Migratory Insertion of a Phosphorus Ligand into a Transition Metal-Alkvl Bond

Hiroshi Nakazawa,^{*,†} Yoshitaka Yamaguchi,[†] Tsutomu Mizuta,[†] Satoshi Ichimura,[‡] and Katsuhiko Miyoshi^{*,‡}

Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan, and Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima 739, Japan

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Treatment of $Cp(CO)(R^1)Fe{\dot{PN}(Me)CH_2CH_2\dot{N}Me(OR^2)}$ ($R^1 = R^2 = Me$, 1a; $R^1 = Me$, R^2 = Et, **2a**; $R^1 = CH_2Ph$; $R^2 = Me$, **3a**) with BF₃·OEt₂ and then with PPh₃ yields [Cp(CO)-

 $(PPh_3)Fe{PN(Me)CH_2CH_2NMe(R^1)}]^+$ (R¹ = Me, 1b; R¹ = CH₂Ph, 3b). The reaction proceeds

via the formation of a cationic phosphenium complex, $[Cp(CO)(R^1)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me}]^+$, by the abstraction of an OR group as an anion from a phosphorus atom, and then migratory insertion of the phosphenium ligand into the iron-alkyl bond takes place to give [Cp(CO)-

 $(BF_2OR^2)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me(R^1)}]^+$, which is characterized by spectroscopic data. The cationic complex readily reacts with PPh₃ to give the final product. A η^5 -C₅Me₅ derivative

of 1a and a monoamino-substituted phosphite complex Cp(CO)(Me)Fe{PN(Me)CH₂CH₂O-(OMe)} show the same reactivity. The reaction of silyl complexes Cp(CO)(SiMe₃)Fe-

 $\{\dot{P}N(Me)CH_2CH_2\dot{N}Me(OR)\}\$ (R = Me, Et) with BE₃·OEt₂ affords a phosphenium complex

 $[Cp(CO)(SiMe_3)Fe{PN(Me)CH_2CH_2NMe}]^+$, which does not show the migratory insertion into

an iron-silyl bond. Iron complexes $Cp(CO)(CH_2OMe)Fe{PN(Me)CH_2CH_2NMe(OR)}$ (R = Me, 9a; R = Et, 10a) having an alkoxy group both on a carbon and on a phosphorus react

with BF₃·OEt₂ and then with PPh₃ to give [Cp(CO)(CH₂PPh₃)Fe{PN(Me)CH₂CH₂NMe(OR)}]⁺ (R = Me, 9e; R = Et, 10e). The results prove that the OMe in the CH₂OMe ligand is selectively abstracted to give the methylidene complex which is trapped with PPh_3 to give a phosphine ylide complex. Complexes 1b·BF₄ and 10e·BF₄ have been characterized by X-ray diffraction (crystal data for 1b BF₄, monoclinic, $P2_1/n$, a = 9.099(1) Å, b = 13.727(2) Å, c =23.134 (5) Å, $\beta = 91.48$ (1)°, Z = 4, R = 0.063; for **10e**·BF₄, orthorhombic, *Pcab*, a = 18.033(6) Å, b = 24.619 (6) Å, c = 14.501 (4) Å, Z = 8, R = 0.059).

Introduction

Phosphenium ions $(^{+}PR_{2})$ are unique ligands toward transition metals because they have both lone pair electrons and a vacant p orbital at the phosphorus.¹ Therefore, they can act as a σ -donor and also as a π -acceptor to a transition metal. In that sense, phosphenium complexes resemble singlet carbene complexes



(Customarily, a bond between M and C in a carbene complex is depicted as a double bond, whereas a bond between M and P in a phosphenium complex is described as a dative bond). Although some preparative methods for transition metal phosphenium complexes have been reported,¹⁻⁵ their reactivities still remain to be exploited.

One of the most attracting reactions of carbene complexes is the so-called carbene migratory insertion into a transition metal-alkyl bond (perhaps more appropriately designated simply as a migration of an alkyl ligand to a carbene ligand or as a 1,2-rearrangement).⁶ The related phosphenium migratory insertion into a transition metal-alkyl bond has not been reported so far. In this paper, we report the unprec-

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[†] Institute for Molecular Science.

[‡] Hiroshima University.

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edented example of a migratory insertion reaction of the phosphenium ligand into an iron-alkyl bond (in other words, an alkyl migration from a transition metal to a phosphenium ligand).



Results and Discussion

Migratory Insertion of Phosphenium Ligand into an Fe-C Bond. Iron complexes containing an alkyl group and (amino-substituted) phosphite (L) were synthesized from $Cp(CO)_2$ FeMe and L by the photoreaction for the methyl complex (eq 1), and from Cp(CO)-



IFeL, NaK_{2.8}, and ClCH₂Ph for the benzyl complex. The complexes were characterized by IR, ¹H, ¹³C, and ³¹P NMR spectra as well as elemental analyses. The two methyl groups and two methylene groups in an N(Me)-CH₂CH₂NMe substituent on a phosphorus ligand for **1a-3a** and **6a** were observed to be diastereotopic in the ¹H and ¹³C NMR spectra due to the chiral iron center. Complex **4a** has two chiral centers (Fe and P), so the diastereomeric pair is expected to be obtained. In the photoreaction, both were formed in a similar ratio.

These complexes obtained thus far were subjected to the reaction with $BF_3 \cdot OEt_2$ and then PPh_3 . Complex 1a was dissolved in CH_2Cl_2 and cooled at -78 °C. $BF_3 \cdot OEt_2$ and then PPh_3 were added to the solution to give a yellow powder. For the following reasons, we concluded that the complex obtained is formulated

as $[Cp(CO)(PPh_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me(Me)}]BF_4$ (1b·BF₄) (eq 2): (i) An IR absorption band due to ν_{CO}



was observed 56 cm⁻¹ higher in frequency than that for the starting complex, indicating that the product is cationic. (ii) The ¹H and ¹³C NMR spectra showed that the amino-substituted phosphorus has no OMe group (no doublet at ca. 3.2 ppm in ¹H NMR or at ca. 52 ppm in ¹³C NMR) but has a Me group (a doublet at 1.53 ppm in ¹H NMR and at 23.46 ppm in ¹³C NMR). (iii) In the ³¹P NMR spectrum, two resonances were observed at 159.48 and 65.29 ppm as doublets with $J_{\rm PP} = 60.5$ Hz,

indicating that $\dot{P}N(Me)CH_2CH_2\dot{N}Me(Me)$ and PPh₃ are both coordinated to the same iron atom. For further confirmation of the structure of **1b**·BF₄, the X-ray diffraction analysis was performed (vide infra).

In the above reaction, a Me group on the phosphorus in the product can be thought to come from the iron. The migration of an alkyl group from iron to phosphorus is proved by the reactions of 2a and 3a. Complex 2ahas an OEt group in place of an OMe group on the P in 1a, and 3a has a CH₂Ph group in place of a Me group on the Fe in 1a. The products in the reactions of 2aand 3a with BF₃·OEt₂ and then PPh₃ were 1b·BF₄ and

 $[Cp(CO)(PPh_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me(CH_2Ph)}]BF_4$ (**3b**·BF₄), respectively (eq 2). These results clearly show that an OR group on the phosphorus is eliminated and an alkyl group on the iron migrates to the phosphorus coordinating to the iron.

It has been reported that cationic phosphenium complexes of group 6 transition metals can be synthesized by the abstraction of an OR group on the coordinating phosphite as an anion by BF₃ OEt₂ (Scheme 1).⁵ The stability of the cationic phosphenium complexes is influenced by the substituents on the phosphorus. The stability decreases with decreasing number of amino substituents on a phosphenium phosphorus in the following order: diamino- > monoamino-monoalkoxy- >> dialkoxy-substituents. Diamino- and monoaminophosphenium complexes are stable in solution at room temperature for several days, whereas dialkoxyphosphenium complexes, which have not been detected even spectroscopically due to their high reactivity, pick up an F⁻ anion to become electrically neutral complexes with a $P(OR)_2F$ ligand.

In the reaction of 1a-3a with BF₃·OEt₂, formation of a cationic iron phosphenium complex can be proposed. In order to examine the effect of a substituent on a phosphorus on the alkyl migration from Fe to P, we attempted the reactions of 4a having a monoaminosubstituted phosphite and 5a having a typical phosphite. In the former reaction, the formation of an alkyl



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Scheme 1



migration product was confirmed (eq 3). In contrast, the reaction of **5a** with BF₃OEt₂ and then PPh₃ yielded an unidentified product but no F-introduced products, for example Cp(CO)(Me)Fe{P(OMe)₂F}, were detected even in the reaction mixture according to the ³¹P NMR measurement. The details will be reported elsewhere.

The reaction of **6a** having η^5 -C₅Me₅ in place of η^5 -C₅H₅ in **1a** with BF₃·OEt₂ then PPh₃ was also examined. The product was **6b** (eq 4), revealing that the modification of Cp to Cp* has no significant influence on the alkyl migration reaction from Fe to P.



Consideration of a Reaction Intermediate. In the reaction of iron phosphite complexes with BF₃·OEt₂, an OR group on a phosphorus is strongly suggested to be abstracted by BF_3 ·OEt₂ as an anion to give a cationic iron phosphenium complex. Thus, we examined the reaction of 1a in CH₂Cl₂ with BF₃·OEt₂ only, in hopes of detecting an iron phosphenium complex, [Cp(CO)- $(Me)Fe{PN(Me)CH_2CH_2NMe}]^+$, as an intermediate (c in Scheme 2). The isolation of the complex formed was unsuccessful, but the spectroscopic data of the reaction mixture gave information about the complex formed at this stage. The IR spectrum (in CH_2Cl_2) showed one absorption band at 1997 cm⁻¹ in a $\nu_{\rm CO}$ region which is 87 cm^{-1} higher than that for **1a**, indicating the formation of a cationic complex. The ³¹P NMR spectrum (in CH_2Cl_2) showed a singlet at 214.58 ppm being 37.65 ppm lower in the magnetic field than that for 1a. This suggests that the product may not be phosphenium

complex [Cp(CO)(Me)Fe{PN(Me)CH₂CH₂NMe}]⁺ because the ³¹P NMR resonances of the phosphenium complexes shown in Scheme 1 were observed 104–137 ppm lower in magnetic field than those of the parent phosphite complexes.⁵ The ¹³C NMR spectrum (in CH₂-Cl₂) showed five resonances: 22.95 (d, $J_{PC} = 12.2$ Hz, PCH₃), 32.96 (d, $J_{PC} = 12.2$ Hz, NCH₃), 51.57 (s, NCH₂),





83.00 (s, C₅H₅), 215.14 (d, $J_{PC} = 29.3$ Hz, CO). A doublet at 22.95 ppm with $J_{PC} = 12.2$ Hz is assigned to a Me on a phosphorus, but no resonances due to an OMe on a phosphorus or due to a Me on an iron presented in the starting complex 1a were observed. Therefore, the product is proposed to have a [Cp(CO)Fe{PN(Me)CH₂-

 $CH_2NMe(Me)$]⁺ moiety.

The reaction mixture of **2a** with BF₃·OEt₂ showed similar data (IR (ν_{CO}), 1994 cm⁻¹; ³¹P NMR (δ), 214.44 ppm) to those obtained in the corresponding reaction of **1a**. However, the small difference in the ³¹P NMR chemical shifts was not due to the experimental error but was significant, because the two resonances were observed even when a mixture of **1a** and **2a** was treated with BF₃·OEt₂.

We thus propose the reaction sequences in Scheme 2. In the reaction of **a** with $BF_3 \cdot OEt_2$, an OR^2 group on a phosphorus atom is abstracted by BF_3 as an anion to give phosphenium complex **c** and $[BF_3OR^2]^-$, the latter of which may react with BF_3 to give BF_2OR^2 and BF_4^- serving as a counteranion of the final product **b**. Phosphenium complex **c** itself could not be detected, presumably due to its high reactivity. The R^1 group on an iron atom then migrates to the phosphenium phos-

phorus to give $[Cp(CO)Fe{PN(Me)CH_2CH_2NMe(R^1)}]^+$, a 16-electron species, which is stabilized presumably by the coordination of BF₂OR² generated through the lone pair of the oxygen to give **d**. Therefore, an OR² group exerts a small but not negligible effect on the ³¹P NMR resonance of **d**. The BF_2OR^2 in **d** is readily replaced by a more strong base such as PPh_3 to give a stable complex **b**.

Alkyl migration to CO ligand to give an acyl ligand on a transition metal is well-known.⁷ Complex c has a terminal carbonyl ligand as well as a phosphenium ligand. It is thus notable that an alkyl group migrates exclusively to a phosphenium ligand in the present reaction.

Some examples⁸ and theoretical studies⁹ have been reported for the migration of an alkyl (or aryl) group from a coordinating phosphorus ligand to the transition metal to which it is coordinating. Our findings correspond to the reversed movement of an alkyl group (from a transition metal to a coordinating phosphorus), which is unprecedented.

Reaction of Iron Complexes Having a Silyl Group and Phosphite with BF₃·OEt₂. The reaction of a silyl iron complex corresponding to the alkyl complex 1a with BF₃·OEt₂ showed very significant results from the mechanistic aspect. Silyl complexes 7a and **8a** were prepared from $Cp(CO)_2Fe(SiMe_3)$ and the corresponding phosphite by the photolysis. The reaction of **7a** with $BF_3 \cdot OEt_2$ in CH_2Cl_2 gives a homogeneous solution, which shows very informative spectroscopic data about the product (7c in eq 5). The IR absorption



band due to $v_{\rm CO}$ was observed 51 cm⁻¹ higher in frequency than that for the starting complex 7a. The ³¹P NMR spectrum shows a singlet at 309.33 ppm. The very low chemical shift (132.69 ppm lower than that of the starting complex, 176.64 ppm) indicates the formation of a phosphenium complex (vide supra). In the 29 Si NMR spectrum, one doublet was observed at 37.42 ppm with $J_{PSi} = 37.6$ Hz. The chemical shift and coupling constant are similar to those for the starting complex 7a (δ = 36.62 ppm, J_{PSi} = 43.0 Hz), indicating that the SiMe₃ group in 7c remains bound to the Fe. The 13 C NMR spectrum (in CH₂Cl₂) showed five resonances: 8.73 (s, $J_{CSi} = 48.8$ Hz, Si(CH₃)₃), 34.46 (d, J_{PC} = 12.2 Hz, NCH₃), 54.09 (s, NCH₂), 84.71 (s, C₅H₅), 214.06 (d, $J_{PC} = 28.1$ Hz, CO). A resonance due to $POCH_3$ was not detected, though it was observed at 51.04 ppm with $J_{PC} = 13.4$ Hz for the starting complex, **7a**. It should be noted that two NMe carbons and two NCH_2 carbons for **7c** are not diastereotopic, though

those for 7a are so, which is consistent with a planar geometry of the phosphorus atom in 7c.

The reaction mixture of 8a (having an OEt group in place of an OMe group in 7a) with BF₃·OEt₂ showed exactly the same spectroscopic data as those obtained from the reaction of 7a with BF₃·OEt₂. This observation strongly suggests the formation of 7c and that the phosphenium phosphorus in 7c has no contact with BF2-OMe or BF_2OEt generated.

Addition of PPh₃ to the solution containing 7c caused no reaction. No silvl migration to the phosphenium phosphorus may be due to a stronger transition metalsilyl bond than -alkyl bond. Complex 7c is stable in a solution at room temperature unless exposed to air. Although the isolation of 7c has been unsuccessful so far, the detection of the phosphenium complex 7c supports the reaction sequence proposed in Scheme 2 for the migratory insertion of a phosphenium ligand into an alkyl-iron bond.

Reaction of Iron Complexes Having both C-OR and P-OR Groups with BF3 OEt2 and PPh3. Cationic iron carbene complexes have been prepared by the abstraction of an OR group as an anion from $(C_5X_5)L_2$ - $Fe(CY_2OR)$ (X = H, Me; L = CO, tertiary phosphine; Y = H, alkyl; R = alkyl, silyl).¹⁰ So we attempted the reaction of Cp(CO)(CH₂OMe)Fe{PN(Me)CH₂CH₂NMe-(OMe) (9a) with BF₃·OEt₂ because it seemed interesting to examine which OMe group on the carbon or on the phosphorus is abstracted. If an OMe is abstracted from the carbon, a methylidene complex would be formed, whereas if abstraction from the phosphorus takes place, a phosphenium complex would be prepared.

Complex 9a was prepared from $Cp(CO)IFe{\dot{P}N(Me)}$ -

CH₂CH₂NMe(OMe)}, NaK_{2.8}, and ClCH₂OMe. The treatment of 9a with BF₃OEt₂ and then PPh₃ led to isolation of an orange complex. For the following reasons, we concluded that the product is a phosphine-stabilized methylidene complex formulated as $[Cp(CO)(CH_2PPh_3)]$ -

 $Fe{PN(Me)CH_2CH_2NMe(OMe)}]BF_4$ (9e-BF₄) (eq 6). (i)



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^{67, 1.}



Figure 1. ORTEP drawing of [Cp(CO)(PPh₃)Fe-

 ${\rm [PN(Me)CH_2CH_2NMe(Me)]^+}$ (1b) with atom-labeling scheme (the BF₄⁻ counterion is omitted for clarity). The thermal ellipsoids are drawn at the 30% probability level.



Figure 2. ORTEP drawing of [Cp(CO)(CH₂PPh₃)Fe-

 ${[\dot{P}N(Me)CH_2CH_2\dot{N}Me(OEt)]}^+$ (10e) with atom-labeling scheme (the BF₄⁻ counterion is omitted for clarity). The thermal ellipsoids are drawn at the 30% probability level.

One ν_{CO} absorption band was observed in the IR spectrum, indicating the complex has a terminal CO ligand. (ii) In the ³¹P NMR spectrum, two resonances were observed at 40.35 and 164.87 ppm, which were assigned to PPh₃ and PN(Me)CH₂CH₂NMe(OMe), respectively; they are not coupled with each other. (iii) In the ¹H NMR spectrum, two diastereotopic CH₂ protons were observed as an apparent triplet of doublets and a double doublet due to the coupling to two kinds of phosphorus atoms and to the mutually geminal proton. (iv) The resonance due to P-OMe was observed, but that due to C-OMe was not.

The reaction may proceed as follows: the OMe abstraction on the carbon atom by BF_3 takes place to give a methylidene complex, which is then trapped by PPh_3 to give an ylide complex. However, another reaction pathway cannot be ruled out in which an OMe

Table 1. Summary of Crystal Data for 1b·BF4 and10e·BF4

	1b·BF ₄	10e·BF ₄
formula	C ₂₉ H ₃₃ BF ₄ FeN ₂ OP ₂	C ₃₁ H ₃₇ BF ₄ FeN ₂ O ₂ P ₂
fw	630.19	674.20
cryst syst	monoclinic	orthorhombic
spece group	$P2_1/n$	Pcab
cell constants		
a, Å	9.099(1)	18.003(6)
b, Å	13.727(2)	24.619(6)
c, Å	23.134(5)	14.501(4)
α, deg		
β , deg	91.48(1)	
γ, deg		
V, Å ³	2889(1)	6427(3)
Z	4	8
$D_{\rm calcd}, {\rm g} {\rm cm}^{-3}$	1.45	1.39
μ , cm ⁻¹	6.85	5.68
cryst size, mm ³	0.32 imes 0.12 imes 0.10	0.45 imes 0.40 imes 0.30
radiation	Μο Κα	Μο Κα
	$(\lambda = 0.710 \ 69 \ \text{\AA})$	$(\lambda = 0.710 \ 69 \ \text{\AA})$
scan technique	$\omega - 2\theta$	$\omega - 2\theta$
scan range, deg	$3 < 2\theta < 55$	$3 < 2\theta < 50$
scan rate, deg min ⁻¹	5.1	6.0
no. of unique data	6972	5661
no. of unique data with $F_0 > 3\sigma(F_0)$	2773	3788
R	0.063	0.059
R_{w}	0.054	0.064

group on the phosphorus is abstracted and then an OMe group on the carbon migrates to the phosphorus to give the methylidene complex. In order to elucidate the reaction pathway, complex 10a was subjected to the reaction with BF₃·OEt₂ then PPh₃. The product was an

ylide complex, $[Cp(CO)(CH_2PPh_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}-Me(OEt)}]BF_4$ (10e-BF₄) (eq 6), which was identified by an X-ray crystallographic study (vide infra) in addition to its spectroscopic data. Therefore, it was concluded that an OR group is abstracted selectively from the carbon but not from the phosphorus.

The reason for the selectivity may come from the difference in bond energy between C-O and P-O, or may come from the difference in overall stability between a methylidene complex and a phosphenium complex. Although the real reason for the selectivity is not clear now, our findings will give a clue when we compare transition-metal complexes with carbene and phosphenium as a ligand.

Crystal Structures of 1b·BF₄ and 10e·BF₄. X-ray structure analyses of 1b·BF₄ and 10e·BF₄ were undertaken. The ORTEP drawings of 1b and 10e are displayed in Figures 1 and 2, respectively. The crystal data and the selected bond distances and angles are listed in Tables 1-3.

An X-ray crystal structure of 1b shows a normal piano stool configuration. The iron has a cyclopentadienyl ligand in a η^5 fashion, a terminal CO ligand, a PPh₃ group, and a diamino-substituted tertiary phosphine,

 $\dot{P}N(Me)CH_2CH_2\dot{N}Me(Me)$. Angles between three monodentate ligands are slightly greater than 90°: C1-Fe1-P1 = 90.6°, P1-Fe1-P2 = 95.8°, and P2-Fe1-C1 = 93.4°. P1 basically takes a tetrahedral geometry, though the N1-P1-N2 angle (93.4°) is smaller than the ideal angle due to the five-membered ring. N1 has a planar geometry (sum of the bond angles around N1 is 356.9°), whereas N2 is not planar (sum of the bond angles around N2 is 344.6°), presumably due to avoid-

Bond Distances					
Fe1-P1	2.201(2)	P2-C24	1.810(7)		
Fe1-P2	2.237(2)	01-C1	1.177(8)		
Fe1-C1	1.727(7)	N1-C3	1.457(10)		
P1-N1	1.651(6)	N1-C4	1.449(10)		
P1-N2	1.676(6)	N2-C5	1.461(9)		
P1-C2	1.800(8)	N2-C6	1.467(9)		
P2-C12	1.833(7)	C4-C5	1.52(1)		
P2-C18	1.842(7)				
	Bond	Angles			
P1-Fe1-P2	95.80(8)	C12-P2-C18	103.4(3)		
P1-Fe1-C1	90.6(3)	C12-P2-C24	97.6(3)		
P2-Fe1-C1	93.4(3)	C18-P2-C24	106.3(3)		
Fe1-P1-N1	120.0(2)	P1-N1-C3	125.1(6)		
Fe1-P1-N2	117.7(2)	P1-N1-C4	114.0(6)		
Fe1-P1-C2	111.3(3)	C3-N1-C4	117.8(7)		
N1-P1-N2	93.4(3)	P1-N2-C5	109.9(6)		
N1-P1-C2	104.5(4)	P1-N2-C6	119.8(6)		
N2-P1-C2	107.9(4)	C5-N2-C6	114.9(7)		
Fe1-P2-C12	114.2(2)	Fe1-C1-O1	175.6(7)		
Fe1-P2-C18	111.9(2)	N1-C4-C5	106.4(8)		
Fe1-P2-C24	121.3(2)	N2-C5-C4	105.7(7)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for

$[Cp(CO)(CH_2PPh_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me(OEt)}]^+$ (10e)

Bond Distances					
Fe1-P1	2.164(2)	P2-C26	1.817(4)		
Fe1-C7	1.741(6)	O1-C6	1.440(7)		
Fe1-C8	2.072(4)	O2-C7	1.158(7)		
P1-01	1.625(4)	N1-C3	1.446(10)		
P1-N1	1.649(7)	N1-C4	1.45(1)		
P1-N2	1.662(7)	N2-C1	1.41(1)		
P2-C8	1.768(4)	N2-C2	1.45(1)		
P2-C14	1.797(4)	C2-C3	1.45(2)		
P2-C20	1.802(4)	C5-C6	1.41(1)		
Bond Angles					
P1-Fe1-C7	92.9(2)	C20-P2-C26	104.7(2)		
P1-Fe1-C8	92.1(1)	P1-01-C6	120.7(3)		
C7-Fe1-C8	97.3(2)	P1-N1-C3	115.2(7)		
Fe1-P1-O1	109.7(1)	P1-N1-C4	124.6(5)		
Fe1-P1-N1	119.9(2)	C3-N1-C4	119.5(8)		
Fe1-P1-N2	119.3(2)	P1-N2-C1	125.4(6)		
01-P1-N1	107.9(3)	P1-N2-C2	113.6(8)		
01P1N2	105.9(3)	C1-N2-C2	119.7(9)		
N1-P1-N2	92.4(3)	N2-C2-C3	109.9(9)		
C8-P2-C14	113.7(2)	N1-C3-C2	107.6(9)		
C8-P2-C20	113.0(2)	O1-C6-C5	112.3(6)		
C8-P2-C26	111.5(2)	Fe1-C7-O2	174.1(5)		
C14-P2-C20	104.4(2)	Fe1-C8-P2	119.1(2)		
C14-P2-C26	108.9(2)				

ance of steric repulsion between the methyl group on N2 and the PPh_3 ligand.

The structure of **10e** is basically similar to that of **1b**. However, the iron has a methylene group to which PPh₃ bonds. The bond lengths of Fe1-C8 (2.072 Å) and C8-P2 (1.768 Å) and the bond angle Fe1-C8-P2 (119.1°) resemble those of the iron ylide complexes reported so far ([Cp*(CO)₂FeCH₂PPh₃]⁺,^{10c} Fe-C = 2.11 Å, C-P = 1.78 Å, \angle Fe-C-P = 118.1°, and (CO)₄FeCH₂PPh₃,¹¹ Fe-C = 2.122 Å, C-P = 1.755 Å, \angle Fe-C-P = 118.6°). The two nitrogen atoms on a phosphorus have planar geometries (the sum of the bond angles around N1 is 359.3°, and that around N2 is 358.7°).

Experimental Section

General Remarks. All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. Column chromatography was done quickly in the air. Benzene, THF, hexane, and pentane were distilled from sodium metal, CH_2Cl_2 was distilled from P_2O_5 , and these solvents were stored under nitrogen atmosphere. Acetone as an eluent was obtained from a common commercial source and was used without further purification. BF_3 ·OEt₂ was distilled prior to use.

IR spectra were recorded on a Shimadzu FTIR-8100A spectrometer. JEOL PMX-60, EX-270, and EX-400 instruments were used to obtain ¹H, ¹³C, ³¹P, and ²⁹Si NMR spectra. ¹H, ¹³C, and ²⁹Si NMR data were referenced to $(CH_3)_4Si$, and ³¹P NMR data were referenced to 85% H₃PO₄.

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Preparation of Cp(CO)(Me)Fe{\dot{P}N(Me)CH_2CH_2NMe}(OMe)} (1a). Cp(CO)_2FeMe (907 mg, 4.72 mmol), benzene (25
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mL), and PN(Me)CH2CH2NMe(OMe) (0.65 mL, 656 mg, 4.43 mmol) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 1 h. After the solvent had been removed, the residue was loaded on an alumina column and eluted with CH₂Cl₂. The second eluted orange band was collected, and the solvent was removed in vacuo to give a yellow powder of 1a (1011 mg, 3.24 mmol, yield 68%). Anal. Calcd for C₁₂H₂₁FeN₂O₂P: C, 46.18; H, 6.78; N, 8.97. Found: C, 46.35; H, 6.75; N, 8.88. IR (ν_{CO} , in CH₂Cl₂): 1910. ³¹P NMR (δ , in CH₂Cl₂): 176.93 (s). ¹H NMR (δ , in CDCl₃): -0.19 (d, $J_{PH} =$ 5.0 Hz, 3H, FeCH₃), 2.72 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 2.74 $(d, J_{PH} = 9.9 \text{ Hz}, 3H, \text{NCH}_3), 3.10 (m, 2H, \text{NCH}_2), 3.23 (d, J_{PH})$ = 10.9 Hz, 3H, OCH₃), 3.45 (m, 2H, NCH₂), 4.38 (s, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): -25.49 (d, J_{PC} = 30.5 Hz, FeCH₃), $33.23 (d, J_{PC} = 9.8 Hz, NCH_3), 33.44 (d, J_{PC} = 12.2 Hz, NCH_3),$ $51.42 (d, J_{PC} = 13.5 Hz, OCH_3), 51.61 (d, J_{PC} = 2.5 Hz, NCH_2),$ 51.73 (d, J_{PC} = 4.8 Hz, NCH₂), 82.64 (s, C₅H₅), 222.50 (d, J_{PC} = 47.6 Hz, CO).

Preparation of $Cp(CO)(Me)Fe{PN(Me)CH_2CH_2NMe}(OEt)$ (2a). Complex 2a was prepared from $Cp(CO)_2FeMe$

and $\dot{P}N(Me)CH_2CH_2\dot{N}Me(OEt)$ in the same manner as that for **1a** (yield 85%). Anal. Calcd for $C_{13}H_{23}FeN_2O_2P$: C, 47.87; H, 7.11; N, 8.59. Found: C, 47.65; H, 6.96; N, 8.27. IR (ν_{CO} , in CH_2Cl_2): 1912. ³¹P NMR (δ , in CH_2Cl_2): 174.86 (s). ¹H NMR (δ , in $CDCl_3$): -0.18 (d, $J_{PH} = 5.0$ Hz, 3H, FeCH₃), 1.09 (t, $J_{PH} = 7.1$ Hz, 3H, OCH_2CH_3), 2.71 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 2.73 (d, $J_{PH} = 10.2$ Hz, 3H, NCH₃), 3.12 (m, 2H, NCH₂), 3.36 (m, 2H, NCH₂), 3.56 (m, 2H, OCH_2CH_3), 4.38 (s, 5H, C_5H_5). ¹³C NMR (δ , in $CDCl_3$): -25.11 (d, $J_{PC} = 30.5$ Hz, FeCH₃), 16.24 (d, $J_{PC} = 6.1$ Hz, OCH_2CH_3), 33.32 (d, $J_{PC} = 9.8$ Hz, NCH₃), 33.53 (d, $J_{PC} = 12.2$ Hz, NCH₃), 51.54 (d, $J_{PC} =$ 2.4 Hz, NCH₂), 51.60 (d, $J_{PC} = 6.1$ Hz, NCH₂), 59.63 (d, $J_{PC} =$ 13.4 Hz, OCH_2CH_3), 82.64 (s, C_5H_5), 222.55 (d, $J_{PC} = 46.4$ Hz, CO).

Preparation of Cp(CO)(CH₂Ph)Fe{PN(Me)CH₂CH₂NMe-(OMe)} (3a). Cp(CO)₂FeI (1526 mg, 5.02 mmol), benzene (60

mL), and $\dot{P}N(Me)CH_2CH_2\dot{N}Me(OMe)$ (0.75 mL, 757 mg, 5.11 mmol) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 1.5 h. After filtration, the solvent was removed under reduced pressure, and the residue was loaded on an alumina column and eluted with CH_2Cl_2 . The green band was collected, and the solvent was removed in vacuo to give a dark

green powder of Cp(CO)IFe{ $PN(Me)CH_2CH_2NMe(OMe)$ } (1016 mg, 2.40 mmol, yield 48%). Anal. Calcd for C₁₁H₁₈FeIN₂O₂P: C, 31.16; H, 4.28; N, 6.61. Found: C, 31.40; H, 4.18; N, 6.63. IR (ν_{CO} , in CH₂Cl₂): 1950. ³¹P NMR (δ , in CH₂Cl₂): 165.88 (s). ¹H NMR (δ , in CDCl₃): 2.83 (d, $J_{PH} = 10.9$ Hz, 3H, NCH₃), 2.97 (d, $J_{PH} = 9.9$ Hz, 3H, NCH₃), 3.21 (m, 2H, NCH₂), 3.32

⁽¹¹⁾ Toupet, P. L.; Weinberger, B.; Abbayes, H. D.; Gross, U. Acta Crystallogr. 1984, C40, 2056.

(d, $J_{PH} = 11.6$ Hz, 3H, OCH₃), 3.38 (m, 2H, NCH₂), 4.62 (d, $J_{PH} = 1.3$ Hz, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): 33.45 (d, $J_{PC} = 11.0$ Hz, NCH₃), 34.36 (d, $J_{PC} = 9.8$ Hz, NCH₃), 51.77 (s, NCH₂), 51.81 (s, NCH₂), 52.18 (d, $J_{PC} = 12.2$ Hz, OCH₃), 81.35 (s, C₅H₅), 220.51 (d, $J_{PC} = 45.1$ Hz, CO).

NaK_{2.8} (0.9 mL, 756 mg, 5.71 mmol) was added to a solution

of Cp(CO)IFe{PN(Me)CH₂CH₂NMe(OMe)} (961 mg, 2.27 mmol) of THF (50 mL), and the solution was stirred for about 30 min at room temperature, causing the color of the solution to change from green to brown. After filtration, the filtrate was added dropwise to a solution of ClCH₂Ph (0.27 mL, 297 mg, 2.35 mmol) of THF (20 mL), and the resulting solution was stirred overnight at room temperature. After insoluble materials had been removed by filtration, the solvent was removed from the filtrate under reduced pressure. The soluble product was extracted with pentane $(20 \text{ mL} \times 2)$ and removing the solvent under reduced pressure gave 3a as a dark yellow oil (428 mg, 1.10 mmol, 49%). The complex was so unstable that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained. IR (ν_{CO} , in CH_2Cl_2): 1912. ³¹P NMR (δ , in CH_2Cl_2): 173.69 (s). ¹H NMR (δ , in CDCl₃): 1.89 (dd, $J_{PH} = 9.6$ Hz, $J_{HH} = 8.2$ Hz, 1H, $FeCH_2$), 2.60 (dd, $J_{PH} = 4.6$ Hz, $J_{HH} = 7.9$ Hz, 1H, $FeCH_2$), 2.77 (d, $J_{PH} = 9.9$ Hz, 3H, NCH₃), 2.80 (d, $J_{PH} = 9.6$ Hz, 3H, NCH_3), 3.16 (m, 2H, NCH_2), 3.29 (d, $J_{PH} = 10.9 \text{ Hz}$, 3H, OCH_3), 3.37 (m, 2H, NCH₂), 4.21 (d, $J_{PH} = 1.0$ Hz, 5H, C₅H₅), 6.85 (t, $J_{\rm HH} = 7.3$ Hz, 1H, p-C₆H₅), 7.90 (m, 4H, o- and m-C₆H₅). ¹³C NMR (δ , in CDCl₃): 3.39 (d, $J_{PC} = 25.6$ Hz, FeCH₂), 33.28 (d, $J_{PC} = 12.2 \text{ Hz}, \text{ NCH}_3$, 51.60 (d, $J_{PC} = 13.5 \text{ Hz}, \text{ OCH}_3$), 51.67 $(d, J_{PC} = 3.7 \text{ Hz}, \text{NCH}_2), 51.79 (d, J_{PC} = 4.9 \text{ Hz}, \text{NCH}_2), 83.41$ (s, C_5H_5), 121.20 (s, p- C_6H_5), 126.86 (s, o- C_6H_5), 127.51 (s, m-C₆H₅), 157.86 (d, $J_{PC} = 2.4$ Hz, ϵ -C₆H₅), 222.80 (d, $J_{PC} =$ 46.4 Hz, CO).

Preparation of $Cp(CO)(Me)Fe{\dot{P}N(Me)CH_2CH_2\dot{O}(OMe)}$ (4a). Complex 4a was prepared from $Cp(CO)_2FeMe$ and

 $\dot{P}N(Me)CH_2CH_2\dot{O}(OMe)$ in the same manner as that for 1a. In this case, the complexes eluted with CH₂Cl₂ from an alumina column were loaded again on a silica gel column and eluted with CH₂Cl₂. The orange band eluted after a yellow band containing Cp(CO)₂FeMe was collected and dried in vacuo to give 4a as an orange oil (yield 37%). Anal. Calcd for C₁₁H₁₈FeNO₃P: C, 44.17; H, 6.07; N, 4.68. Found: C, 44.24; H, 6.04; N, 4.60. IR (ν_{CO} , in CH₂Cl₂): 1919. ³¹P NMR (δ , in CH₂Cl₂): 195.96 (s), 195.73 (s). ¹H NMR (δ , in CDCl₃): -0.28 $(d, J_{PH} = 5.6 \text{ Hz}, 1.5 \text{H}, \text{FeCH}_3), -0.24 (d, J_{PH} = 5.9 \text{ Hz}, 1.5 \text{H},$ FeCH₃), 2.73 (d, $J_{PH} = 9.9$ Hz, 1.5H, NCH₃), 2.79 (d, $J_{PH} =$ 10.6 Hz, 1.5H, NCH₃), 3.17 (m, 1H, NCH₂), 3.33 (m, 1H, NCH₂), $3.42 (d, J_{PH} = 11.2 Hz, 1.5H, OCH_3), 3.44 (d, J_{PH} = 10.9 Hz,$ 1.5 Hz, OCH₃), 4.21 (m, 1H, OCH₂), 4.33 (m, 1H, OCH₂), 4.49 (s, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): -26.19 (d, $J_{PC} = 33.0$ Hz, FeCH₃), -25.63 (d, $J_{PC} = 32.9$ Hz, FeCH₃), 32.16 (d, J_{PC} = 10.9 Hz, NCH₃), 32.25 (d, J_{PC} = 10.9 Hz, NCH₃), 51.37 (s, NCH_2 , 51.50 (s, NCH_2), 51.58 (d, $J_{PC} = 11.0 \text{ Hz}$, OCH_3), 51.70 $(d, J_{PC} = 9.7 \text{ Hz}, \text{ OCH}_3), 67.11 (d, J_{PC} = 11.0 \text{ Hz}, \text{ OCH}_2), 67.34$ (d, $J_{PC} = 11.0$ Hz, OCH₂), 82.66 (s, C₅H₅), 83.04 (s, C₅H₅), 221.16 (d, J_{PC} = 46.4 Hz, CO), 221.46 (d, J_{PC} = 45.1 Hz, CO).

Preparation of Cp(CO)(Me)Fe{P(OMe)₃} (5a). The complex was prepared according to the literature method¹² (yield 65%). IR (ν_{CO} , in CH₂Cl₂): 1924. ³¹P NMR (δ , in CH₂Cl₂): 192.97 (s). ¹H NMR (δ , in CDCl₃): -0.17 (d, $J_{PH} = 4.6$ Hz, 3H, FeCH₃), 3.57 (d, $J_{PH} = 11.2$ Hz, 9H, OCH₃), 4.50 (s, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): -26.15 (d, $J_{PC} = 32.9$ Hz, FeCH₃), 51.45 (d, $J_{PC} = 3.6$ Hz, OCH₃), 82.91 (s, C₅H₅), 220.82 (d, $J_{PC} = 46.4$ Hz, CO).

Preparation of $Cp^*(CO)(Me)Fe\{PN(Me)CH_2CH_2NMe-(OMe)\}$ (6a). Complex 6a was prepared from $Cp^*(CO)_2FeMe$

and $\dot{P}N(Me)CH_2CH_2\dot{N}Me(OMe)$ by photolysis in the same

manner as that for **1a**. In this case, the reaction mixture was loaded on a silica gel column and eluted with CH₂Cl₂. The second eluted band was collected and loaded again on a new silica gel column. After the band that eluted with hexane was discarded, the orange band that eluted with CH₂Cl₂ was collected and the solvent was removed in vacuo to give 6a as a dark yellow powder (yield 69%). Anal. Calcd for C₁₇H₃₁FeN₂O₂P: C, 53.42; H, 8.17; N, 7.33. Found: C, 53.54; H, 8.19; N, 6.90. IR (ν_{CO} , in CH₂Cl₂): 1894. ³¹P NMR (δ , in CH₂Cl₂): 175.02 (s). ¹H NMR (δ , in CDCl₃): -0.41 (d, $J_{PH} =$ 4.6 Hz, 3H, FeCH₃), 1.61 (s, 15H, $C_5(CH_3)_5$), 2.62 (d, $J_{PH} = 9.6$ Hz, 3H, NCH₃), 2.73 (d, $J_{PH} = 9.9$ Hz, 3H, NCH₃), 3.18 (d, J_{PH} = 10.6 Hz, 3H, OCH₃), 3.35 (m, 4H, NCH₂). ¹³C NMR (δ , in $CDCl_3$): -14.74 (d, $J_{PC} = 30.5 \text{ Hz}$, $FeCH_3$), 9.29 (s, $C_5(CH_3)_5$), $32.74 (d, J_{PC} = 12.2 Hz, NCH_3), 33.09 (d, J_{PC} = 11.0 Hz, NCH_3),$ $51.73 (d, J_{PC} = 12.2 Hz, OCH_3), 51.79 (d, J_{PC} = 4.9 Hz, NCH_2),$ 52.23 (d, $J_{PC} = 6.1$ Hz, NCH₂), 91.14 (s, $C_5(CH_3)_5$), 223.75 (d, $J_{\rm PC} = 44.0$ Hz, CO).

Preparation of $Cp(CO)(SiMe_3)Fe{\dot{P}N(Me)CH_2CH_2NMe}(OMe)$ } (7a). $Cp(CO)_2Fe(SiMe_3)$ (1328 mg, 5.31 mmol), ben-

zene (60 mL), and PN(Me)CH2CH2NMe(OMe) (1.16 mL, 1172 mg, 7.91 mmol) were put in a Pyrex Schlenk tube, and the solution was irradiated with a 400 W medium-pressure mercury arc lamp at 0 °C for 3.5 h. After some insoluble materials were removed by filtration, the filtrate was concentrated under reduced pressure and loaded on an alumina column. The yellow band that eluted with CH₂Cl₂ was collected, and the solvent was removed in vacuo. Pentane was added to the residue. After filtration to remove insoluble materials, the solvent was removed in vacuo to give 7a as a yellow powder (1742 mg, 4.70 mmol, 89%). Anal. Calcd for C₁₄H₂₇FeN₂O₂PSi: C, 45.41; H, 7.35; N, 7.56. Found: C, 45.46; H, 7.12: N, 7.49. IR (ν_{CO} , in CH₂Cl₂): 1902. ³¹P NMR (δ , in CH₂Cl₂): 176.64 (s). ¹H NMR (δ , in CDCl₃): 0.26 (s, 9H, Si- $(CH_3)_3$, 2.72 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 2.75 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 3.10 (m, 2H, NCH₂), 3.17 (d, $J_{PH} = 11.2$ Hz, 3H, OCH₃), 3.32 (m, 2H, NCH₂), 4.35 (d, $J_{PH} = 1.3$ Hz, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): 8.80 (s, $J_{CSi} = 40.3$ Hz, Si-(CH₃)₃), 33.50 (d, $J_{PC} = 11.0$ Hz, NCH₃), 33.58 (d, $J_{PC} = 12.2$ Hz, NCH₃), 51.04 (d, $J_{PC} = 13.4$ Hz, OCH₃), 51.37 (d, $J_{PC} =$ 2.4 Hz, NCH₂), 51.71 (d, $J_{PC} = 3.7$ Hz, NCH₂), 81.13 (s, C_5H_5), 219.39 (d, $J_{PC} = 42.7$ Hz, CO). ²⁹Si NMR (δ , in CH₂Cl₂): 37.23 $(d, J_{PSi} = 41.7 \text{ Hz}).$

Preparation of $Cp(CO)(SiMe_3)Fe\{PN(Me)CH_2CH_2NMe(OEt)\}$ (8a). Complex 8a was prepared from $Cp(CO)_2Fe$ -

(SiMe₃) and PN(Me)CH₂CH₂NMe(OEt) in the same manner as that for **7a** (yellow powder, yield 85%). Anal. Calcd for C₁₅H₂₉FeN₂O₂PSi: C, 46.88; H, 7.61; N, 7.29. Found: C, 46.88; H, 7.36: N, 7.15. IR (ν_{CO} , in CH₂Cl₂): 1901. ³¹P NMR (δ , in CH₂Cl₂): 174.13 (s). ¹H NMR (δ , in CDCl₃): 0.28 (s, 9H, Si-(CH₃)₃), 1.10 (t, J_{HH} = 6.9 Hz, 3H, OCH₂CH₃), 2.70 (d, J_{PH} = 10.9 Hz, 3H, NCH₃), 2.74 (d, J_{PH} = 10.6 Hz, 3H, NCH₃), 3.10 (m, 2H, NCH₂), 3.27 (m, 2H, NCH₂), 3.50 (m, 2H, OCH₂), 4.34 (s, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): 8.93 (s, J_{CSi} = 39.0 Hz, Si(CH₃)₃), 16.16 (d, J_{PC} = 6.1 Hz, OCH₂CH₃), 33.44 (d, J_{PC} = 12.2 Hz, NCH₃), 33.65 (d, J_{PC} = 11.0 Hz, NCH₃), 51.30 (d, J_{PC} = 2.4 Hz, NCH₂), 51.59 (d, J_{PC} = 4.9 Hz, NCH₂), 59.76 (d, J_{PC} = 13.5 Hz, OCH₂), 81.11 (s, C₅H₅), 219.32 (d, J_{PC} = 42.8 Hz, CO). ²⁹Si NMR (δ , in CH₂Cl₂): 36.62 (d, J_{PSi} = 43.0 Hz).

Preparation of Cp(CO)(CH₂OMe)Fe{ $PN(Me)CH_2CH_2N-Me(OMe)$ } (9a). NaK_{2.8} (0.95 mL, 798 mg, 6.02 mmol) was

added to a solution of Cp(CO)IFe{ $PN(Me)CH_2CH_2NMe(OMe)$ } (987 mg, 2.33 mmol) in THF (50 mL), and the solution was stirred for about 30 min at room temperature, causing the color of the solution to change from green to brown. After filtration, the filtrate was added dropwise to a solution of ClCH₂OMe (0.18 mL, 191 mg, 2.37 mmol) in THF (20 mL) and stirred overnight at room temperature. After removing insoluble materials by filtration, the solvent was removed from the

⁽¹²⁾ Alt, H. G.; Herberhold, M.; Rausch, M. D.; Edwards, B. H. Z. Naturforsch. 1979, 34b, 1070.

filtrate under reduced pressure. The soluble product was extracted with pentane (30 mL × 2) and removing the solvent under reduced pressure gave **9a** as a yellow powder (353 mg, 1.03 mmol, 44%). Anal. Calcd for $C_{13}H_{23}FeN_2O_3P$: C, 45.63; H, 6.77; N, 8.19. Found: C, 45.72; H, 6.66; N, 8.15. IR (ν_{CO} , in CH₂Cl₂): 1911. ³¹P NMR (δ , in CH₂Cl₂): 175.71 (s). ¹H NMR (δ , in CDCl₃): 2.68 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 2.72 (d, $J_{PH} = 10.2$ Hz, 3H, NCH₃), 3.10 (m, 2H, NCH₂), 3.21 (d, $J_{PH} = 8.3$ Hz, 3H, POCH₃), 3.22 (s, 3H, CH₂OCH₃), 3.31 (m, 2H, NCH₂), 3.95 (t, J = 5.3 Hz, 1H, FeCH₂), 4.49 (s, 5H, C₅H₅), 5.32 (t, J = 4.5 Hz, 1H, FeCH₂). ¹³C NMR (δ , in CDCl₃): 32.79 (d, $J_{PC} = 11.0$ Hz, NCH₃), 33.39 (d, $J_{PC} = 12.2$ Hz, NCH₃), 51.37 (d, $J_{PC} = 13.5$ Hz, POCH₃), 51.56 (s, NCH₂), 51.61 (s, NCH₂), 60.45 (s, CH₂OCH₃), 67.86 (d, $J_{PC} = 30.5$ Hz, FeCH₂), 83.27 (s, C₅H₅), 222.45 (d, $J_{PC} = 45.1$ Hz, CO).

$Preparation of Cp(CO)(CH_2OMe)Fe\{ \dot{P}N(Me)CH_2CH_2\dot{N} -$

 $\label{eq:metric} \begin{array}{l} \textbf{Me(OEt)} \ \textbf{(10a).} \ Cp(CO)IFe\{PN(Me)CH_2CH_2NMe(OEt)\} \ was \\ prepared from Cp(CO)_2FeI \ and \ PN(Me)CH_2CH_2NMe(OEt) \ by \\ photolysis in the same manner as that for Cp(CO)IFe\{PN(Me)-$

CH₂CH₂NMe(OMe)] (green powder, yield 31%). Anal. Calcd for C₁₂H₂₀FeIN₂O₂P: C, 32.90; H, 4.60; N, 6.40. Found: C, 32.93; H, 4.43; N, 6.43. IR (ν_{C0} , in CH₂Cl₂): 1953. ³¹P NMR (δ , in CH₂Cl₂): 163.76 (s). ¹H NMR (δ , in CDCl₃): 1.58 (t, J_{HH} = 7.3 Hz, 3H, CH₂CH₃), 2.83 (d, J_{PH} = 10.9 Hz, 3H, NCH₃), 2.94 (d, J_{PH} = 10.2 Hz, 3H, NCH₃), 3.25 (m, 4H, NCH₂), 3.66 (m, 2H, OCH₂), 4.61 (d, J_{PH} = 1.3 Hz, 5H, C₅H₅). ¹³C NMR (δ , in CDCl₃): 16.15 (d, J_{PC} = 4.9 Hz, CH₂CH₃), 33.65 (d, J_{PC} = 11.0 Hz, NCH₃), 34.30 (d, J_{PC} = 9.8 Hz, NCH₃), 51.67 (d, J_{PC} = 3.7 Hz, NCH₂), 51.75 (d, J_{PC} = 2.4 Hz, NCH₂), 60.74 (d, J_{PC} = 12.2 Hz, OCH₂), 81.40 (s, C₅H₅), 220.71 (d, J_{PC} = 44.0 Hz, CO).

Complex 10a was prepared from Cp(CO)IFe{PN(Me)CH₂-

CH₂NMe(OEt)}, Nak_{2.8}, and ClCH₂OMe in the same manner as that for 9a (greenish yellow oil, yield 49%). The complex was so unstable that the correct elemental analysis data could not be obtained, though satisfactory spectroscopic data were obtained. IR (ν_{CO} , in CH_2Cl_2): 1911. ³¹P NMR (δ , in CH_2Cl_2): 173.43 (s). ¹H NMR (δ , in CDCl₃): 1.09 (t, $J_{HH} = 6.9$ Hz, 3H, $POCH_2CH_3$), 2.67 (d, $J_{PH} = 10.6$ Hz, 3H, NCH_3), 2.71 (d, J_{PH} = 10.6 Hz, 3H, NCH₃), $3.08 (m, 2H, NCH_2)$, $3.23 (s, 3H, CH_2-$ OCH₃), 3.25 (m, 2H, NCH₂), 3.53 (m, 2H, POCH₂CH₃), 3.95 (t, J = 5.6 Hz, 1H, FeCH₂), 4.48 (s, 5H, C₅H₅), 5.35 (t, J = 4.6Hz, 1H, FeCH₂). ¹³C NMR (δ , in CDCl₃): 16.16 (d, $J_{PC} = 4.9$ Hz, POCH₂CH₃), 32.88 (d, $J_{PC} = 11.0$ Hz, NCH₃), 33.46 (d, J_{PC} = 12.2 Hz, NCH₃), 51.45 (s, NCH₂), 51.50 (s, NCH₂), 59.65 (d, $J_{\rm PC} = 13.4$ Hz, POCH₂), 60.40 (s, CH₂OCH₃), 68.40 (d, $J_{\rm PC} =$ 30.5 Hz, FeCH₂), 83.27 (s, C_5H_5), 222.51 (d, $J_{PC} = 45.2$ Hz, CO).

[Cp(CO)(PPh₃)Fe{ $\dot{P}N(Me)CH_2CH_2\dot{N}Me(Me)$ }]BF₄ (1b·BF₄) from 1a. A solution of 1a (275 mg, 0.88 mmol) of CH₂Cl₂ (20 mL) was cooled to -78 °C, and then BF₃·OEt₂ (0.22 mL, 248 mg, 1.75 mmol) was added. After the solution had been stirred for several minutes, PPh₃ (500 mg, 1.91 mmol) was added, and then the solution warmed to room temperature. After the solvent had been removed under reduced pressure, the residue was loaded on a silica gel column. After elution with CH₂Cl₂, an orange complex that eluted with CH₂-Cl₂/acetone (8/1) was collected and dried in vacuo to give a yellowish orange powder of 1b·BF₄ (381 mg, 0.61 mmol, 68%). Anal. Calcd for C₂₉H₃₃BF₄FeN₂OP₂: C, 55.27; H, 5.28; N, 4.44. Found: C, 54.85; H, 5.21; N, 4.51. IR (ν_{CO} , in CH₂Cl₂): 1966. ³¹P NMR (δ , in CH₂Cl₂): 65.29 (d, $J_{PP} = 60.5$ Hz, PPh₃), 159.48

(d, $J_{PP} = 60.5 \text{ Hz}$, $\dot{P}N(Me)CH_2CH_2\dot{N}Me(Me)$). ¹H NMR (δ , in CDCl₃): 1.59 (d, $J_{PH} = 5.9 \text{ Hz}$, 3H, PCH₃), 2.12 (m, 2H, NCH₂), 2.41 (d, $J_{PH} = 10.9 \text{ Hz}$, 3H, NCH₃), 2.63 (d, $J_{PH} = 11.9 \text{ Hz}$, 3H, NCH₃), 2.94 (m, 2H, NCH₂), 4.80 (s, 5H, C₅H₅), 7.36-7.51 (m, 15H, C₆H₅). ¹³C NMR (δ , in CDCl₃): 23.57 (d, $J_{PC} = 8.5 \text{ Hz}$,

PCH₃), 33.72 (d, $J_{PC} = 6.1$ Hz, NCH₃), 33.82 (d, $J_{PC} = 7.3$ Hz, NCH₃), 50.78 (s, NCH₂), 51.48 (s, NCH₂), 85.93 (s, C₅H₅), 128.69 (d, $J_{PC} = 11.0$ Hz, o-C₆H₅), 130.91 (d, $J_{PC} = 2.4$ Hz, p-C₆H₅), 133.32 (d, $J_{PC} = 8.6$ Hz, m-C₆H₅), 134.18 (d, $J_{PC} = 47.6$ Hz, ϵ -C₆H₅), 217.26 (dd, $J_{PC} = 28.1$, 35.4 Hz, CO).

[Cp(CO)(PPh₃)Fe{PN(Me)CH₂CH₂NMe(CH₂Ph)]BF₄ (**3b·BF**₄) from 3a. Complex 3b was prepared from 3a, BF₃·OEt₂, and PPh₃ in the same manner as that for 1b. The crude product was purified by a silica gel column chromatography. After yellow and green bands that eluted with CH₂-Cl₂ were discarded, an orange band that eluted with acetone was collected and the solvent was removed in vacuo. The resulting powder was washed with benzene (10 mL × 2) and dried in vacuo to give an orange powder of **3b·B**F₄ (yield 55%). Anal. Calcd for C₃₅H₃₇BF₄FeN₂OP₂: C, 59.52; H, 5.28; N, 3.97. Found: C, 59.31; H, 5.23; N, 4.21. IR (ν_{CO} , in CH₂Cl₂): 1963. ³¹P NMR (δ , in CH₂Cl₂): 64.65 (d, $J_{PP} = 52.2$ Hz, PPh₃), 161.78

(d, $J_{PP} = 52.2$ Hz, $\dot{P}N(Me)CH_2CH_2\dot{N}Me(CH_2Ph)$). ¹H NMR (δ , in CD₂Cl₂): 2.38 (m, 4H, NCH₂), 2.40 (d, $J_{PH} = 9.3$ Hz, 3H, NCH₃), 2.84 (d, $J_{PH} = 9.8$ Hz, 3H, NCH₃), 3.22 (d, $J_{PH} = 14.7$ Hz, 1H, PCH₂), 3.41 (d, $J_{PH} = 14.7$ Hz, 1H, PCH₂), 4.84 (s, 5H, C₅H₅), 7.05–7.48 (m, 20H, C₆H₅). ¹³C NMR (δ , in CD₂-Cl₂): 34.24 (d, $J_{PC} = 5.4$ Hz, NCH₃), 34.32 (d, $J_{PC} = 5.4$ Hz, NCH₃), 51.37 (s, NCH₂), 52.21 (s, NCH₂), 52.62 (d, $J_{PC} = 5.4$ Hz, NCH₃), 129.05 (d, $J_{PC} = 10.7$ Hz, P- σ -C₆H₅), 129.98 (s, C-m-C₆H₅), 131.40 (s, P-p-C₆H₅), 133.68 (d, $J_{PC} = 8.1$ Hz, P-m-C₆H₅), 134.61 (d, $J_{PC} = 10.8$ Hz, C- ϵ -C₆H₅), 134.79 (d, $J_{PC} = 45.7$ Hz, P- ϵ -C₆H₅), 218.05 (dd, $J_{PC} = 26.9$, 32.2 Hz, CO).

[Cp(CO)(PPh₃)Fe{ $\dot{P}N(Me)CH_2CH_2\dot{O}(Me)$ }]BF₄ (4b·BF₄) from 4a. Complex 4b·BF₄ was prepared from 4a, BF₃·OEt₂, and PPh₃ in the same manner as that for 1b·BF₄ (yield 19%). Anal. Calcd for C₂₈H₃₀BF₄FeNO₂P₂: C, 54.49; H, 4.90; N, 2.27. Found: C, 54.61; H, 5.09; N, 1.95. IR (ν_{CO} , in CH₂Cl₂): 1977. ³¹P NMR (δ , in CH₂Cl₂): 65.33 (d, J_{PP} = 64.4 Hz, PPh₃), 66.74

(d, $J_{PP} = 71.7$ Hz, PPh₃), 203.51 (d, $J_{PP} = 71.7$ Hz, $\dot{P}N(Me)CH_2$ -

 $CH_2O(Me)$), 203.95 (d, $J_{PP} = 64.4 \text{ Hz}$, $PN(Me)CH_2CH_2O(Me)$). ¹H NMR (δ , in CDCl₃): 1.06 (d, $J_{PH} = 6.3$ Hz, 1.5H, PCH₃), 1.69 (d, $J_{\rm PH} = 6.3$ Hz, 1.5H, PCH₃), 2.71 (d, $J_{\rm PH} = 11.9$ Hz, 1.5H, NCH₃), 2.77 (d, $J_{PH} = 11.9$ Hz, 1.5H, NCH₃), 3.01 (m, 1H, NCH₂), 3.31 (m, 1H, NCH₂), 3.51 (m, 1H, OCH₂), 3.98 (m, 0.5H, OCH₂), 4.16 (m, 0.5H, OCH₂), 4.80 (t, $J_{PH} = 1.7$ Hz, 2.5H, C_5H_5), 4.87 (t, $J_{PH} = 1.7$ Hz, 2.5H, C_5H_5), 7.39–7.63 (m, 15H, C₆H₅). ¹³C NMR (δ , in CDCl₃): 22.68 (d, $J_{PC} = 17.1$ Hz, PCH₃), $25.34 (d, J_{PC} = 17.1 Hz, PCH_3), 31.93 (d, J_{PC} = 4.9 Hz, NCH_3),$ 32.01 (d, $J_{\rm PC} = 6.1$ Hz, NCH₃), 49.54 (s, NCH₂), 49.63 (s, NCH₂), 67.27 (d, $J_{PC} = 11.0$ Hz, OCH₂), 67.96 (d, $J_{PC} = 9.8$ Hz, OCH₂), 86.29 (s, C₅H₅), 86.56 (s, C₅H₅), 128.77 (d, $J_{PC} =$ 9.7 Hz, o-C₆H₅), 128.92 (d, $J_{PC} = 11.0$ Hz, o-C₆H₅), 130.98 (d, $J_{\rm PC} = 2.4$ Hz, p-C₆H₅), 131.18 (d, $J_{\rm PC} = 2.5$ Hz, p-C₆H₅), 133.08 (d, $J_{PC} = 9.8$ Hz, m-C₆H₅), 133.48 (d, $J_{PC} = 9.8$ Hz, m-C₆H₅), 133.81 (d, $J_{PC} = 54.9$ Hz, ϵ -C₆H₅), 133.92 (d, $J_{PC} = 51.2$ Hz, ϵ -C₆H₅), 214.94 (dd, $J_{PC} = 26.9$, 35.4 Hz, CO), 215.44 (dd, J_{PC} = 26.9, 33.0 Hz, CO).

[Cp*(CO)(PPh₃)Fe{PN(Me)CH₂CH₂NMe(Me)}]BF₄ (**6b·BF**₄) from 6a. Complex **6b·**BF₄ was prepared from 6a, BF₃·OEt₂, and PPh₃ in the same manner as that for 1b·BF₄ (yield 74%). Anal. Calcd for C₃₄H₄₃BF₄FeN₂OP₂: C, 58.31; H, 6.19; N, 4.00. Found: C, 58.04; H, 5.97; N, 3.59. IR (ν_{CO} , in CH₂Cl₂): 1939. ³¹P NMR (δ , in CH₂Cl₂): 64.04 (d, J_{PP} = 49.5 Hz, PPh₃), 158.28 (d, J_{PP} = 49.5 Hz, PN(Me)CH₂CH₂NMe-(Me)). ¹H NMR (δ , in CDCl₃): 0.69 (d, J_{PH} = 5.4 Hz, 3H, PCH₃), 1.49 (s, 15H, C₅Me₅), 2.46 (d, J_{PH} = 11.2 Hz, 3H, NCH₃), 2.64 (d, J_{PC} = 12.2 Hz, 3H, NCH₃), 2.94 (m, 4H, NCH₂) 7.32– 7.69 (m, 15H, C₆H₅). ¹³C NMR (δ , in CDCl₃): 9.60 (s, C₅(CH₃)₅), 18.05 (d, J_{PC} = 8.6 Hz, PCH₃), 33.85 (d, J_{PC} = 6.1 Hz, NCH₃), 34.51 (d, J_{PC} = 8.5 Hz, NCH₃), 51.33 (d, J_{PC} = 3.7 Hz, NCH₂), 51.63 (d, J_{PC} = 3.6 Hz, NCH₂), 97.38 (s, C₅(CH₃)₅), 128.59 (d,

 $J_{PC} = 9.7 \text{ Hz}, o-C_6H_5), 130.91 \text{ (s, } p-C_6H_5), 133.31 \text{ (d, } J_{PC} = 41.5 \text{ (d, } J_{PC} = 41.5$ Hz, ϵ -C₆H₅), 133.84 (d, $J_{PC} = 8.6$ Hz, m-C₆H₅), 221.45 (dd, J_{PC} = 33.0, 25.7 Hz, CO).

 $[Cp(CO)(SiMe_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me}]^+$ (7c) from 7a. A solution of 7a (195 mg, 0.53 mmol) in CH₂Cl₂ (4 mL) was cooled to -78 °C, and then BF₃·OEt₂ (0.14 mL, 158 mg, 1.11 mmol) was added. After the solution had warmed to room temperature, it was concentrated to about 0.5 mL under reduced pressure and then subjected to spectroscopic measurements. IR (ν_{CO} , in CH₂Cl₂): 1953. ³¹P NMR (δ , in CH₂Cl₂): 309.33 (s). ¹³C NMR (δ , in CH₂Cl₂): 8.73 (s, $J_{CSi} = 48.8$ Hz, Si(CH₃)₃), 34.46 (d, $J_{PC} = 12.2$ Hz, NCH₃), 54.09 (s, NCH₂), 84.71 (s, C₅H₅), 214.06 (d, J_{PC} = 28.1 Hz, CO). ²⁹Si NMR (δ , in CH₂Cl₂): 37.42 (d, $J_{PSi} = 37.6$ Hz).

 $[C_{D}(CO)(CH_{2}PPh_{3})Fe{PN(Me)CH_{2}CH_{2}NMe(OMe)}]$ BF₄ (9e·BF₄) from 9a. A solution of 9a (1502 mg, 4.39 mmol) of CH₂Cl₂ (100 mL) was cooled to -78 °C, and then BF₃ OEt₂ (1.20 mL, 1355 mg, 9.55 mmol) was added. After the solution had been stirred for several minutes, PPh₃ (2300 mg, 8.79 mmol) was added, and then the solution was warmed to room temperature. After the solvent had been removed under reduced pressure, the residue was loaded on a silica gel column. After elution with CH₂Cl₂, an orange complex that eluted with CH₂Cl₂/acetone (8/1) was collected and dried in vacuo to give an orange powder of 9e-BF4 (837 mg, 1.27 mmol, 29%). Anal. Calcd for C₃₃H₄₁BF₄FeN₂O₃P₂ (9e·BF₄·acetone): C, 55.25; H, 5.76; N, 3.91. Found: C, 55.48; H, 5.75; N, 3.72. IR (ν_{CO}, in CH₂Cl₂): 1939. ³¹P NMR (δ, in CH₂Cl₂): 40.35 (s,

PPh₃), 164.87 (s, $\dot{P}N(Me)CH_2CH_2\dot{N}Me(OMe)$). ¹H NMR (δ , in acetone- d_6): 1.45 (ddd, J = 23.1, 12.9, 10.2 Hz, 1H, FeCH₂), 2.41 (td, J = 13.2, 1.0 Hz, 1H, FeCH₂), 2.76 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 3.04 (d, $J_{PH} = 10.6$ Hz, 3H, NCH₃), 3.42 (m, 3H, NCH₂), 3.55 (d, J_{PH} = 11.2 Hz, 3H, OCH₃), 3.61 (m, 1H, NCH₂), 4.20 (d, $J_{PH} = 1.3$ Hz, 5H, C₅H₅), 7.56-7.95 (m, 15H, C₆H₅). ¹³C NMR (δ , in acetone- d_6): -23.38 (dd, J_{PC} = 29.3, 25.6 Hz, FeCH₂), 32.89 (d, $J_{PC} = 11.0$ Hz, NCH₃), 33.29 (d, $J_{PC} = 10.9$ Hz, NCH₃), 52.42 (s, NCH₂), 52.44 (d, $J_{PC} = 3.7$ Hz, NCH₂), 52.66 (d, $J_{PC} = 13.4 \text{ Hz}$, OCH₃), 84.04 (s, C₅H₅), 126.48 (d, J_{PC} = 81.8 Hz, ϵ -C₆H₅), 130.21 (d, J_{PC} = 11.0 Hz, m-C₆H₅), 134.21 (d, $J_{PC} = 2.5$ Hz, p-C₆H₅), 134.42 (d, $J_{PC} = 8.5$ Hz, o-C₆H₅), 222.09 (dd, $J_{PC} = 46.4$, 6.1 Hz, CO).

 $[Cp(CO)(CH_2PPh_3)Fe{\dot{P}N(Me)CH_2CH_2\dot{N}Me(OEt)}]$ -BF₄ (10e·BF₄) from 10a. Complex 10e·BF₄ was prepared from 10a, BF₃·OEt₂, and PPh₃ in the same manner as that for **9e**·BF₄ (yield 19%). Anal. Calcd for $C_{31}H_{37}BF_4FeN_2O_2P_2$: C, 55.22; H, 5.53; N, 4.15. Found: C, 55.16; H, 5.53; N, 4.18. IR $(\nu_{CO}, \text{ in } CH_2Cl_2)$: 1936. ³¹P NMR (δ , in CH₂Cl₂): 40.20 (s, PPh₃), 162.44 (s, $\dot{P}N(Me)CH_2CH_2\dot{N}Me(OEt)$). ¹H NMR (δ , in acetone- d_6): 1.34 (t, $J_{\rm HH} = 7.1$ Hz, 3H, CH₃), 1.49 (dd, $J_{\rm PH} =$ 13.7, 11.0 Hz, 1H, FeCH₂), 2.43 (t, $J_{PH} = 12.9$ Hz, 1H, FeCH₂), $2.76 (d, J_{PH} = 10.7 Hz, 3H, NCH_3), 3.04 (d, J_{PH} = 10.3 Hz, 3H,$ NCH₃), 3.39 (m, 2H, NCH₂), 3.59 (br, 2H, OCH₂), 3.91 (m, 2H, $NCH_2),\,4.19\,(s,\,5H,\,C_5H_5),\,7.69-7.95\,(m,\,15H,\,C_6H_5).$ ^{13}C NMR (δ , in acetone- d_6): -23.17 (dd, $J_{PC} = 25.7, 29.3$ Hz, FeCH₂),

16.56 (d, $J_{PC} = 6.1$ Hz, OCH_2CH_3), 32.88 (d, $J_{PC} = 12.2$ Hz,

 NCH_3), 33.24 (d, $J_{PC} = 11.0 Hz$, NCH_3), 52.31 (s, NCH_2), 61.65 (d, $J_{PC} = 12.2$ Hz, OCH₂), 84.04 (s, C₅H₅), 126.58 (d, $J_{PC} =$ 81.8 Hz, ϵ -C₆H₅), 130.19 (d, $J_{PC} = 11.0$ Hz, m-C₆H₅), 134.25 (d, $J_{PC} = 2.4$ Hz, $p-C_6H_5$), 134.45 (d, $J_{PC} = 9.8$ Hz, $o-C_6H_5$), 222.18 (dd, $J_{PC} = 6.1$, 46.4 Hz, CO).

X-ray Structure Determination for 1b-BF4 and 10e-BF4. Single crystals of 1b-BF4 grown from CH2Cl2/hexane at room temperature and 10e-BF4 grown from CH2Cl2/hexane in a refrigerator were individually mounted on an Enraf-Nonius CAD4 diffractometer and a Mac Science MXC3 diffractometer, respectively, and irradiated with graphite-monochromated Mo Ka radiation ($\lambda = 0.710$ 69 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 (for $1b \cdot BF_4$) and 30 (for 10e BF₄) carefully centered reflections in the range $3^{\circ} <$ $2\theta < 55^{\circ}$ corresponded to a monoclinic cell with dimensions of a = 9.099(1) Å, b = 13.727(2) Å, c = 23.134(5) Å, $\beta = 91.48$ -(1)°, Z = 4, and V = 2889(1) Å³ for 1b·BF₄ and corresponded to an orthorhombic cell with dimensions of a = 18.003(6) Å, b = 24.619(6) Å, c = 14.501(4) Å, Z = 8, and V = 6427(3) Å³ for 10e·BF₄. $P2_1/n$ and Pcab were selected as space groups for 1b-BF₄ and 10e-BF₄, respectively, which led to successful refinements. The data were collected at temperature of 23 \pm 1 °C using the $\omega - 2\theta$ scan technique. The intensities of three representative reflections were measured after every 200 reflections. No decay correction was applied.

The structures were solved by a direct method with the DIRDIF program system¹³ for 1b·BF₄ and with the program Monte Carlo-Multan¹⁴ for 10e BF₄. The positions of all hydrogen atoms were calculated by assuming idealized geometries. Absorption and extinction corrections were then applied,^{15,16} and several cycles of a full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms led to final R_w values of 0.054 and 0.064 for 1b-BF₄ and 10e-BF₄, respectively. All calculations were performed using the program system teXsan¹⁷ for 1b·BF₄ and the program system Crystan-G¹⁴ for 10e-BF₄.

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Supporting Information Available: Additional structural data for complexes 1b-BF4 and 10e-BF4, including tables of positional parameters and thermal parameters (10 pages). Ordering information is given on any current masthead page.

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