

# Reactions of Cationic Piano Stool Iron Complexes Containing Phosphorus Ligands with Phosphorus Ylide

Hiroshi Nakazawa,\* Yoshiko Ueda, Keiichi Nakamura, and Katsuhiko Miyoshi\*

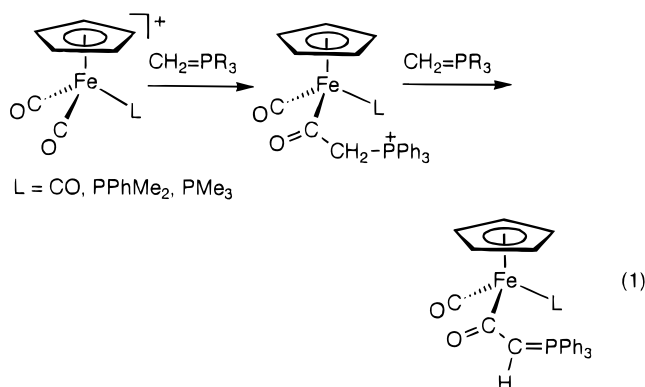
Department of Chemistry, Faculty of Science, Hiroshima University,  
Higashi-Hiroshima 739, Japan

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Reactions of  $\text{PF}_6^-$  salts of cationic piano stool iron complexes with a phosphorus ylide,  $\text{CH}_2\text{PPh}_3$ , were examined. In the reaction of the dicarbonyl complex  $[\text{Cp}(\text{CO})_2\text{FeL}]^+$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{P}(\text{OEt})_3, \text{PPh}_2(\text{OMe})$ ),  $\text{Cp}(\text{CO})\text{LFe}\{\text{C}(\text{O})\text{CH}=\text{PPh}_3\}$  is formed by the nucleophilic attack of the carbene carbon of  $\text{CH}_2\text{PPh}_3$  on the carbonyl carbon of the complex. In contrast, the reaction of the monocarbonyl complex  $[\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{OR})_3\}]^+$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{R} = \text{Me}; \text{L} = \text{PMe}_3, \text{R} = \text{Me}; \text{L} = \text{P}(\text{OEt})_3, \text{R} = \text{Et}$ ) yields  $\text{Cp}(\text{CO})\text{LFe}\{\text{P}(\text{O})(\text{OR})_2\}$  by the Arbuzov-like dealkylation reaction.  $[\text{Cp}(\text{PMe}_3)_2\text{Fe}\{\text{P}(\text{OMe})_3\}]^+$ , having no CO ligand, also exhibits the Arbuzov-like dealkylation reaction under forced conditions. These results indicate that increasing the back donation ability from a central transition metal to a ligand induces a change in the reaction site from a carbonyl carbon in a CO ligand to an  $\alpha$ -carbon in a phosphite ligand. In the reaction of  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{PPh}_2\text{H}\}]^+$ , proton abstraction from the  $\text{PPh}_2\text{H}$  ligand takes place to give a phosphide complex  $\text{Cp}(\text{CO})_2\text{FePPh}_2$ .

## Introduction

Phosphorus ylides, being one of the most well-investigated compounds in organic chemistry, have attracted significant attention in organometallic chemistry over the past few decades. The results have been nicely reviewed.<sup>1,2</sup> Although many reactions with phosphorus ylides have been reported for most of the transition metals in the periodic table, a systematic approach, such as the study of an influence of changing ancillary ligands on a certain transition metal on the reactivity or reaction site, seems rather sparse. In the case of cationic piano stool iron complexes, the reactions of  $[\text{CpFe}(\text{CO})_2\text{L}]^+$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ,  $\text{L} = \text{CO}, \text{PPhMe}_2, \text{PMe}_3$ ) with  $\text{CH}_2=\text{PR}_3$  have been examined and it was found that the carbene carbon of  $\text{CH}_2=\text{PR}_3$  nucleophilically attacks the carbonyl carbon of  $[\text{CpFe}(\text{CO})_2\text{L}]^+$  to give  $[\text{Cp}(\text{CO})\text{LFe}-\text{C}(\text{O})\text{CH}_2\text{PR}_3]^+$ , which reacts successively with another  $\text{CH}_2=\text{PR}_3$  to give  $\text{Cp}(\text{CO})\text{LFe}-\text{C}(\text{O})\text{CH}=\text{PR}_3$  (eq 1).<sup>3</sup> However, the reaction of cationic piano stool iron complexes containing phosphite with a phosphorus ylide has not been reported so far. It is well-known that cationic complexes containing phosphite react with a nucleophile to give a phosphonate complex by the Arbuzov-like dealkylation reaction.<sup>4,5</sup> We also have been engaged in the study of piano stool Fe and Ru complexes with a phosphonate ligand.<sup>6</sup> Since  $\text{CH}_2\text{PR}_3$  is a very nice nucleophile, two plausible reactions are expected when cationic piano stool iron complexes containing phosphite are treated with  $\text{CH}_2\text{PR}_3$ : (i) a carbonyl attack, as shown in eq 1, and (ii) an Arbuzov-like dealkylation reaction to give a phosphonate complex. In order to elucidate which type of reactions take



place for what kind of complexes, we examined the reaction of several kinds of cationic piano stool iron complexes containing phosphite with a phosphorus ylide.

## Results and Discussion

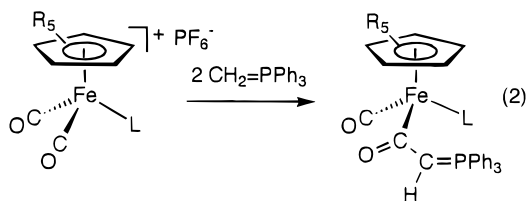
The phosphorus ylide used in this paper is confined to  $\text{CH}_2\text{PPh}_3$ .  $\text{PF}_6^-$  salts of several kinds of cationic piano stool iron complexes are subjected to the reaction with  $\text{CH}_2\text{PPh}_3$ , which can be classified into three groups:  $[\text{Cp}(\text{CO})_2\text{FeL}]^+$ ,  $[\text{Cp}(\text{CO})\text{FeLL}']^+$ , and  $[\text{CpFeLL}'_2]^+$ . The spectroscopic data of the starting complexes and products are summarized in Table 1.

**Reaction of  $[\text{Cp}(\text{CO})_2\text{FeL}]^+$ .** A  $\text{PF}_6^-$  salt of  $[\text{Cp}(\text{CO})_2\text{Fe}\{\text{P}(\text{OMe})_3\}]^+$ , **1a**, was suspended in benzene, and 2 equiv of  $\text{CH}_2\text{PPh}_3$  was added. The color of the solution immediately changed from yellow to reddish orange. After work up, a yellow powder was isolated. The product was assigned to  $[\text{Cp}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Fe}\{\text{C}(\text{O})\text{CH}=\text{PPh}_3\}]$  (**2a**, eq 2) for the following reasons: (i) The IR spectrum exhibits one absorption at  $1914\text{ cm}^{-1}$  in the  $\nu_{\text{CO}}$  region, which is more than  $100\text{ cm}^{-1}$  lower in frequency than those for the starting complex ( $2071$  and  $2028\text{ cm}^{-1}$ ), indicating that the product has one terminal CO ligand and is electrically neutral. (ii)

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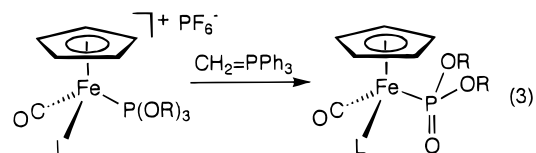
<b>1a</b>	R = H	L = P(OMe) <sub>3</sub>	<b>2a</b>
<b>1b</b>	R = H	L = P(OEt) <sub>3</sub>	<b>2b</b>
<b>1c</b>	R = H	L = PPh <sub>2</sub> (OMe)	<b>2c</b>
<b>1d</b>	R = Me	L = P(OMe) <sub>3</sub>	<b>2d</b>

In the <sup>31</sup>P NMR spectrum, two resonances are observed at 2.02 and 189.05 ppm as doublets with  $J_{PP} = 9.2$  Hz. (iii) The <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the existence of a  $-\text{C}(\text{O})\text{CH}=\text{PPh}_3$  ligand. The elemental analysis data also support the formation of **2a**. Although the isolation yield was 49%, the conversion of **1a** into **2a** proceeded cleanly, which was evidenced by the IR and <sup>31</sup>P NMR measurements of the reaction mixture. Two more dicarbonyl complexes  $[\text{Cp}(\text{CO})_2\text{FeL}]\text{PF}_6$  (L = P(OEt)<sub>3</sub> (**1b**), PPh<sub>2</sub>(OMe) (**1c**)) were subjected to the reaction with CH<sub>2</sub>PPh<sub>3</sub>. The products were **2b** and **2c**, respectively (see eq 2). These results show that the carbonyl carbon in  $[\text{Cp}(\text{CO})_2\text{FeL}]^+$  is the most reactive site toward CH<sub>2</sub>PPh<sub>3</sub>.

The Cp\* analogue of **1a** (**1d**) showed the same reactivity indicating that the carbonyl carbon is still the reaction site, though the electrophilicity of the CO seems to be reduced by a more electron-donating Cp\* ligand than a Cp ligand.

**Reaction of  $[\text{Cp}(\text{CO})\text{FeLL}]^+$ .** For the monocarbonyl complexes  $[\text{Cp}(\text{CO})\text{FeLL}]^+$  (L = L' = P(OMe)<sub>3</sub> (**3a**); L = P(OMe)<sub>3</sub>, L' = PMe<sub>3</sub> (**3b**); L = L' = P(OEt)<sub>3</sub> (**3c**)), it is expected that the electrophilicity of the carbonyl carbon is reduced compared with that of the dicarbonyl complexes  $[\text{Cp}(\text{CO})_2\text{FeL}]^+$ . Actually, the  $\nu_{\text{CO}}$ 's of **3a–c** are considerably lower in frequency than those for **1a–d** (see Table 1).

The reaction of **3a** with CH<sub>2</sub>PPh<sub>3</sub> under similar reaction conditions to those of **1a** resulted in the formation of a yellow powder in 86% yield. The spectroscopic data of the product indicate the formation of  $\text{Cp}(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Fe}\{\text{P}(\text{O})(\text{OMe})_2\}$  (**4a**, eq 3). The <sup>31</sup>P



<b>3a</b>	L = P(OMe) <sub>3</sub> , R = Me	<b>4a</b>
<b>3b</b>	L = PMe <sub>3</sub> , R = Me	<b>4b</b>
<b>3c</b>	L = P(OEt) <sub>3</sub> , R = Et	<b>4c</b>

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NMR spectrum showed two doublets at 123.95 and 181.91 ppm with  $J_{PP} = 137.8$  Hz. These are reasonably attributed to P(O)(OMe)<sub>2</sub> and P(OMe)<sub>3</sub> ligands, respectively. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra, two diastereotopic OMe groups in the P(O)(OMe)<sub>2</sub> ligand were observed, indicating that the iron is a chiral center and the racemization either does not occur or is slow on the NMR time scale. Complexes **3b** and **3c** were also converted into the corresponding phosphonate complexes, **4b** and **4c**, respectively, by the reaction with CH<sub>2</sub>PPh<sub>3</sub> (eq 3).

These results show that the reactions proceed by the nucleophilic attack of the carbene carbon of CH<sub>2</sub>PPh<sub>3</sub> at the  $\alpha$ -carbon in the coordinating phosphite rather than at the coordinating CO carbon to give the corresponding phosphonate complexes (the Arbuzov-like dealkylation reaction). This is the first example in which a phosphorus ylide induces the Arbuzov-like dealkylation reaction leading to a transition-metal-phosphonate complex. It has been reported that CO ligands with a CO stretching frequency at 2000 cm<sup>-1</sup> or above will be subjected to nucleophilic attack to give  $\text{M}-\text{C}(\text{O})\text{CH}_2\text{PPh}_3^+$  rather than substitution to give  $\text{M}-\text{CH}_2-\text{PPh}_3^+$ .<sup>2,7</sup> Likewise, complexes with carbonyl stretching modes below 2000 cm<sup>-1</sup> appear to give substitution products. This rule holds in our case in the sense that complexes **1a–d**, having carbonyl stretching modes above 2000 cm<sup>-1</sup>, suffer nucleophilic attack at CO and complexes **3a–c**, having  $\nu_{\text{CO}}$  below 2000 cm<sup>-1</sup>, do not sustain nucleophilic attack. The latter complexes undergo the Arbuzov-like dealkylation reaction rather than the CO substitution.

**Reaction of  $[\text{CpFeLL}_2]^+$ .** We chose  $[\text{CpFe}\{\text{P}(\text{OMe})_3\}\{\text{P}(\text{Me})_2\}]\text{PF}_6$  (**5a**) as an example of cationic piano stool complexes containing no carbonyl ligand and

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**Table 1. Spectroscopic Data**

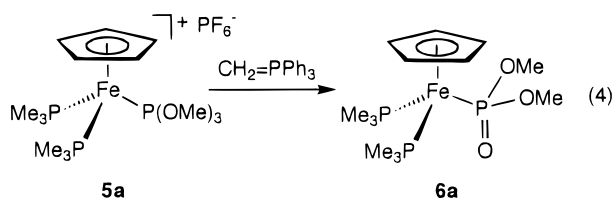
complex	IR (CH <sub>2</sub> Cl <sub>2</sub> ) $\nu(\text{CO})$ , (cm <sup>-1</sup> )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) $\delta$ (ppm)	<sup>31</sup> P NMR (CH <sub>2</sub> Cl <sub>2</sub> ) $\delta$ (ppm) <sup>a</sup>	<sup>13</sup> C NMR (CDCl <sub>3</sub> ) $\delta$ (ppm)
<b>1a</b>	2071, 2028	3.84 (d, $J_{\text{PH}} = 12.2$ Hz, 9H, OMe), 5.43 (s, 5H, Cp)	159.80 (s, P(OMe) <sub>3</sub> )	54.85 (d, $J_{\text{PC}} = 7.9$ Hz, P(OMe) <sub>3</sub> ), 87.19 (s, Cp), 206.82 (d, $J_{\text{PC}} = 39.1$ Hz, CO)
<b>1b</b>	2068, 2025	1.38 (t, $J_{\text{HH}} = 6.9$ Hz, 9H, CH <sub>3</sub> ), 4.16 (qui, $J_{\text{HH}} = 7.1$ Hz, 6H, OCH <sub>2</sub> ), 5.39 (s, 5H, Cp)	152.70 (s, P(OEt) <sub>3</sub> )	15.87 (d, $J_{\text{PC}} = 6.7$ Hz, OCH <sub>2</sub> CH <sub>3</sub> ), 64.77 (d, $J_{\text{PC}} = 7.9$ Hz, OCH <sub>2</sub> CH <sub>3</sub> ), 87.15 (s, Cp), 207.20 (d, $J_{\text{PC}} = 39.1$ Hz, CO)
<b>1c</b>	2061, 2020	3.64 (d, $J_{\text{PH}} = 12.8$ Hz, 3H, OMe), <sup>b</sup> 5.54 (d, $J_{\text{PH}} = 1.7$ Hz, 5H, Cp), 7.64–7.78 (m, 10H, Ph)	164.91 (s, PPh <sub>2</sub> (OMe))	56.35 (d, $J_{\text{PC}} = 9.3$ Hz, P(OMe) <sub>3</sub> ), <sup>b</sup> 89.60 (s, Cp), 130.49 (d, $J_{\text{PC}} = 11.2$ Hz, <i>m</i> -Ph), 132.05 (d, $J_{\text{PC}} = 11.8$ Hz, <i>o</i> -Ph), 134.00 (d, $J_{\text{PC}} = 2.5$ Hz, <i>p</i> -Ph), 134.52 (d, $J_{\text{PC}} = 55.3$ Hz, $\epsilon$ -Ph), 209.93 (d, $J_{\text{PC}} = 27.3$ Hz, CO)
<b>1d</b>	2047, 2001	1.90 (s, 15H, Cp*), 3.82 (d, $J_{\text{PH}} = 10.4$ Hz, 9H, OMe)	160.19 (s, P(OMe) <sub>3</sub> )	9.47 (s, C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> ), 55.72 (d, $J_{\text{PC}} = 8.7$ Hz, P(OMe) <sub>3</sub> ), 100.89 (s, C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> ), 209.93 (d, $J_{\text{PC}} = 36.0$ Hz, CO)
<b>1e</b>	2061, 2016	5.65 (d, $J_{\text{PH}} = 2.0$ Hz, 5H, Cp), <sup>b</sup> 7.56 (d, $J_{\text{PH}} = 410.8$ Hz, 1H, PH), 7.49–7.59 (m, 6H, Ph), 7.67–7.75 (m, 4H, Ph)	32.59 (s, PPh <sub>2</sub> )	89.68 (s, Cp), <sup>b</sup> 130.43 (d, $J_{\text{PC}} = 54.1$ Hz, $\epsilon$ -Ph), 131.15 (d, $J_{\text{PC}} = 11.2$ Hz, <i>m</i> -Ph), 133.60 (d, $J_{\text{PC}} = 2.5$ Hz, <i>p</i> -Ph), 133.62 (d, $J_{\text{PC}} = 10.6$ Hz, <i>o</i> -Ph), 210.31 (d, $J_{\text{PC}} = 24.2$ Hz, CO)
<b>2a</b>	1914 <sup>d</sup>	3.62 (d, $J_{\text{PH}} = 10.8$ Hz, 9H, OMe), <sup>c</sup> 4.55 (d, $J_{\text{PH}} = 38.0$ Hz, 1H, CH=P), 4.75 (d, $J_{\text{PH}} = 0.8$ Hz, 5H, Cp), 7.00–7.25 (m, 15H, Ph)	2.02 (d, $J_{\text{PP}} = 9.2$ Hz, PPh <sub>3</sub> ), 189.05 (d, $J_{\text{PP}} = 9.2$ Hz, P(OMe) <sub>3</sub> )	51.99 (d, $J_{\text{PC}} = 4.6$ Hz, OMe), <sup>c</sup> 60.16 (dd, $J_{\text{PC}} = 73.1$ and 10.1 Hz, CH=P), 84.77 (s, Cp), 128.46 (d, $J_{\text{PC}} = 9.2$ Hz, <i>m</i> -Ph), 130.51 (d, $J_{\text{PC}} = 86.4$ Hz, $\epsilon$ -Ph), 131.04 (d, $J_{\text{PC}} = 2.8$ Hz, <i>p</i> -Ph), 133.41 (d, $J_{\text{PC}} = 10.1$ Hz, <i>o</i> -Ph), 221.49 (dd, $J_{\text{PC}} = 49.2$ and 3.7 Hz, CO), 230.06 (dd, $J_{\text{PC}} = 31.7$ and 10.1 Hz, C(O)CH)
<b>2b</b>	1913 <sup>d</sup>	1.15 (t, $J_{\text{HH}} = 7.0$ Hz, 9H, CH <sub>3</sub> ), <sup>c</sup> 4.15 (qui, $J_{\text{HH}} = 7.0$ Hz, 6H, OCH <sub>2</sub> ), 4.55 (d, $J_{\text{PH}} = 37.8$ Hz, 1H, CH=P), 4.74 (s, 5H, Cp), 7.02–7.16 (m, 9H, Ph), 7.72–7.78 (m, 6H, Ph)	1.80 (d, $J_{\text{PP}} = 9.8$ Hz, PPh <sub>3</sub> ), 184.07 (d, $J_{\text{PP}} = 9.8$ Hz, P(OEt) <sub>3</sub> )	16.60 (d, $J_{\text{PC}} = 6.6$ Hz, OCH <sub>2</sub> CH <sub>3</sub> ), <sup>c</sup> 59.85 (dd, $J_{\text{PC}} = 71.7$ and 8.1 Hz, CH=P), 60.50 (d, $J_{\text{PC}} = 8.8$ Hz, OCH <sub>2</sub> CH <sub>3</sub> ), 84.86 (s, Cp), 128.40 (d, $J_{\text{PC}} = 12.4$ Hz, <i>m</i> -Ph), 130.60 (d, $J_{\text{PC}} = 86.4$ Hz, $\epsilon$ -Ph), 131.00 (d, $J_{\text{PC}} = 2.9$ Hz, <i>p</i> -Ph), 133.37 (d, $J_{\text{PC}} = 9.5$ Hz, <i>o</i> -Ph), 211.82 (dd, $J_{\text{PC}} = 50.0$ and 2.9 Hz, CO), 230.06 (dd, $J_{\text{PC}} = 31.5$ and 10.2 Hz, C(O)CH)
<b>2c</b>	1902 <sup>d</sup>	3.49 (d, $J_{\text{PH}} = 12.3$ Hz, 3H, OMe), <sup>c</sup> 4.43 (s, 5H, Cp), 4.62 (d, $J_{\text{PH}} = 37.0$ Hz, 1H, CH=P), 6.82–7.15, 7.64–7.70, 8.02 (m, 30H, Ph)	2.25 (d, $J_{\text{PP}} = 6.7$ Hz, PPh <sub>3</sub> ), 182.05 (d, $J_{\text{PP}} = 6.7$ Hz, PPh <sub>2</sub> (OMe))	52.80 (s, OMe), <sup>c</sup> 60.94 (dd, $J_{\text{PC}} = 70.9$ and 6.8 Hz, CH=P), 85.95 (s, Cp), 127.83 (d, $J_{\text{PC}} = 5.6$ Hz, <i>m</i> -Ph in PPh <sub>2</sub> (OMe)), 128.54 (d, $J_{\text{PC}} = 11.8$ Hz, <i>m</i> -Ph in PPh <sub>3</sub> ), 129.47 (s, <i>p</i> -Ph in PPh <sub>3</sub> ), 130.38 (d, $J_{\text{PC}} = 86.4$ Hz, $\epsilon$ -Ph in PPh <sub>3</sub> ), 131.11 (d, $J_{\text{PC}} = 2.5$ Hz, <i>p</i> -Ph in PPh <sub>2</sub> (OMe)), 132.21 (d, $J_{\text{PC}} = 11.2$ Hz, <i>o</i> -Ph in PPh <sub>2</sub> (OMe)), 133.35 (d, $J_{\text{PC}} = 9.9$ Hz, <i>o</i> -Ph in PPh <sub>3</sub> ), 141.78 (d, $J_{\text{PC}} = 45.4$ Hz, $\epsilon$ -Ph in PPh <sub>2</sub> (OMe)), 142.50 (d, $J_{\text{PC}} = 44.1$ Hz, $\epsilon$ -Ph in PPh <sub>2</sub> (OMe)), 222.95 (dd, $J_{\text{PC}} = 37.9$ and 3.7 Hz, CO), 231.76 (dd, $J_{\text{PC}} = 23.6$ and 10.6 Hz, C(O)CH)
<b>2d</b>	1893 <sup>c</sup>	1.86 (s, 15H, Cp*), <sup>c</sup> 3.69 (d, $J_{\text{PH}} = 10.5$ Hz, 9H, OMe), 4.44 (d, $J_{\text{PH}} = 39.4$ Hz, 1H, CH=P), 7.10, 7.73, 7.88 (m, 15H, Ph)	3.28 (d, $J_{\text{PP}} = 11.1$ Hz, PPh <sub>3</sub> ), 185.04 (d, $J_{\text{PP}} = 11.1$ Hz, P(OMe) <sub>3</sub> )	9.93 (s, C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> ), <sup>c</sup> 52.00 (d, $J_{\text{PC}} = 5.3$ Hz, P(OMe) <sub>3</sub> ), 57.80 (dd, $J_{\text{PC}} = 70.2$ and 9.2 Hz, CH=P), 94.03 (s, C <sub>5</sub> (CH <sub>3</sub> ) <sub>5</sub> ), 128.17 (d, $J_{\text{PC}} = 11.4$ Hz, <i>m</i> -Ph), 130.79 (d, $J_{\text{PC}} = 3.1$ Hz, <i>p</i> -Ph), 130.80 (d, $J_{\text{PC}} = 86.2$ Hz, $\epsilon$ -Ph), 133.54 (d, $J_{\text{PC}} = 9.9$ Hz, <i>o</i> -Ph), 223.57 (dd, $J_{\text{PC}} = 45.0$ and 5.3 Hz, CO), 239.57 (dd, $J_{\text{PC}} = 32.8$ and 9.9 Hz, C(O)CH)
<b>3a</b>	1999	3.76 (vt, $J_{\text{PH}} = 5.8$ Hz, 18H, OMe), 5.03 (s, 5H, Cp)	169.07 (s, P(OMe) <sub>3</sub> )	53.99 (vt, $J_{\text{PC}} = 4.0$ Hz, OMe), 84.54 (s, Cp), 212.41 (d, $J_{\text{PC}} = 40.3$ Hz, CO)
<b>3b</b>	1986	1.18 (d, $J_{\text{PH}} = 10.8$ Hz, 9H, CH <sub>3</sub> ), <sup>b</sup> 3.38 (d, $J_{\text{PH}} = 11.0$ Hz, 9H, OCH <sub>3</sub> ), 5.20 (dd, $J_{\text{PH}} = 1.1$ and 1.7 Hz, 5H, Cp)	30.52 (d, $J_{\text{PP}} = 98.4$ Hz, PMe <sub>3</sub> ), 170.90 (d, $J_{\text{PP}} = 98.4$ Hz, P(OMe) <sub>3</sub> )	20.41 (d, $J_{\text{PC}} = 34.2$ Hz, PMe <sub>3</sub> ), <sup>b</sup> 54.37 (d, $J_{\text{PC}} = 8.7$ Hz, P(OMe) <sub>3</sub> ), 85.32 (s, Cp), 215.26 (dd, $J_{\text{PC}} = 40.4$ and 28.0 Hz, CO)
<b>3c</b>	1996	1.28 (t, $J_{\text{HH}} = 6.6$ Hz, 18H, CH <sub>3</sub> ), 4.02 (vt, $J_{\text{HH}} = 3.3$ Hz, 12H, OCH <sub>2</sub> ), 4.89 (s, 5H, Cp)	162.87 (s, P(OEt) <sub>3</sub> )	16.06 (vt, $J_{\text{PC}} = 3.1$ Hz, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 63.34 (d, $J_{\text{PC}} = 4.4$ Hz, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 84.74 (s, Cp), 212.83 (t, $J_{\text{PC}} = 41.0$ Hz, CO)
<b>4a</b>	1967	3.55 (d, $J_{\text{PH}} = 11.2$ Hz, 3H, P(O)(OMe) <sub>2</sub> ), 3.56 (d, $J_{\text{PH}} = 10.8$ Hz, 3H, P(O)(OMe) <sub>2</sub> ), 3.73 (d, $J_{\text{PH}} = 11.2$ Hz, 9H, P(OMe) <sub>3</sub> ), 4.80 (s, 5H, Cp)	123.95 (d, $J_{\text{PP}} = 137.8$ , P(O)(OMe) <sub>2</sub> ), 181.91 (d, $J_{\text{PP}} = 137.8$ Hz, P(OMe) <sub>3</sub> )	49.86 (d, $J_{\text{PC}} = 9.2$ Hz, P(O)(OMe) <sub>2</sub> ), 50.05 (d, $J_{\text{PC}} = 9.2$ Hz, P(O)(OMe) <sub>2</sub> ), 52.68 (d, $J_{\text{PC}} = 5.5$ Hz, P(OMe) <sub>3</sub> ), 83.81 (s, Cp), 216.29 (t, $J_{\text{PC}} = 43.2$ Hz, CO)
<b>4b</b>	1945 <sup>d</sup>	1.51 (d, $J_{\text{PH}} = 10.1$ Hz, 9H, CH <sub>3</sub> ), 3.51 (d, $J_{\text{PH}} = 10.6$ Hz, 3H, OMe), 3.53 (d, $J_{\text{PH}} = 10.8$ Hz, 3H, OMe), 4.63 (s, 5H, Cp)	35.91 (d, $J_{\text{PP}} = 106.8$ Hz, PMe <sub>3</sub> ), 128.42 (d, $J_{\text{PP}} = 106.9$ Hz, P(O)(OMe) <sub>2</sub> )	20.28 (d, $J_{\text{PC}} = 31.7$ Hz, PMe <sub>3</sub> ), 49.19 (d, $J_{\text{PC}} = 8.7$ Hz, OMe), 50.08 (d, $J_{\text{PC}} = 7.5$ Hz, OMe), 83.09 (s, Cp), 217.28 (dd, $J_{\text{PC}} = 43.5$ and 29.8 Hz, CO)

Table 1 (Continued)

complex	IR (CH <sub>2</sub> Cl <sub>2</sub> ) $\nu(\text{CO})$ , (cm <sup>-1</sup> )	<sup>1</sup> H NMR (CDCl <sub>3</sub> ) $\delta$ (ppm)	<sup>31</sup> P NMR (CH <sub>2</sub> Cl <sub>2</sub> ) $\delta$ (ppm) <sup>a</sup>	<sup>13</sup> C NMR (CDCl <sub>3</sub> ) $\delta$ (ppm)
<b>4c</b>	1963	1.21 (t, $J_{\text{HH}} = 7.3$ , 3H, P(O)(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ), 1.25 (t, $J_{\text{HH}} = 7.3$ Hz, 3H, P(O)(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ), 1.30 (t, $J_{\text{HH}} = 7.3$ Hz, 9H, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 3.95 (qui, $J_{\text{HH}} = 7.3$ and 7.3 Hz, 4H, P(O)(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ), 4.06–4.18 (m, 6H, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 4.75 (s, 5H, Cp)	121.05 (d, $J_{\text{PP}} = 137.3$ Hz, P(O)(OEt) <sub>2</sub> ), 175.67 (d, $J_{\text{PP}} = 137.3$ Hz, P(OEt) <sub>3</sub> )	16.18 (d, $J_{\text{PC}} = 7.4$ Hz, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 16.75 (d, $J_{\text{PC}} = 6.4$ Hz, P(O)(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ), 58.26 (d, $J_{\text{PC}} = 9.1$ Hz, P(O)(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> ), 61.44 (d, $J_{\text{PC}} = 5.5$ Hz, P(OCH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub> ), 84.07 (s, Cp), 216.84 (t, $J_{\text{PC}} = 43.2$ Hz, CO)
<b>5a</b>		1.43 (vt, $J_{\text{PH}} = 4.4$ Hz, 18H, PMe <sub>3</sub> ), 3.72 (d, $J_{\text{PH}} = 10.6$ Hz, 9H, P(OMe) <sub>3</sub> ), 4.39 (s, 5H, Cp)	27.54 (d, $J_{\text{PP}} = 100.7$ Hz, PMe <sub>3</sub> ), 177.94 (t, $J_{\text{PP}} = 100.7$ Hz, P(OMe) <sub>3</sub> )	22.26 (vt, $J_{\text{PC}} = 15.2$ Hz, PMe <sub>3</sub> ), 53.20 (d, $J_{\text{PC}} = 9.3$ Hz, P(OMe) <sub>3</sub> ), 79.57 (s, Cp)
<b>6a</b>		1.31 (t, $J_{\text{PH}} = 4.4$ Hz, 18H, PMe <sub>3</sub> ), 3.44 (d, $J_{\text{PH}} = 9.9$ Hz, 6H, P(O)(OMe) <sub>2</sub> ), 4.04 (s, 5H, Cp)	34.14 (d, $J_{\text{PP}} = 112.9$ Hz, PMe <sub>3</sub> ), 143.60 (t, $J_{\text{PP}} = 112.9$ Hz, P(O)(OMe) <sub>2</sub> )	22.42 (t, $J_{\text{PC}} = 13.7$ Hz, PMe <sub>3</sub> ), 49.09 (d, $J_{\text{PC}} = 9.2$ Hz, P(O)(OMe) <sub>2</sub> ), 78.28 (s, Cp)
<b>7e</b>	2008, <sup>d</sup> 1956		8.77 (s, PPh <sub>2</sub> ) <sup>d</sup>	
<b>8e</b>	2031, <sup>d</sup> 1983	1.29 (q, $J_{\text{BH}} = 96.5$ Hz, 3H, BH <sub>3</sub> ), <sup>b</sup> 5.07 (s, 5H, Cp), 7.23 (s, 4H, Ph), 7.58 (s, 6H, Ph)	32.72 (d, $J_{\text{PB}} = 61.5$ Hz, PPh <sub>2</sub> )	88.25 (s, Cp), <sup>b</sup> 128.72 (d, $J_{\text{PC}} = 8.7$ Hz, <i>m</i> -Ph), 129.69 (d, $J_{\text{PC}} = 1.9$ Hz, <i>p</i> -Ph), 133.54 (d, $J_{\text{PC}} = 8.1$ Hz, <i>o</i> -Ph), 140.92 (d, $J_{\text{PC}} = 28.0$ Hz, <i>c</i> -Ph), 214.10 (d, $J_{\text{PC}} = 18.6$ Hz, CO)

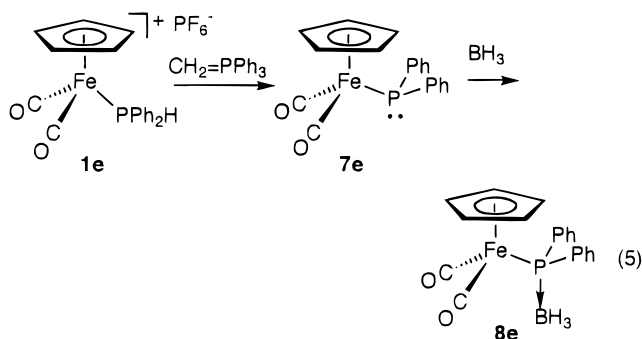
<sup>a</sup> For **1a–e**, **3a–c**, and **5a**, a septet at  $-143.80$  ppm with  $J_{\text{PP}} = 711.0$  Hz due to PF<sub>6</sub><sup>-</sup> was observed in addition to the resonance(s) shown in the table. <sup>b</sup> In acetone-*d*<sub>6</sub>. <sup>c</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>d</sup> In C<sub>6</sub>H<sub>6</sub>.

examined the reaction with CH<sub>2</sub>PPh<sub>3</sub>. The result is depicted in eq 4, showing the Arbuzov-like dealkylation reaction takes place, though refluxing is required to promote the reaction. This shows that an  $\alpha$ -carbon of



the coordinating P(OMe)<sub>3</sub> in **5a** still serves as an electrophilic active site toward a carbene carbon of CH<sub>2</sub>PPh<sub>3</sub>, though the electrophilicity is surely reduced compared with that for **3a–c**. The electrophilic property of an  $\alpha$ -carbon of **5a** has been demonstrated in the reaction with KOH in the presence of dibenzo-18-crown-6 under benzene refluxing conditions to give **6a** by the Arbuzov-like dealkylation reaction.<sup>6j</sup>

**Reaction of [Cp(CO)<sub>2</sub>Fe(PPh<sub>2</sub>H)]PF<sub>6</sub> (**1e**).** **1e** belongs to the category of [Cp(CO)<sub>2</sub>Fe(phosphine)]<sup>+</sup> and has similar  $\nu_{\text{CO}}$  absorptions to those of **1a–c**. Therefore, **1e** may be expected to react with CH<sub>2</sub>PPh<sub>3</sub> at the CO ligand. However, **1e** did not undergo the reaction shown in eq 1. The product in this reaction was a phosphide complex, **7e** (eq 5). Although **7e** is too reactive to be isolated as a solid, the formation was confirmed by the comparison of its IR spectrum with that reported in the literature.<sup>8</sup> For further confirmation, **7e** was converted into an isolable metallaphosphine borane by addition of BH<sub>3</sub>. **8e** that was thus isolated was fully characterized. This is the first example in which a phosphorus ylide creates a transition-metal–phosphide complex. The reaction shows that the P–H is more reactive than



the CO ligands toward CH<sub>2</sub>PPh<sub>3</sub>, which serves, in this reaction, as a Lewis base rather than a nucleophile.

## Conclusion

Reactions of cationic piano stool iron complexes, [Cp(CO)<sub>2</sub>FeL]<sup>+</sup>, [Cp(CO)FeLL']<sup>+</sup>, and [CpFeLL'<sub>2</sub>]<sup>+</sup>, with CH<sub>2</sub>PPh<sub>3</sub> were examined. On going from [Cp(CO)<sub>2</sub>FeL]<sup>+</sup> to [Cp(CO)FeLL']<sup>+</sup>, the electrophilic site changes from a CO carbon to an  $\alpha$ -carbon in the phosphite ligand. One of the reasons may come from the number of reactive ligands: **1a–d** have two CO ligands and one phosphite while **3a** and **3c** have one CO and two phosphites. Another reason, which seems to be more important, is that the electrophilicity of a CO ligand is much more sensitive to the electron density of a central metal than that of an  $\alpha$ -carbon in phosphite is. The reaction of **3b**, having one CO and one phosphite, with CH<sub>2</sub>PPh<sub>3</sub> shows that a phosphite is more attractive than a CO toward a phosphorus ylide. A phosphite is still a reactive site in **5a**, which has two electron-donating PMe<sub>3</sub> ligands. The reaction of **1e** revealed that a P–H is more reactive than a CO ligand toward CH<sub>2</sub>PPh<sub>3</sub>.

## Experimental Section

**General Remarks.** All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube

(8) (a) Burckett-St. J. C. T. R.; Haines, L. R. J.; Nolte, C. R.; Steen, N. D. C. T. *Inorg. Chem.* **1980**, *19*, 577. (b) Ashby, M. T.; Enemark, J. H. *Organometallics* **1987**, *6*, 1323.

techniques. Column chromatography was performed quickly in the air. Benzene, pentane, ether, and hexane were purified by distillation from sodium/benzophenone. These solvents were stored under an N<sub>2</sub> atmosphere. Other solvents, as eluents of column chromatography, were used without further purification. CH<sub>2</sub>PPh<sub>3</sub> was obtained in the reported method.<sup>9</sup> Complexes **1a**,<sup>6j</sup> **1c**,<sup>6h</sup> **1e**,<sup>10</sup> and **5a**<sup>6j</sup> were prepared according to the literature methods.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were measured on a JEOL EX-270, EX-400, or LA-300 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR data were referenced to Si(CH<sub>3</sub>)<sub>4</sub> as an internal standard. <sup>31</sup>P NMR data were referenced to 85% H<sub>3</sub>PO<sub>4</sub> as an external standard. Elemental analyses were performed on a Perkin-Elmer 2400CHN elemental analyzer.

**Preparation of 1b and 1d.** **1b** and **1d** were synthesized in a manner similar to that for **1a**. For **1b**, yield 96%. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>F<sub>6</sub>FeO<sub>5</sub>P<sub>2</sub>: C, 31.99; H, 4.13. Found: C, 32.19; H, 4.12. For **1d**, yield 54%. Anal. Calcd for C<sub>15</sub>H<sub>24</sub>F<sub>6</sub>FeO<sub>5</sub>P<sub>2</sub>: C, 34.91; H, 4.69. Found: C, 35.01; H, 4.69.

**Preparation of 3a.** Although **3a** has been prepared,<sup>11</sup> we employed the following method. P(OMe)<sub>3</sub> (0.26 mL, 2.20 mmol) was added to a suspension of **1a** (942 mg, 2.11 mmol) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (20 mL), and the reaction mixture was refluxed for 5 h. The solvent was removed under reduced pressure, and the residue was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> and loaded on a silica gel column. The yellow band that eluted with CH<sub>2</sub>Cl<sub>2</sub>/acetone (4/1) was collected. Removal of the solvent in vacuo resulted in the formation of a yellow powder of **3a** (1092 mg, 2.01 mmol, 95%). Anal. Calcd for C<sub>12</sub>H<sub>23</sub>F<sub>6</sub>FeO<sub>7</sub>P<sub>3</sub>: C, 26.59; H, 4.28. Found: C, 26.77; H, 4.18.

**Preparation of 3b.** AlCl<sub>3</sub> (1000 mg, 7.5 mmol) and P(OMe)<sub>3</sub> (1.3 mL, 11.0 mmol) were added to a solution of CpFe(CO)(PMe<sub>3</sub>)Cl (962 mg, 3.69 mmol) in benzene (80 mL). A dark green oil was immediately formed. The oil that separated from the supernatant was treated with H<sub>2</sub>O (40 mL) and NH<sub>4</sub>PF<sub>6</sub> (700 mg, 4.29 mmol). Then, CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added to the solution. The organic layer was dried with MgSO<sub>4</sub>, concentrated under reduced pressure, and loaded on a silica gel column. The yellow band that eluted with CH<sub>2</sub>Cl<sub>2</sub>/acetone (3/1) was collected. Removal of the solvent yielded a yellow powder, which was washed with ether and dried in vacuo to give **3b** (970 mg, 1.96 mmol, 53%). Anal. Calcd for C<sub>12</sub>H<sub>23</sub>F<sub>6</sub>FeO<sub>4</sub>P<sub>3</sub>: C, 29.17; H, 4.69. Found: C, 29.20; H, 4.62.

**Preparation of 3c.** P(OEt)<sub>3</sub> (0.86 mL, 5.02 mmol) was added to a solution of [Cp(CO)<sub>2</sub>Fe(THF)]PF<sub>6</sub> (897 mg, 2.28 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL), and the solution was stirred at room temperature for 24 h. After concentration under reduced pressure, the solution was loaded on a silica gel column and eluted with CH<sub>2</sub>Cl<sub>2</sub>. The first-eluted orange band and the second-eluted red band were discarded, and the third-eluted yellow band was collected. Removal of the solvent in vacuo resulted in the formation of a yellow powder of **3c** (919 mg, 1.47 mmol, 64%). Anal. Calcd for C<sub>18</sub>H<sub>35</sub>F<sub>6</sub>FeO<sub>7</sub>P<sub>3</sub>: C, 34.52; H, 5.63. Found: C, 34.82; H, 5.67.

**Preparation of 2a from 1a.** CH<sub>2</sub>PPh<sub>3</sub> (437 mg, 1.58 mmol) in benzene (4 mL) was added dropwise to a suspension of **1a** (307 mg, 0.69 mmol) in benzene (6 mL), which immediately caused the color of the solution to change from light yellow to reddish orange. After the solution was stirred at room temperature for 8 h, the reaction mixture was filtered. The solvent was removed from the filtrate under reduced pressure. The residue was washed with pentane several times and dried

in vacuo to give **2a** as a yellow powder (196 mg, 0.34 mmol, 49%). Anal. Calcd for C<sub>29</sub>H<sub>30</sub>FeO<sub>5</sub>P<sub>2</sub>: C, 60.44; H, 5.25. Found: C, 60.56; H, 5.13.

**Preparation of 2b from 1a.** **2b** was prepared from **1b** in the same manner as that of **2a** (yield 59%). Anal. Calcd for C<sub>32</sub>H<sub>36</sub>FeO<sub>5</sub>P<sub>2</sub>: C, 62.15; H, 5.87. Found: C, 62.02; H, 5.88.

**Preparation of 2c from 1c.** **2c** was prepared from **1c** in the same manner as that of **2a**. This complex was purified from benzene/pentane (1/4) (yield 28%). Anal. Calcd for C<sub>39</sub>H<sub>34</sub>FeO<sub>3</sub>P<sub>2</sub>: C, 70.07; H, 5.13. Found: C, 69.87; H, 5.22.

**Preparation of 2d from 1d.** **2d** was prepared from **1d** in the same manner as that of **2a**. The complex was purified from benzene/pentane (1/4) (yield 38%). Anal. Calcd for C<sub>34</sub>H<sub>40</sub>FeO<sub>5</sub>P<sub>2</sub>: C, 63.17; H, 6.24. Found: C, 63.19; H, 5.99.

**Preparation of 4a from 3a.** CH<sub>2</sub>PPh<sub>3</sub> (307 mg, 1.11 mmol) was added to a suspension of **3a** (407 mg, 0.74 mmol) in benzene (4 mL). After the reaction mixture was stirred at room temperature for 24 h (or was alternatively refluxed for 6 h), the solvent was removed under reduced pressure and the residue was loaded on a silica gel column. After a few yellow bands that eluted with acetone were discarded, a yellow band that eluted with acetone/EtOH (1/1) was collected and the solvent was removed under reduced pressure. The yellow oil thus formed was suspended in ether, and removal of the solvent in vacuo resulted in a yellow powder of **4a** (244 mg, 0.64 mmol, 86%). Anal. Calcd for C<sub>11</sub>H<sub>20</sub>FeO<sub>7</sub>P<sub>2</sub>: C, 34.58; H, 5.28. Found: C, 34.48; H, 5.19.

**Preparation of 4b from 3b.** **4b** was prepared from **3b** in the same manner as that of **4a** (yield 72%). The complex was so hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

**Preparation of 4c from 3c.** CH<sub>2</sub>PPh<sub>3</sub> (502 mg, 1.82 mmol) was added to a suspension of **3c** (685 mg, 1.10 mmol) in benzene (13 mL), and the reaction mixture was refluxed for 2 days. After purification in the same manner as that of **4a**, a yellow powder of **4c** (312 mg, 0.67 mmol, 61%) was obtained. The complex was so hygroscopic that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained.

**Preparation of 6a from 5a.** **6a** was prepared from **5a** in the same manner as that of **4a**. In this case, refluxing the benzene solution for 6 h was required to complete the reaction (yield 91%). Anal. Calcd for C<sub>13</sub>H<sub>29</sub>FeO<sub>3</sub>P<sub>3</sub>: C, 40.86; H, 7.65. Found: C, 40.93; H, 7.71.

**Preparation of 8e from 1e.** CH<sub>2</sub>PPh<sub>3</sub> (80 mg, 0.29 mmol) was added to a suspension of **1e** (137 mg, 0.27 mmol) in benzene (7 mL), and the reaction mixture was stirred at room temperature for 30 min. Then BH<sub>3</sub>·THF (0.32 mL of a 1.07 M BH<sub>3</sub>·THF solution, 0.32 mmol) was added to the solution, and the solution was stirred at room temperature for 30 min, causing the color of the solution to change from red to yellow. After the solvent was removed under reduced pressure, the residue was loaded on a silica gel column. After elution with benzene, a yellow band that eluted with benzene/CH<sub>2</sub>Cl<sub>2</sub> (1/1) was collected and the solvents were removed under reduced pressure. The residue was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (1 mL), and then hexane (20 mL) was added. The solvents were removed in vacuo to give **8e** as a yellow powder (67 mg, 0.18 mmol, 66%). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>BF<sub>6</sub>O<sub>2</sub>P: C, 60.69; H, 4.82. Found: C, 60.62; H, 4.55.

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