

# Study of the Amination Reaction of the Coordinated Cyclopentadienyl Ring in $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$ Derivatives. Crystal and Molecular Structure of $(\eta^5\text{-C}_5\text{H}_4\text{NET}_2)\text{Fe}(\text{CO})[\text{PhP}(\text{OEt})_2]\text{Br}$

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The influence of the nature of X, L<sup>1</sup>, L<sup>2</sup>, and the NR<sub>2</sub> anions on the reaction between LiNR<sub>2</sub> and  $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$  derivatives **6** (L<sup>1</sup> = CO, L<sup>2</sup> = PR<sub>3</sub>; L<sup>1</sup> = L<sup>2</sup> = PR<sub>3</sub>; X = Cl, Br) has been investigated in order to explore the extent and potential in synthesis of the amination reaction of the coordinated cyclopentadienyl ring in **6**. A rather complex situation was found with up to five different reaction products isolated or identified: the main derivatives that formed were the aminated adducts  $(\eta^5\text{-C}_5\text{H}_4\text{NR}_2)\text{FeL}^1\text{L}^2\text{X}$  (**9**) and  $(\eta^5\text{-C}_5\text{H}_4\text{NR}_2)\text{FeL}^1\text{L}^2\text{H}$  (**10**) and the diiron species  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{L})(\mu\text{-CO})_2]$  (**13**). The results show indeed that there is a significant influence of the nature of the halogen X, the ligands L<sup>1</sup> and L<sup>2</sup>, and the amide anions NR<sub>2</sub><sup>-</sup> on the amination process. (i) It leads to C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> adducts only when R ≠ H. (ii) Much higher yields in aminated derivatives **9** and/or **10** are obtained starting from the  $(\eta^5\text{-Cp})\text{FeL}(\text{CO})\text{X}$  or  $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$  derivatives than from the  $(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2\text{X}$  adducts while, on electronic grounds, the latter were expected to be the most suitable candidates: this illustrates the prominent role played by the steric effects of the ligands. (iii) The  $\pi$ -acceptor character of the ligand L plays, however, an important role and favors the amination process: in the case of  $(\eta^5\text{-Cp})\text{FeL}(\text{CO})\text{X}$  derivatives, when L = P(OPh)<sub>3</sub> or PhP(OR)<sub>2</sub>, C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> compounds (**9** and **10**) are obtained in 57–88% yields while for the bulkier PPh<sub>3</sub> ligand the yield is only of 31%. This effect is even more drastic in the case of  $(\eta^5\text{-Cp})\text{FeL}_2\text{Br}$  derivatives: while, for L = PhP(OEt)<sub>2</sub>, the amination reaction occurs in good yield (74%), no aminated adduct was detected for L<sub>2</sub> = dppe which is a better donating ligand than PhP(OEt)<sub>2</sub>. (iv) The brominated derivatives **6** are much better starting materials than their chlorinated analogues. Compound **9d**,  $(\eta^5\text{-C}_5\text{H}_4\text{NET}_2)\text{Fe}(\text{CO})[\text{PhP}(\text{OEt})_2]\text{Br}$  (C<sub>20</sub>H<sub>28</sub>BrFeNO<sub>3</sub>P), crystallizes in the triclinic space group P $\bar{1}$  with *a* = 10.926 (3) Å, *b* = 11.407 (2) Å, *c* = 10.399 (2) Å,  $\alpha$  = 106.53 (1)°,  $\beta$  = 109.40 (2)°,  $\gamma$  = 99.35 (2)°, and *Z* = 2. Its structure shows the nitrogen atom to be coplanar with its substituents; the Cp ring lies approximately in the same plane; the N–C2(Cp) bond is short (1.332 (4) Å) and the C2–Fe distance long (2.304 (3) Å).

## Introduction

Recent studies on the interplay between transition-metal derivatives and phosphorus-based ligands led us to obtain the transition-metal phosphoranides **4**<sup>1,2</sup> and **5**<sup>3</sup> from complexes **2** under the action of LiMe (Scheme I). The cyclic P/N ligand **1'** (the open tautomeric form of **1**) readily coordinates to the metal through P and N, as in **2**, thereby facilitating the abstraction of the N-bound hydrogen atom initially located on phosphorus in **1**. An intramolecular intraligand P–N bond closing process then takes place in the amido-phosphane chelate **3**, leading to phosphoranide **4**. The question obviously arose as to whether this approach could be extended to acyclic analogues of **3** such as **7** and led us to investigate the possibility of an intramolecular interligand reaction as an access to other phosphoranide complexes.

We failed in the synthesis of the cationic derivative **14** from the iron-phosphane adduct **6d** and HNEt<sub>2</sub>, and we therefore investigated the action of LiNEt<sub>2</sub> on **6d**, which was expected to yield **7d** and subsequently phosphoranide **8d** (Scheme II). As reported in a preliminary communication,<sup>4</sup> it led in fact to **9d**, i.e. to the amination of the cyclopentadienyl ring, thus providing an easy and direct access (one step from **6d**, 88% yield) to a ((diethyl-amino)cyclopentadienyl)iron complex.

Although cyclopentadienyl derivatives have found extraordinarily wide applications as ligands in organometallic chemistry, few cyclopentadienylamines (C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub>) and even fewer of their complexes are known compared to

other functionalized cyclopentadienyl rings.<sup>5</sup> The C<sub>5</sub>H<sub>4</sub>NMe<sub>2</sub><sup>-</sup> anion has been obtained in 44% yield by electrophilic amination of C<sub>5</sub>H<sub>5</sub>Li followed by deprotonation, and only three metallocene-type complexes have been prepared directly from this ligand in overall yield not exceeding 30%.<sup>6</sup> Indirect methods led to the preparation of a few other C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> derivatives including ferrocenylamines,<sup>7a</sup> aminocobalticinium salts,<sup>7b,c</sup>  $(\eta^5\text{-C}_5\text{H}_4\text{NH}_2)\text{M}(\text{CO})_3$  (M = Mn,<sup>8</sup> Re<sup>9</sup>), and  $(\eta^5\text{-C}_5\text{H}_4\text{NH}_2)\text{Cr}(\text{CO})_2\text{NO}$ <sup>10</sup> but through multistep processes that usually gave only poor yields. Finally, the synthesis of a 1,2,3-triaminocyclopentadienide anion, isolated in 40–60% yield in its diprotonated form, has also been reported.<sup>11</sup>

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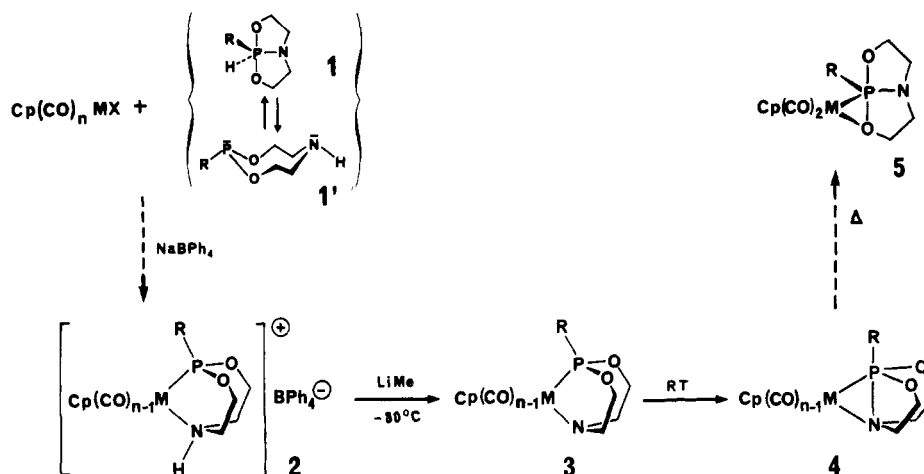
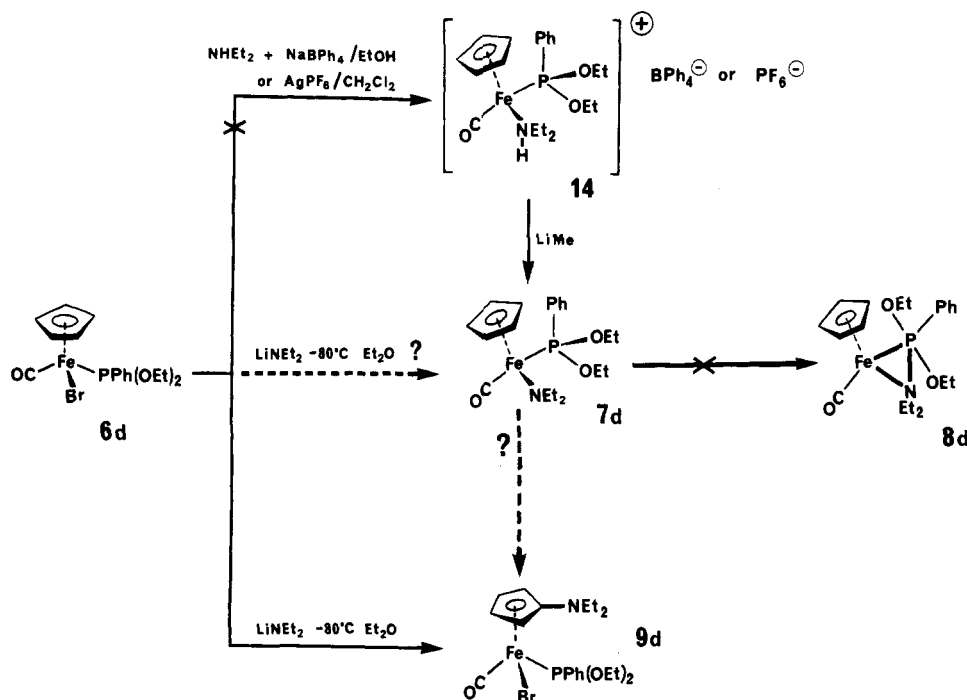
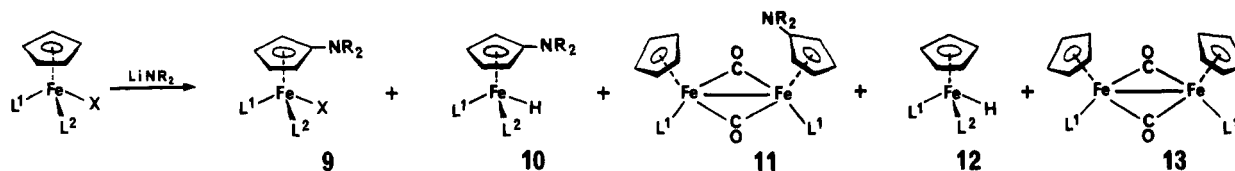
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**Scheme I. Intramolecular Intraligand Access to the Metal Phosphoranides 4 (M = Mo, W,  $n = 3$ ; M = Fe, Ru,  $n = 2$ ) and 5 (M = Mo, W)****Scheme II. The Intramolecular Interligand Approach to the Iron Phosphoranide 8d Which Led in Fact to 9d, i.e. to the Amination of the Cyclopentadienyl Ring****Scheme III. The Different Compounds Resulting from the Reaction between  $\text{LiNR}_2$  and  $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$  Derivatives 6**

Our initial observation led us therefore to investigate whether, and to what extent, the amination of the coordinated Cp ring could be developed into a more general method of preparation of functionalized five-membered rings useful as well in organic as in organometallic chemistry.

We report now on the effect of the nature of R,  $\text{L}^1$ ,  $\text{L}^2$ , and X on the reaction of  $\text{LiNR}_2$  on  $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$  derivatives 6 (Scheme III). These results bring some further

insight in the reaction sequence involved. The detailed X-ray analysis of 9d is also presented.

In parallel to our work, Reger et al. have shown very recently that the action of  $\text{LiNHPh}$  and  $\text{LiNPh}_2$  on cationic cyclopentadienyl iron  $\eta^2$ -alkyne complexes also resulted into the amination of the cyclopentadienyl ring.<sup>12</sup> They mentioned in the same paper that  $\eta^5\text{-CpFe}(\text{CO})[\text{P}(\text{OPh})_3]\text{I}$  when treated with  $\text{LiNEt}_2$  undergoes a "very surprising" ring substitution to yield  $(\eta^5\text{-C}_5\text{H}_4\text{NEt}_2)\text{Fe}$

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Table I. Product Distribution (% Yield) as a Function of R, L<sup>1</sup>, L<sup>2</sup>, and X

	6	9	10	11	12	13
LiNR <sub>2</sub> = LiNEt <sub>2</sub>						
X = Br, L <sup>1</sup> = L <sup>2</sup> = CO	a	6		2		59
X = Cl, L <sup>1</sup> = L <sup>2</sup> = CO	a'					61
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = PPh <sub>3</sub>	b	31	ε		8	
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = P(OPh) <sub>3</sub>	c	42-10	15-70			ε
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = PhP(OEt) <sub>2</sub>	d	88				ε
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = PhP(OMe) <sub>2</sub>	e	28	30			
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = P(OEt) <sub>3</sub>	f	?	?			?
X = Br, L <sup>1</sup> = L <sup>2</sup> = PhP(OEt) <sub>2</sub>	g		74			
X = Br, L <sup>1</sup> , L <sup>2</sup> = Ph <sub>2</sub> P(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub>	h					
X = Cl, L <sup>1</sup> = CO, L <sup>2</sup> = PhP(OEt) <sub>2</sub>	d'	15				?
LiNR <sub>2</sub> = LiNMe <sub>2</sub>						
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = PhP(OEt) <sub>2</sub>	d''	72			ε	
LiNR <sub>2</sub> = LiNH- <i>t</i> -Bu or LiNHCH <sub>2</sub> Ph						
X = Br, L <sup>1</sup> = CO, L <sup>2</sup> = PhP(OEt) <sub>2</sub>						99
X = Br, L <sup>1</sup> = L <sup>2</sup> = PhP(OEt) <sub>2</sub>						

Table II. Spectroscopic Data of Compounds 6 and 9-13

	ν(CO), cm <sup>-1</sup>	ν(C=C), cm <sup>-1</sup>	δ( <sup>1</sup> H)				δ( <sup>31</sup> P)
			C <sub>5</sub> H <sub>5</sub> <sup>a</sup>	C <sub>5</sub> H <sub>4</sub> <sup>b</sup>	NR <sub>2</sub> <sup>c</sup>	FeH <sup>d</sup>	
6a	2060-1990		5.05 (s)				
6a'	2065-1995		5.04 (s)				
6b	1960		4.46				65
6c	1975		4.17				169
6d	1940		4.48				194
6d'	1950		4.48				194
6e	1965		4.50				199
6f	1960		4.66				169
6g							199
6h			4.11 (t)				97
9a	2040-1960	1585		4.33-4.50	1.22 (t), 3.26 (q)		
9b	1900	1550		3.55-3.98	1.1 (t), 3.11 (q)		71
9c	1950-1930	1570		3.30-3.75	1.0 (t), 2.95 (q)		171
9d	1920	1570		T	0.85 (t), 3.08 (q)		198
9d'	1920	1575		T	1.08 (t), 3.10 (q)		198
9e	1915-1935	1550-1570		T	1.08 (t), 3.10 (q)		204
9f	1940	1560					
9d''	1925	1570		T	2.76 (s)		198
10b				3.95	0.94 (t), 2.76 (q)	-13.3 (d, <i>J</i> = 72 Hz)	
10c	1930-1910	1540		3.30-4.07	0.84 (t), 2.54 (q)	-13.2 (d, <i>J</i> = 92 Hz)	185
10e	1890	1535		T	1.07 (t), 2.98 (q)	-19.4 (d, <i>J</i> = 41 Hz)	169
10f	1920	1530		T	0.90 (t), 2.80 (q)	-13.3 (d, <i>J</i> = 89 Hz)	
10g		1515		3.21-4.18	1.11 (t), 2.75 (q)	-13.5 (t, <i>J</i> = 75 Hz)	210
11a	1980-1930, 1745	1555	4.71 (s)	3.89-4.46	1.23 (t), 3.18 (q)		
12b	1930		4.24			-12.9 (d, <i>J</i> = 72 Hz)	
12d''	1940		4.24			-13.15 (d, <i>J</i> = 82 Hz)	
13a	1960-1940, 1760		4.77 (s)				
13c	1720		4.40				
13d	1700		4.40				
13f	1720						

<sup>a</sup> Doublet (if not specified); <sup>3</sup>J<sub>H,P</sub> = 1 Hz. <sup>b</sup> A<sub>2</sub>B<sub>2</sub> (or AA'BB') system; T, masked by the ligand resonance. <sup>c</sup> <sup>3</sup>J<sub>H,H</sub> = 7 Hz. <sup>d</sup> <sup>2</sup>J<sub>H,P</sub>.

(CO)[P(OPh)<sub>3</sub>]I, in accordance with what we had already reported when (η<sup>5</sup>-Cp)Fe(CO)[PhP(OEt)<sub>2</sub>]Br (6d) was treated with LiNEt<sub>2</sub>.<sup>4</sup>

### Results and Discussion

**Occurrence.** All the reactions have been performed by dropwise addition of a THF solution of the (η<sup>5</sup>-Cp)-FeL<sup>1</sup>L<sup>2</sup>X complexes 6 to a solution of LiNR<sub>2</sub> in ether at -80 °C. Chromatography of the crude reaction product on silica allowed the separation of up to five different compounds, depending on the nature of R, L<sup>1</sup>, L<sup>2</sup>, and X (Scheme III). The results are summarized in Table I.

The compounds isolated consist mainly in the expected C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> compounds 9 and 10 and in the undesirable diiron adducts 13. Complexes 12 have been isolated or identified in a few cases while the formation of the disymmetric diiron adducts 11 was shown in one case only.

**Characterizations.** The amination of the Cp ring has been unambiguously established by an X-ray diffraction study on compound 9d (vide infra). The presence of the C<sub>5</sub>H<sub>4</sub>NET<sub>2</sub> ring in this compound is also responsible for the following spectroscopic data: (i) its infrared spectrum shows a relatively intense ν(C=C) absorption at 1560 cm<sup>-1</sup> that is not seen in the spectrum of the unsubstituted C<sub>5</sub>H<sub>5</sub> derivative 6d; (ii) its <sup>1</sup>H NMR spectrum exhibits the print of the NET<sub>2</sub> group—a quadruplet and a triplet centered at 3.08 and 0.85 ppm, respectively (<sup>3</sup>J<sub>H,H</sub> ≈ 7 Hz) (the <sup>1</sup>H resonances of the C<sub>5</sub>H<sub>4</sub> ring in 9d could not be assigned as they are masked by the complex OCH<sub>2</sub> pattern of the phosphane ligand); (iii) its mass spectrum shows the molecular peak and those of the C<sub>5</sub>H<sub>4</sub>NET<sub>2</sub><sup>+</sup>, C<sub>5</sub>H<sub>5</sub>NET<sub>2</sub><sup>+</sup>, and C<sub>5</sub>H<sub>5</sub>NHET<sub>2</sub><sup>+</sup> fragments.

These data are highly characteristic of the presence of a C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> ring and allowed the unambiguous identifica-

Table III. Crystallographic Data for 9d

formula	C <sub>20</sub> H <sub>29</sub> BrFeNO <sub>3</sub> P
fw	498.2
triclinic space group	P $\bar{1}$
a, Å	10.926 (3)
b, Å	11.407 (2)
c, Å	10.399 (2)
$\alpha$ , deg	106.53 (1)
$\beta$ , deg	109.40 (2)
$\gamma$ , deg	99.35 (2)
V, Å <sup>3</sup>	1123.7
Z	2
$\mu$ , cm <sup>-1</sup>	25.2
cryst size, mm	0.45 × 0.35 × 0.30
Mo K $\alpha$ radiatn	graphite monochromatized
$d_{\text{calc}}$ , g·cm <sup>-3</sup>	1.47
scan mode	$\omega$ -2 $\theta$
scan range, deg	1.00 + 0.35 tan $\theta$
detector aperture, mm	2.00 + 0.50 tan $\theta$
2 $\theta$ limits, deg	1-28
total measurements	5711
data used ( $I > \sigma(I)$ )	3412
final R	0.041
final R <sub>w</sub>	0.045

Table IV. Selected Bond Lengths (Å) and Angles (deg)

Bond Lengths			
Br-Fe	2.437 (0)	N-C2	1.332 (4)
Fe-P	2.163 (1)	N-C13	1.465 (4)
Fe-C1	1.744 (3)	N-C15	1.457 (4)
Fe-C2	2.304 (3)	C2-C3	1.425 (4)
Fe-C3	2.131 (3)	C2-C6	1.424 (4)
Fe-C4	2.039 (3)	C3-C4	1.414 (5)
Fe-C5	2.034 (3)	C4-C5	1.410 (5)
Fe-C6	2.133 (3)	C5-C6	1.397 (5)
C1-O1	1.136 (4)		
Bond Angles			
Br-Fe-P	91.73 (3)	C3-C2-C6	106.1 (3)
P-Fe-C1	95.0 (1)	C2-N-C13	120.8 (3)
N-C2-C3	127.5 (3)	C2-N-C15	121.3 (3)
N-C2-C6	126.3 (3)	C13-N-C15	117.8 (3)

tion of the subsequently synthesized compounds **9** and **10** whose spectroscopic data are listed in Table II. For instance, a  $\nu(\text{C}=\text{C})$  vibration is systematically found between 1515 and 1585 cm<sup>-1</sup> for all these derivatives. Their <sup>1</sup>H NMR spectra show the expected NR<sub>2</sub> pattern, triplet/quadruplet system with <sup>3</sup>J<sub>HH</sub>  $\approx$  7 Hz for the NEt<sub>2</sub> or a singlet for the NMe<sub>2</sub> group, and an AA'BB' spin system for the C<sub>5</sub>H<sub>4</sub> moiety in compounds **9b**, **9c**, **10c**, and **10g** (pseudo A<sub>2</sub>B<sub>2</sub> for **9a**). The hydride in derivatives **10** is clearly evidenced by the presence, at high fields, of a doublet (or a triplet for **10g**), resulting from a <sup>2</sup>J<sub>HP</sub> coupling; this coupling is confirmed by <sup>31</sup>P NMR. As observed for **9d**, the mass spectra of **9a**, **9c**, and **10c** exhibit the C<sub>5</sub>H<sub>4</sub>NET<sub>2</sub><sup>+</sup> fragment at  $m/e$  136.

The dissymmetric diiron complex **11a** is characterized in the IR spectrum by  $\nu(\text{CO})$  bands at 1980, 1930 (terminal CO), and 1745 cm<sup>-1</sup> (bridging CO) and a  $\nu(\text{C}=\text{C})$  vibration at 1555 cm<sup>-1</sup> and in the <sup>1</sup>H NMR spectrum by the triplet/quadruplet system corresponding to the NEt<sub>2</sub> group, the pseudo A<sub>2</sub>B<sub>2</sub> spin system of the amino-substituted ring protons, and a singlet assigned to the unsubstituted Cp ligand. The structure of **11a** is further confirmed by the presence of the molecular peak in its mass spectrum.

**X-ray Structure Determination of the (Diethylamino)cyclopentadienyl Adduct 9d.** Figure 1 shows an ORTEP representation of the molecule with its labeling scheme; Tables III and IV collect the crystallographic data and selected bond distances and angles respectively.

As shown in Figure 1, the iron atom is surrounded by the Br, CO, and PhP(OEt)<sub>2</sub> ligands and, indeed, by the aminated C<sub>5</sub>H<sub>4</sub>-NET<sub>2</sub> ring. Although two structures of

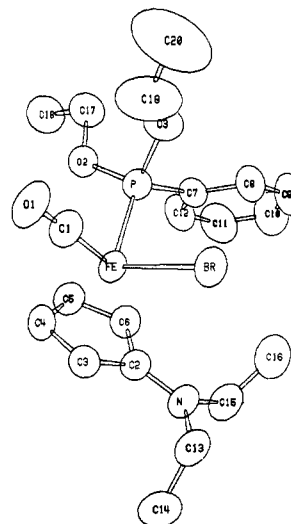


Figure 1. ORTEP view of 9d with its labeling scheme.

amino-substituted metallocenes are known (vide infra), this appears to be the first structure determination to be reported on a mono((dialkylamino)cyclopentadienyl)metal carbonyl complex: it is therefore of interest to discuss the changes provoked in the metal-ring moiety by the presence of the NR<sub>2</sub> substituent with respect to unsubstituted and differently monosubstituted cyclopentadienyl analogues.

The distances from iron to the NR<sub>2</sub>-substituted Cp carbon (Fe-C2 = 2.304 (3) Å) and to the two carbon in  $\beta$  from C2 (Fe-C4 = 2.039 (3) and Fe-C5 = 2.034 (3) Å) are significantly longer and shorter, respectively, than those usually found in unsubstituted Cp iron derivatives (Fe-C(Cp)  $\approx$  2.10 Å).<sup>1a,13a</sup> The former is among the longest reported so far. The shorter two are in the range found for ferrocenes or even for bridged ferrocenes,<sup>13b,c</sup> which are known to have Fe-C(Cp) distances shorter than those of ( $\eta^5$ -Cp)FeL<sup>1</sup>L<sup>2</sup>L<sup>3</sup>-type derivatives.<sup>13a</sup> The ring displays geometrical distortion similar to those observed for other monosubstituted rings:<sup>13a</sup> the C-C bond lengths vary from 1.397 (5) to 1.425 (4) Å (but stay in the expected range<sup>14</sup>), and the ring bond angle at the substituted carbon (C3C2C6 = 106.1 (3)°) is slightly smaller than the "ideal" value of 108.0°.<sup>13c</sup>

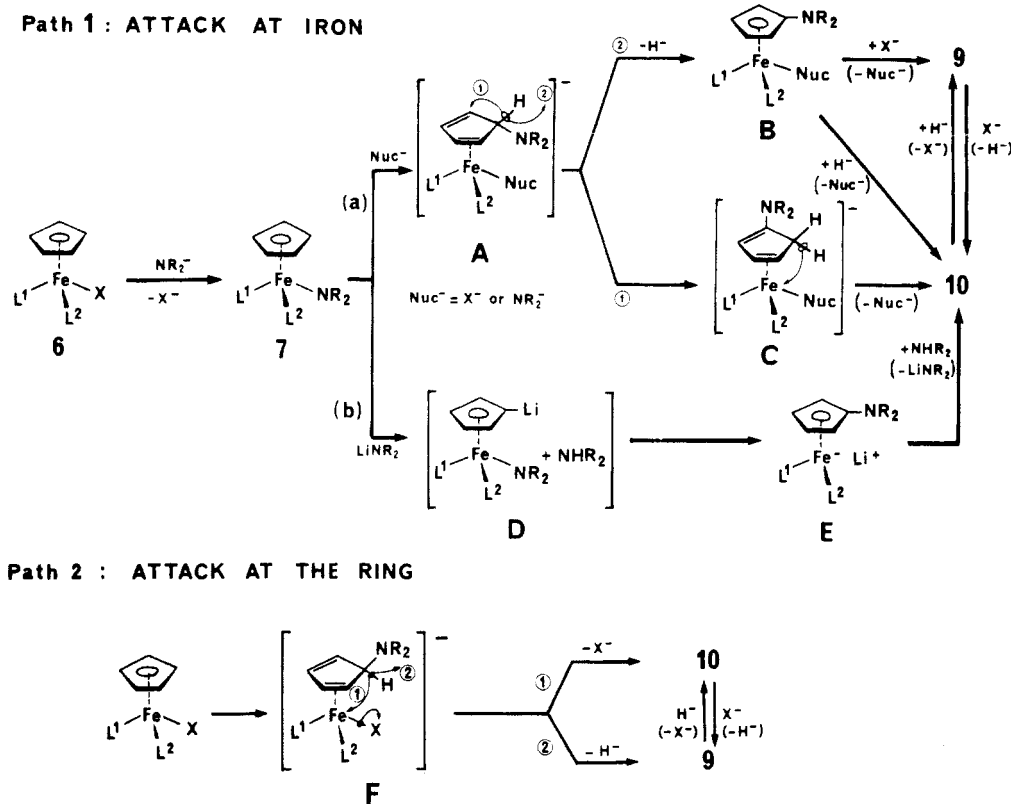
The N-C2 distance (1.332(4) Å) is markedly shorter than the 1.40-1.44 Å standard given for a N(sp<sup>3</sup>)-C(sp<sup>2</sup>) single bond but longer than a "pure" N(sp<sup>2</sup>)=C(sp<sup>2</sup>) double bond (1.25-1.28 Å).<sup>15,17a</sup> It is also much shorter than those found in a tris(ferrocenyl)amine (average 1.414 Å)<sup>13d</sup> and in a ferrocene derivative where the two Cp rings are linked together by a -SO<sub>2</sub>-NH- bridge (C-N = 1.419 (11) Å).<sup>13b</sup> It is also noteworthy that the nitrogen atom is nearly coplanar with its substituents (sum of the angles around N,  $\Sigma_N$  = 359.9°; the distance from N to the C2-C13-C15 plane is only 0.023 (3) Å). The angle of this plane with that of the Cp ring is of only 5.3°, a value which is consistent with a  $\pi$ -bond delocalization over the whole C<sub>5</sub>H<sub>4</sub>NET<sub>2</sub> moiety. This is further in the line with the structural data reported for 1,1'-bis(dimethylamino)-titanocene dichloride,<sup>16</sup> where a very short (Cp)C-NMe<sub>2</sub>

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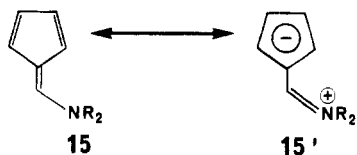
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Scheme IV. Possible Mechanisms of Formation of 9 and 10 from 6



bond (1.347 (4) Å) and an unusually long Ti-C(NMe<sub>2</sub>) bond (2.564 (4) Å) compared to those between Ti and the cyclopentadienyl β-carbons (2.318 (4) and 2.329 (4) Å) were also found. The nitrogen atom is also nearly coplanar with its substituents ( $\sum_N = 358.7^\circ$ ) with a small distance from N to its substituent plane (0.092 Å) and a small angle between this plane and the Cp ring plane ( $3.2^\circ$ ).

An interesting parallel can furthermore be drawn with 6-(dimethylamino)pentafulvene (15) and its transition metal complexes,<sup>17</sup> in which the nitrogen atom also adopts a planar configuration and in which the C-N bond lengths lie in the same range: 1.331 (6) Å in the uncomplexed aminofulvene<sup>17a</sup> and 1.303 (9) and 1.337 (3) Å in its Cr<sup>17b</sup> and Fe<sup>17c</sup> adducts, respectively. In these cases the shortening of the C-N bond has similarly been interpreted as implying the highly delocalized π-system 15' (the angles between the N plane and the ring were  $2.6^\circ$  in the uncomplexed aminofulvene<sup>17a</sup> and  $14.5^\circ$  in its chromium complex).<sup>17b</sup>



In 9d the immediate consequence of the substantial overlap between the nitrogen's 2p orbital and a  $\pi^*$ -orbital of the Cp ring is that the C<sub>5</sub>H<sub>4</sub>NR<sub>2</sub> entity should be a better electron-donating ligand than the unsubstituted C<sub>5</sub>H<sub>5</sub> ring; this is reflected to some extent by the 30 cm<sup>-1</sup> shift to lower frequencies found for the  $\nu(\text{CO})$  vibration

when the adducts of type 6 are compared to their amino derivatives 9 (see Table II).

**Factors Influencing the Amination Reaction.** The influence of the nature of X, L<sup>1</sup>, L<sup>2</sup>, and the NR<sub>2</sub> anions on the reaction of LiNR<sub>2</sub> on  $(\eta^5\text{-Cp})\text{FeL}^1\text{L}^2\text{X}$  was investigated in order to explore the extent and potential in synthesis of this ring amination reaction.

A rather complex situation was found with up to five different reaction products isolated or identified. The main derivatives that formed were the aminated adducts 9 and 10 and the diiron species 13.

Our results can be rationalized by considering the most probable mechanisms of formation of these derivatives.

**Formation of the Dinuclear Compounds 13.** The reductive character of the NR<sub>2</sub> nucleophile is thought to be responsible for the formation of  $(\eta^5\text{-Cp})\text{Fe}(\text{CO})\text{L}^*$  radicals leading through dimerization to 13 whose formation is, for our purpose, to be avoided. It is expected that this reductive process will be favored by the presence of good π-accepting L ligands while the dimerization will be disfavored by bulky L ligands. In this regard, the dicarbonyl derivatives 6a,a' would be the best candidates. This is effectively the case as both compounds investigated gave quite high yield of the adduct 13a. It should be added further that such radicals may also arise from the homolytic rupture of the Fe-N bond in derivatives of type 7 whose formation cannot be excluded.

**Formation of the Aminated Adducts 9 and 10.** Nucleophilic attacks on cationic cyclopentadienyl metal carbonyl complexes are well-known to occur at either the Cp ring or the metal atom or the carbonyl group, although the factors that affect the regioselectivity of these attacks remain unclear.<sup>18</sup> By contrast, the case of neutral ana-

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logues is poorly documented. However we expect the neutral complexes **6** to undergo nucleophilic attack by the amide anion similarly.

**Attack at the Carbonyl Group.** If initial attack at the carbonyl group leading to a transient intermediate containing the Fe-CO-NR<sub>2</sub> sequence, then, after subsequent rearrangements, to the final aminated adducts, cannot be completely ruled out, the fact that the aminated adduct **9g** (74% yield) was obtained in the case of derivative ( $\eta^5$ -Cp)FeL<sub>2</sub>Br (L = PhP(OEt)<sub>2</sub>) (**6g**) indicates that the attack occurs either at the iron atom or at the ring rather than at the carbonyl in the case of the monocarbonyl complexes **6**.

**Attack at Iron (Scheme IV, Path 1).** A few examples of (i) base-induced migrations of metal-bonded groups to  $\pi$ -cyclopentadienyl ligands (Ph<sub>3</sub>Ge from molybdenum,<sup>19</sup> aryl from cobalt,<sup>20</sup> acetyl from rhenium<sup>21</sup> and iron,<sup>22</sup> R<sub>3</sub>Si groups from iron,<sup>23</sup> and rhenium<sup>24</sup> to Cp or substituted Cp rings) and (ii) thermal-induced migrations, in the presence of PPh<sub>3</sub>, of alkyl groups from manganese to Cp and methyl-substituted Cp rings<sup>31</sup> have been reported. These migrations support the idea of an initial formation of compounds like **7** resulting from nucleophilic substitution of X at iron. At this stage, two main routes become possible:

Route a involves a X<sup>-</sup> or NR<sub>2</sub><sup>-</sup> nucleophilic-assisted migration of the NR<sub>2</sub> group from iron to the Cp ring to produce intermediate A that may evolve either (i) by expulsion of H<sup>-</sup> ( $\rightarrow$  B) and formation of Fe-H or Fe-X bond giving compounds **9** and **10** or (ii) by a 1,2 shift of the exo H atom to the carbon ring atom ( $\rightarrow$  C) followed by the migration of the endo H atom thus produced to the iron atom leading to **10**. A subsequent exchange of H by X would then lead to **9**.

In route b, the migration process of the NR<sub>2</sub> group is shown to occur through a mechanism similar to that reported by Berryhill et al.<sup>23d</sup> However, in the base-induced migrations cited above, 1 equiv of the base (RLi or LiNR<sub>2</sub>) is needed for the quantitative formation of adducts of type E (RH or HNR<sub>2</sub> are formed during these reactions). In the present case, the formation of Fe-H compounds such as **10** and **12** may indicate a base-catalyzed migration process. However, when LiNR<sub>2</sub>-induced migrations<sup>23</sup> are performed, the formation of metal hydrides, which involves abstraction of H<sup>+</sup> from HNR<sub>2</sub> (step E  $\rightarrow$  **10**), has never been observed.

Despite the very mild reaction conditions, we could neither isolate nor even detect any compound of structure **7**,<sup>30</sup> which is indeed surprising; this and the fact that a transformation like E  $\rightarrow$  **10** is not known up to now argues to some extent against both routes depicted in path 1.

**Attack at the Cp Ring (Scheme IV, Path 2).** It has been shown that the PPh<sub>2</sub><sup>-</sup> anion attacks directly the Cp ring in ( $\eta^5$ -Cp)Fe(CO)<sub>3</sub><sup>+</sup> to give neutral ( $\eta^4$ -C<sub>5</sub>H<sub>5</sub>PPh<sub>2</sub>)Fe(CO)<sub>3</sub>;<sup>25</sup> this might be taken to indicate that a direct attack

of the NR<sub>2</sub><sup>-</sup> anion on the exo face of the Cp ring in **6** can also be considered: it would produce the intermediate F that would evolve to give **10** by migration of the endo H<sup>-</sup> hydride to iron and X<sup>-</sup> expulsion or **9** by liberation of H<sup>-</sup> in the medium. A subsequent H/X exchange would interconvert **9** and **10**.

**Notice.** The presence of H<sup>-</sup> anions in the medium is strongly suggested by the isolation of derivatives **12** that are formed through the exchange of X by H in **6** (the liberation of H<sup>-</sup> is involved in both mechanisms depicted in Scheme IV).

The conclusion up to now is difficult since we have no spectroscopic evidence to localize the initial site of attack;<sup>30</sup> furthermore, the action of the amide anion on compounds **6** may occur either selectively at only one of the two sites or not. However, the direct attack at the ring would probably be the most selective route to the aminated compounds; attack at iron, unlikely for the reasons mentioned above, is furthermore expected to be less selective since the intermediates of type **7** thus produced are supposed to be also good sources of radicals through Fe-N homolytic bond cleavage.

Nevertheless, if one considers the two mechanisms depicted in Scheme IV as the most probable ones, it becomes obvious that for a given nucleophile, the electronic and steric properties of the ligands L<sup>1</sup>, L<sup>2</sup>, and X should influence the initial site of attack of the nucleophile, hence the issue of the reaction. Bulky ligands will favor (i) the direct attack at the Cp ring (ii) the migration, in the intermediate **7**, of the amido group from Fe to the Cp ring by release of steric constraints at the metal center and disfavor the dimerization of the ( $\eta^5$ -Cp)Fe(CO)L• radicals. The latter is inhibited in the case of ( $\eta^5$ -Cp)FeL<sup>1</sup>L<sup>2</sup>• radicals.

It is furthermore expected that the nucleophilic attack by an amide anion on ( $\eta^5$ -Cp)FeL<sup>1</sup>L<sup>2</sup>X complexes will also be favored by  $\pi$ -accepting ligands.

Our results show indeed that there is a significant influence of the nature of the halogen, the ligands L<sup>1</sup> and L<sup>2</sup>, and the amide anions on the amination process.

**(a) Influence of the Halogen.** Better yields in aminated compounds are obtained for X = Br than for X = Cl (88% and 15% for **9d** and **9d'**, respectively; 6% for **9a** while the chlorinated analogue was not detected). This difference may indicate a specific mechanism of attack for each halogen: the steric hindrance of the bromine atom would orient the nucleophilic attack of the NR<sub>2</sub><sup>-</sup> ion on the Cp ligand rather than on the metal, the latter being favored in the case of the chlorine atom.

**(b) Influence of CO-Phosphane.** Much higher yields in aminated derivatives are obtained starting from the ( $\eta^5$ -Cp)FeL(CO)X adducts **6** (31–88% yield) or ( $\eta^5$ -Cp)Fe[PhP(OEt)<sub>2</sub>]<sub>2</sub>Br (74% yield) than from the ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>X species while, on electronic grounds, the latter were expected to be the most suitable candidates. This illustrates not only that these reactions are controlled by the electronic effects of the ligands (see next section) and but also that their steric effects play a prominent role.

The  $\pi$ -acceptor character of the phosphine ligand plays, however, an important role and favors the amination process as reflected by the better yields in aminated adducts obtained (i) in the case of ( $\eta^5$ -Cp)FeL(CO)X derivatives for L = P(OPh)<sub>3</sub> (57–80% for **9c** and **10c**) or PhP(OR)<sub>2</sub> (58% for **9e** and **10e**; 88% for **9d**) compared to the

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bulkier L = PPh<sub>3</sub> (31% for **9b**) and (ii) essentially in the case of ( $\eta^5$ -Cp)FeL<sup>1</sup>L<sup>2</sup>Br derivatives, for L<sup>1</sup> = L<sup>2</sup> = PhP(OEt)<sub>2</sub>, **6g** (74% for **10g**), compared to L<sup>1</sup>L<sup>2</sup> = dppe, **6h**, which is a better donating ligand than PhP(OEt)<sub>2</sub>; in the latter case no aminated adduct was even detected.

(c) **Influence of the Amide Anion.** The behavior of the amide ion on the issue of the reaction is directly related to its degree of substitution: thus, the reaction of ( $\eta^5$ -Cp)FeL(CO)Br (**6d**) with NEt<sub>2</sub><sup>-</sup> and NMe<sub>2</sub><sup>-</sup> gives similar yields in Cp-aminated product (88 and 74%, respectively), while no aminated compounds are detected with *t*-BuNH<sup>-</sup> or PhCH<sub>2</sub>NH<sup>-</sup>, the diiron adduct **13d** being formed in nearly quantitative yields. The reaction between **6g** and a RNH<sup>-</sup> anion, designed to circumvent dimerization, was also unsuccessful.

### Experimental Section

All reactions were carried out under dry oxygen-free argon. All solvents were freshly distilled from appropriate drying agents. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Bruker WH 90 spectrometer. Chemical shifts are given in parts per million downfield from internal Me<sub>4</sub>Si for the <sup>1</sup>H and <sup>13</sup>C shifts and from external H<sub>3</sub>PO<sub>4</sub> for the <sup>31</sup>P shifts. Infrared spectra were obtained on a Perkin-Elmer 577 grating spectrophotometer and mass spectra on a R10 Riberlag L10 spectrometer. Elemental analysis was performed by the Service Central de Microanalyse of the CNRS, France.

**Synthesis of the ( $\eta^5$ -Cp)FeL<sup>1</sup>L<sup>2</sup>X Derivatives 6.** Complexes ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>X (X = Br, Cl), <sup>22</sup> ( $\eta^5$ -Cp)Fe(CO)(PPh<sub>3</sub>)Br (**6b**),<sup>23</sup> and ( $\eta^5$ -Cp)Fe(dppe)Br<sup>24</sup> (**6h**) were prepared according to published procedures. A procedure similar to that described for **6b** was applied to the preparation of all the other derivatives of 6.

**General Procedure.** A toluene solution of 1 equiv of the phosphine ligand L (two for the synthesis of **6g**) and 1 equiv of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>X are exposed to UV irradiation (HP lamp, 125 W) under magnetic stirring; the reaction is monitored by IR, and irradiation is stopped as soon as the dicarbonyl complex has been consumed. Filtration, evaporation of toluene, and further chromatography of the residue on a SiO<sub>2</sub> column leads to derivatives 6.

( $\eta^5$ -Cp)Fe(CO)[P(OPh)<sub>3</sub>]Br (**6c**). This procedure applied to 3.43 g (13.4 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br and 4.15 g (13.4 mmol) of P(OPh)<sub>3</sub> leads after 22 h of UV irradiation followed by chromatography by elution with ether to 4.30 g (8.04 mmol, 60%) of **6c** as a brown powder: IR (KBr)  $\nu$ (CO) 1975 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.17 (d, <sup>3</sup>J<sub>HP</sub> = 1 Hz, C<sub>5</sub>H<sub>5</sub>, 5 H); 7.39 (m, C<sub>6</sub>H<sub>5</sub>, 15 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  169 (s).

( $\eta^5$ -Cp)Fe(CO)[PhP(OEt)<sub>2</sub>]Br (**6d**). The same procedure applied to 3.50 g (13.6 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br and 2.62 g (13.6 mmol) of PhP(OEt)<sub>2</sub> leads after 9 h of UV irradiation and chromatography with elution with a ether/pentane (2/1) mixture to 4.75 g (8.98 mmol, 66%) of **6d** as a red-brown powder: IR (KBr)  $\nu$ (CO) 1940 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.28 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 3.80 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4 H), 4.48 (d, <sup>3</sup>J<sub>HP</sub> = 1 Hz, C<sub>5</sub>H<sub>5</sub>, 5 H), 7.40, 7.75 (m, C<sub>6</sub>H<sub>5</sub>, 5 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  194 (s).

( $\eta^5$ -Cp)Fe(CO)[PhP(OEt)<sub>2</sub>]Cl (**6d'**). The synthesis of **6d'** has been performed without UV irradiation. A toluene solution of 0.45 g (2.12 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Cl and 0.41 g (2.12 mmol) of PhP(OEt)<sub>2</sub> is stirred for 4 h. Chromatography with elution with ether followed by recrystallization from a THF/pentane mixture gives 0.23 g (0.59 mmol, 28%) of **6d'** as red crystals: IR (KBr)  $\nu$ (CO) 1950 cm<sup>-1</sup>. <sup>1</sup>H and <sup>31</sup>P NMR spectra are identical with those described for **6d**.

( $\eta^5$ -Cp)Fe(CO)[PhP(OMe)<sub>2</sub>]Br (**6e**). The general procedure applied to 6.86 g (26.7 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br and 4.54 g (26.7 mmol) of PhP(OMe)<sub>2</sub> leads after 24 h of UV irradiation and chromatography with elution with CH<sub>2</sub>Cl<sub>2</sub> to 8.50 g (21.4 mmol, 80%) of **6e** as a red-brown powder: IR (KBr)  $\nu$ (CO) 1965 cm<sup>-1</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.72 (m, CH<sub>3</sub>, 6 H), 4.50 (d, <sup>3</sup>J<sub>HP</sub> = 1 Hz, C<sub>5</sub>H<sub>5</sub>, 5 H), 7.85, 7.50 (m, C<sub>6</sub>H<sub>5</sub>, 5 H); <sup>31</sup>P{<sup>1</sup>H} NMR (CH<sub>2</sub>Cl<sub>2</sub>)  $\delta$  199 (s).

( $\eta^5$ -Cp)Fe(CO)[P(OEt)<sub>3</sub>]Br (**6f**). ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br (1.90 g, 7.40 mmol) and 1.23 g (7.41 mmol) of P(OEt)<sub>3</sub> yields, after 17 h of UV irradiation and chromatography with elution with toluene, 0.80 g (2.22 mmol, 30%) of a brown oil consisting in **6f**: IR (KBr)

$\nu$ (CO) 1960 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.30 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 9 H), 4.12 (m, CH<sub>2</sub>, 6 H), 4.66 (d, <sup>3</sup>J<sub>HP</sub> = 1 Hz, C<sub>5</sub>H<sub>5</sub>, 5 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  169 (s).

( $\eta^5$ -Cp)Fe(PhP(OEt)<sub>2</sub>)Br (**6g**). ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br (2.50 g, 9.73 mmol) and 4.2 g (21.9 mmol) of PhP(OEt)<sub>2</sub> lead, after 30 h of UV irradiation and evaporation of toluene, to a oily residue. Recrystallization from pentane at -30 °C yields 4.35 g (7.29 mmol, 75%) of dark green crystals consisting in **6g**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.22 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 12 H), 3.99 (m, CH<sub>2</sub> and C<sub>5</sub>H<sub>5</sub>, 13 H), 7.34, 7.79 (m, C<sub>6</sub>H<sub>5</sub>, 10 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  199 (s).

**General Procedure for the Amination Reaction of Derivatives 6.** The same experimental procedure has been applied to all reactions: dropwise addition at -90 °C of a THF solution of **6** to a LiNR<sub>2</sub> solution freshly prepared by action of LiMe on HNR<sub>2</sub> in ether; the resulting mixture is stirred for 1 h at this temperature and then allowed to warm to room temperature. It is important to follow strictly the order of addition of the reagents, the opposite order of addition greatly favoring the formation of dimers **13** at the expenses of the aminated derivatives **9** and **10**. The various compounds were isolated by column chromatography on SiO<sub>2</sub> of the crude residues obtained after evaporation of the solvent.

**Action of LiNEt<sub>2</sub> on ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br (**6a**).** The above procedure is applied to 1.49 g (5.8 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Br in 50 mL of THF and to a solution in ether in LiNEt<sub>2</sub> (6.2 mmol). A deep red fraction is first eluted with toluene and recrystallized from an ether/pentane (1/1) mixture to give 590 mg (3.4 mmol, 59%) of red crystals of **13a**: IR (KBr)  $\nu$ (CO) 1960, 1940, 1760 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.77 (s, C<sub>5</sub>H<sub>5</sub>). These spectroscopic data are consistent with those given in literature.

The solution remaining after the separation of **13a** is concentrated and cooled to -30 °C; 25 mg of red crystals of **11a** (2%) is collected: IR (KBr)  $\nu$ (CO) 1980, 1930, 1745,  $\nu$ (C=C) 1555 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.23 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 3.18 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4 H), 3.89, 4.46 (A<sub>2</sub>B<sub>2</sub>, C<sub>5</sub>H<sub>4</sub>, 2 H, 2 H), 4.71 (s, C<sub>5</sub>H<sub>5</sub>, 5 H); MS (CI, NH<sub>3</sub>), *m/e* (relative intensity) 426 [(M + H)<sup>+</sup>; 99], 258 [(CpFe(C<sub>5</sub>H<sub>4</sub>NHET<sub>2</sub>)<sup>+</sup>; 40], 249 [(Fe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NHET<sub>2</sub>)<sup>+</sup>; 20], 138 [(C<sub>5</sub>H<sub>5</sub>NHET<sub>2</sub>)<sup>+</sup>; 71], 137 [(C<sub>5</sub>H<sub>4</sub>NHET<sub>2</sub>)<sup>+</sup>; 48].

A second orange fraction is eluted with ether; recrystallization from an ether/pentane (2/1) mixture yields 120 mg (0.36 mmol, 6%) of orange crystals of **9a**: IR (KBr)  $\nu$ (CO) 2040, 1960,  $\nu$ (C=C) 1585 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.22 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 3.26 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4 H), 4.33, 4.50 (A<sub>2</sub>B<sub>2</sub>, C<sub>5</sub>H<sub>4</sub>, 2 H, 2 H); MS (CI, NH<sub>3</sub>), *m/e* (relative intensity) 299, 301 [(M - CO)<sup>+</sup>; 9, 10], 271, 273 [(M - 2CO)<sup>+</sup>; 51, 51], 136 [(C<sub>5</sub>H<sub>4</sub>NET<sub>2</sub>)<sup>+</sup>; 100]. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>BrFeNO<sub>2</sub> (*M<sub>r</sub>* 328): C, 40.24; H, 4.27; N, 4.27; Br, 24.39. Found: C, 40.17; H, 4.25; N, 3.94; Br, 23.71.

**Action of LiNEt<sub>2</sub> on ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Cl.** The same procedure is applied to 830 mg (3.91 mmol) of ( $\eta^5$ -Cp)Fe(CO)<sub>2</sub>Cl in 30 mL of THF and to a solution of LiNEt<sub>2</sub> (3.92 mmol) in ether. The red fraction eluted with toluene yields, after recrystallization in a THF/pentane (2/1) mixture, 420 mg (2.38 mmol, 61%) of red crystals of **13a**.

**Action of LiNEt<sub>2</sub> on **6b**.** Likewise 480 mg (0.98 mmol) of **6b** in 30 mL of THF were treated with a solution of LiNEt<sub>2</sub> (1.10 mmol) in ether. A yellow fraction is first eluted with toluene and, after recrystallization in a toluene/pentane (2/1) mixture, yields 32 mg (0.08 mmol, 8%) of yellow crystals of the known compound **12b**.

The presence of traces of **10b** has been established by the <sup>1</sup>H NMR spectrum of the remaining solution after isolation of **12b**: <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>)  $\delta$  0.94 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 2.76 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4 H), 3.95 (m, C<sub>5</sub>H<sub>4</sub>, 4 H), -13.3 (d, <sup>2</sup>J<sub>HP</sub> = 72 Hz, FeH, 1 H).

Then, a green fraction is eluted with toluene, giving after recrystallization in a THF/pentane (2/1) mixture 171 mg (0.30 mmol, 31%) of deep green crystals of **9b**: IR (KBr)  $\nu$ (CO) 1900,  $\nu$ (C=C) 1550 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  1.10 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 3.11 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4 H), 3.55, 3.98 (m, C<sub>5</sub>H<sub>4</sub>, 4 H), 7.38, 7.57 (m, C<sub>6</sub>H<sub>5</sub>, 15 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  71 (s). Anal. Calcd for C<sub>28</sub>H<sub>29</sub>BrFeNOP (*M<sub>r</sub>* 562): C, 59.79; H, 5.16; N, 2.49; P, 5.52. Found: C, 59.69; H, 5.15; N, 2.42; P, 5.29.

**Action of LiNEt<sub>2</sub> on **6c**.** The procedure is applied to 690 mg (1.28 mmol) of **6c** in 30 mL of THF and to a solution of LiNEt<sub>2</sub> (1.50 mmol) in ether. Elution with a pentane/ether (10/1) mixture leads to a yellow fraction which, concentrated and cooled at -30



Table V. Positional Parameters and Their Estimated Standard Deviations<sup>a</sup>

atom	x	y	z	B, Å <sup>2</sup>	atom	x	y	z
Br	0.44400 (4)	0.22941 (4)	-0.00367 (4)	4.52 (1)	H3	0.282 (4)	-0.121 (3)	-0.143 (4)
Fe	0.21431 (5)	0.09996 (5)	-0.07762 (5)	3.14 (1)	H4	0.001 (4)	-0.120 (4)	-0.112 (4)
P	0.1399 (1)	0.2660 (1)	-0.0517 (1)	3.60 (2)	H5	-0.043 (4)	-0.001 (4)	-0.253 (4)
O1	0.2436 (3)	0.0885 (3)	0.2037 (3)	5.56 (8)	H6	0.105 (4)	0.071 (3)	-0.363 (4)
O2	-0.0133 (2)	0.2294 (2)	-0.0643 (3)	4.38 (7)	H8	0.302 (4)	0.466 (3)	-0.082 (4)
O3	0.2150 (3)	0.3938 (3)	0.0903 (3)	5.13 (8)	H9	0.306 (4)	0.542 (3)	-0.255 (4)
N	0.3268 (3)	-0.0150 (3)	-0.3383 (3)	3.94 (8)	H10	0.134 (4)	0.464 (4)	-0.460 (4)
C1	0.2348 (4)	0.0973 (4)	0.0951 (4)	4.1 (1)	H11	-0.060 (4)	0.312 (4)	-0.505 (4)
C2	0.2334 (3)	-0.0253 (3)	-0.2831 (4)	3.44 (9)	H12	-0.047 (4)	0.223 (4)	-0.340 (4)
C3	0.2278 (4)	-0.0849 (3)	-0.1811 (4)	3.73 (9)	H131	0.470 (4)	-0.053 (3)	-0.192 (4)
C4	0.1033 (4)	-0.0867 (4)	-0.1670 (4)	4.1 (1)	H132	0.512 (4)	-0.016 (4)	-0.298 (4)
C5	0.0384 (4)	-0.0166 (4)	-0.2460 (4)	4.1 (1)	H141	0.474 (4)	-0.232 (4)	-0.376 (4)
C6	0.1210 (4)	0.0259 (4)	-0.3109 (4)	3.65 (9)	H142	0.338 (4)	-0.257 (4)	-0.379 (4)
C7	0.1318 (4)	0.3398 (3)	-0.1859 (4)	3.73 (9)	H143	0.388 (4)	-0.215 (4)	-0.492 (4)
C8	0.2411 (4)	0.4360 (4)	-0.1627 (5)	4.6 (1)	H151	0.224 (4)	0.021 (3)	-0.513 (4)
C9	0.2307 (5)	0.4838 (4)	-0.2697 (5)	6.2 (1)	H152	0.357 (4)	-0.000 (4)	0.518 (4)
C10	0.1289 (6)	0.4363 (5)	-0.4013 (5)	6.9 (1)	H161	0.358 (4)	0.209 (3)	-0.466 (4)
C11	0.0219 (5)	0.3402 (4)	-0.4273 (5)	6.1 (1)	H162	0.326 (4)	0.216 (4)	-0.336 (4)
C12	0.0223 (4)	0.2930 (4)	-0.3194 (5)	4.7 (1)	H163	0.469 (4)	0.193 (4)	-0.343 (4)
C13	0.4414 (4)	-0.0672 (4)	-0.2952 (4)	4.5 (1)	H171	-0.058 (4)	0.389 (4)	-0.082 (4)
C14	0.4055 (5)	-0.2061 (5)	-0.3862 (5)	5.9 (1)	H172	-0.055 (4)	0.366 (4)	0.043 (4)
C15	0.3134 (4)	0.0401 (4)	-0.4518 (4)	4.9 (1)	H181	-0.277 (4)	0.319 (4)	-0.094 (4)
C16	0.3701 (6)	0.1810 (5)	-0.3942 (5)	6.6 (1)	H182	-0.259 (4)	0.213 (4)	-0.228 (4)
C17	-0.0879 (4)	0.3229 (4)	-0.0464 (5)	5.5 (1)	H183	-0.255 (4)	0.189 (4)	-0.080 (4)
C18	-0.2328 (5)	0.2586 (5)	-0.1160 (6)	6.2 (1)	H191	0.352 (4)	0.350 (3)	0.230 (4)
C19	0.2085 (8)	0.3985 (7)	-0.2338 (6)	10.0 (2)	H192	0.238 (4)	0.374 (3)	0.288 (4)
C20	0.337 (1)	0.5083 (7)	0.3401 (8)	16.1 (3)				

<sup>a</sup> Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as  $(4/3)a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ac(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)$ .

<sup>o</sup>C, yields yellow crystals of **10c**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  0.84 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6H), 2.54 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4H), 4.07, 3.30 (m, C<sub>5</sub>H<sub>4</sub>, 4H), 7.02, 7.30 (m, C<sub>6</sub>H<sub>5</sub>, 15H), -13.2 (d, <sup>2</sup>J<sub>HP</sub> = 92 Hz, FeH, 1H); <sup>31</sup>P NMR (THF)  $\delta$  185 (d, <sup>2</sup>J<sub>HP</sub> = 92 Hz); MS (CI, NH<sub>3</sub>), *m/e* (relative intensity) 531 (M<sup>+</sup>; 86), 530 [(M - H)<sup>+</sup>; 100], 502 [(M - CO - H)<sup>+</sup>; 32], 311 [(P(OPh)<sub>3</sub> + H)<sup>+</sup>; 73], 138 [(C<sub>5</sub>H<sub>5</sub>NHET<sub>2</sub>)<sup>+</sup>; 54].

A second red fraction is eluted with ether and yields, after recrystallization in a THF/pentane (2/1) mixture, red crystals of **9c**: IR (KBr)  $\nu$ (CO) 1950, 1930,  $\nu$ (C=C) 1570 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.00 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6H), 2.95 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4H), 3.30, 3.75 (m, C<sub>5</sub>H<sub>4</sub>, 4H), 7.32 (m, C<sub>6</sub>H<sub>5</sub>, 15H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  171 (s); MS (CI, NH<sub>3</sub>), *m/e* (relative intensity) 311 [(P(OPh)<sub>3</sub> + H)<sup>+</sup>; 100], 138 [(C<sub>5</sub>H<sub>5</sub>NHET<sub>2</sub>)<sup>+</sup>; 47]. Anal. Calcd for C<sub>28</sub>H<sub>28</sub>BrFeNO<sub>3</sub>P (M<sub>r</sub> 610): C, 55.08; H, 4.75; N, 2.30; P, 5.08. Found: C, 54.71; H, 4.73; N, 2.26; P, 4.87.

The yields of **9c** and **10c** vary from 15 to 70% for **10c** and from 42 to 10% for **9c**, depending on the experiment.

**Action of LiNEt<sub>2</sub> on 6d.** The procedure is applied to 640 mg (1.5 mmol) of **6d** in 20 mL of THF and to a solution of LiNEt<sub>2</sub> (1.6 mmol) in ether. Elution with ether followed by recrystallization in a ether/pentane (1/2) mixture gives 660 mg (1.3 mmol, 88%) of red crystals of **9d**: IR (KBr)  $\nu$ (CO) 1920,  $\nu$ (C=C) 1570 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  0.85 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>CH<sub>3</sub>, 6H), 1.13, 1.30 (t, <sup>3</sup>J<sub>HJ</sub> = 7 Hz, OCH<sub>2</sub>CH<sub>3</sub>, 6H), 3.08 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>, 4H), 3.90 (m, C<sub>5</sub>H<sub>4</sub> and OCH<sub>2</sub>, 8H), 7.42, 7.82 (m, C<sub>6</sub>H<sub>5</sub>, 5H); <sup>31</sup>P{<sup>1</sup>H} NMR (CHCl<sub>3</sub>)  $\delta$  198 (s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  13.3 (s, NCH<sub>2</sub>CH<sub>3</sub>); 16.6 (d, <sup>3</sup>J<sub>CP</sub> = 6.6 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 46.3 (s, NCH<sub>2</sub>), 54.7 (d, <sup>3</sup>J<sub>CP</sub> = 7.3 Hz, OCH<sub>2</sub>CH<sub>3</sub>), 62.2 (d, <sup>2</sup>J<sub>CP</sub> = 5.9 Hz, OCH<sub>2</sub>), 63.65 (d, <sup>3</sup>J<sub>CP</sub> = 7.3 Hz, OCH<sub>2</sub>), 63.7, 72.5, 75.4 [s, C(Cp)], 128.1, 129.7 (d, <sup>1</sup>J<sub>CP</sub> = 9 and 12 Hz, C(Ph) ortho and meta), 130.4 (s, C(Ph) para), 141.1 (d, <sup>1</sup>J<sub>CP</sub> = 44 Hz, PC(Ph)), 142.8 (s, NC(Cp)); the off-resonance <sup>13</sup>C NMR spectrum agrees with these assignments; MS (CI, NH<sub>3</sub>), *m/e* (relative intensity) 500 and 498 (M + H)<sup>+</sup>, 499 and 497 (M<sup>+</sup>), 472 and 470 [(M + H - CO)<sup>+</sup>; 43 and 52], 471 and 469 [(M - CO)<sup>+</sup>; 37], 418 [(M - Br)<sup>+</sup>; 18], 390 [(M - CO - Br)<sup>+</sup>; 8], 273 and 271 [(M - CO - PhP(OEt)<sub>2</sub>)<sup>+</sup>; 55 and 60], 199 [(PhP(OEt)<sub>2</sub> + H)<sup>+</sup>; 100], 136 [(C<sub>5</sub>H<sub>5</sub>NEt<sub>2</sub>)<sup>+</sup>; 92], 137 [(C<sub>5</sub>H<sub>5</sub>NEt<sub>2</sub>)<sup>+</sup>; 69], 138 [(C<sub>5</sub>H<sub>5</sub>NHET<sub>2</sub>)<sup>+</sup>; 72]. Anal. Calcd for C<sub>20</sub>H<sub>29</sub>BrFeNO<sub>3</sub>P (M<sub>r</sub> 498): C, 48.20; H, 5.82; N, 2.81; P, 6.22. Found: C, 49.00; H, 5.95; N, 2.83; P, 6.10.

**Action of LiNEt<sub>2</sub> on 6e.** The procedure is applied to 1.04 g (2.61 mmol) of **6e** in 50 mL of THF and to a solution of LiNEt<sub>2</sub> (3.00 mmol) in ether. The first orange fraction eluted with toluene

yields 310 mg (0.78 mmol, 30%) of **10e** as an orange oil: IR (KBr film)  $\nu$ (CO) 1890,  $\nu$ (C=C) 1535 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  1.07 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6H), 2.98 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4H), 4.10 (m, OCH<sub>3</sub> and C<sub>5</sub>H<sub>4</sub>, 10H), 7.20, 8.10 (m, C<sub>6</sub>H<sub>5</sub>, 5H), -19.4 (d, <sup>2</sup>J<sub>HP</sub> = 41 Hz, FeH, 1H); <sup>31</sup>P NMR (THF)  $\delta$  169 (d).

The fraction subsequently eluted with a toluene/ether (2/1) mixture yields, after recrystallization in an ether/pentane (1/2) mixture, 340 mg (0.73 mmol, 28%) of red crystals of **9e**: IR (KBr)  $\nu$ (CO) 1915-1935,  $\nu$ (C=C) 1550-1570 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.08 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6H), 3.10 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>, 4H), 3.68 (m, OCH<sub>3</sub> and C<sub>5</sub>H<sub>4</sub>, 10H), 7.45-7.84 (m, C<sub>6</sub>H<sub>5</sub>, 5H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  204 (s). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>BrFeNO<sub>3</sub>P (M<sub>r</sub> 470): C, 45.96; H, 5.32; N, 2.98; P, 6.60. Found: C, 45.80; H, 5.33; N, 2.96; P, 6.56.

**Action of LiNEt<sub>2</sub> on 6f.** The procedure is applied to 550 mg (1.39 mmol) of **6f** in 40 mL of THF and to a solution of LiNEt<sub>2</sub> (1.45 mmol) in ether. The IR and <sup>1</sup>H NMR spectra of the first brown fraction eluted with toluene show the presence of **10f**: IR (KBr film)  $\nu$ (CO) 1920,  $\nu$ (C=C) 1530 cm<sup>-1</sup>; <sup>1</sup>H NMR (toluene-d<sub>8</sub>)  $\delta$  0.90-1.50 (m, NCH<sub>2</sub>CH<sub>3</sub> and OCH<sub>2</sub>CH<sub>3</sub>, 15H), 2.80 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>, 4H), 3.80, 4.30 (m, OCH<sub>2</sub> and C<sub>5</sub>H<sub>4</sub>, 10H), -13.3 (d, <sup>2</sup>J<sub>HP</sub> = 89 Hz, FeH, 1H). The IR spectrum (KBr film) of an another brown fraction eluted with a toluene/ether (1/1) mixture presumes presence of both **9f** and **13f**:  $\nu$ (CO) 1940, 1720,  $\nu$ (C=C) 1560 cm<sup>-1</sup>.

**Action of LiNEt<sub>2</sub> on 6d'.** The procedure is applied to 510 mg (1.50 mmol) of **6d'** in 40 mL of THF and to a solution of LiNEt<sub>2</sub> (1.75 mmol) in ether. The green fraction eluted with toluene yields **13d** as a green powder that decomposes rapidly at room temperature: IR (KBr)  $\nu$ (CO) 1700 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.40 (d, <sup>3</sup>J<sub>HP</sub> 1 Hz, C<sub>5</sub>H<sub>5</sub>).

A second fraction, eluted with a toluene/ether (1/1) mixture, leads to a red oil which, by recrystallization from pentane at -30 °C, yields 88 mg (0.22 mmol, 15%) of red crystals of **9d'**: IR (KBr)  $\nu$ (CO) 1920,  $\nu$ (C=C) 1575 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.08 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>CH<sub>3</sub>, 6H), 1.32 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, OCH<sub>2</sub>CH<sub>3</sub>, 6H), 3.10 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>, 4H), 3.70, 4.10 (m, OCH<sub>2</sub> and C<sub>5</sub>H<sub>4</sub>, 8H), 7.43-7.84 (m, C<sub>6</sub>H<sub>5</sub>, 5H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF)  $\delta$  198 (s).

**Action of LiNEt<sub>2</sub> on 6g.** The procedure is applied to 400 mg (0.67 mmol) of **6g** in 40 mL of THF and to a solution of LiNEt<sub>2</sub> (0.75 mmol) in ether. The fraction eluted with toluene yields 290 mg of **10g** (0.497 mmol, 74%) as a yellow oil: IR (KBr film)  $\nu$ (C=C) 1515 cm<sup>-1</sup>; <sup>1</sup>H NMR (toluene-d<sub>8</sub>)  $\delta$  1.11 (m, NCH<sub>2</sub>CH<sub>3</sub> and OCH<sub>2</sub>CH<sub>3</sub>, 18H); 2.75 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, NCH<sub>2</sub>, 4H), 3.77 (m,



OCH<sub>2</sub>, 8 H), 3.21, 4.18 (m, C<sub>5</sub>H<sub>4</sub>, 4 H), 7.23, 7.79 (m, C<sub>6</sub>H<sub>5</sub>, 10 H), -13.5 (t, <sup>2</sup>J<sub>HP</sub> = 75.2 Hz, FeH, 1 H); <sup>31</sup>P NMR (THF) δ 210 (d).

**Action of LiNEt<sub>2</sub> on 6h.** The procedure is applied to **6h** and to a solution of LiNEt<sub>2</sub>. No product could be eluted from the silica column whatever solvent was used; other attempts of isolation have failed.

**Action of LiNMe<sub>2</sub> on 6d.** The procedure is applied to 240 mg (0.56 mmol) of **6d** in 40 mL of THF and to a solution of LiNMe<sub>2</sub>, (0.63 mmol) in ether. The first fraction eluted with toluene yields in fairly quantities **12d''** as a yellow oil: IR (KBr film) ν(CO) 1940 cm<sup>-1</sup>; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 1.11 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 3.80 (m, CH<sub>2</sub>, 4 H), 4.24 (s, C<sub>5</sub>H<sub>5</sub>, 5 H), 7.18, 7.84 (m, C<sub>6</sub>H<sub>5</sub>, 5 H), -13.15 (d, <sup>2</sup>J<sub>HP</sub> = 82 Hz, FeH, 1 H).

The second fraction eluted with a toluene/ether (10/1) mixture yields after recrystallization in an ether/pentane (2/1) mixture 190 mg (0.40 mmol, 72%) of **9d''** as red crystals: IR (KBr) ν(CO) 1925, ν(C=C) 1570 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.31 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>3</sub>, 6 H), 2.76 (s, NCH<sub>3</sub>, 6 H), 3.92 (m, OCH<sub>2</sub> and C<sub>5</sub>H<sub>4</sub>, 8 H), 7.47, 7.87 (m, C<sub>6</sub>H<sub>5</sub>, 5 H); <sup>31</sup>P{<sup>1</sup>H} NMR (THF) δ 198 (s). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>BrFeNO<sub>3</sub>P (*M*<sub>r</sub> 470): C, 45.96; H, 5.32; N, 2.98; P, 6.60. Found: C, 46.68; H, 5.36; N, 2.98; P, 6.87.

**Action of LiNHR on 6d.** The procedure is applied to **6d** and to a solution of LiNHR (R = *t*-Bu, CH<sub>2</sub>Ph). No aminated product is characterized. Only one fraction is eluted by chromatography with toluene, which consists of **13d** (an unstable green solid) that forms quasi-quantitatively.

**Action of LiNH-*t*-Bu on 6g.** The procedure is applied to **6g** and to a solution of LiNH-*t*-Bu in ether. The IR and <sup>1</sup>H NMR spectra of the only fraction eluted with a CH<sub>2</sub>Cl<sub>2</sub>/acetone mixture indicate the absence of aminated products; no compounds could be characterized or isolated.

**X-ray Study of 9d. Space Group Determination and Data Collection.** Crystals suitable for X-ray work were obtained by slow crystallization at -30 °C in a 2/1 pentane/ether mixture. Crystals of Fe[C<sub>5</sub>H<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>](CO)[P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>][Br] (**9d**) are red, air-stable parallelepipeds. A summary of crystal data and intensity collection, on an Enraf-Nonius CAD-4 automatic diffractometer, with the monocrystal used, is given in Table III. The unit cell parameters were refined by using the angular settings of 25 reflections measured on the diffractometer. Owing to the size of the crystal and to the value of the linear absorption coefficient, no absorption corrections were applied. The program package for the calculations was Enraf-Nonius SPD.<sup>29</sup>

(29) Frenz, B. A. In *The Enraf-Nonius CAD-4 SDP, a Real Time for Concurrent X-ray Data Collection and Crystal Structure Determination*; Schenk, H., Olthof-Hazekamp, R., Van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1978.

**Solution and Refinement of the Structure.** Atomic positions for the heavy atoms and many of the other non-hydrogen atoms were obtained from the MULTAN program. Subsequent difference Fourier synthesis allowed the location of the remaining non-hydrogen atoms.

Least-squares refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of the 27 non-hydrogen atoms of the molecule, constitute the asymmetric unit, led to values of  $R = [\sum(F_o - F_c)/\sum F_o]$  of 0.047 and  $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$  of 0.057.

At this stage, 26 hydrogen atoms were introduced in the refinement (owing to the large value of the equivalent isotropic thermal parameter of the terminal carbon atom of one OC<sub>2</sub>H<sub>5</sub> group, i.e. C20, the three hydrogen atoms bonded to C20 were not introduced). Most of these H atoms were located on a difference Fourier synthesis. Two last cycles of refinement of coordinates and anisotropic thermal parameters of the 27 non-hydrogen atoms and of coordinates of the 26 hydrogen atoms (with isotropic thermal parameters fixed at 5 Å<sup>2</sup>) led to final values of  $R = 0.041$  and  $R_w = 0.045$ .

Final atomic parameters are given in Table V. The labeling scheme is shown in Figure 1, which gives an ORTEP view of the molecule. Selected bond distances and bond angles are given in Table IV.

**Registry No.** **6a**, 12078-20-5; **6a'**, 12107-04-9; **6b**, 12099-12-6; **6c**, 32993-40-1; **6d**, 104627-13-6; **6d'**, 107474-24-8; **6e**, 89199-72-4; **6f**, 107474-22-6; **6g**, 107474-23-7; **6h**, 32843-50-8; **9a**, 107494-86-0; **9b**, 107474-25-9; **9c**, 107474-26-0; **9d**, 104627-12-5; **9d'**, 107474-28-2; **9d''**, 107474-29-3; **9e**, 107513-91-7; **9f**, 107474-27-1; **10b**, 107474-30-6; **10c**, 107474-31-7; **10e**, 107474-32-8; **10f**, 107474-33-9; **10g**, 107474-34-0; **11**, 107474-35-1; **12b**, 32660-22-3; **12d''**, 107474-36-2; **13**, 12154-95-9; LiNEt<sub>2</sub>, 816-43-3; LiNMe<sub>2</sub>, 3585-33-9; LiNH-*t*-Bu, 37828-54-9; LiNHCH<sub>2</sub>Ph, 38225-27-3.

**Supplementary Material Available:** Tables of all bond distances, bond angles, and least-squares planes (3 pages), a listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

(30) <sup>1</sup>H NMR is the only spectroscopy that would allow the localization of the initial site of attack. However, NMR monitoring of the reaction could not be conclusively run due to the demanding experimental conditions.

(31) Colomer, E.; Corriu, R. J. P.; Vioux, A. *J. Organomet. Chem.* **1984**, 267, 107.