaction is initiated by a proton abstraction on the Cp ring by LDA, followed by migration of the phosphorane fragment to the Cp ring to give  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}(\text{CO})_2\text{Fe}^-$ , which is converted into  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}(\text{CO})_2\text{FeR}$  by the treatment of alkyl halide. The reaction of  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}$  containing two NH groups with LDA proceeds first with NH proton abstraction to give  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{N}^-)\}$  and then with Cp proton abstraction followed by phosphorane migration to give  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{N}^-)\}(\text{CO})_2\text{Fe}^-$ . The addition of MeI finally led to the isolation of  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{NH})\}(\text{CO})_2\text{FeMe}$  and  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{NMe})\}(\text{CO})_2\text{FeMe}$ .

## Introduction

It is widely accepted that hypervalent compounds have more than eight electrons in the valence shell of the central element, resulting in the formation of three-center four-electron bonds, that is, hypervalent bonds. The chemistry of hypervalent compounds is one of the most vigorously growing areas of research. Nowadays, many such compounds have been isolated, characterized, and structurally determined for several main group elements (groups 13–17).<sup>1–9</sup> Parallel to these studies, their

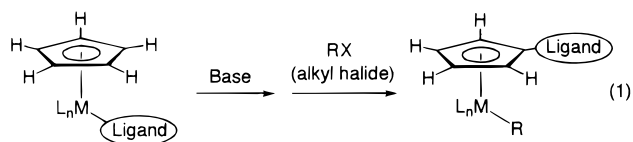
reactivities have also been investigated.<sup>4,7–12</sup> However, migration of a hypervalent fragment<sup>13</sup> has not been reported, to our knowledge, for any kinds of hypervalent elements.

It has been reported for  $\eta^5$ -cyclopentadienyl (Cp)-containing complexes that one of the ligands undergoes base-induced migration to the Cp ring (eq 1). The first example of this type of migration reaction was reported by Dean and Graham in 1977 for  $\text{Cp}(\text{CO})_3\text{M}(\text{GePh}_3)$  (M = Mo, W).<sup>14</sup> Since then, several types of ligand have been illustrated to migrate from a transition metal to the Cp ring: acyl,<sup>15</sup> alkoxy carbonyl,<sup>15c</sup> formyl,<sup>15e,f</sup> silyl,<sup>16</sup> germyl,<sup>17</sup> stannyl,<sup>17</sup> plumbyl,<sup>17</sup> hydride,<sup>18</sup> and phosphonate<sup>19</sup> migration. These ligands, except hydride, have two common properties: The coordinating atom does not have a

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typical dative bond but has a covalent bond with a transition metal and has an empty orbital such as a  $\pi^*$  or d orbital.

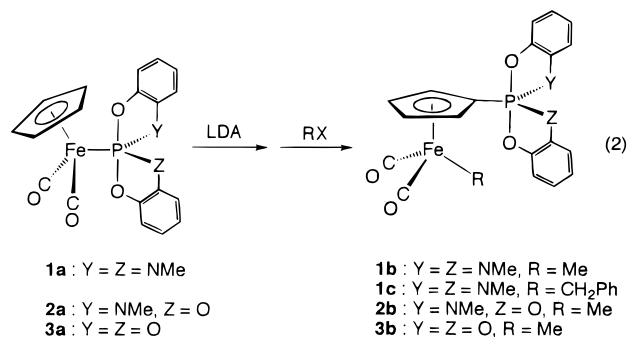


We have been engaged in the study of metalated hypervalent phosphorus compounds by a transition metal, metallaphosphoranes. The M–P bond is considered to be a covalent bond, and an empty orbital may exist on the phosphorane phosphorus. This rough sketch let us seek the possibility of base-induced migration of a phosphorane fragment to the Cp ring. This paper reports the first example of a hypervalent fragment migration: phosphorane migration from iron to the Cp ring for  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$  (Y = Z = NMe (**1a**); Y = NMe, Z = O (**2a**); Y = Z = O (**3a**)) (although the complex should be described as  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$ , the tie lines are omitted in this paper for clarity).

## Results and Discussion

**Reaction of  $\text{Cp}(\text{CO})_2\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$  with LDA and Then RX.** Three iron phosphorane complexes,  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{Y})(\text{OC}_6\text{H}_4\text{Z})\}$  (**1a**, **2a**, and **3a**), were subjected to the reaction with lithium diisopropylamide (LDA) and then alkyl halide. The results obtained are shown in eq 2. The spectroscopic data for the products are summarized in Table 1.

In a typical reaction, **1a** having two N and two O atoms in addition to one Fe atom on the hypervalent phosphorus was treated with LDA in THF at  $-78^\circ\text{C}$ . The color of the solution changed immediately from yellow to deep orange. After it had been stirred at  $-78^\circ\text{C}$  for 15 min, the reaction mixture was treated with MeI and was warmed to room temperature. The product was purified by column chromatography and isolated as a pale yellow powder in a considerable yield. The following points of its spectroscopic data should be noted. (i) The  $^{31}\text{P}$  NMR spectrum of the product shows a singlet at  $-45.80$  ppm, which is ca. 62 ppm higher in magnetic field than that of the



starting complex and is close to those of the related organic phosphorane compounds such as  $\text{MeP}(\text{OC}_6\text{H}_4\text{NMe})_2$  ( $-32.0$  ppm)<sup>20</sup> and  $\text{PhP}(\text{OC}_6\text{H}_4\text{NH})_2$  ( $-35.1$  ppm).<sup>21</sup> (ii) In the  $^1\text{H}$  NMR spectrum, the starting complex shows a doublet at 4.86 ppm ( $J = 0.7$  Hz) due to the cyclopentadienyl protons, whereas the product exhibits a characteristic splitting pattern involving multiplets at 4.71, 5.16, and 5.22 ppm with an intensity ratio of 2:1:1 (Figure 1a). This observation indicates that the product has a monosubstituted cyclopentadienyl ligand. (iii) The  $^{13}\text{C}$  NMR spectrum exhibits five doublets at 85.87 ( $J_{\text{PC}} = 16.1$  Hz), 86.41 ( $J_{\text{PC}} = 15.5$  Hz), 92.27 ( $J_{\text{PC}} = 255.1$  Hz), 94.57 ( $J_{\text{PC}} = 15.5$  Hz), and 95.91 ( $J_{\text{PC}} = 15.5$  Hz) in the cyclopentadienyl carbon region (Figure 1b), suggesting that the product has a phosphorus-substituted Cp ligand, presumably  $\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe})_2$ . (iv) In the IR spectrum, two absorption bands due to  $\nu_{\text{CO}}$  are observed at 2011 and 1956  $\text{cm}^{-1}$ . These are very close to those for  $\text{CpFe}(\text{CO})_2\text{Me}$ .<sup>22</sup> From these data together with elemental analysis and mass spectroscopic data, we concluded that the product is  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe})_2\}\text{Fe}(\text{CO})_2\text{Me}$  (**1b**). The reaction of **1a** with LDA and then  $\text{PhCH}_2\text{Cl}$  in place of MeI gave  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe})_2\}\text{Fe}(\text{CO})_2\text{CH}_2\text{Ph}$  (**1c**), the structure of which was confirmed by the X-ray analysis (vide infra) in addition to the spectroscopic data. It should be noted that these complexes are the migration products of a phosphorane fragment from an iron to the Cp ring and the hypervalent structure is retained even after the migration reaction.

Let us consider the assignment of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1b**. Holmes et al. reported analysis of the aromatic region of the  $^1\text{H}$  NMR spectra of some phenyl-substituted pentacoordinated compounds of main group elements (Si, Pb, P, As, Sb, S, Te, and I) (when the compound assumes a trigonal bipyramidal geometry, the phenyl group occupies one of the equatorial sites) and drew the conclusion that the ortho protons are more deshielded than the meta and para protons. The reason arises from the delocalization of  $\pi$ -electron density from the phenyl ring to the vacant d orbital of the attached central element in the pentacoordinate state as well as a strengthening of the central element  $\sigma$  bond.<sup>23</sup> A similar explanation would be invoked to interpret signals of the cyclopentadienyl ring bonding to a pentacoordinate phosphorus. With **1b**, two downfield resonances ( $\delta$  5.16 and 5.22) relative to the other ( $\delta$  4.71) are assignable to  $\beta$ -protons on the substituted Cp ligand and the multiplet at 4.71 ppm to  $\gamma$ -protons. In this complex, two  $\beta$ -protons are observed diastereotopically. The resonances of the diastereotopic  $\gamma$ -protons are superimposed. The  $^1\text{H}$ – $^{13}\text{C}$  shift correlation spectroscopy revealed that the doublets at 94.57 and 95.91 ppm are assigned to  $\beta$ -carbons and those at 85.87

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**Table 1.** Spectroscopic Data

complex	IR, $\nu(\text{CO})$ ( $\text{cm}^{-1}$ ) <sup>a</sup>	<sup>1</sup> H NMR, $\delta$ (ppm) <sup>b</sup>	<sup>31</sup> P{ <sup>1</sup> H} NMR, $\delta$ (ppm) <sup>a</sup>	<sup>13</sup> C{ <sup>1</sup> H} NMR, $\delta$ (ppm) <sup>b</sup>
<b>1b</b>	2011, 1956	0.10 (s, 3H, FeCH <sub>3</sub> ), 3.23 (d, $J_{\text{PH}} = 10.1$ Hz, 6H, NCH <sub>3</sub> ), 4.71 (m, 2H, C <sub>5</sub> H <sub>4</sub> P), 5.16 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.22 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 6.66–6.89 (m, 8H, OC <sub>6</sub> H <sub>4</sub> N)	–45.80 (s)	–23.15 (s, FeCH <sub>3</sub> ), 32.47 (d, $J_{\text{PC}} = 3.1$ Hz, NCH <sub>3</sub> ), 85.87 (d, $J_{\text{PC}} = 16.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 86.41 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 92.27 (d, $J_{\text{PC}} = 255.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 94.57 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 95.91 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>5</sub> P), 108.31 (d, $J_{\text{PC}} = 7.4$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 108.98 (d, $J_{\text{PC}} = 11.8$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 119.57 (s, OC <sub>6</sub> H <sub>4</sub> N), 120.41 (s, OC <sub>6</sub> H <sub>4</sub> N), 135.16 (d, $J_{\text{PC}} = 21.1$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 146.06 (s, OC <sub>6</sub> H <sub>4</sub> N), 215.98 (s, CO), 216.17 (s, CO)
<b>1c</b>	2009, 1957	2.63 (m, 2H, FeCH <sub>2</sub> ), 3.22 (d, $J_{\text{PH}} = 9.9$ Hz, 6H, NCH <sub>3</sub> ), 4.45 (m, 2H, C <sub>5</sub> H <sub>4</sub> P), 5.10 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.17 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 6.64–7.14 (m, 13H, OC <sub>6</sub> H <sub>4</sub> N and C <sub>6</sub> H <sub>5</sub> )	–45.35 (s)	5.46 (s, FeCH <sub>2</sub> ), 32.50 (d, $J_{\text{PC}} = 2.5$ Hz, NCH <sub>3</sub> ), 87.63 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 88.71 (d, $J_{\text{PC}} = 14.9$ Hz, C <sub>5</sub> H <sub>4</sub> P), 91.52 (d, $J_{\text{PC}} = 255.0$ Hz, C <sub>5</sub> H <sub>4</sub> P), 94.29 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 97.09 (d, $J_{\text{PC}} = 14.9$ Hz, C <sub>5</sub> H <sub>4</sub> P), 108.40 (d, $J_{\text{PC}} = 6.9$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 109.10 (d, $J_{\text{PC}} = 11.8$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 127.40 (s, OC <sub>6</sub> H <sub>4</sub> N), 127.99 (s, OC <sub>6</sub> H <sub>4</sub> N), 135.07 (d, $J_{\text{PC}} = 21.7$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 146.03 (s, OC <sub>6</sub> H <sub>4</sub> N), 119.71 (s, C <sub>6</sub> H <sub>5</sub> ), 120.54 (s, C <sub>6</sub> H <sub>5</sub> ), 123.11 (s, C <sub>6</sub> H <sub>5</sub> ), 152.57 (s, C <sub>6</sub> H <sub>5</sub> ), 215.00 (s, CO), 216.02 (s, CO)
<b>2b</b>	2014, 1960	0.14 (s, 3H, FeCH <sub>3</sub> ), 3.37 (d, $J_{\text{PH}} = 10.5$ Hz, 3H, NCH <sub>3</sub> ), 4.78 (m, 2H, C <sub>5</sub> H <sub>4</sub> P), 5.21 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.36 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 6.75–7.06 (m, 8H, OC <sub>6</sub> H <sub>4</sub> O and OC <sub>6</sub> H <sub>4</sub> N)	–28.34 (s)	–23.04 (s, FeCH <sub>3</sub> ), 32.69 (d, $J_{\text{PC}} = 2.5$ Hz, NCH <sub>3</sub> ), 86.37 (d, $J_{\text{PC}} = 16.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 87.26 (d, $J_{\text{PC}} = 256.3$ Hz, C <sub>5</sub> H <sub>4</sub> P), 87.98 (d, $J_{\text{PC}} = 16.7$ Hz, C <sub>5</sub> H <sub>4</sub> P), 94.61 (d, $J_{\text{PC}} = 16.7$ Hz, C <sub>5</sub> H <sub>4</sub> P), 96.50 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 109.02 (d, $J_{\text{PC}} = 8.7$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 109.59 (d, $J_{\text{PC}} = 13.0$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 109.74 (d, $J_{\text{PC}} =$ 10.0 Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 111.63 (d, $J_{\text{PC}} = 15.5$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 120.57 (s, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 120.63 (s, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 120.77 (s, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 122.91 (s, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 133.64 (d, $J_{\text{PC}} = 23.0$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 142.86 (d, $J_{\text{PC}} = 3.7$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 145.61 (s, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 146.00 (d, $J_{\text{PC}} = 2.5$ Hz, OC <sub>6</sub> H <sub>4</sub> O or OC <sub>6</sub> H <sub>4</sub> N), 215.29 (s, CO), 215.43 (s, CO)
<b>3b</b>	2010, 1952	not available	–11.46 (s)	–22.96 (s, FeCH <sub>3</sub> ), 81.09 (d, $J_{\text{PC}} = 252.6$ Hz, C <sub>5</sub> H <sub>4</sub> P), 88.24 (d, $J_{\text{PC}} = 16.8$ Hz, C <sub>5</sub> H <sub>4</sub> P), 95.09 (d, $J_{\text{PC}} = 16.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 110.75 (d, $J_{\text{PC}} = 14.3$ Hz, OC <sub>6</sub> H <sub>4</sub> O), 122.15 (s, OC <sub>6</sub> H <sub>4</sub> O), 143.51 (d, $J_{\text{PC}} = 4.3$ Hz, OC <sub>6</sub> H <sub>4</sub> O), 214.25 (s, CO)
<b>4b</b>	2011, 1955	0.11 (s, 3H, FeCH <sub>3</sub> ), 4.71 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 4.75 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.15 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.26 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.31 (d, $J_{\text{PH}} = 20.0$ Hz, 2H, NH), 6.71–6.83 (m, 8H, OC <sub>6</sub> H <sub>4</sub> N)	–38.45 (s)	–22.90 (s, FeCH <sub>3</sub> ), 84.60 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 87.53 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 91.36 (d, $J_{\text{PC}} = 242.6$ Hz, C <sub>5</sub> H <sub>4</sub> P), 93.08 (d, $J_{\text{PC}} = 16.8$ Hz, C <sub>5</sub> H <sub>4</sub> P), 95.70 (d, $J_{\text{PC}} = 16.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 109.43 (d, $J_{\text{PC}} = 7.5$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 109.65 (d, $J_{\text{PC}} = 16.1$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 120.27 (d, $J_{\text{PC}} = 1.2$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 120.53 (s, OC <sub>6</sub> N <sub>4</sub> H), 130.72 (d, $J_{\text{PC}} = 17.4$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 146.50 (d, $J_{\text{PC}} = 1.2$ Hz, OC <sub>6</sub> H <sub>4</sub> N), 216.03 (s, CO), 216.11 (s, CO)
<b>4c</b>	2011, 1955	0.13 (s, 3H, FeCH <sub>3</sub> ), 3.26 (d, $J_{\text{PH}} = 10.1$ Hz, 3H, NCH <sub>3</sub> ), 4.72 (m, 2H, C <sub>5</sub> H <sub>4</sub> P), 5.17 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.26 (m, 1H, C <sub>5</sub> H <sub>4</sub> P), 5.34 (d, $J_{\text{PH}} = 19.3$ Hz, 1H, NH), 6.67–6.94 (m, 8H, OC <sub>6</sub> H <sub>4</sub> NMe and OC <sub>6</sub> H <sub>4</sub> NH)	–42.77 (s)	–23.01 (s, FeCH <sub>3</sub> ), 32.00 (d, $J_{\text{PC}} = 2.5$ Hz, NCH <sub>3</sub> ), 85.33 (d, $J_{\text{PC}} = 16.1$ Hz, C <sub>5</sub> H <sub>4</sub> P), 86.92 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 91.64 (d, $J_{\text{PC}} = 247.6$ Hz, C <sub>5</sub> H <sub>4</sub> P), 93.82 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 95.67 (d, $J_{\text{PC}} = 15.5$ Hz, C <sub>5</sub> H <sub>4</sub> P), 108.46 (d, $J_{\text{PC}} = 6.8$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 109.12 (d, $J_{\text{PC}} = 12.4$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 109.31 (d, $J_{\text{PC}} = 8.1$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 109.44 (d, $J_{\text{PC}} = 15.5$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 119.86 (s, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 120.26 (s, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 120.39 (s, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 130.83 (d, $J_{\text{PC}} = 16.7$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 134.95 (d, $J_{\text{PC}} = 22.4$ Hz, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 146.20 (s, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 146.40 (s, OC <sub>6</sub> H <sub>4</sub> NMe or OC <sub>6</sub> H <sub>4</sub> NH), 216.00 (s, CO), 216.13 (s, CO)

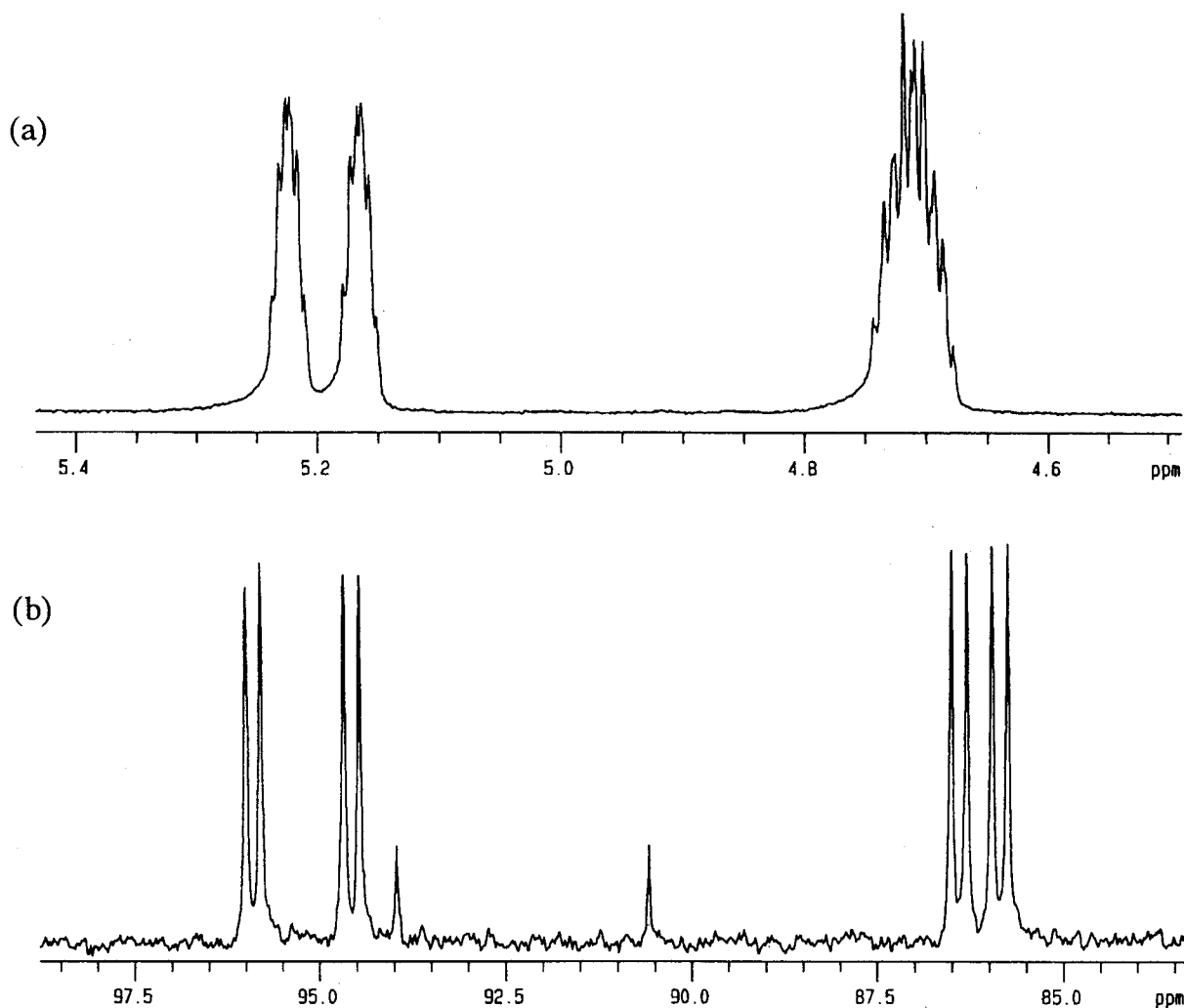
<sup>a</sup> In THF. <sup>b</sup> In CDCl<sub>3</sub>.

and 86.41 ppm to  $\gamma$ -carbons. The doublet at 92.27 ppm is uniquely assigned to the  $\alpha$ -carbon due to the lack of a proton on it and the largest P–C coupling constant.

The reactions of **2a**, having one N, three O, and one Fe atoms on the hypervalent phosphorus, and **3a**, having four O and one Fe atoms, with LDA and then MeI led to the formation of **2b** and **3b**, respectively, which correspond to the phosphorane fragment migration products. Although **3b** was too reactive to be isolated as a solid, the formation was confirmed by the <sup>31</sup>P, <sup>13</sup>C, and IR spectra. **2b** was isolated in 58% yield. These results show that the phosphorane migration reaction seems to be general, irrespective of substituents on the phosphorane phos-

phorus. The phosphorus of **1b–3b** is a chiral center in principle, causing observation of diastereotopic  $\beta$ - and  $\gamma$ -carbons in the Cp ring in the <sup>13</sup>C NMR spectra if the racemization in the Berry pseudorotation (BPR) process is slower than the NMR time scale. For **1b**, **1c**, and **2b**, diastereotopic resonances were observed, whereas **3b** did not show such resonances. Therefore, it can be said that BPR is slower for **1b**, **1c**, and **2b**, if it occurs at all, whereas BPR occurs faster for **3b** than the NMR time scale. This tendency is the same as that exhibited by the parent complexes.<sup>24</sup>

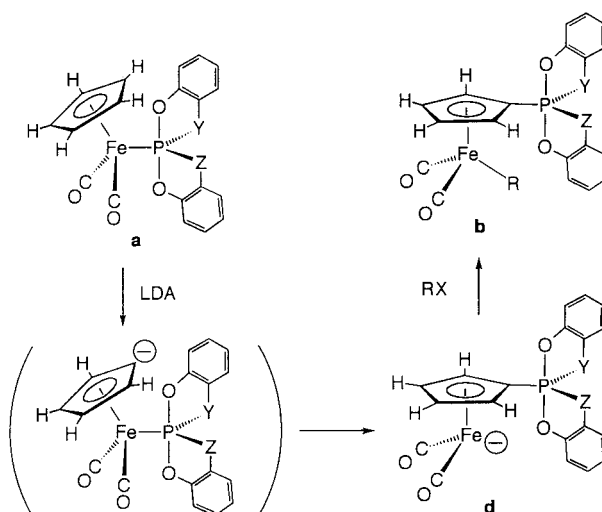
(24) Kubo, K.; Nakazawa, H.; Mizuta, T.; Miyoshi, K. *Organometallics*. In press.



**Figure 1.** Cyclopentadienyl region in the  $^1\text{H}$  NMR spectrum (a) and the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (b) for  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe}_2)_2\text{Fe}(\text{CO})_2\text{Me}$  (**1b**) in  $\text{CDCl}_3$ .

**Consideration of Phosphorane Fragment Migration Process.** To obtain a clue to the migration process, we measured the  $^{31}\text{P}$  NMR and IR spectra of the reaction mixture of the starting metallaphosphorane complexes with LDA. In the reaction of **3a** with LDA, complicated spectra were obtained, presumably due to the formation of an unstable complex. However, when **1a** and **2a** were used as the starting complex, clear spectra were observed due to the formation of relatively stable complexes (**1d** and **2d**, respectively) (see Scheme 1): For **1d**.  $^{31}\text{P}$  NMR (THF):  $\delta$   $-38.30$  (s). IR ( $\nu_{\text{CO}}$ , THF): 1891, 1878, 1822, 1789, 1772  $\text{cm}^{-1}$ . For **2d**.  $^{31}\text{P}$  NMR (THF):  $\delta$   $-19.91$  (s). IR ( $\nu_{\text{CO}}$ , THF): 1884, 1828, 1813, 1773  $\text{cm}^{-1}$ . These IR absorption bands are close to those for  $[\text{CpFe}(\text{CO})_2]^- \text{Li}^+$ ,<sup>25</sup> indicating that the products here are  $[\text{CpFe}(\text{CO})_2]^-$  derivatives. On going from **1a** to **1d** and then to **1b**, the  $^{31}\text{P}$  NMR chemical shift moves upfield by 54.59 ppm and by 7.50 ppm, respectively. Similarly, changing from **2a** to **2b** causes upfield shifts of 65.30 and 8.43 ppm. This behavior of the  $^{31}\text{P}$  NMR chemical shift resembles that observed in the reaction of  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{O})(\text{OEt})_2\}$  with LDA to produce  $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{O})(\text{OEt})_2\}\text{Fe}(\text{CO})_2]^-$  (62.1 ppm upfield shift) which reacts with MeI to give  $[\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{O})(\text{OEt})_2\}\text{Fe}(\text{CO})_2\text{Me}]$  (6.1 ppm upfield shift).<sup>19</sup> Therefore, it is highly

**Scheme 1**

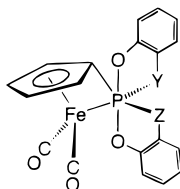


likely that the complex (**d**) formed in the reaction of **a** with LDA is a phosphorane migrated anionic iron complex (see Scheme 1).

The migration reaction may proceed as shown in Scheme 1. This reaction is initiated by a proton abstraction on the Cp ring by LDA, followed by migration of the phosphorane fragment

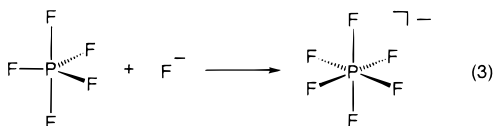
(25) (a) Pannel, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443.  
(b) Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23.

## Chart 1

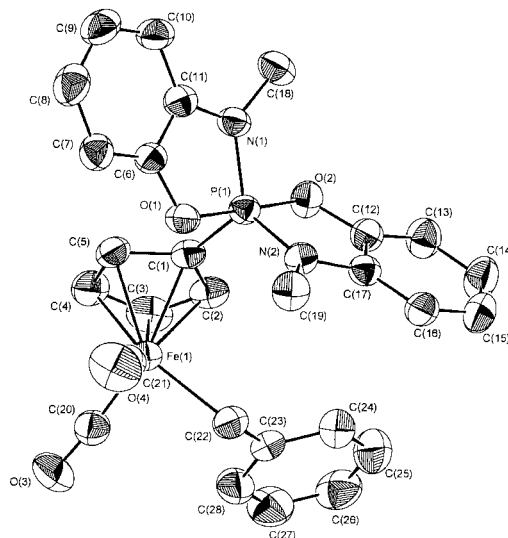


to give **d** which is relatively stable in solution and is converted into an isolable complex (**b**) by treatment with alkyl halide.

Next, let us consider the transition state of a phosphorane fragment migration process from iron to the Cp ring. Berryhill and Gladysz suggested that the migrating ligand should have a low-lying unoccupied orbital (i.e.,  $\pi^*$  or d orbitals) to accept the electron density on the cyclopentadienyl ring carbon.<sup>15e,16c</sup> It is known that a phosphorus atom can accept up to 12 valence electrons forming three hypervalent bonds. In a pentacoordinated phosphorus with a TBP structure, the central phosphorus atom is estimated to have a considerable positive charge due to polarization of apical hypervalent bonds.<sup>26</sup> This polarization allows the phosphorane phosphorus to act as a Lewis acid to react with nucleophiles yielding anionic hexacoordinate phosphorus species. For example,  $\text{PF}_5$  readily reacts with  $\text{F}^-$  to give a stable hexacoordinated anionic species  $\text{PF}_6^-$  (eq 3). In the case of base-induced silyl migration, an intramolecular and concerted reaction has been established.<sup>16c</sup> Therefore, the phosphorane fragment migration would be best described to proceed through a metalated hypervalent hexacoordinated phosphorus species (Chart 1), and this transition state (or an intermediate in some cases) should make the energy barrier of the migration lower. However, a reaction pathway not via a hexacoordinated phosphorus species cannot be ruled out, where, for example, heterolytic cleavage of a P–O (or P–Y or P–Z) bond takes place with Cp–P bond formation and then an Fe–P bond breaks with P–O bond formation, resulting in phosphorane migration.



**Crystal Structure of  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NMe}_2)\text{Fe}(\text{CO})_2\text{-CH}_2\text{Ph}$  (**1c**).** The structure of **1c** was determined by X-ray diffraction analysis. The ORTEP drawing is displayed in Figure 2. The crystallographic data and selected bond lengths and angles are summarized in Tables 2 and 3, respectively. The complex has a normal piano stool configuration where the central iron atom has two carbonyls, a benzyl group, and  $\eta^5$ -cyclopentadienyl ligand with a phosphorane fragment on one of the Cp carbons. The phosphorane fragment has a distorted TBP geometry with two oxygens in the apical positions and two nitrogens and one Cp group in the equatorial positions. The two apical bonds form an almost straight line (the O1–P1–O2 angle is 178.9°). The geometries around N1 and N2 atoms are planar (the sums of the bond angles around N1 and N2 are both 359.9°), and both of the planes contain the apical O1–P1–O2 bond. These observations indicate that the two nitrogens undergo  $\text{sp}^2$  hybridization and the remaining p orbital containing lone pair electrons lies on the equatorial plane of the phosphorus atom. This orientation is suitable for  $\pi$  donation of the lone pair electrons to the equatorial  $\sigma^*$  bonds. In addition, it seems



**Figure 2.** ORTEP drawing of **1c** (50% probability ellipsoids) showing the numbering system. All hydrogen atoms are omitted for clarity.

**Table 2.** Summary of Crystal Data for **1c**

formula	$\text{C}_{28}\text{H}_{25}\text{O}_4\text{N}_2\text{FeP}$
fw	540.30
cryst syst	Monoclinic
space group	$P2_1/n$
$a$ , Å	13.986 (4)
$b$ , Å	22.971 (6)
$c$ , Å	7.799 (2)
$\beta$ , deg	99.28 (2)
$V$ , Å <sup>3</sup>	2472.6 (12)
$Z$	4
$D_{\text{calcd}}$ , g $\text{cm}^{-3}$	1.451
$\mu$ , $\text{cm}^{-1}$	7.082
cryst size, mm	0.38 × 0.25 × 0.15
radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.710 73)
scan technique	$\omega - 2\theta$
scan range, deg	3 < $2\theta$ < 50
no. of unique data	4357
no. of unique data with $F_o > 3\sigma(F_o)$	3169
$R^a$	0.032
$R_w^b$	0.040
$F_A, F_B^b$	10.0, 0.00030

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

that the C1 atom can donate some  $\pi$ -electron density on the Cp ring to the equatorial  $\sigma^*$  orbitals, although the torsion angles for O1–P1–C1–C5 (32.2°) and O2–P1–C1–C2 (26.5°) indicate that the  $\pi$  orbital on C1 is not exactly in the equatorial plane of the phosphorus. The low-field shift of  $\beta$ -protons on the Cp ring in the <sup>1</sup>H NMR spectrum may be attributed to this electron donation to the hypervalent phosphorus atom.

**Reaction of  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH}_2)\}$  (**4a**) with LDA and Then MeI.** Complex **4a** has two amino protons in a phosphorane fragment, which led to some interesting results in the reaction with LDA and then MeI (Scheme 2). The treatment of **4a** with 2 equiv of LDA and then MeI gave several kinds of products. One of them was very reactive, causing difficulty in its separation from others. Therefore, we followed the reaction and estimated the products by the <sup>31</sup>P NMR measurement. The reaction mixture of **4a** with 2 equiv of LDA exhibited a complicated spectrum. After the addition of MeI, the resulting solution showed a better spectrum which involved mainly three sharp singlets at 24.18, 21.90, and –38.45 ppm with an intensity ratio of 1:2:1. In the proton nondecoupled <sup>31</sup>P NMR measurement, they were observed as a triplet, a broad singlet, and a

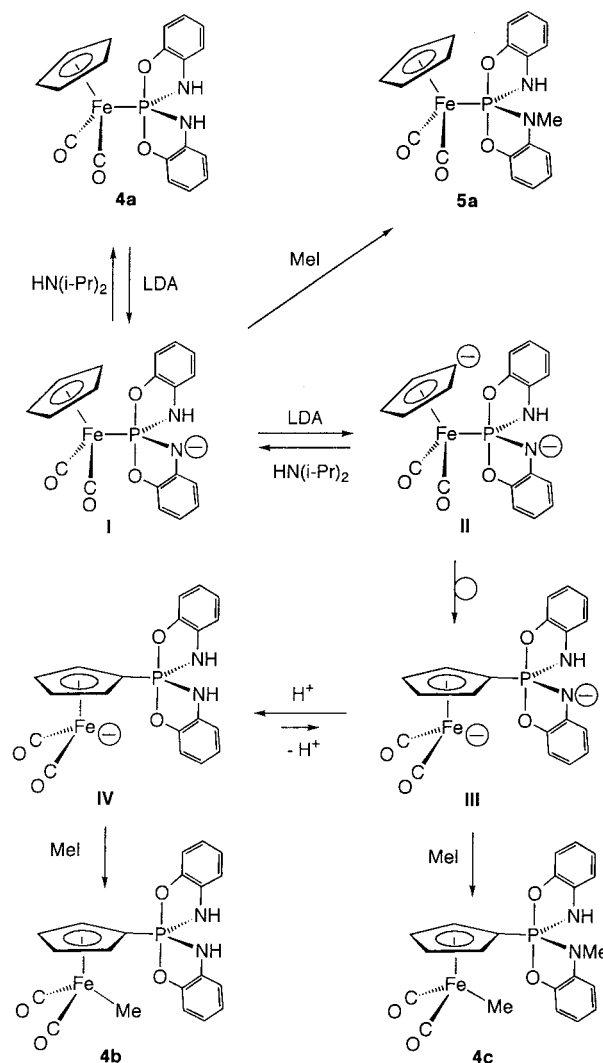
(26) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses for **1c**

Bond Lengths			
Fe(1)–C(1)	2.112(2)	Fe(1)–C(2)	2.134(2)
Fe(1)–C(3)	2.116(2)	Fe(1)–C(4)	2.108(2)
Fe(1)–C(5)	2.084(2)	Fe(1)–C(20)	1.745(2)
Fe(1)–C(21)	1.753(3)	Fe(1)–C(22)	2.090(2)
P(1)–O(1)	1.711(2)	P(1)–O(2)	1.709(1)
P(1)–N(1)	1.701(2)	P(1)–N(2)	1.689(2)
P(1)–C(1)	1.809(2)	O(1)–C(6)	1.358(3)
O(2)–C(12)	1.359(2)	O(3)–C(20)	1.150(3)
O(4)–C(21)	1.145(3)	N(1)–C(11)	1.393(2)
N(1)–C(18)	1.454(2)	N(2)–C(17)	1.401(3)
N(2)–C(19)	1.461(3)	C(1)–C(2)	1.425(2)
C(1)–C(5)	1.446(3)	C(2)–C(3)	1.406(3)
C(3)–C(4)	1.418(3)	C(4)–C(5)	1.403(3)
C(6)–C(7)	1.377(2)	C(6)–C(11)	1.388(3)
C(7)–C(8)	1.402(3)	C(8)–C(9)	1.381(3)
C(9)–C(10)	1.390(3)	C(10)–C(11)	1.391(3)
C(12)–C(13)	1.367(3)	C(12)–C(17)	1.399(3)
C(13)–C(14)	1.405(3)	C(14)–C(15)	1.377(3)
C(15)–C(16)	1.393(3)	C(16)–C(17)	1.380(3)
C(22)–C(23)	1.495(3)		
Bond Angles			
C(20)–Fe(1)–C(21)	91.2(1)	C(20)–Fe(1)–C(22)	90.7(1)
C(21)–Fe(1)–C(22)	88.1(1)	O(1)–P(1)–O(2)	178.9(1)
O(1)–P(1)–N(1)	88.8(1)	O(1)–P(1)–N(2)	90.9(1)
O(1)–P(1)–C(1)	90.3(1)	O(2)–P(1)–N(1)	90.4(1)
O(2)–P(1)–N(2)	89.0(1)	O(2)–P(1)–C(1)	90.8(1)
N(1)–P(1)–N(2)	126.7(1)	N(1)–P(1)–C(1)	115.6(1)
N(2)–P(1)–C(1)	117.6(1)	P(1)–O(1)–C(6)	114.5(2)
P(1)–O(2)–C(12)	114.6(1)	P(1)–N(1)–C(11)	113.8(1)
P(1)–N(1)–C(18)	127.4(1)	C(11)–N(1)–C(18)	118.7(2)
P(1)–N(2)–C(17)	114.5(2)	P(1)–N(2)–C(19)	128.5(2)
C(17)–N(2)–C(19)	116.9(2)	P(1)–C(1)–C(2)	126.9(2)
P(1)–C(1)–C(5)	126.3(2)	C(2)–C(1)–C(5)	106.6(2)
C(1)–C(2)–C(3)	108.6(2)	C(2)–C(3)–C(4)	108.3(2)
C(3)–C(4)–C(5)	108.3(2)	C(1)–C(5)–C(4)	108.1(2)
O(1)–C(6)–C(7)	125.6(2)	O(1)–C(6)–C(11)	111.7(2)
C(7)–C(6)–C(11)	122.7(2)	C(6)–C(7)–C(8)	117.2(2)
C(7)–C(8)–C(9)	120.9(2)	C(8)–C(9)–C(10)	121.2(2)
C(9)–C(10)–C(11)	118.4(2)	N(1)–C(11)–C(6)	110.9(2)
N(1)–C(11)–C(10)	129.4(2)	C(6)–C(11)–C(10)	119.7(2)
O(2)–C(12)–C(13)	126.1(2)	O(2)–C(12)–C(17)	111.8(2)
C(13)–C(12)–C(17)	122.0(2)	C(12)–C(13)–C(14)	117.8(2)
C(13)–C(14)–C(15)	120.7(2)	C(14)–C(15)–C(16)	121.1(2)
C(15)–C(16)–C(17)	118.6(2)	N(2)–C(17)–C(12)	109.9(2)
N(2)–C(17)–C(16)	130.2(2)	C(12)–C(17)–C(16)	119.9(2)
Fe(1)–C(20)–O(3)	175.3(2)	Fe(1)–C(21)–O(4)	178.9(2)
Fe(1)–C(22)–C(23)	115.6(2)		

triplet, respectively. The resonance at 24.18 ppm is assigned to the starting complex **4a**. The chemical shift at 21.90 ppm is almost the average of 24.18 ppm due to **4a** and 16.29 ppm due to **1a**, and the signal is observed as a broad singlet in the proton nondecoupled  $^{31}\text{P}$  NMR. Therefore, the signal at 21.90 ppm is reasonably attributed to  $\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{NMe})\}$  (**5a**) corresponding to a singly N-methylated derivative of **4a**. The resonance at  $-38.45$  ppm is assigned to a phosphorane-migrated complex (**4b**) (vide infra).

The reaction of **4a** with 4 equiv of LDA and then MeI gave different products. The  $^{31}\text{P}$  NMR spectrum of the resulting solution exhibits mainly two singlets at  $-39.71$  (corresponding to a resonance at  $-38.45$  ppm in the above experiment) and  $-42.77$  ppm in the ratio of 4:1, and the signals ascribed to **4a** and **5a** were not observed in this case. These two products were separated and isolated as yellow powders by HPLC. The spectroscopic measurements revealed that the products are  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NH})_2\}\text{Fe}(\text{CO})_2\text{Me}$  (**4b**, 46% yield) showing a singlet at  $-39.71$  ppm in the  $^{31}\text{P}$  NMR and  $\{\eta^5\text{-C}_5\text{H}_4\text{P}(\text{OC}_6\text{H}_4\text{NH})(\text{OC}_6\text{H}_4\text{NMe})\}\text{Fe}(\text{CO})_2\text{Me}$  (**4c**, 14% yield) showing a singlet at  $-42.77$  ppm.

**Scheme 2**

We propose the reaction pathway as follows (see Scheme 2). In the reaction of **4a** with 2 equiv of LDA, not the Cp proton but the amino proton is abstracted by LDA to give **I** where the remaining NH proton may be shuttling between the two nitrogens. The basicity of LDA may not be strong enough to abstract completely even one of the amino protons; therefore, **4a** and **I** may be in equilibrium under the present reaction conditions. Complex **I** reacts with MeI at the amido position to give **5a**.

When 4 equiv of LDA is used in the reaction of **4a**, the equilibrium between **4a** and **I** may shift to the right, and moreover, **I** can react with extra LDA. In this reaction, the Cp proton, not the remaining NH proton, may be abstracted to give **II**, which undergoes an anionic phosphorane fragment migration to yield **III**. If the basicity at the amido group increases on going from **II** to **III**, the amido group in **III** picks up either an amino proton of **4a**, a Cp proton of **I**, or an amino proton of  $\text{HN}(i\text{-Pr})_2$  to give **IV**. **III** and **IV** are in equilibrium in favor of **IV**. MeI reacts with both **III** and **IV** to give **4c** and **4b**, respectively.

It should be noted that, in the reaction of **4a** with 2 equiv of LDA and then MeI, **5a** is the main product and **4b** is a minor one. This indicates that **4b** may not be produced by the proton abstraction on the Cp ring in **4a**, followed by the phosphorane migration. **4b** and **4c** are reasonably assumed to be derived from **IV** and **III**, respectively. Therefore, the following two

points should be noted: (i) LDA selectively abstracts an amino proton in **4a** and does not abstract the Cp proton, (ii) an anionic phosphorane fragment migrates to the Cp ring; in other words, an anionic phosphorane fragment still can accept a nucleophilic attack.

## Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Column chromatography was done quickly in the air. THF, diethyl ether, benzene, and hexane were freshly distilled from sodium metal prior to use. Other organic solvents, HN-(*i*-Pr)<sub>2</sub>, *n*-BuLi (0.66 M of hexane solution), MeI, and PhCH<sub>2</sub>Cl, were obtained from common commercial sources and used without further purification. A 0.5 N THF solution of LDA was prepared from HN-(*i*-Pr)<sub>2</sub> and *n*-BuLi prior to use. CpFe(CO)<sub>2</sub>{P(OC<sub>6</sub>H<sub>4</sub>NMe)<sub>2</sub>} (**1a**), CpFe(CO)<sub>2</sub>{P(OC<sub>6</sub>H<sub>4</sub>NMe)(OC<sub>6</sub>H<sub>4</sub>O)} (**2a**), CpFe(CO)<sub>2</sub>{P(OC<sub>6</sub>H<sub>4</sub>O)<sub>2</sub>} (**3a**), and CpFe(CO)<sub>2</sub>{P(OC<sub>6</sub>H<sub>4</sub>NH)<sub>2</sub>} (**4a**) were prepared by published procedures.<sup>24</sup>

HPLC was performed using a JAI LC-908 recycling preparative HPLC instrument with JAIGEL-1H and -2H columns. IR spectra were recorded on either a Shimadzu FTIR-8100A or an FTIR-4000 spectrometer. JEOL LA-300 and EX-400 multinuclear spectrometers were used to obtain <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra. <sup>1</sup>H and <sup>13</sup>C NMR data were referenced to Me<sub>4</sub>Si, and <sup>31</sup>P NMR data were referenced to 85% H<sub>3</sub>PO<sub>4</sub>. 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 1b.** A solution of **1a** (232 mg, 0.52 mmol) in THF (3 mL) was treated with LDA (1.3 mL, 0.65 mmol) at -78 °C. The color of the solution changed immediately from yellow to deep orange. After it has been stirred at -78 °C for 15 min, the reaction mixture was treated with MeI (60 μL, 0.96 mmol), warmed to room temperature, and then stirred for 30 min to complete the reaction. The solvent was removed under reduced pressure, and the residue was extracted with a small amount of hexane/benzene (7/3). The extract was loaded on a silica gel column and eluted with a mixture of hexane/benzene (7/3). The yellow band eluted first was collected, and the solvents were removed in vacuo to give **1b** as a pale yellow powder (151 mg, 0.32 mmol, 63%). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>FeN<sub>2</sub>O<sub>4</sub>P: C, 56.92; H, 4.56; N, 6.03. Found: C, 56.89; H, 4.51; N, 5.86. MS (EI, 70 eV): *m/z* (relative intensity) 464 (3, M<sup>+</sup>), 436 (2, M<sup>+</sup> - CO), 408 (40, M<sup>+</sup> - 2CO), 393 (100, M<sup>+</sup> - 2CO - Me), 273 (21), 152 (87).

**Preparation of 1c.** A treatment of **1a** (179 mg, 0.40 mmol) with LDA (1.0 mL, 0.5 mol) followed by PhCH<sub>2</sub>Cl (90 μL, 0.78 mmol) in a manner similar to that for **1b** gave a pale yellow powder of **1c** (155 mg, 0.29 mmol, 72%). Anal. Calcd for C<sub>28</sub>H<sub>25</sub>FeN<sub>2</sub>O<sub>4</sub>P: C, 62.24; H, 4.66; N, 5.18. Found: C, 62.09; H, 4.71; N, 5.04. MS (EI, 70 eV): *m/z* (relative intensity) 521 (4, M<sup>+</sup> - CO), 484 (19, M<sup>+</sup> - 2CO), 393 (89, M<sup>+</sup> - 2CO - CH<sub>2</sub>Ph), 152 (67), 91 (100).

**Preparation of 2b.** A solution of **2a** (198 mg, 0.45 mmol) in THF (3 mL) was treated with LDA (1.4 mL, 0.70 mmol) at -78 °C, and the mixture was stirred for 15 min. The solution was then treated with MeI (60 μL, 0.96 mmol) and warmed to room temperature. Procedures similar to those described above yielded **2b** as a pale yellow powder (119 mg, 0.26 mmol, 58%). Anal. Calcd for C<sub>21</sub>H<sub>18</sub>FeNO<sub>5</sub>P: C, 55.90; H, 4.02; N, 3.10. Found: C, 55.76; H, 4.02; N, 2.96. MS (EI, 70 eV): *m/z* (relative intensity) 451 (2, M<sup>+</sup>), 395 (42, M<sup>+</sup> - 2CO), 380 (100, M<sup>+</sup> - 2CO - Me), 288 (18), 152 (18).

**Preparation of 3b.** **3a** (136 mg, 0.32 mmol) was dissolved in THF (3 mL) and treated with LDA (1.0 mL, 0.50 mmol) at -78 °C. After it had been stirred at -78 °C for 15 min, the reaction mixture was treated with MeI (40 μL, 0.64 mmol) and warmed to room temperature. The solvent was removed in vacuo from the mixture, and the residue was extracted with ether. The ether solution was filtered, and the

solvent was removed under reduced pressure to give a crude product of **3b** as a brown oil. Although the product was too unstable to be purified, the satisfactory IR spectrum and <sup>13</sup>C and <sup>31</sup>P NMR data of **3b** were obtained.

**Preparation of 4b and 4c.** LDA (6.1 mL, 3.1 mmol) was added to a solution of **4a** (320 mg, 0.76 mmol) in THF (6 mL) at -78 °C, and the reaction mixture was stirred for 15 min. The solution was treated with MeI (250 μL, 4.01 mmol), warmed to room temperature, and then stirred for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with a small amount of benzene. The benzene extract was charged on a silica gel column and eluted with benzene. The yellow band was collected, and the solvent was removed in vacuo to give a yellow oil which was a mixture of **4b** and **4c**. These products were separated by HPLC with chloroform as an eluent to give a yellow powder of **4b** (152 mg, 0.35 mmol, 46%) and a yellow powder of **4c** (49 mg, 0.11 mmol, 14%). **4b.** Anal. Calcd for C<sub>20</sub>H<sub>17</sub>FeN<sub>2</sub>O<sub>4</sub>P: C, 55.07; H, 3.93; N, 6.42. Found: C, 54.97; H, 3.69; N, 6.28. MS (EI, 70 eV): *m/z* (relative intensity) 436 (3, M<sup>+</sup>), 408 (7, M<sup>+</sup> - CO), 380 (52, M<sup>+</sup> - 2CO), 365 (100, M<sup>+</sup> - 2CO - Me), 228 (26). **4c.** Anal. Calcd for C<sub>21</sub>H<sub>19</sub>FeN<sub>2</sub>O<sub>4</sub>P: C, 56.02; H, 4.25; N, 6.22. Found: C, 55.78; H, 4.11; N, 5.99. MS (EI, 70 eV): *m/z* (relative intensity) 450- (1, M<sup>+</sup>), 422(6, M<sup>+</sup> - CO), 394 (37, M<sup>+</sup> - 2CO), 379 (100, M<sup>+</sup> - 2CO - Me), 242 (13), 176 (14), 152 (30), 56 (26).

**Stability of the Migration Products.** All migration products in the present paper except **3b**, that is, **1b**, **1c**, **2b**, **4b**, and **4c**, are as stable as they can be purified by column chromatography in air for about 30 min. Complex **3b** decomposes if it exposed to air.

**X-ray Structure Determination.** Crystallographic and experimental details of X-ray crystal structure analysis for **1c** are given in Table 2. A suitable crystal of **1c** was obtained through recrystallization from hot toluene. The crystal was mounted on a Mac Science MXCκ diffractometer and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit-cell dimensions were obtained by least squares from the angular setting of 26 accurately centered reflections with 32° < 2θ < 35°. P<sub>2</sub>/n was selected as the space group, which led to successful refinement. Reflection intensities were collected in the usual manner at 25 °C, and three reflections checked after every 300 reflections showed no decrease in intensity.

The structure was solved by a direct method with the program SIR92.<sup>27</sup> The positions of the hydrogen atoms were determined from subsequent difference Fourier maps. 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 = 0.032 and R<sub>w</sub> = 0.040. All calculations were performed on an SGI Indy R5000 computer using the program system CRYSTAN-GM<sup>28</sup> with neutral atom scattering factors from Cromer and Weber.<sup>29</sup>

**Acknowledgment.** This work was supported by Grant-in-Aids for Scientific Research (07404037 and 07740523) and a Grant-in-Aid on Priority Area of Interelement Chemistry (No. 09239235) from the Ministry of Education, Science, Sports and Culture of Japan.

**Supporting Information Available:** Tables giving positional and thermal parameters for **1c** (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA980146M

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