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2011

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UNIVERSITY OF CALIFORNIA  
RIVERSIDE

New Routes to Phosphametallocene Derivatives

A Dissertation submitted in partial satisfaction  
of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

Aholibama J. Escobar

December 2011

Dissertation Committee:

Dr. Francois Mathey, Co-Chairperson  
Dr. Guy Bertrand, Co-Chairperson  
Dr. Michael Marsella

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2011

The Dissertation of Aholibama J. Escobar is approved:

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Committee Co-Chairperson

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Committee Co-Chairperson

University of California, Riverside

## Acknowledgements

I would first and foremost like to thank Dr. Francois Mathey for allowing me to work in his research group. His advice on the subjects of chemistry and life in general has been and will continue to be greatly appreciated. I would like to express a great deal of gratitude to Dr. Guy Bertrand for opening his research lab to me during the last year of my graduate studies and giving me the opportunity to be a part of his group.

I've had the great opportunity to work along side two different research groups while in graduate school. Both groups have been filled with outstanding amounts knowledge and I am truly grateful for all the advise and memories. The Mathey group members deserve special appreciation for putting up with me and my mess the longest. I need to especially thank Matt Duffy for making the lab a fun place to be around, even when it meant making phosphole until 2 in the morning; Evelyn Duffy for being the coolest adopted member of the group; Duanghathai Panichakul for showing me how much Thailand rocks and being the best room-mate/lab-mate combination ever; Magali Clochard for helping the transition to the Mathey lab go smoothly; and Dr. R. Tian for his help on the phosphaferrocene/azacymantrene project.

I also would like to convey my appreciation of the Bertrand group members. I am grateful to my officemates, Gregorio and Jean, for their useful chemistry suggestions and for bringing my baking skills to a whole new level. I need to thank Amos and David W. for providing an escape from NPR with

baseball games, classic rock, and mariachi music. Big thanks to Oliver and Martin, for breaking the silence with an occasional scream down the hall; Daniel, David R., Rei Kinjo and Gael for their generosity in sharing their compounds and knowledge. I am thankful to have worked with the CNRS gang; Michelle for working through the Garden experience with me and understanding what it's like to have two full time jobs; Mo and David M. for being test subjects to my baking adventures while not living on the roto vap and for their insight on phosphorus chemistry; and Bruno for his optimism in trying out any crystal. Last, but certainly not least, I would like to thank Alan DeHope and Aden for making everyday a wonderful adventure.

The text, tables, schemes, and figures of the following chapters, in part or in their entirety, are reproduced from the following published and accepted manuscripts.

- Chapter 1: **From Functional Phospholide Ions to Bifunctional 1,1' - Diphosphaferrocenes**  
Aholibama Escobar, Bruno Donnadieu; Francois Mathey. *Organometallics* **2008**, 27 (8) 1887-1891.
- Chapter 2: **Synthesis of 2,5-Difunctional Phosphaferrocenes**  
Aholibama Escobar and Francois Mathey.  
*Organometallics* **2010**, 29 (4) 1053-1056.
- Chapter 3: **A New P,N-Chelating Ligand Combining Phosphaferrocene and Azacymantrene Units**  
Rongqiang Tian, Aholibama Escobar, Francois Mathey.  
*Organometallics*, **2011**, 30(6) 1738-1740.

## ABSTRACT OF THE DISSERTATION

### New Routes to Phosphametallocene Derivatives

by

Aholibama J. Escobar

Doctor of Philosophy, Graduate Program in Chemistry

University of California, Riverside, December 2011

Dr. Francois Mathey, Co-Chairperson

Dr. Guy Bertrand, Co-Chairperson

While the syntheses of phosphaferrocene and diphosphaferrocene have been known for several decades, derivatization of these molecules has been limited. Prior to our work, functionalization of the phosphametallocenes has been through two routes: electrophilic aromatic substitution (EAS) and functionalization of phospholide ions that are later coordinated to an iron source. The most common method, EAS, is limited to alpha carbon substitution and only with acetyl or benzoyl groups.

A small number of 2,5-silyl substituted phosphametallocenes have been reported in literature, via coordination of substituted phospholide ions with Cp\*FeCl or FeCl<sub>2</sub>. However, the 2,5-silyl substituted phosphaferrocene and diphosphaferrocene have not been found to be useful precursors of phosphametallocene macrocycles.

Our group has explored other routes for making substituted phosphaferrocene molecules and this work is presented hereafter. Using

phospholide ions that are carbonyl substituted at the alpha position to react with iron (II) chloride in the presence of zinc chloride, we were able to prepare the corresponding 2,2'-difunctional-1,1' diphosphaferrocenes as mixtures of *meso* and *rac* diastereomers. When the 2,5-bis(ethoxycarbonyl)phospholide was reacted under the same conditions however the product was found to be the tetrafunctional 1,1'-biphospholyl which lead us to believe that the reaction is occurring through a bis( $\eta^1$ -phospholyl) iron intermediate.

We were successful at synthesizing 2,5-bis(ethoxycarbonyl)phosphaferrocene, 2,5-dibenzoylphosphaferrocene, and the 2,2',5,5'-tetrapivaloyl-1,1'-diphosphaferrocene by reacting iron (II) chloride with a 1:1 mixture of Cp<sup>\*</sup>Li and the corresponding 2,5 substituted phospholide ion in the presence of zinc chloride. We attributed the stability of the 2,5-substituted phosphametallocenes to a push-pull type stabilization, where the Cp<sup>\*</sup> unit acts as an electron donor to the metal center and the phospholide plays the role of an electron acceptor.

Our new protocol for making phosphaferrocene derivatives was used in the synthesis of a new 2-(azacymanthrenylmethyl)phosphaferrocene ligand, and in the preparation of building blocks for phosphametallocene macrocycles 2,5-bis(hydroxymethyl)phosphaferrocene and 2,5-bis(pyrrolylmethyl)phosphaferrocene.

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The generic term “phosphametallocene” can be used to describe 3 general structures as illustrated in figure 0.1. The first structure (**1**) is a half sandwich complex; the second (**2**) is a metal bound by a  $\eta^5$ -phospholyl and  $\eta^5$ -cyclopentadienyl (Cp) such as in complex 2; and the third (**3**), where a metal is surrounded by two  $\eta^5$ -phospholyl metal complexes.<sup>1</sup> The work presented in this thesis will primarily focus on the iron and manganese derivatives of these types of phosphametallocenes.

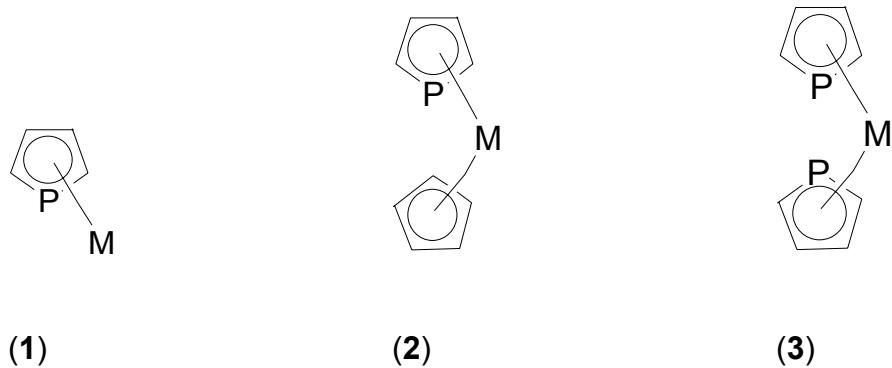
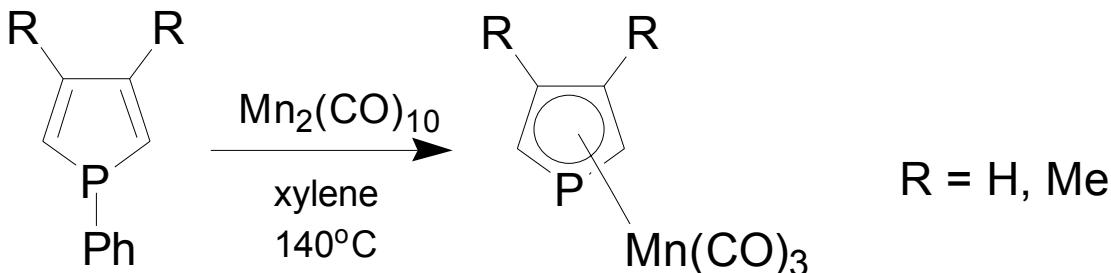


Figure 0.1: General structures of phosphametallocenes

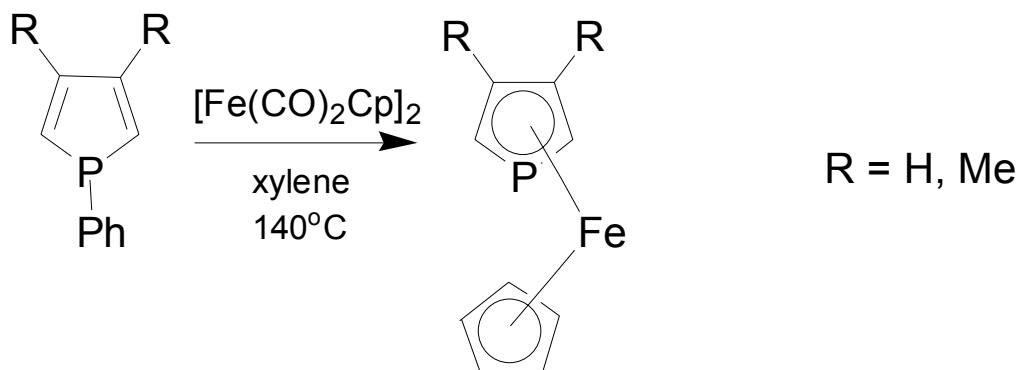
#### History of Phosphametallocenes:

The first successful reported exploration of reactions between phospholes and metal complexes to make phosphametallocenes was<sup>2</sup> by the group of Mathey. The phosphorous analog of cymantrene, phosphacymantrene, was synthesized in 1976 by the coordination of a substituted phosphole with dimanganese decacarbonyl (scheme 0.1).

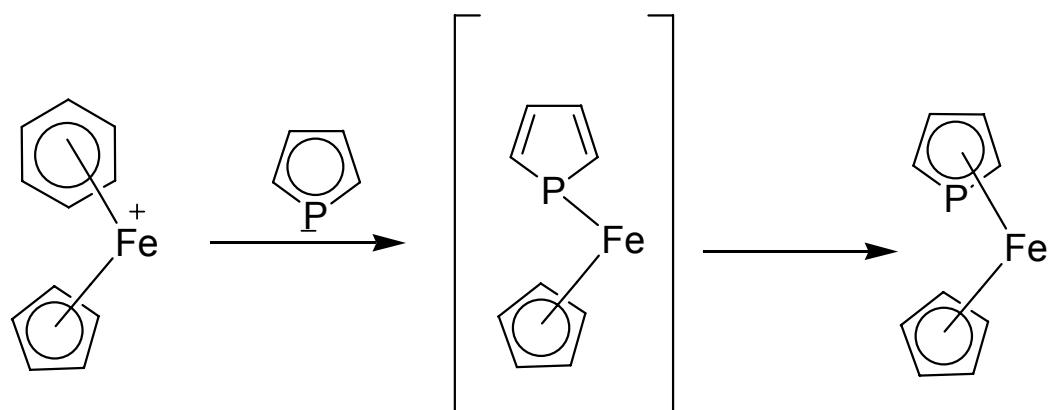


Scheme 0.1: Synthesis of phosphacymantrene

During the same period of time the Mathey group extended the synthetic phosphacymantrene route utilizing cyclopentadienyliron dicarbonyl dimer as a metal source to make the first phosphaferrocene<sup>3,4</sup> (scheme 0.2). Although the one pot synthesis is straightforward, its disadvantages include low yields and the formation of side products requiring purification. The synthesis was improved upon by Roberts and Wells in 1986.<sup>5</sup> Roberts and Wells used a method that incorporated the use of an  $\eta^6$ -arene- $\eta^5$ -cyclopentadienyliron (II) cation that would release the weakly coordinated  $\eta^6$ -arene when subjected to nucleophilic attack by a phospholide ion, as illustrated in scheme 0.3. This not only improved the yield of the desired product but is also currently the only known route to form phosphaferrocenes with a substituted Cp ring coordinated to the iron center.

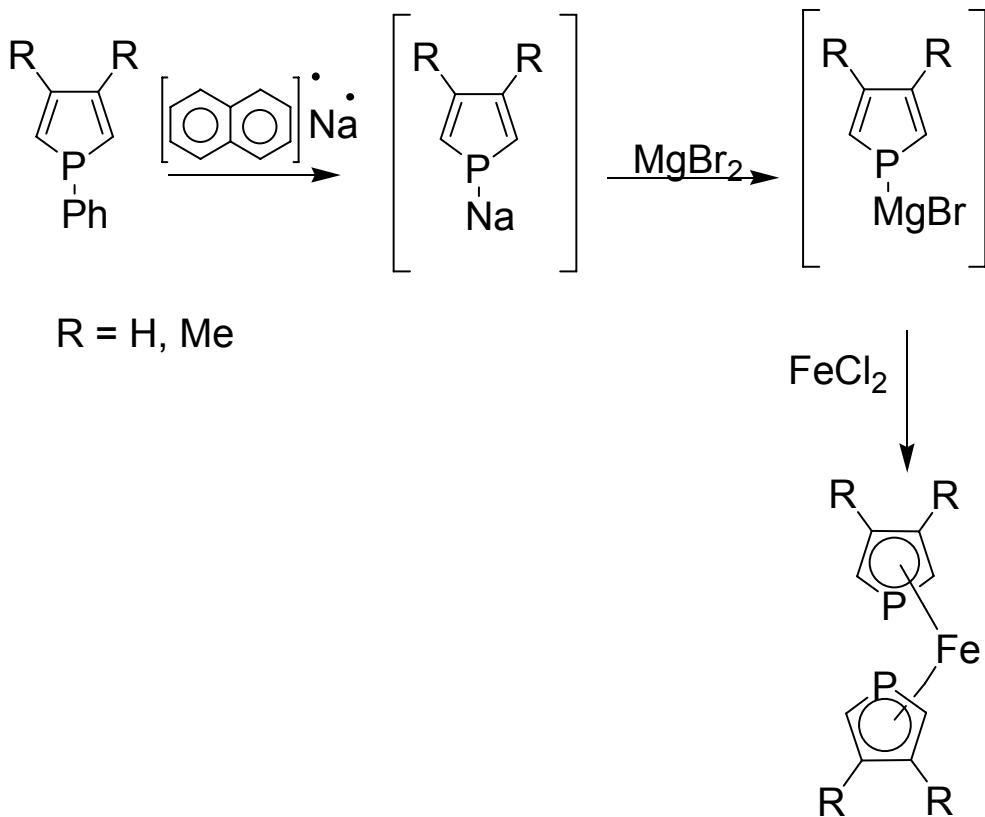


Scheme 0.2: Synthesis of phosphaferrocene



Scheme 0.3: Synthesis of phosphaferrocene using  $\eta^6$ -arene -  $\eta^5$ -cyclopentadienyliron(II)

The last of the phosphametallocene series, diphosphaferrocene, was discovered by Mathey et al in 1980.<sup>6</sup> The synthesis of diphosphaferrocene relies on the formation of a phospholide ion from a substituted phosphole. Once formed, the phospholide can then react with iron (II) chloride to form the product (scheme 0.4).



Scheme 0.4: Synthesis of diphosphapherrocene

The biggest obstacle of this type of reaction is the formation of the phospholide ion. The one electron transfer of the alkali metal to the phosphorous phenyl bond releases a phenyl radical that can react with the formed phosphapherrocene. The addition of a Lewis acid, such as AlCl<sub>3</sub>, has been shown to improve the synthesis.

### Chemistry of phosphametallocenes

The lone pair of the phosphorous atom in phosphacyclopentadienes does not act as a nucleophile as demonstrated by the inability of phosphacyclopentadiene to

react with I<sub>2</sub> or with benzyl bromide even using aggressive conditions.<sup>7</sup>

Phosphaferrocene and diphosphaferrocene contain a lone pair that is sufficiently donating to form P-metal bonds as well as react with benzyl bromide under moderate conditions.<sup>8</sup> Recent examples of phosphaferrocene and diphosphaferrocene metal complexes are illustrated in figures 0.2<sup>9</sup> and figure 0.3<sup>10</sup> respectively.

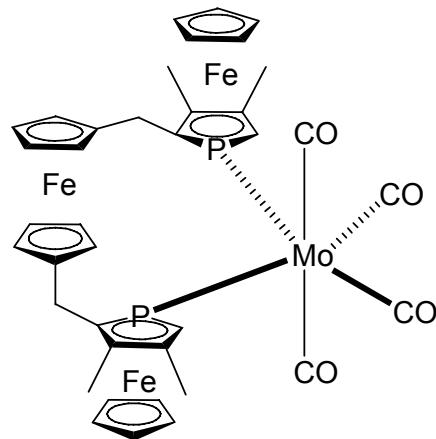


Figure 0.2: Molybdenum complex of phosphaferrocene

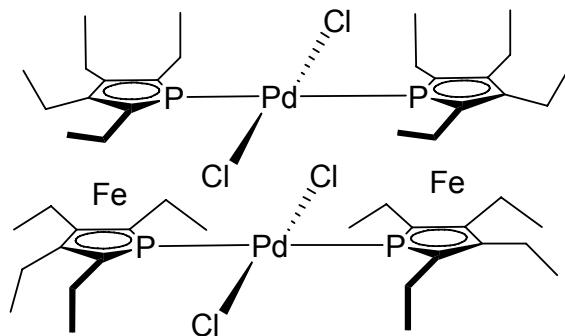
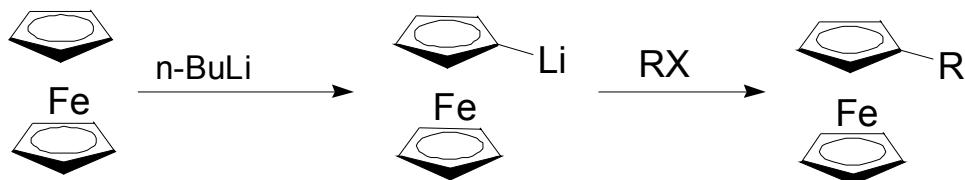
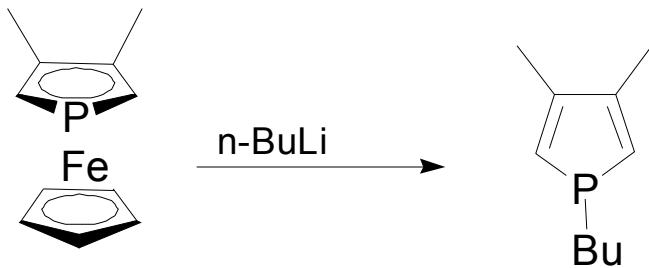


Figure 0.3: Platinum complex of diphosphaferrocene

In addition to the slight nucleophilicity of the phosphorous atom in phosphaferrocene and diphosphaferrocene, these complexes as well as the phosphacymantrene also behave as electrophiles. The high reactivity of the phosphorus atom towards nucleophiles makes functionalizing phosphaferrocenes more complicated than its organic ferrocene analogue. For example, the reaction of ferrocene with one equivalent of n-butyllithium gives the lithiation at one carbon on the cyclopentadiene ring that can react as a nucleophile (figure 0.5) whereas the same reaction conditions with 3,4-dimethylphosphaferrocene yields 1-butyl-3,4-dimethylphosphole (figure 0.6).<sup>11</sup>

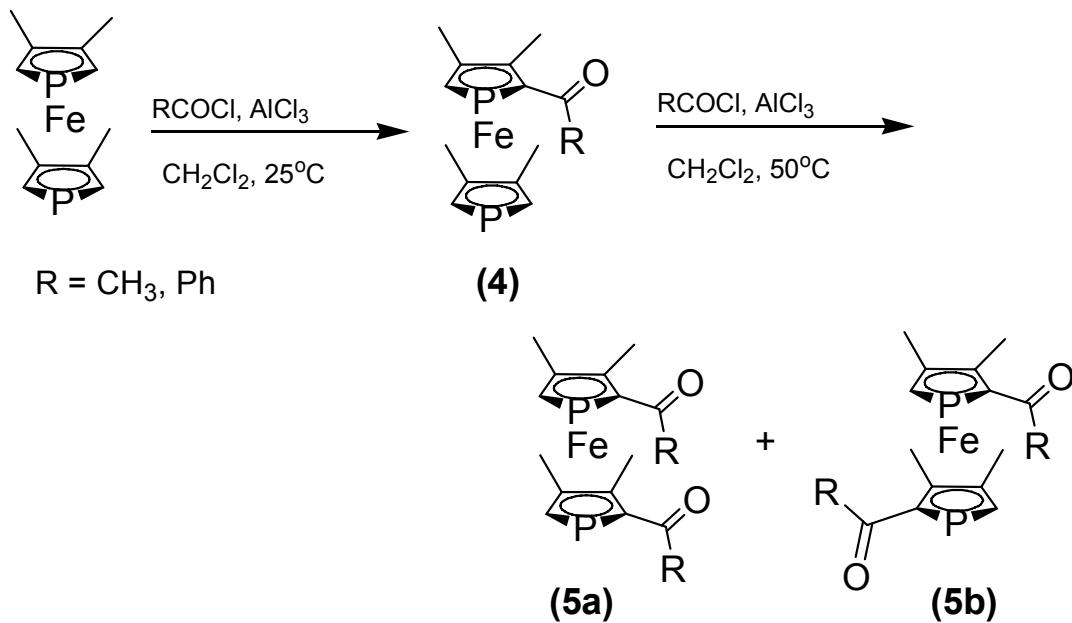


Scheme 0.5: Substitution reaction of ferrocene using n-BuLi and an organohalogen

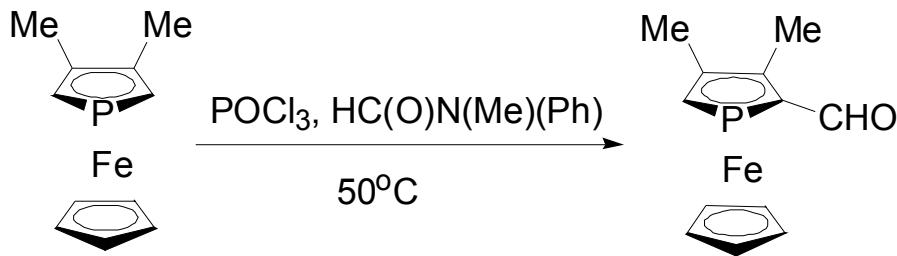


Scheme 0.6: Reaction of phosphaferrocene with n-BuLi to form a substituted phosphole

The low reactivity of phosphorus towards electrophiles, allows for substitution reactions on the phospholyl ring through the use of electrophilic aromatic substitution. In fact, the most common path to obtaining functionalized phosphametallocenes is through Friedel-Crafts acetylation of a non-functionalized phosphametallocenes. For example, diphosphaferrrocene can be substituted at the alpha carbon of one phosphole ring to give compound **4** (scheme 0.7).<sup>8</sup> A second equivalent of reagents does not substitute at the 5 position of the ring, but instead substitution at the alpha carbon of the second phosphole ring produces two stereoisomers of the 2,2' bifunctional-1,1' diphosphaferrrocenes (meso isomer **5a** and rac isomer **5b**). This type of bifunctional substitution so far is limited to acetyl<sup>6</sup> and benzoyl<sup>12</sup> groups to date.



Scheme 0.7: Electrophilic aromatic substitution of diphosphaferrrocene

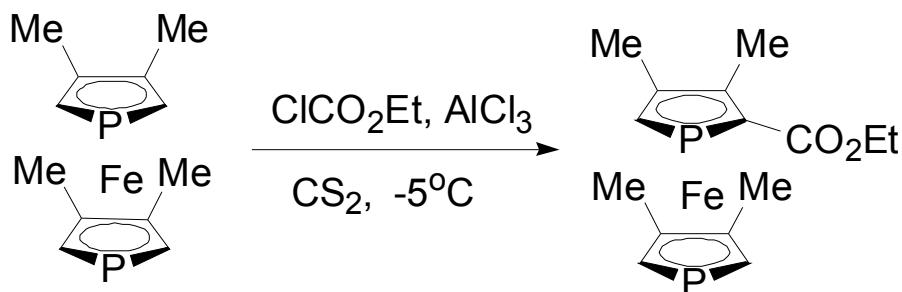


Scheme 0.8: Vilsmeier reactions of phosphapherrocene

The formyl derivatives of phosphapherrocene can also be easily prepared by classical Vilsmeier reaction conditions illustrated in scheme 0.8.

Phosphacymantrenes containing three CO ligands on the manganese metal will not react with such conditions to give the formyl substituted phosphacymantine. The reactivity of the ring must be enhanced by exchanging one of the carbon monoxides ligands of the metal with a sigma donating ligand, such as triphenylphosphine.<sup>13</sup>

The carboxylation of diphosphapherrocene can also be carried out using alkyl chloroformates and aluminum chloride under typical conditions (scheme 0.9)<sup>14</sup>.



Scheme 0.9: Carboxylation of diphosphapherrocene

The use of phosphametallocenes in asymmetric catalysis was initiated by the groups of Fu<sup>15</sup> and Ganter<sup>16</sup> in the late 1990's. The group of Fu first reported the catalytic nature of compound **6** in the ring opening reaction of epoxides with TMSCl in 1997.

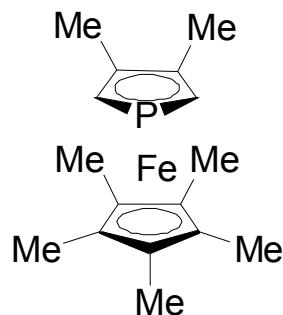
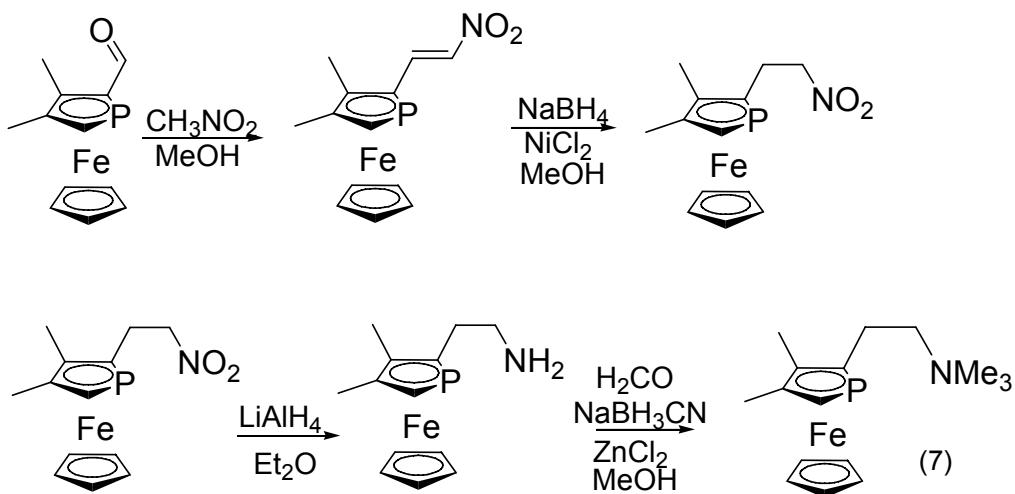


Figure 0.4: Heptamethylphosphaphrocene **6**

Ganter first reported the synthesis and use of bidentate chelating phosphaphrocene ligands in catalysis around the same time. The substituted ligand **7** was prepared by manipulation of the 3,4-dimethylphosphaphrocene as illustrated in scheme 0.10.



Scheme 0.10: Synthesis of bidentate phosphaphrocene **7**

Taking this type of synthesis one step further, substitution at the 2 and 5 position of the phospholyl ring, would allow formation of macrocycles and polymers that would incorporate the phospholyl ring of the phosphametallocenes. While much is known about heteroatom substituted macrocycles containing oxygen, sulfur, or nitrogen, the phosphorous substituted macrocycles have in the past been much more elusive in literature. Macrocycles containing a phosphorous atom have the advantage of having an atom with sigma donating and whose pi accepting ability could potentially be tuned while O, S, or N derivatives only exhibit sigma donor properties. In 1988 the group of Mathey synthesized a series of dicoordinate phosphinine ring-based macrocycles with strong pi-aromaticity properties that formed stable complexes with low-valent transition-metals, an example is illustrated in figure 0.5.<sup>17</sup>

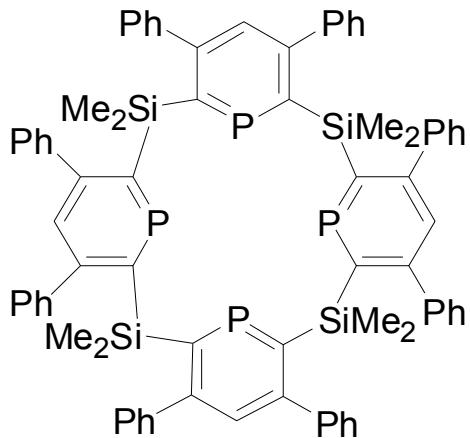
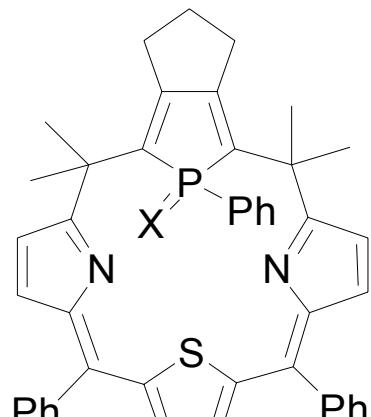


Figure 0.5: Dicoordinate phosphinine ring-based macrocycle



$X = S$  or lone pair

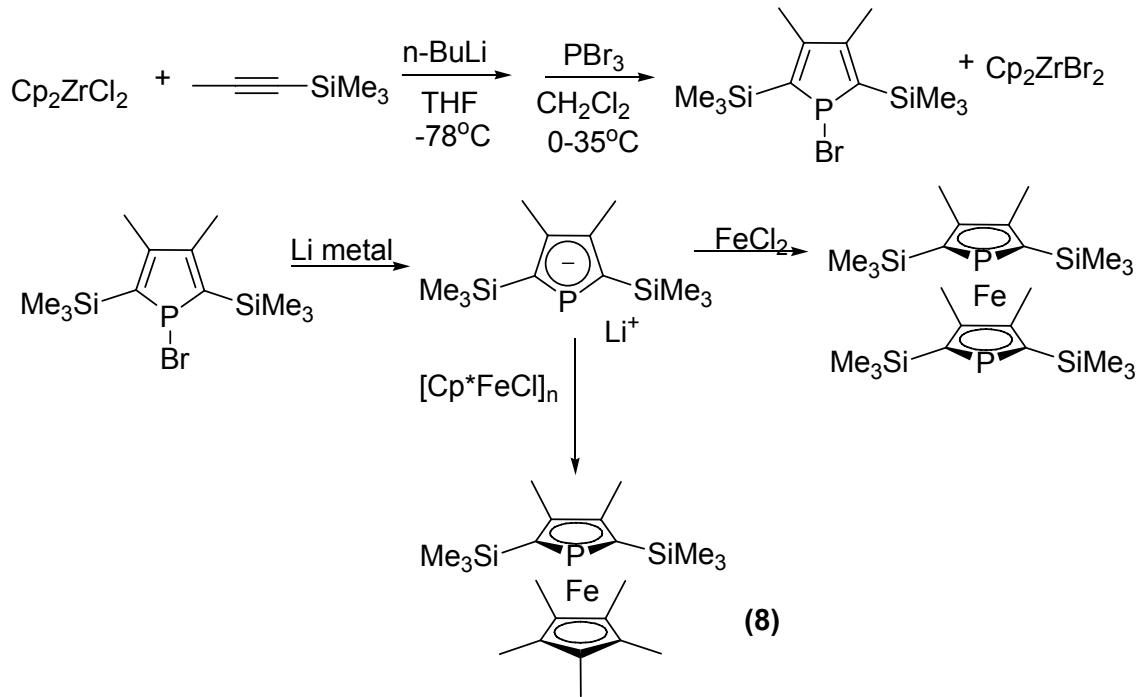
Figure 0.6: Phosphole substituted calixphyrin

More recently the group of Matano reported the only known modified porphyrin that replaced one of the pyrroles by a phosphole to form a calixphyrin molecule (figure 0.6).<sup>18</sup> Modifying the porphyrin structure further by replacing pyrroles by phosphaferrocene seems to be the next logical step in the sequence. With the incorporation of phosphaferrocene the structure is improved for many reasons. The poorly aromatic phosphole ring would be replaced by a highly aromatic five membered ring; the electron donating heteroatom would become a sp<sup>2</sup>-hybridized P with significant pi-acceptor ability; the tricoordinated phosphorus atom in the phosphole would also be replaced with dicoordinate phosphorus. Besides the benefits of exchanging the heteroatom the Cp\* group has the potential of adding steric protection to the molecule that would be useful in differentiating between the two sides of the resulting macrocycles.

The limitations of using electrophilic aromatic substitution conditions to make a 2,5 substituted phosphaferrocene have been previously mentioned. The substitution is allowed in the 2-position of the phospholyl ring but even under aggressive conditions, the desired disubstituted product is unattainable.

Previous to 2010, the only known 2,5-disubstituted phosphaferrocenes were a small number of 2,5 -silyl-substitued derivatives (scheme 0.11).<sup>19,20</sup> The 2,5-silyl-substitued phosphaferrocenes and diphosphaferrocenes are produced through the zirconocene-mediated coupling of two equivalents of silyl substituted alkynes. The resulting zirconacyclopentadiene can be converted into the corresponding bromophosphole by treatment with PBr<sub>3</sub>. The phospholide anion

is formed through the reduction of bromophosphole by elemental lithium. Once formed, the substituted phospholide anion can react with  $\text{Cp}^*\text{FeCl}$  to form the silyl-substituted phosphaferrocene **8**, or  $\text{FeCl}_2$  to give the corresponding substituted diphosphaferrocene.



Scheme 0.11: Synthesis of 2,5-disiyl-substituted phosphaferrocene **8**

Incorporating substitutions in the 2 and 5 position of the phosphole ring is limited by the functional groups and their reactivities. The substituents must be suitable to build upon while not reacting with other reagents in preceding synthetic steps. For example, formyl or acyl groups would be interesting handles to build upon but the groups would not be suitable for the reaction conditions of the trimethylsilyl derivatives.

An alternative approach would be to use substituted phospholide ions to react with some source of iron such as  $(CpFeCl)_n$  to make the corresponding phosphaferrocene or  $FeCl_2$  to form the diphosphaferrocene. The synthesis of functional phospholide ions based on the chemistry of parent  $1H$ - phosphole (**9**) and its tautomer  $2H$ -phosphole (**10**) has been well established by the Mathey group (Figure 0.7)<sup>21a,b</sup>.

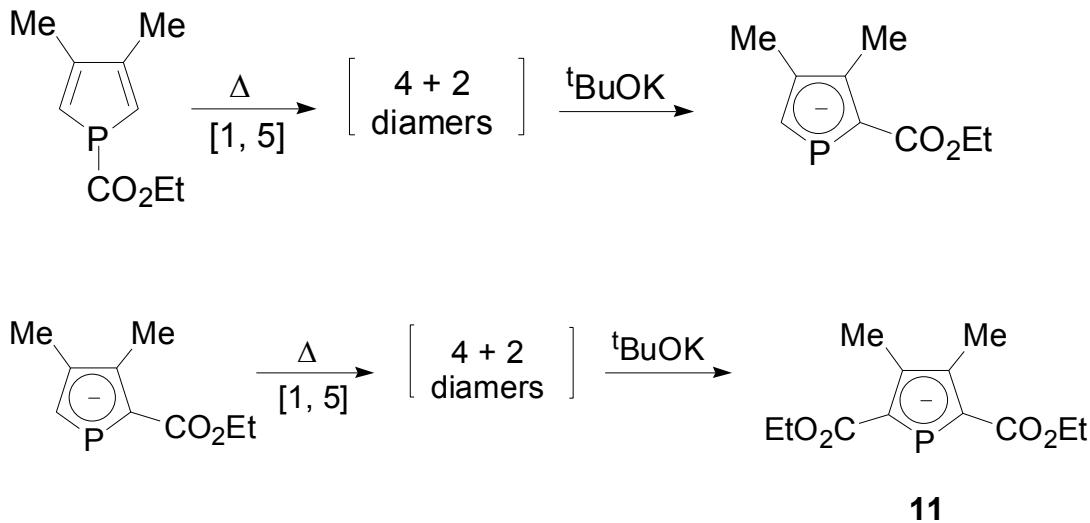


Figure 0.7: Parent  $1H$  phosphole **9** and tautomer  $2H$ -phosphole **10**

The [1,5] shift of the functional group from P to  $C\alpha$  in the  $2H$ -phosphole is the simplest known method to functionalize an preexisting phosphole, but is heavily dependent on migration ability of the substituent as well as compatibility with the base used to deprotonate the phosphole. Alkyl and alkoxy groups for example have been found to lack the ability to migrate. Substituents such as  $CO_2Et$ ,  $C(O)R$ , and  $SiR_3$  are reactive enough to form  $[4 + 2]$  diamers at room temperature. Upon the addition of potassium tert-butoxide, the result is a phospholide ion that is substituted at the alpha carbon position. Other groups such as phenyl, 2-(diphenylphosphino)-phenyl, 2-pyridyl, N-methyl-2-pyrrolyl, and

1,2,3,4-tetramethyl-cyclopentadienyl, require heating the phosphole in the presence of potassium tert-butoxide before the migration of the group takes place.

A great benefit to this type of reaction is the potential for a second substitution taking place at the 5 position of the phosphole<sup>21a</sup> as illustrated for CO<sub>2</sub>Eт (11) in scheme 0.12.



Scheme 0.12: Synthesis of 2,5-substituted phospholide ion 11

The use of carbonyl substituted phospholide ions to synthesize phosphaferrocene molecules and their use as building blocks is described hereafter.

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## Chapter 1

### From Functional Phospholide Ions to Bifunctional 1,1' Diphosphaferrocenes

Together with phosphinines (A), phosphaferrocenes (B) and 1,1'-diphosphaferrocenes (C) are certainly the most accessible and representative species incorporating a  $\text{sp}^2$ -phosphorus center into an aromatic system. In all of these cases, the parent species are isolable<sup>1,2</sup> because the aromatic stabilization energy eliminates the need for kinetic stabilization by bulky substituents, as is the case for phosphaalkenes. This situation is exceptionally favorable since it has been demonstrated that bulky substituents significantly alter the chemistry of low-coordinate phosphorus centers.<sup>3</sup>

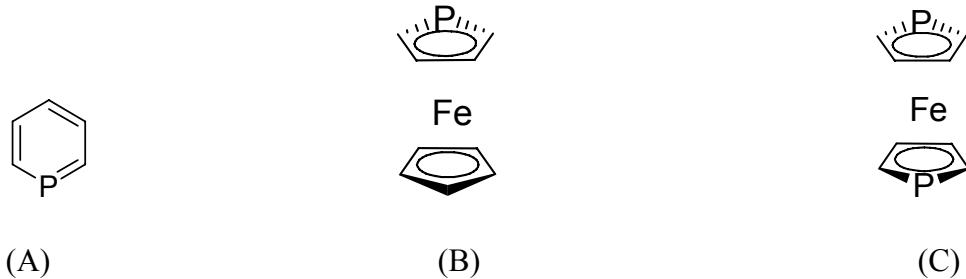
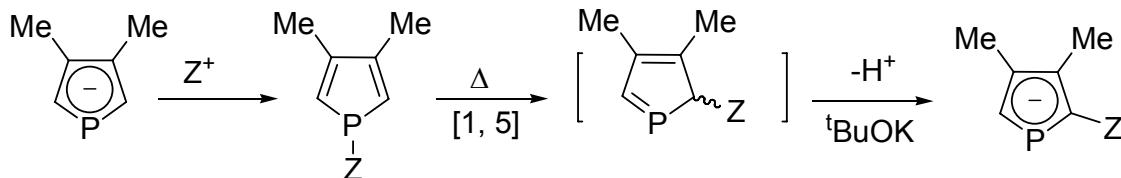


Figure 1.1: Aromatic systems **A**, **B**, and **C** incorporating  $\text{sp}^2$  phosphorus centers

Phosphaferrocenes have already found interesting applications as ligands for transition metals in homogeneous catalysis.<sup>4</sup> A logical further development of their chemistry would be to incorporate them into macrocyclic structures. The phosphinine ring has indeed been incorporated into macrocyclic structures,<sup>5</sup> and

the resulting macrocycles have shown an exceptional ability to stabilize low oxidation state metallic centers.<sup>6</sup> A prerequisite for the synthesis of phosphaferrocene-based macrocycles is an easy access to difunctional phosphaferrocenes. Aside from silylsubstituted derivatives,<sup>7</sup> the only described difunctional derivative is a 2,2'-diacetyl-1,1'-diphosphaferrocene obtained by Friedel–Crafts acetylation of a nonfunctional diphosphaferrocene.<sup>2</sup> Some time ago, we devised a synthesis of functional phospholide ions based on the [1,5] shift of the functional group from P to C $\alpha$  (scheme 1.1).<sup>8</sup>



Scheme 1.1: Synthesis of a functionalized phospholide

The simplicity of this one-pot synthesis of functional phospholides is quite attractive, and it was tempting to investigate their reaction with iron(II) derivatives in order to get bifunctional phosphaferrocenes. In this context, we were intrigued by a report of Ganter et al.<sup>7</sup> stating that they had been unable to convert 2,5-difunctional phospholide ions into the corresponding Fe or Ru sandwich complexes. We thus decided to investigate this reaction more closely.

Chapter one is based on the initial exploration of substituted phospholide ions with FeCl<sub>2</sub> to produce substituted 1,1' diphosphaferrocenes. The point of

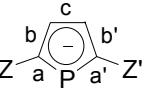
reference for this work came from the use of the 3,4-dimethyl phospholide ion that had been used as a starting point in making the first known diphosphaferrocene.<sup>2</sup>

Unlike the simple 1,1'-diphosphaferrocene reaction, it was soon discovered that the carbonyl substituted phospholides did not react in the way we desired with FeCl<sub>2</sub>. Instead the experiments gave way to a complex mixture that contained oxidized iron without any phosphorous signals in the <sup>31</sup>P. In order to prevent the oxidation of iron, we began a study to find potential salts to lessen the ionicity of the phospholide ion. The study began with three potential salts: aluminium chloride, tin (II) chloride, and zinc chloride. The results of experiments using aluminium chloride and tin (II) chloride were discouraging but the salt exchange using zinc chloride did yield the desired products.

Both the 2-ethoxycarbonyl and the 2-benzoyl phospholides (**1** and **2**) react with FeCl<sub>2</sub> in the presence of ZnCl<sub>2</sub> to give the corresponding 2,2'-difunctional 1,1'-diphosphaferrocenes as mixtures of *meso* and *rac* diastereomers. Stable rotamers were also detected by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Under the same conditions, the 2,5-bis(ethoxycarbonyl)phospholide (**3**) gives the tetrafunctional 1,1'-biphospholyl (**6**). The diphosphaferrocenes and the 1,1'-biphospholyl are probably formed from a common type of intermediates with a bis( $\eta^1$ -phospholyl)iron structure.

## Results and Discussion

This work being focused on carbonyl functionalities, we first decided to investigate the influence of a carbonyl substituent on the electronic structure of a phospholide ion. A comparative theoretical study was carried out on the parent phospholide (D), the 2-formylphospholide (E), and the 2,5-diformylphospholide (F) by DFT at the B3LYP/6-311G++(3df,2p) level.<sup>9</sup> The counterion was not included since it has been shown previously that it has only a limited influence on the structure of the anion,<sup>10</sup> the results are collected in Table 1.1.

	a (a')	b (b')	c	NICS(1) <sup>a</sup>	Charge at P <sup>b</sup>	Charge at O <sup>b</sup>	$\pi$ sym (eV)	$\pi$ asym (eV)	I.p. (eV)
Z, Z'=H (D)	1.764	1.393	1.413	-10.86	-0.43	-	-0.24	-0.84	-2.04
Z=CHO, Z'=H (E)	1.786 (1.743)	1.414 (1.408)	1.391	-10.18	-0.24	-0.69	-1.09	-1.74	-2.37
Z,Z'=CHO (F)	1.766	1.421	1.378	-10.09	-0.09	-0.67	-1.77	-2.48	-2.99

<sup>a</sup>RHF/6-311+G\*\*; see re11.<sup>b</sup> Mulliken

Table 1.1: Computed Data on Phospholides

Grafting one or two carbonyls on the ring significantly alters its structure. Anions E and F are better represented by the mesomeric formulations shown in figure 1.3.

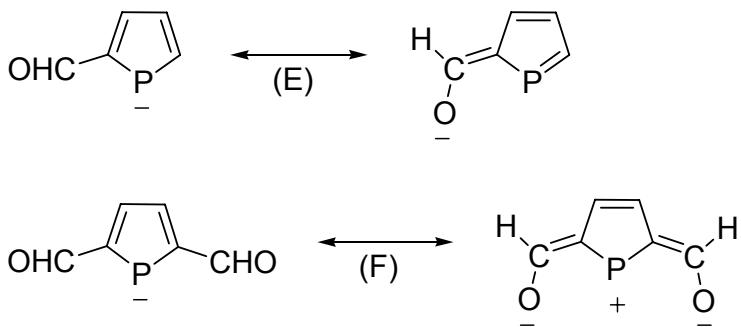


Figure 1.2: Mesomeric formulation of anions **E** and **F**

The negative charge at P sharply decreases from D to E and F, but the aromaticity does not according to the NICS(1) index. The highest occupied orbitals are shown in Figure 1 for F. The HOMO and HOMO-1 that are involved in the  $\pi$ -bonding with Fe(II) are shifted to lower energies to such an extent that  $\pi_{\text{asym}}$  is lower for F than the lone pair orbital for D. This cast some doubt on the ability of F to give a stable  $\pi$ -complex with iron. Indeed, the energetic gap between these orbitals and the  $d_{xz}$  and  $d_{yz}$  orbitals of iron might become too large to allow the formation of a stable  $\eta^5$ -structure.

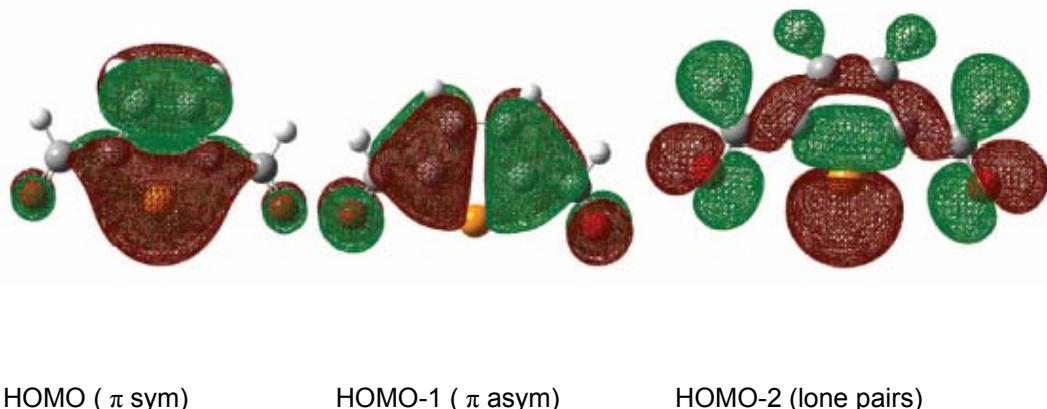


Figure 1.3: Highest occupied orbitals of anion **F**

For our experimental work, we chose to investigate the reaction of the three easily accessible functional phospholides **1-3**<sup>8,12</sup> with FeCl<sub>2</sub>. Our initial experiments were carried out with **1**.

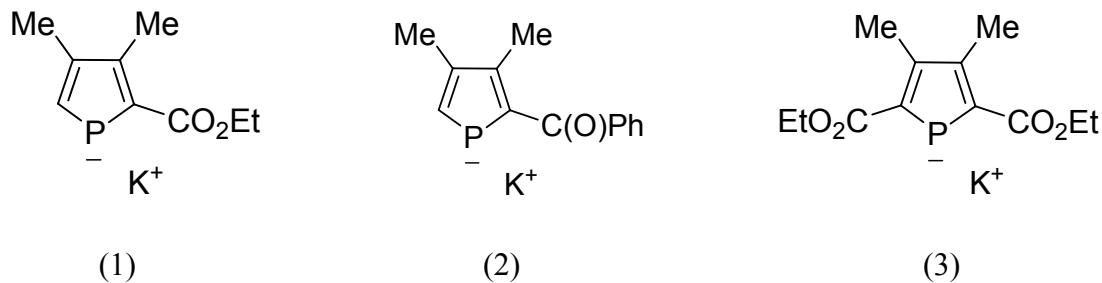
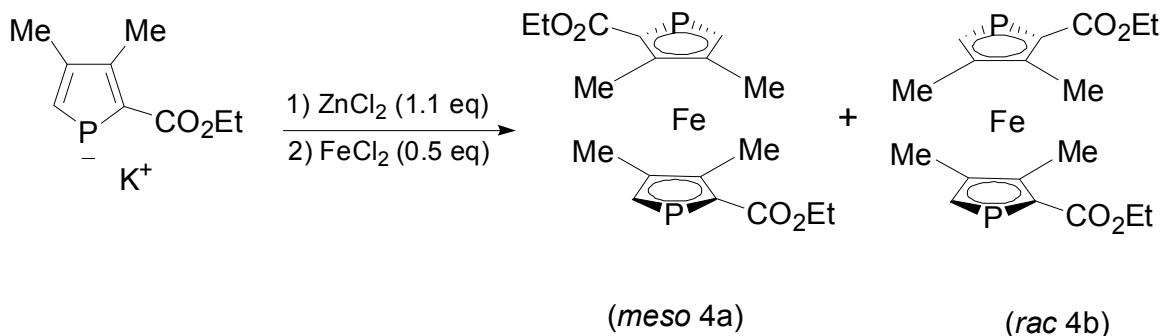


Figure 1.4: Functionalized phospholides **1**, **2**, and **3**

The reaction of **1** with FeCl<sub>2</sub> in THF at RT afforded only a mixture of decomposition products. We suspected that Fe(II) was partly reduced by the anion, and we chose to reduce the ionicity of the potassium phospholide by metathesis with ZnCl<sub>2</sub>. The zinc phospholide cleanly reacted with FeCl<sub>2</sub> to give a 70:30 mixture of the expected *meso* (**4a**) ( $\delta^{31}\text{P}$  -45.9 ppm) and *rac* (**4b**) ( $\delta^{31}\text{P}$  -50.5 ppm) difunctional 1,1'-diphosphaferrocenes (scheme 1.2).

After a preliminary purification by chromatography, the pure *meso* diastereomer was obtained in the pure state by extraction with pentane. The X-ray crystal structure of **4a** is shown in Figure 2.

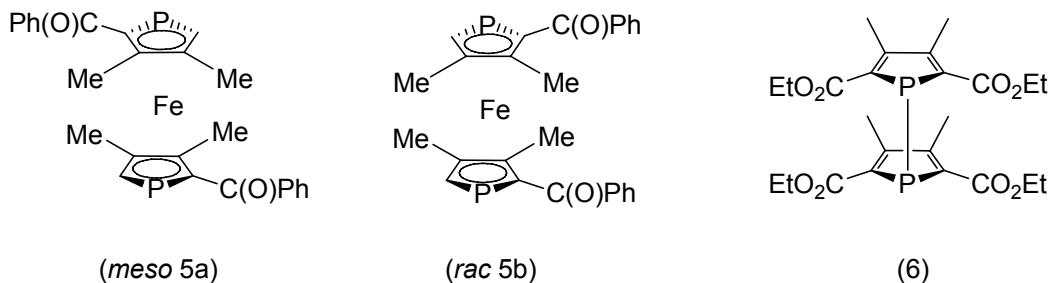


Scheme 1.2: Synthesis of meso **4a** and rac **4b** isomers of difunctional 1,1'-disphosphaferrrocene

The two phospholyl rings are in a head-to-tail disposition. The carbonyls are lying in the planes of the rings and are directed toward the methyl substituents. The  $^1\text{H}$  NMR spectrum shows two types of ethyl groups whose methyl resonances appear at 0.88 (37%) and 1.05 ppm (63%). These methyl resonances are correlated with two closely spaced  $^{13}\text{C}$  resonances at 14.31 (minor) and 14.41 ppm (major). Two sets of  $\text{OCH}_2$  resonances also appear on the  $^1\text{H}$  spectrum, but they are very close. We interpret this phenomenon as resulting from the presence of two stable rotamers. In the minor one, the carbonyls would lie opposite of the methyl substituents. Upon heating at 60–70 °C, the minor rotamer is slowly and irreversibly transformed into the major one. We prefer this explanation rather than the other possibility involving a blocked rotation around the Fe axis because only the ethyl resonances are different in the two rotamers.

Using the same experimental protocol, we were able to prepare the 2,2'-dibenzoyl-1,1'-diphosphaferrrocene (**5**) from the functional phospholide **2**. Like **4**,

**5** is obtained as a mixture of *meso* (**5a**) and *rac* (**5b**) diastereomers. The <sup>1</sup>H and <sup>13</sup>C NMR spectra show that **5b** is a mixture of two rotamers.



Always using the same protocol, the reaction of the difunctional phospholide **3** with FeCl<sub>2</sub> yielded the tetrafunctional biphenophospholyl **6** in 20% overall yield. Due to the paramagnetism of the solution, it proved impossible to monitor the reaction by <sup>31</sup>P NMR. However, after filtration on silica gel, we checked that **6** was the sole important product and that no diphosphaferrrocene was formed. Obviously, the modest overall yield partly reflects the moderate yield of the functionalization step. The X-ray crystal structure of **6** is shown in Figure 1.8. The P-P distance is normal at 2.2289(14) Å. The two rings are in a staggered conformation. The phosphorus atoms are highly pyramidal; Σangles at P = 290.9°. The strong alternation between the C-C single and the C=C double bonds of the rings confirms the absence of electronic delocalization. The carbonyls are directed toward the methyl substituents but are not coplanar with the rings.

These results suggest that the reaction of phospholides with  $\text{FeCl}_2$  proceeds via a  $\sigma$  P-Fe complex such as **7** (figure 1.5). A  $\eta^1 \rightarrow \eta^5$  fluctuation would yield the diphosphferrocene, whereas a reductive elimination would yield the 1,1'-biphospholyl.

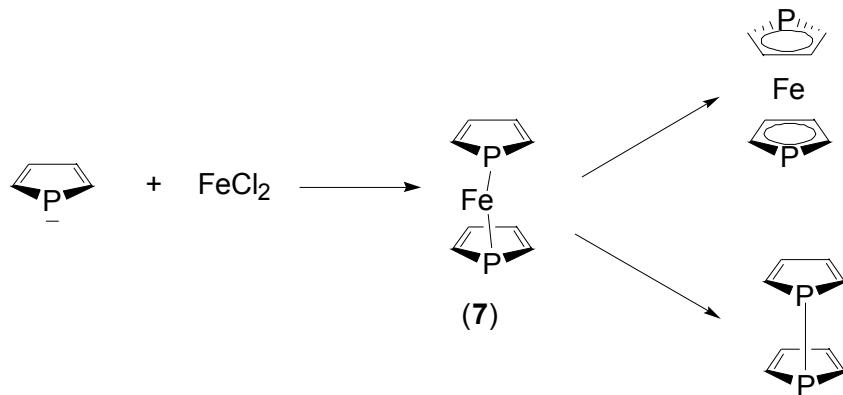


Figure 1.5: Reactions of phospholides with  $\text{FeCl}_2$  via  $\sigma$  P-Fe complex **7**

In order to give some support to this proposition, we decided to compute the structure of **7** with two molecules of THF as additional ligands. The computation was carried out by DFT at the B3LYP/6-31G(d) (C, H, O, P) and lanl2dz (Fe) level. The computed structure is shown in figure 1.6. It corresponds to a genuine minimum (no negative frequency). The most interesting feature is that the phosphorus atoms are pyramidal ( $\Sigma$ angles at P =  $336.9^\circ$ ), although less than in a normal phosphole. As a result, the phosphole ring is poorly delocalized and a strong alternation between the single and the double bonds is still present (1.443 vs 1.370 Å). We note a good agreement with the X-ray crystal structure analysis of a  $\eta^1$ -phospholyltungsten complex.<sup>13</sup>

One of the driving forces for the formation of the diphosphaferroocene is thus the aromatization of the rings during the  $\eta^1 \rightarrow \eta^5$  fluctuation. Such a driving force does not exist in the case of pyrrolyl complexes (both  $\eta^1$ - and  $\eta^5$ -pyrrolyl complexes are aromatic), and this might explain why diazaferrocenes are more difficult to prepare than diphosphaferrocenes.<sup>14</sup>

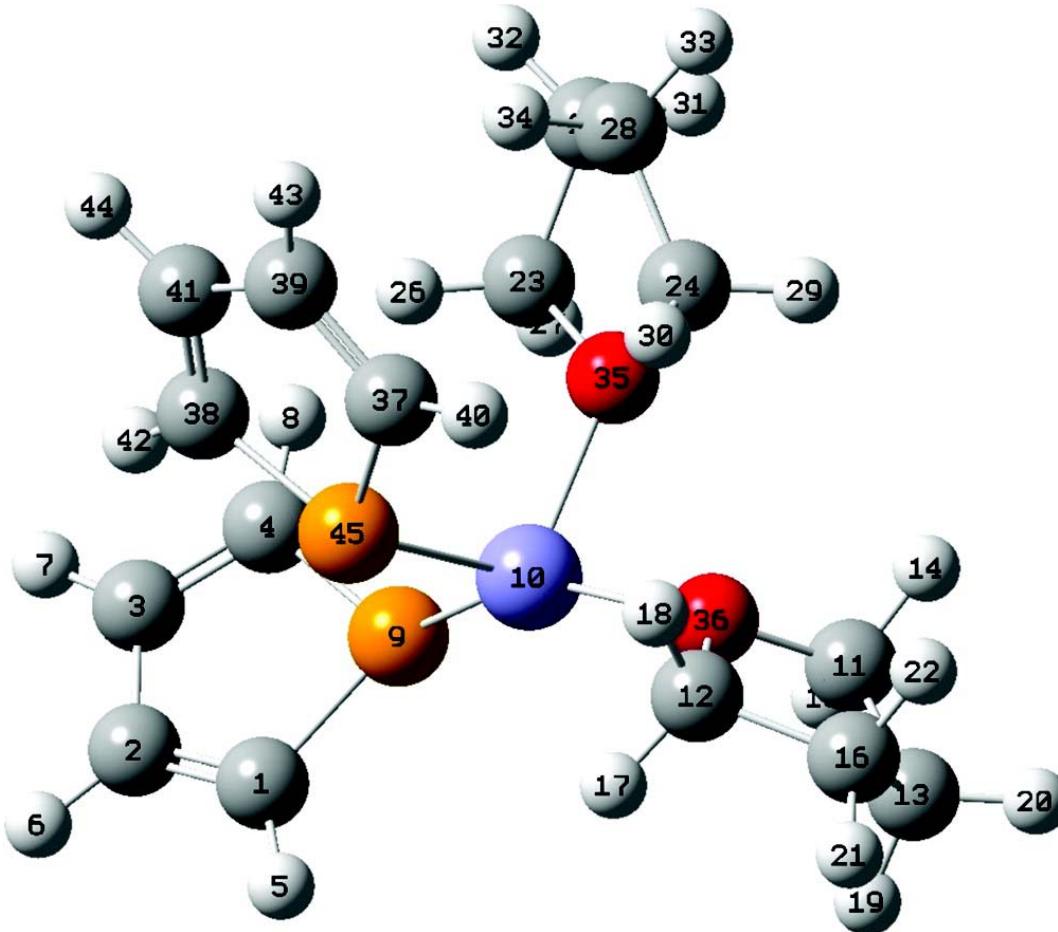


Figure 1.6: Computed structure of the  $\sigma$ -complex  $(7)(\text{THF})_2$ . Main bond lengths ( $\text{\AA}$ ) and angles (deg): Fe-P9 2.278, P9-C1 1.791, P9-C4 1.792, C1-C2 1.369, C2-C3 1.443, C3-C4 1.370, Fe-P45 2.253; P9-Fe-P45 103.84, C1-P9-C4 91.08, C1-P9-Fe 115.35, C4-P9-Fe 130.44

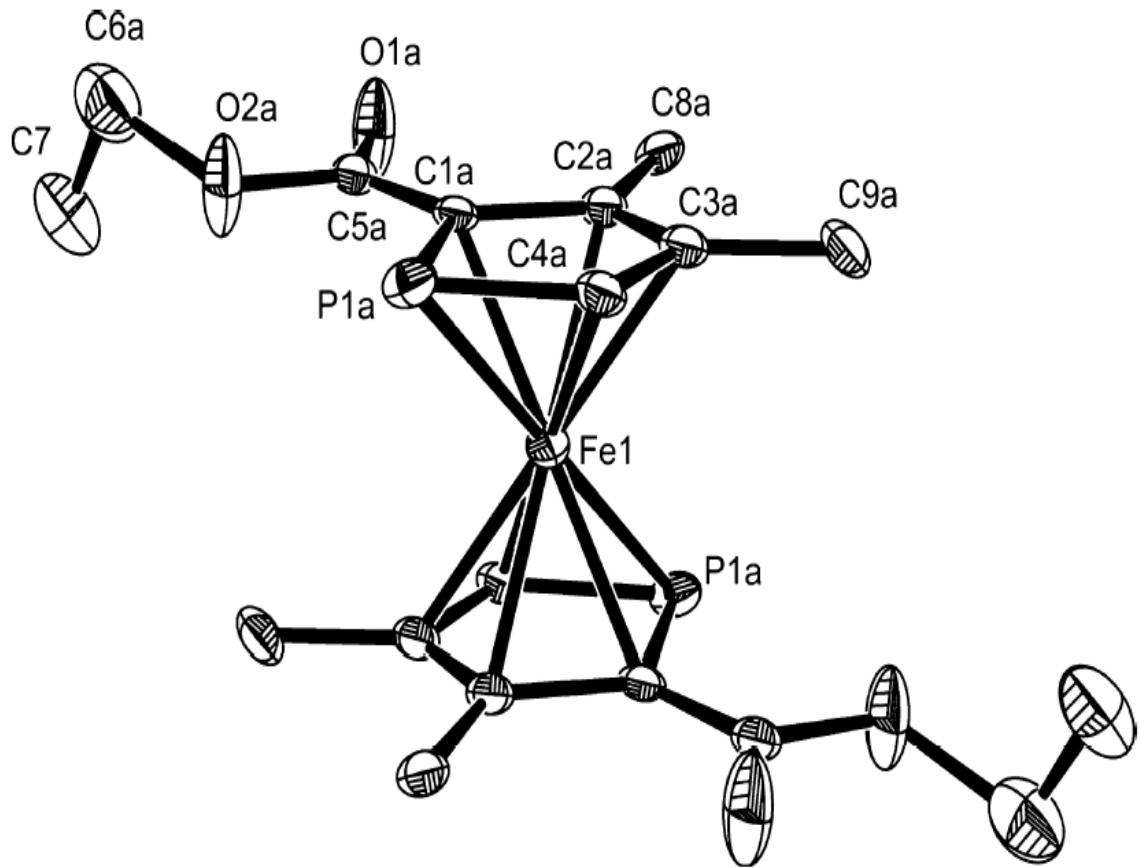


Figure 1.7: X-ray crystal structure of *meso*-2,2'-bis(ethoxycarbonyl)-1,1'-diphosphapherrocene (**4a**). Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P1-C1 1.87(5), P1-C4 1.76(5), C1-C2 1.451(16), C2-C3 1.407(18), C3-C4 1.374(18), Fe1-C1 2.11(5), Fe1-C4 2.04(3), Fe1-P1 2.221(38); C1-P1-C4 86(2).

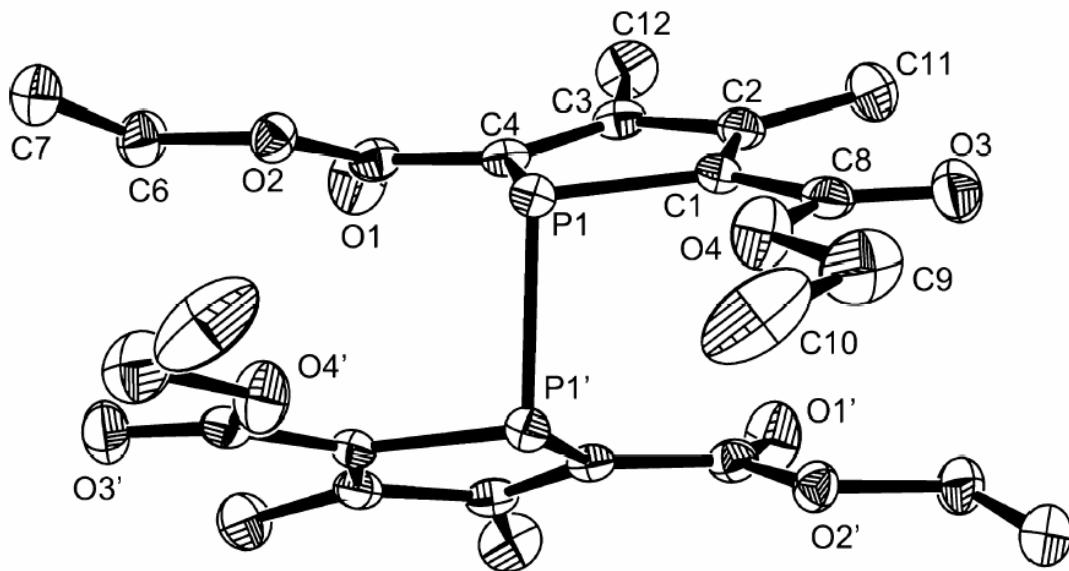


Figure 1.8: X-ray crystal structure of 3,3',4,4'-tetramethyl-2,2',5,5'-tetrakis(ethoxycarbonyl)-1,1'-biphospholyl (**6**). Ellipsoids are scaled to enclose 50% of the electronic density. Main bond lengths (Å) and angles (deg): P1-P1' 2.2289(14), P1-C1 1.809(2), P1-C4 1.805(4), C1-C2 1.358(4), C2-C3 1.466(4), C3-C4 1.362(3); C1-P1-C4 89.66(11), C1-P1-P1' 98.29(9), C4-P1-P1' 102.95(8).

## Experimental Section

Nuclear magnetic resonance spectra were obtained on Bruker Avance 300 and Varian Inova spectrometers operating at 300.13 MHz for  $^1\text{H}$ , 75.45 MHz for  $^{13}\text{C}$ , and 121.496 MHz for  $^{31}\text{P}$ . A Bruker Avance 600 instrument was also used for  $^1\text{H}$  and  $^{13}\text{C}$  (150.925 MHz) spectra. Chemical shifts are expressed in parts per million downfield from external TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). Mass spectra were obtained on VG 7070 and Hewlett-Packard

5989A GC/MS spectrometers. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

**3,3',4,4'-Tetramethyl-2,2'-bis(ethoxycarbonyl)-1,1'-diphosphaferrocene**

**(4a,b).** 1-Phenyl-3,4-dimethylphosphole (2 g, 10.63 mmol) in dry THF (25 mL) was allowed to react with an excess of lithium wire until the P-Ph bond cleavage was completed. After excess lithium was removed, the solution was treated with *tert*butyl chloride (1.2 mL, 10.63 mmol) and heated to 60 °C for 1 h. Ethyl chloroformate (1.1 mL, 11.7 mmol) was added dropwise at -78 °C. The solution was heated at 65 °C for 2.5 h. *t*BuOK was added (1.3 g, 11.7 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. ZnCl<sub>2</sub> (1.4 g, 10.63 mmol) was added at 0 °C and stirred at room temperature for 30 min. FeCl<sub>2</sub> (0.67 g, 5.3 mmol) was added at room temperature. The solution was stirred for 18 h at RT. The crude solution mixture was filtered through silica and concentrated. Purification was performed via column chromatography on silica using 3:2 dichloromethane/ petroleum ether. A red band was collected and, once concentrated, 683 mg of a red solid was obtained (30% yield). The *meso* diastereomer was extracted from the solid with pentane and crystallized from the pentane solution. We were unable to get the *rac* diastereomer in the pure form.

**meso Diastereomer (4a).** <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ -45.3. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.88 (t, Me(Et) minor), 1.05 (t, Me(Et) major), 1.78 (s, Me), 2.40 (s, Me), 3.72 (d, <sup>2</sup>J<sub>HP</sub> = 36.4 Hz, CH-P), 4.04 (2q, OCH<sub>2</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 13.54 (s, Me), 14.41 (s,

Me(Et)), 15.17 (s, Me), 60.30 (s, OCH<sub>2</sub>), 84.40 (d, <sup>1</sup>J<sub>C-P</sub> = 62.3 Hz, =C-P), 86.45 (d, <sup>1</sup>J<sub>C-P</sub> = 58.7 Hz, =CH-P), 98.74 (d, <sup>2</sup>J<sub>CP</sub> = 5.2 Hz, =C(Me)), 102.64 (d, <sup>2</sup>J<sub>CP</sub> = 9.0 Hz, =C(Me)), 171.32 (d, <sup>2</sup>J<sub>CP</sub> = 19.8 Hz, CO). MS (EI): *m/z* 422 (M<sup>+</sup>, 100%).

Anal. Calcd for C<sub>18</sub>H<sub>24</sub>FeO<sub>4</sub>P<sub>2</sub>: C, 51.21; H, 5.73. Found: C, 50.79; H, 5.79.

**3,3',4,4'-Tetramethyl-2,2'-dibenzoyl-1,1'-diphosphaferrocene (5a,b).** 1-Phenyl-3,4-dimethylphosphole (2 g, 10.63 mmol) in dry THF (25 mL) was allowed to react with an excess of lithium wire until the P-Ph bond cleavage was completed. After excess lithium was removed, the solution was treated with *tert*-butyl chloride (1.2 mL, 10.63 mmol) and heated at 60 °C for 1 h. Benzoyl chloride (1.4 mL, 11.7 mmol) was added dropwise at -78 °C. The mixture was warmed to room temperature and stirred for 20 min. *t*BuOK (1.3 g, 11.7 mmol) was added at 0 °C, and the solution was stirred at 60 °C for 2 h. The solution was cooled to 0 °C, ZnCl<sub>2</sub> (1.4 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. FeCl<sub>2</sub> (0.67 g, 5.3 mmol) was added, and the solution was stirred for 18 h. The crude reaction mixture was filtered through silica and concentrated. Purification was performed via column chromatography on silica using 3:2 petroleum ether/dichloromethane solution. A red band was collected and, once concentrated, 863 mg of a red oil was obtained (33% yield). The two diastereomers were separated by a second chromatography with methylene chloride as the eluent and crystallized upon slow evaporation of the solvent.

**meso Diastereomer (5a).** <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>): δ -53.1. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.88 (s, Me), 2.10 (s, Me), 3.93 (m, CH-P), 6.98 – 7.16 (m, Ph), 7.86 (m, Ph *ortho*). <sup>13</sup>C

NMR ( $C_6D_6$ ):  $\delta$  11.40 (s, Me), 12.60 (s, Me), 83.68 (m, =CH-P), 91.34 (m, =C-P), 98.93 (d, =C(Me)), 101.70 (d, =C(Me)), 139.26 (s, Ph *ipso*C), 197.68 (pseudo t, CO).

**rac Diastereomers (5b1 and 5b2): 5b1 (major).**  $^{31}P$  NMR ( $C_6D_6$ ):  $\delta$  -43.7.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  1.87 (s, Me), 2.09 (s, Me), 4.09 (d,  $^2J_{HP}$  = 45 Hz, CH-P), 7.84 (m, Ph *ortho*).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  13.14 (s, Me), 14.37 (s, Me), 87.69 (d,  $^1J_{CP}$  = 74.7 Hz, =CH-P), 96.68 (d,  $^1J_{CP}$  = 79.7 Hz, =C-P), 100.66 (s, =C(Me)), 103.45 (d,  $^2J_{CP}$  = 5.0 Hz, =C(Me)), 141.14 (s, Ph *ipso*C), 199.04 (d,  $^2J_{CP}$  = 22.3 Hz, CO).

**5b2 (minor).**  $^{31}P$  NMR ( $C_6D_6$ ):  $\delta$  -43.4.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  2.07 (s, Me), 2.26 (s, Me), 3.92 (m, CH-P), 7.80 (m, Ph *ortho*).  $^{13}C$  NMR ( $C_6D_6$ ):  $\delta$  15.39 (s, Me), 16.49 (s, Me), 85.31 (m, =CH-P), 93.09 (m, =C-P), 99.90 (d,  $^2J_{CP}$  = 5.0 Hz, =C(Me)), 102.57 (d,  $^2J_{CP}$  = 10.0 Hz, =C(Me)), 141.01 (s, Ph *ipso*C), 199.44 (pseudo t, CO). Anal. Calcd for  $C_{26}H_{24}FeO_2P_2$ : C, 64.22; H, 4.97. Found: C, 64.39; H, 4.94.

**3,3',4,4'-Tetramethyl-2,2',5,5'-tetrakis(ethoxycarbonyl)-1,1'-biphospholy (6).** 1-Phenyl-3,4-dimethylphosphole (2 g, 10.63 mmol) in dry THF (25 mL) was allowed to react with an excess of lithium wire until the P-Ph bond cleavage was complete. After excess lithium was removed, the solution was treated with *tert*butyl chloride (1.2 mL, 10.63 mmol) and heated to 60 °C for 1 h. Ethyl chloroformate (1.1 mL, 11.7 mmol) was added dropwise at -78 °C. The solution was heated at 65 °C for 2.5 h. *t*BuOK was added (1.4 g, 12.8 mmol) at 0 °C, followed by heating at 60 °C for 2 h. A second equivalent of ethyl chloroformate (1.2 mL, 12.8 mmol) was added at -78 °C, immediately followed by addition of a

second equivalent of *t*BuOK (1.4 g, 12.8 mmol) at 0 °C. The resulting mixture was stirred at 40 °C for 18 h. The solution was cooled to 0 °C, ZnCl<sub>2</sub> (1.4 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. FeCl<sub>2</sub> (0.67 g, 5.3 mmol) was added, and the mixture was stirred for 18 h. The crude reaction mixture was filtered through silica and concentrated. Purification was performed via column chromatography on silica using 100:1 dichloromethane/ethyl acetate solution. A yellow band was collected and, once concentrated, 542 mg of a yellow solid was obtained (20% yield). The yellow solid was recrystallized from dichloromethane. <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –6.5. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.29 (t, Me(Et)), 2.34 (m, Me-C=), 4.07 (m, OCH<sub>2</sub>), 4.20 (m, OCH<sub>2</sub>). <sup>13</sup>C NMR CD<sub>2</sub>Cl<sub>2</sub>): δ 14.57 (s, Me(Et)), 15.82 (s, Me-C=), 61.18 (s, OCH<sub>2</sub>), 136.32 (pseudo t, C $\alpha$ ), 158.12 (pseudo t, C $\beta$ ), 165.00 (pseudo t, CO). MS (EI): *m/z* 510 (M, 80%), 254 (M/2, 100%). The compound is sensitive to oxidation. Anal. Calculated for C<sub>24</sub>H<sub>32</sub>O<sub>8</sub>P<sub>2</sub>: C, 56.47; H, 6.32. Found: C, 56.2; H, 6.3.

**X-Ray Structure Determination of 4a and 6.** Compounds were measured at low temperature, *T* ) 100(2) K, on a X8-APEX Bruker Kappa four-circle X-ray diffractometer system (Mo radiation,  $\lambda$  ) 0.71073 Å). An optimized data collection strategy was defined using **Figure 4**. Computed structure of the σ-complex (7)(THF)2. Main bond lengths (Å) and angles (deg): Fe-P9 2.278, P9-C1 1.791, P9-C4 1.792, C1-C2 1.369, C2-C3 1.443, C3-C4 1.370, Fe-P45 2.253; P9-Fe-P45 103.84, C1-P9-C4 91.08, C1-P9-Fe 115.35, C4-P9-Fe 130.44.

Cosmo.15 Frames were integrated with the aid of Bruker Saint software<sup>16</sup> included in the Bruker APEX2 package<sup>17</sup> and using a narrow-frame integration algorithm.

**4a:** The integrated frames yielded a total of 3925 reflections at a maximum  $2\theta$  angle of  $43.94^\circ$ , of which 1127 were independent reflections ( $R_{\text{int}} = 0.0814$ ,  $R_{\text{sig}} = 0.0895$ , completeness = 98.5%) and 871 (77.28%) reflections were greater than  $2\sigma(I)$ . A triclinic cell space group  $P2(1)/n$  was found; the unit cell parameters were  $a = 6.796(5) \text{ \AA}$ ,  $b = 8.163(6) \text{ \AA}$ ,  $c = 16.939(13) \text{ \AA}$ ,  $\alpha = 90.0^\circ$ ,  $\beta = 96.360(9)^\circ$ ,  $\gamma = 90.0^\circ$ ,  $V = 933.9(12) \text{ \AA}^3$ ,  $Z = 4$ , calculated density  $D_c = 1.473 \text{ Mg/m}^3$ . The molecule is statistically disordered on two positions.

**6:** The integrated frames yielded a total of 6858 reflections at a maximum  $2\theta$  angle of  $46.50^\circ$ , of which 1835 were independent reflections ( $R_{\text{int}} = 0.0307$ ,  $R_{\text{sig}} = 0.0294$ , completeness = 99.4%) and 1617 (88.12%) reflections were greater than  $2\sigma(I)$ . A monoclinic cell space group  $C2/c$  was found; the unit cell parameters were  $a = 20.816(5) \text{ \AA}$ ,  $b = 10.489(2) \text{ \AA}$ ,  $c = 12.513(3) \text{ \AA}$ ,  $\beta = 109.335(3)^\circ$ ,  $V = 2578.2(10) \text{ \AA}^3$ ,  $Z = 8$ , calculated density  $D_c = 1.315 \text{ Mg/m}^3$ .

**6** is organized around a  $C2$  axis with the following symmetry transformations used to generate equivalent atoms: #1  $-x, y, -z+3/2$ .

Absorption corrections were applied for data using the SADABS<sup>18</sup> program. The program SIR92<sup>19</sup> was used for phase determination and structure solution, followed by some subsequent differences Fourier maps. From the primary electron density map most of the non-hydrogen atoms were located, and with the

aid of subsequent isotropic refinement all of the non-hydrogen atoms were identified. Atomic coordinates and isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on  $F_2$ . The H atoms were included in the refinement in calculated positions riding on the C atoms to which they were attached. The refinement converged for **4a** at  $R1 = 0.0751$ ,  $wR2 = 0.1862$ , with intensity  $I > 2\sigma(I)$ , and for **6** at  $R1 = 0.0406$ ,  $wR2 = 0.1057$  with intensity  $I > 2\sigma(I)$ .

Drawings of molecules were performed using ORTEP32.<sup>20, 21</sup>

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## Chapter 2

### Synthesis of 2,5-Difunctional Phosphaferrocenes.

Together with phosphinines, phosphaferrocenes are one of the two fundamental classes of aromatic species featuring an  $sp^2$  phosphorus center. They are readily functionalizable, and they have already found a certain number of catalytic applications.<sup>1</sup> At the present time, however, essentially no 2,5-difunctional phosphaferrocene is known aside from the silyl derivatives,<sup>2</sup> thus preventing the easy incorporation of the phosphaferrocene unit into rings or polymers. This point has been raised by Ganter,<sup>2</sup> who unsuccessfully tried to prepare 2,5-diacylphosphaferrocenes. We show hereafter how it is possible to circumvent this limitation.

#### Results and Discussion

Our initial reasoning was that the failure reported by Ganter was due to the very poor  $\pi$ -donating ability of 2,5-diacylphospholides. Indeed, it is well established, on the basis of comparative IR studies of cymantrene and phosphacymantrene, that the nonfunctional  $\eta^5$ -phospholyl is already a poorer  $\pi$ -donor than the  $\eta^5$ -cyclopentadienyl ligand.<sup>3</sup> From another standpoint, this fact seems to contradict the observation that the Friedel-Crafts acylation of phosphaferrocenes selectively takes place at the phospholyl ring.<sup>4</sup>

This contradiction is suppressed if we admit that a sizable electronic transfer from cyclopentadienyl to phospholyl takes place through iron in phosphaferrocenes. This transfer must induce a stabilization of the phosphaferrocene by a classical push-pull effect. In order to evaluate this effect, we decided to compute the energies of the two members of the formal equation (figure 2.1) by DFT at the 6-31G(d)-Lanl2dz (Fe) level.<sup>5</sup>

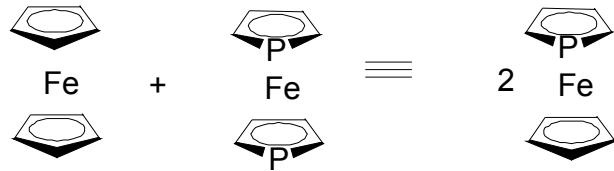
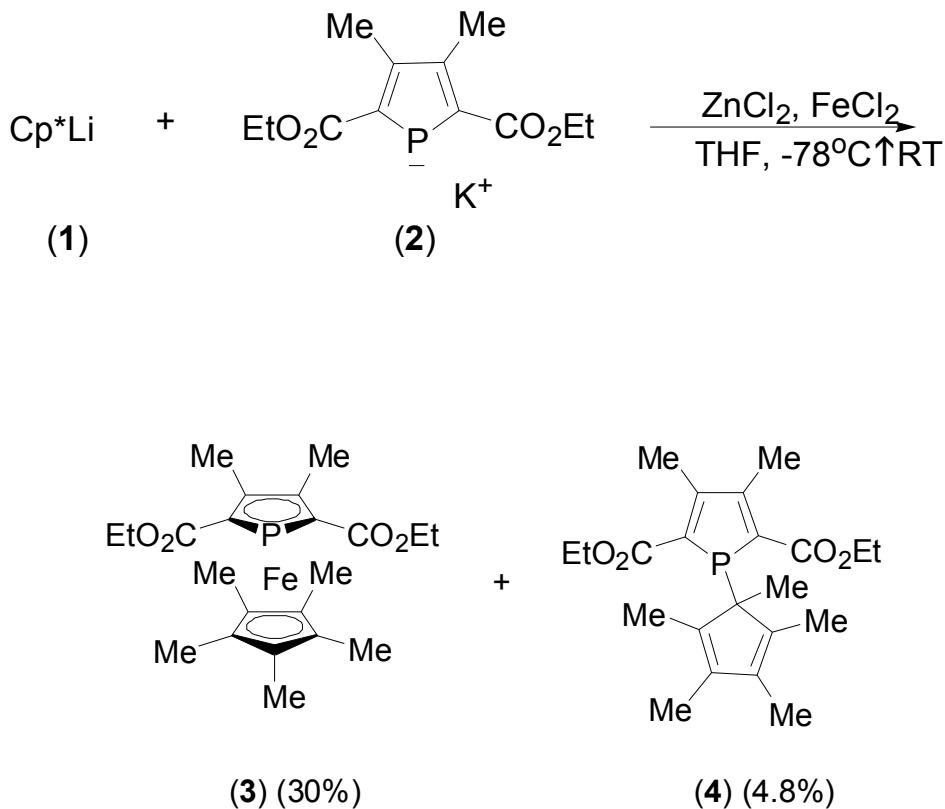


Figure 2.1: 1+1 mixture of ferrocene and 1,1'-diphosphaferrocene

The results are ambiguous. The two molecules of phosphaferrocene appear to be more stable than the 1 + 1 mixture of ferrocene and 1,10-diphosphaferrocene by only 0.9 kcal mol<sup>-1</sup> (ZPE included). Even though this effect is limited, we could expect to enhance it on replacing Cp by Cp\* and the nonfunctional phospholyl by a phospholyl substituted with an electron-withdrawing group. Two practical consequences can be expected: (1) if we react a 1:1 mixture of cyclopentadienide and phospholide with FeCl<sub>2</sub>, we must get more phosphaferrocene than the statistical mixture; (2) we can envisage compensating the very poor  $\pi$ -complexing ability of 2,5-diacylphospholyl by using the strong Cp\* donor as the coligand of iron. This led us to investigate the reaction of a 1:1 mixture of the pentamethylcyclopentadienide **1** and 2,5-

diethoxycarbonyl- 3,4-dimethylphospholide (**2**)<sup>6</sup> with  $\text{FeCl}_2$  in the presence of  $\text{ZnCl}_2$  as acidic coreagent.<sup>7</sup> We were delighted to find that this reaction provides a very simple access to the 2,5-difunctional phosphaferrocene **3** (scheme 2.1).

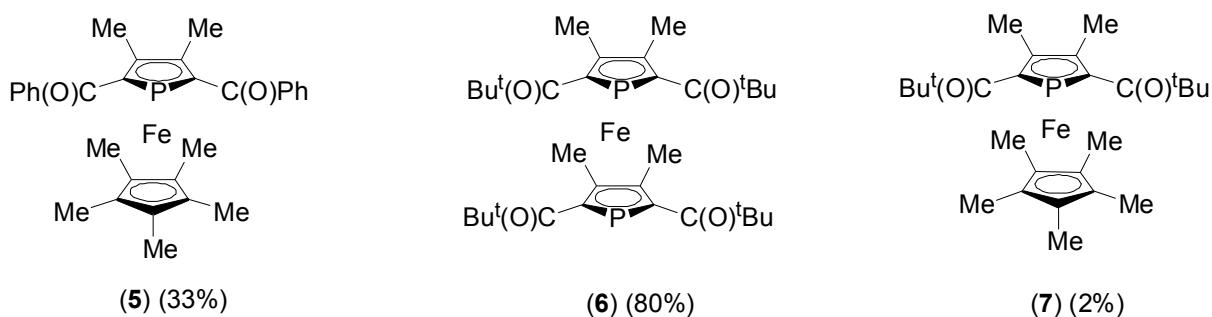


Scheme 2.1: Synthesis of 2,5 difunctional phosphaferrocene **3**

This result is remarkable because we have shown previously that the reaction of **2** with  $\text{FeCl}_2$  leads exclusively to the tetrafunctional P-P coupling product.<sup>7</sup> In line with this previous result, we just get a small quantity of the  $\text{Cp}^*$ -substituted phosphole **4**. Both products were characterized by X-ray crystal structure analysis (Figures 2.2 and 2.3). In phosphaferrocene **3**, both rings are in a staggered conformation. The phosphole ring is quasi planar, the bending

around C1 · · · C4 being only 1.67°. The Cp\* and phospholyl planes are almost parallel (angle 1.33°). The phospholyl plane is closer to iron than the Cp\* plane (1.637 vs 1.670 Å). As expected, the phospholyl ring shows practically no alternation between the C-C bonds. In phosphole **4**, the steric bulk of the Cp\* substituent induces a lengthening of the P-C exocyclic bond at 1.8967(16) Å but the phosphorus pyramid is not flattened ( $\Sigma$  angles at P = 302.6°), the same as in 1-benzylphosphole<sup>8</sup>). The intracyclic P-C bonds are long, and the alternation between C-C and C=C bonds is high. The bending of the ring around C4-C9 is significant at 9.65°.

Using the same experimental protocol, but replacing the 2,5-bis(ethoxycarbonyl) by 2,5-dibenzoylphospholide,<sup>9</sup> we obtained the 2,5-dibenzoylphosphaferrocene **5** in 33% yield. The surprise came when we used the 2,5-bis(pivaloyl)phospholide. In the presence of a stoichiometric amount of Cp\*Li, only traces of the expected phosphaferrocene **7** are obtained. By far the main product of the reaction is the tetrafunctional 1,1'-diphosphaferrocene **6**. In the absence of Cp\*Li, we got an impressive 80% yield of this product. The identity of **6** was unambiguously established by X-ray crystal structure analysis (Figure 2.4).



The conformation of the molecule lies halfway between staggered and eclipsed. One ring is rotated with respect to the other by  $23.24^\circ$ . The two phospholyl planes are almost parallel (interplane angle  $1.26^\circ$ ). The two rings are slightly folded around their  $\text{C}\alpha\text{-C}\alpha'$  axis, both by  $1.78^\circ$ . The two planes are equidistant from iron at  $1.655 \text{ \AA}$ . The preferential formation of **6** vs **7** is somewhat mysterious. It might have something to do with the relative stabilities of the intermediate  $\sigma$ -complexes.

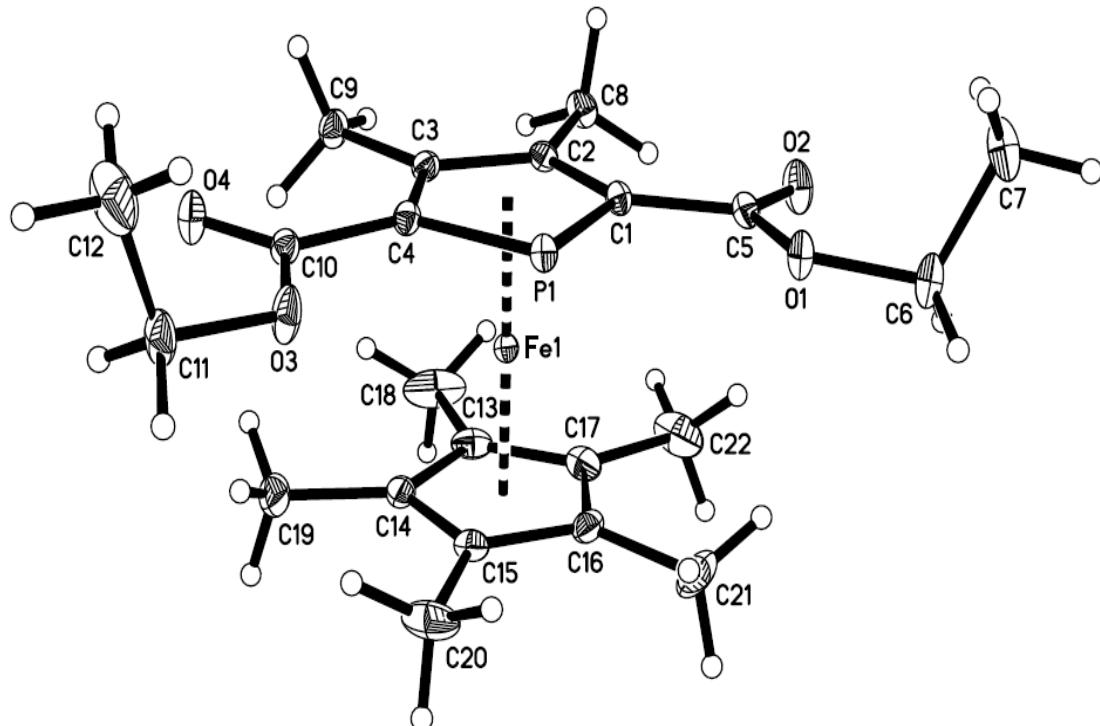


Figure 2.2: X-ray crystal structure of phosphaferrocene **3**. Main distances ( $\text{\AA}$ ) and angles (deg):  $\text{Fe1-P1}=2.2780(3)$ ,  $\text{Fe1-C1}= 2.0643(11)$ ,  $\text{Fe1-C13}=2.0773(12)$ ,  $\text{P1-C1}=1.7868(12)$ ,  $\text{P1- C4}=1.7832(12)$ ,  $\text{C1-C2}=1.4384(16)$ ,  $\text{C2-C3}=1.4254(16)$ ,  $\text{C3-C4} = 1.4386(16)$ ;  $\text{C1-P1-C4} = 87.88(5)$ .<sup>11</sup>

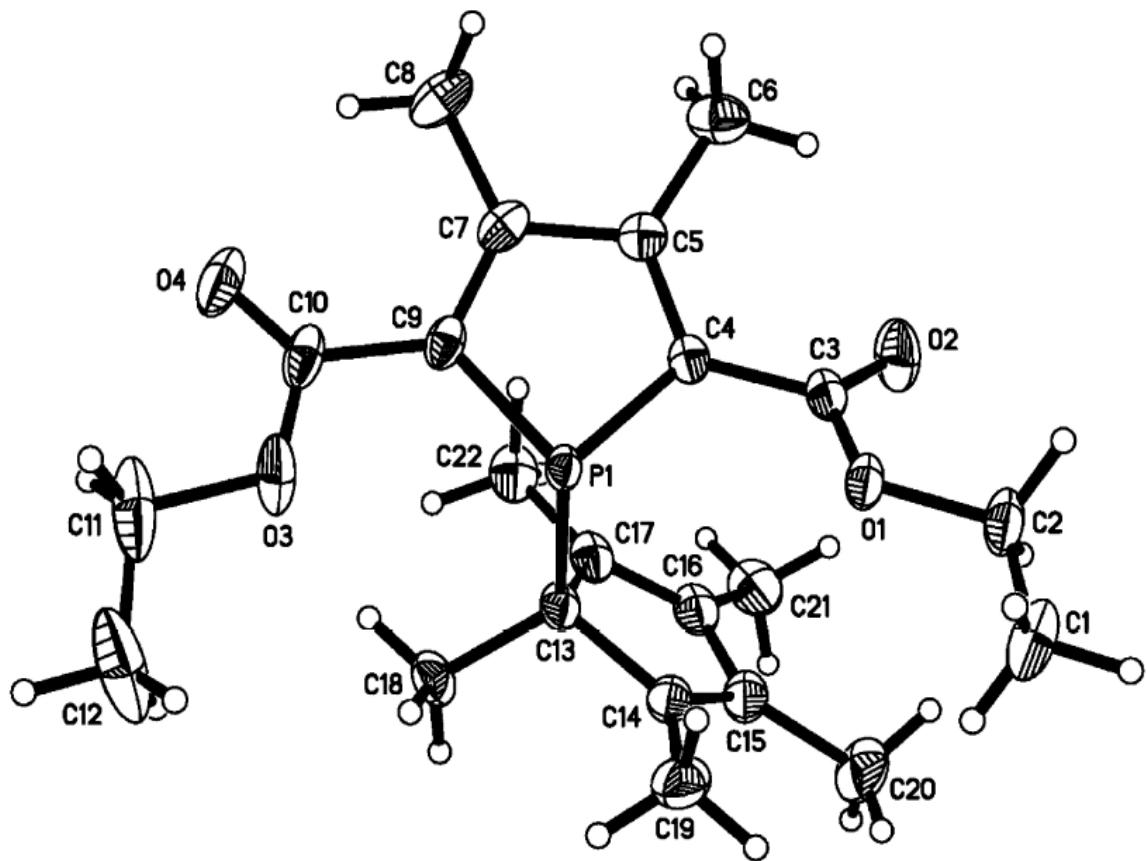


Figure 2.3: X-ray crystal structure of phosphole **4**. Main distances ( $\text{\AA}$ ) and angles (deg): P1-C13=1.8967(16), P1-C9=1.8033(17), P1-C4=1.8011(16), C4-C5=1.362(2), C5-C7= 1.464(2), C7-C9=1.367(2), C4-C3=1.474(2), C9-C10= 1.479(2); C4-P1-C9=89.86(8), C4-P1-C13=103.57(7), C9- P1-C13 = 109.16(7).<sup>11</sup>

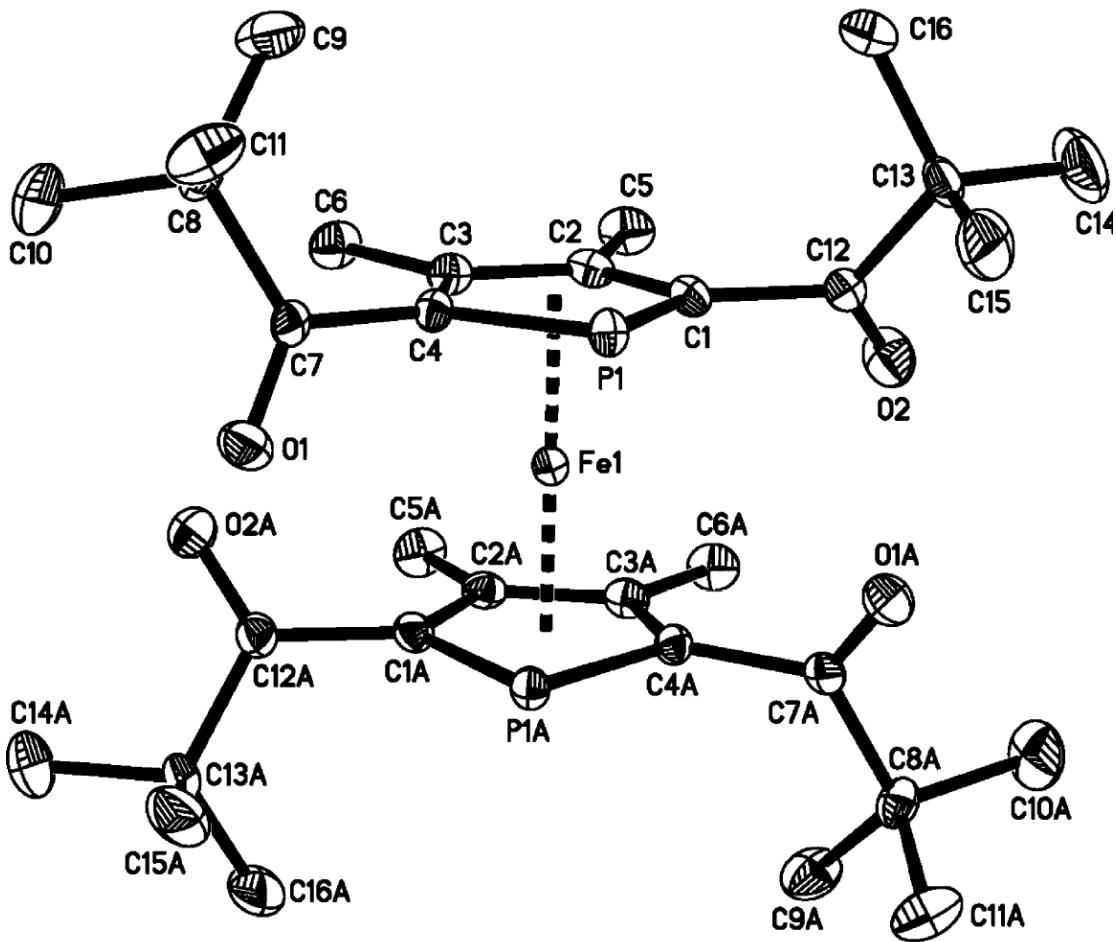


Figure 2.4: X-ray crystal structure of 1,1'-diphosphapherrocene **6**.  
 Main distances ( $\text{\AA}$ ) and angles (deg): Fe1-P1 = 2.2746(9), Fe1-C1=2.092(3), Fe1-C2=2.086(3), P1-C1=1.782(3), C1-C2=1.430(5), C2-C3=1.426(5), C3-C4=1.423(5), P1-C4=1.795(3); C1-P1-C4 = 88.72(15).<sup>11</sup>

## Experimental Section

### **2,5-Bis(ethoxycarbonyl)phosphapherrocene **3** and 1-**

### **pentamethylcyclopentadienylphosphole **4**.**

1-Phenyl-3,4-dimethylphosphole 10 (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After

excess lithium was removed, the solution was treated with tertbutyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Ethyl chloroformate (0.55 mL, 5.85 mmol) was added dropwise at -78 °C. The solution was heated at 65 °C for 2 h. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of ethyl chloroformate (0.6 mL, 5.85 mmol) was added at -78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 40°C for 18 h. The solution was cooled to 0 °C, ZnCl<sub>2</sub> (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. In a separate reaction flask, Cp\*Li was prepared by adding n-BuLi (2.85 mL, 4.5 mmol) to 1,2,3,4,5-pentamethylcyclopentadiene (0.84 mL, 5.32 mmol) in dry THF (15 mL) at -78 °C. The solution was stirred at -78 °C for 30 min and warmed to room temperature for 1 h. The 2,5-bifunctionalized phospholide mixture was then added to the Cp\*Li solution at -78 °C and stirred for 20 min at -78 °C. In a separate flask, FeCl<sub>2</sub> (0.725 g, 5.32 mmol) was stirred in dry THF at room temperature for 30 min. After the FeCl<sub>2</sub> solution was cooled to -78 °C, the 2,5-bifunctionalized phospholide/Cp\*Li solution was added dropwise by cannula. The resulting mixture was stirred at -78 °C for 1 h and at room temperature for 18 h. The crude solution mixture was concentrated, dissolved in methylene chloride, filtered through silica, and concentrated. Purification was performed via cold column chromatography on silica using 1:1 dichloromethane-hexanes. An orange band was collected and, once concentrated, 570 mg (1.28 mmol) of an orange

solid (**3**) was obtained in 30% yield. The product was crystallized by slow evaporation of methylene chloride. When the polarity of the eluent was increased to 2:1 dichloromethane-hexanes, a yellow band was recovered from the same column. On concentration, 100 mg (0.26 mmol) of a yellow solid (**4**) was obtained in 4.8% yield. The solid was crystallized by slow evaporation of methylene chloride.

Data for **3** are as follows.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.31 (t, 6H, Me), 1.64 (s, 15H, Me), 2.24 (s, 6H, Me), 4.12 (q, 4H,  $\text{OCH}_2$ ).  $^{13}\text{C}$  NMR( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.99 (s, Me Cp\*), 11.90 (s, Me), 14.15 (s, Me), 60.00 (s,  $\text{OCH}_2$ ), 82.78 (d,  $^1\text{J}_{\text{PC}} = 56.8$  Hz, C-P), 84.74 (s, C Cp\*), 97.83 (d,  $^2\text{J}_{\text{PC}} = 6.4$  Hz,  $\text{C}\beta$ ), 171.58 (d,  $^2\text{J}_{\text{PC}} = 18.5$  Hz, CO).  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  -29.7. Exact mass: m/z calcd for  $\text{C}_{22}\text{H}_{32}\text{FeO}_4\text{P}$  447.1388, found 447.1386. Anal. Calcd for  $\text{C}_{22}\text{H}_{31}\text{FeO}_4\text{P}$ : C, 59.21; H, 7.00. Found: C, 60.08; H, 7.34.

Data for **4** are as follows.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.23 (d,  $^3\text{J}_{\text{HP}} = 15.6$  Hz, Me Cp\*), 1.31 (t, Me OEt), 1.60 (s, Me Cp\*), 1.67 (s, Me Cp\*), 2.21 (s, Me phosphole), 2.22 (s, Me phosphole), 4.08 and 4.21 (2 m,  $\text{OCH}_2$ ).  $^{13}\text{C}$ NMR( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  10.63 (s, Me Cp\*), 10.77 (d,  $\text{J}_{\text{CP}} = 5.8$  Hz, MeCp\*), 14.09 (s, Me OEt), 15.30 (s, Me phosphole), 18.84 (d,  $^2\text{J}_{\text{CP}} = 12.5$  Hz, Me-C-P), 60.57 (s,  $\text{OCH}_2$ ), 133.52 (s, =C Cp\*), 135.98 (d,  $^1\text{J}_{\text{CP}} = 9.6$  Hz, C-P), 139.74 (s, =C Cp\*), 153.38 (d,  $^2\text{J}_{\text{CP}} = 8.6$  Hz,  $\text{C}\beta$ ), 166.07 (d,  $^2\text{J}_{\text{CP}} = 19.2$  Hz, CO).  $^{31}\text{P}$ NMR( $\text{CD}_2\text{Cl}_2$ )  $\delta$  29.7. Exact mass:m/z calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_4\text{P}$  391.2038, found 391.2043.

### **2,5-Dibenzoylphosphaferrocene 5.**

1-Phenyl-3,4-dimethylphosphole (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After excess lithium was removed, the solution was treated with tert-butyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Benzoyl chloride (0.7 mL, 5.32 mmol) was added dropwise at -78 °C. The solution was warmed to room temperature and stirred for 20 min. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of benzoyl chloride (0.7 mL, 5.32 mmol) was added at -78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 60 °C for 2.5 h. The solution was cooled to 0 °C, ZnCl<sub>2</sub> (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. The resulting 2,5-bifunctional phospholide solution was treated in the same manner as for 3. Purification was performed via cold column chromatography on silica using 1:1 dichloromethane hexanes. A red band was collected and, on concentration, 900 mg (1.76 mmol) of a red oil (5) was obtained in 33% yield.

Data for **5** are as follows. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.61 (s, 15H, Me), 2.19 (s, 6H, Me), 7.38 (t, 4H meta), 7.48 (t, 2H para), 7.74 (d, 4H ortho). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.24 (s, Me Cp\*), 12.83 (s, Me phosphole), 85.27 (s, C Cp\*), 92.45 (d, <sup>1</sup>J<sub>PC</sub> = 61.2 Hz, C-P), 98.60 (d, <sup>2</sup>J<sub>PC</sub>=5.4Hz,Cβ), 127.74 (s, CH *meta*), 128.81 (d, J<sub>PC</sub>= 6.5 Hz, CH *ortho*), 131.47 (s, CH *para*), 141.88 (s, C *ipso*), 200.33 (d, <sup>2</sup>J<sub>PC</sub>=20.4Hz, CO).

<sup>31</sup>PNMR(CD<sub>2</sub>Cl<sub>2</sub>) δ-17.5. Exact mass: m/z calculated for C<sub>30</sub>H<sub>32</sub>FeO<sub>2</sub>P 511.1489, found 511.1475.

**2,2',5,5'-Tetrapivaloyl-1,1'-diphosphaferrrocene 6.**

1-Phenyl- 3,4-dimethylphosphole (1 g, 5.32 mmol) in dry THF (15 mL) was allowed to react with an excess of lithium wire for 5 h at room temperature. After excess lithium was removed, the solution was treated with tert-butyl chloride (0.6 mL, 5.32 mmol) and heated to 60 °C for 1 h. Pivaloyl chloride (0.7 mL, 5.32 mmol) was added dropwise at -78 °C. The solution was warmed to room temperature and stirred for 20 min. tBuOK was added (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was heated at 60 °C for 2 h. Another 1 equiv of pivaloyl chloride (0.7 mL, 5.32 mmol) was added at -78 °C, immediately followed by addition of another 1 equiv of tBuOK (0.597 g, 5.32 mmol) at 0 °C. The resulting mixture was stirred at 60 °C for 2.5 h. The solution was cooled to 0 °C, ZnCl<sub>2</sub> (1.450 g, 10.63 mmol) was added, and the mixture was stirred at room temperature for 30 min. The resulting 2,5-bifunctional phospholide solution was treated in the same manner as for **3**. Purification was performed via cold column chromatography on silica using 3:1 dichloromethanehexanes. An orange band was first collected. After concentration, 50 mg (0.11 mmol) of an orange solid (**7**) was obtained in 2% yield. A second red band corresponding to the diphosphaferrrocene **6** was collected and, on concentration, 320 mg (0.52 mmol) of a red solid was obtained in 20% yield. The product was crystallized by slow evaporation of hexanes. For the optimized synthesis of **6**, the initial preparation

of the 2,5-diacylphospholide was identical. After the addition of ZnCl<sub>2</sub>, FeCl<sub>2</sub> (0.335 g, 2.66 mmol) was added at room temperature. The solution was stirred for 18 h at room temperature. The crude solution mixture was filtered through silica and concentrated. Purification was performed via column chromatography on silica using 3:1 dichloromethane-hexanes. The red band was collected and, on concentration, 1.311 g (2.136 mmol) of a red solid (**6**) was obtained in 80% yield.

Data for **6** are as follows. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.16 (s, 36H, Me <sup>t</sup>Bu), 1.99 (s, 12H, Me phosphole). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 12.99 (s, Me phosphole), 27.15 (s, Me <sup>t</sup>Bu), 45.39 (s, C <sup>t</sup>Bu), 98.79 (d, 1J<sub>PC</sub>=72.5 Hz, C-P), 102.19 (d, 2J<sub>PC</sub>=3.8 Hz, Cβ), 210.41 (d, 2J<sub>PC</sub> = 16.3 Hz, CO). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -61.3.

Exact mass: m/z calcd for C<sub>32</sub>H<sub>49</sub>FeO<sub>4</sub>P<sub>2</sub>: 615.2456, found 615.2466. Anal. Calculated for C<sub>32</sub>H<sub>48</sub>FeO<sub>4</sub>P<sub>2</sub>: C, 62.54; H, 7.87; Found: C, 62.85; H, 8.14.

Data for **7** are as follows. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.21 (s, Me <sup>t</sup>Bu), 1.62 (s, Me Cp\*), 2.04 (s, Me phosphole). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.52 (s, Me Cp\*), 12.05 (s, Me phosphole), 27.63 and 27.71 (2s Me <sup>t</sup>Bu), 45.69 (s, C <sup>t</sup>Bu), 84.72 9 (s, C Cp\*), 91.22 (d, <sup>1</sup>J<sub>PC</sub>=66.7 Hz, C-P), 99.50 (d, <sup>2</sup>J<sub>PC</sub>=4.8 Hz, Cβ), 211.78 (d, <sup>2</sup>J<sub>PC</sub> = 16.8 Hz, CO). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ -66.3. Exact mass: m/z calculated for C<sub>26</sub>H<sub>40</sub>FeO<sub>2</sub>P 471.2115, found 471.2109.

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11. Supporting Information Available: CIF files giving X-raycrystal structure analyses of compounds 3, 4, and 6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## CHAPTER 3

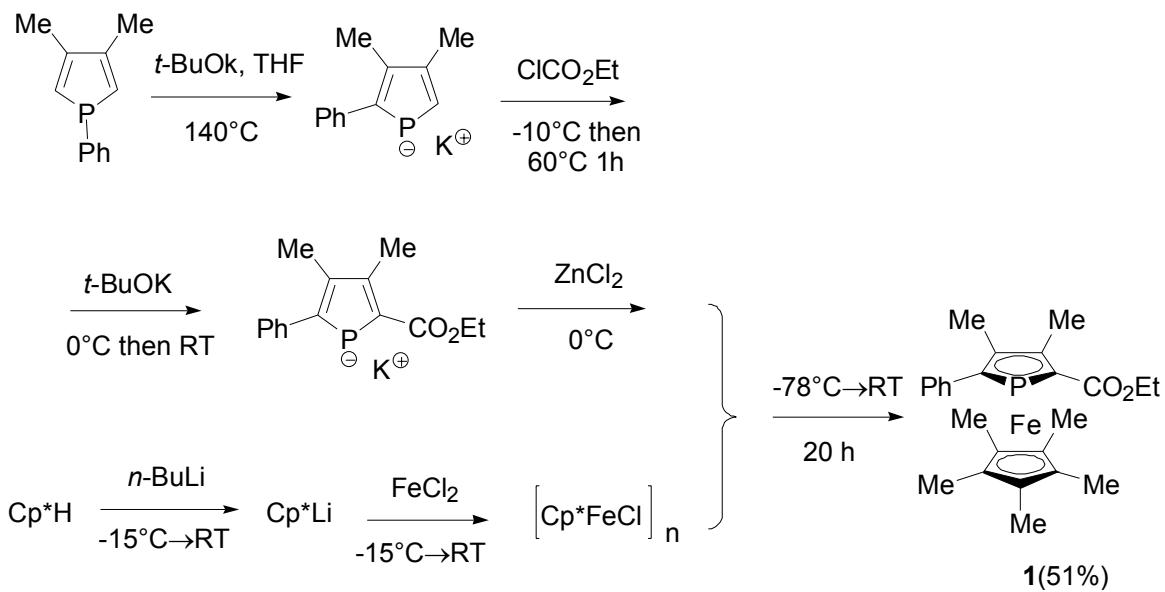
### A New *P,N*-Chelating Ligand Combining Phosphaferrocene and Azacymantrene Units

*P,N*-Chelating ligands deriving from phosphaferrocenes have proven their worth in asymmetric catalysis since the work of Fu on phosphaferrocene-oxazolines.<sup>1,2</sup> Other nitrogen heterocycles such as pyridines, pyrazoles and imidazoles<sup>3-6</sup> have also been combined with phosphaferrocenes in such chelating systems.

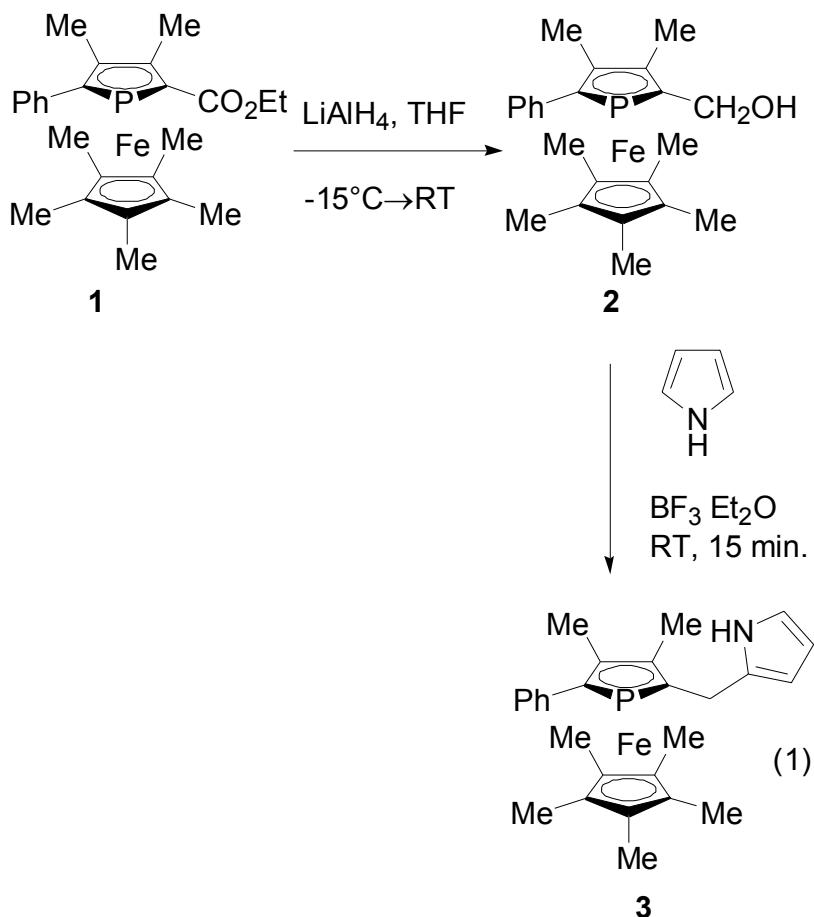
We began by exploring the possibility of combining phosphaferrocenes and azaferrocenes since both molecules have previously been used in asymmetric catalysis. Our attempts to combine the two molecules however were met with great disappointment. The classical conditions to form azaferrocene from a substituted pyrrole require a strong base to deprotonate that would destroy the phosphaferrocene unit as they are sensitive to nucleophilic attack. Experiments using  $[Fe(CO)_2Cp]_2$  as a neutral source of making the azaferrocene unit was unsuccessful as well. Azacymentrene can be easily made under neutral conditions using  $Mn_2(CO)_{10}$ . Chapter 3 describes and characterizes the structure of another member of the P-N chelating family based on phosphaferrocenes and azacymantrenes. The use of azacymantrenes offers additional possibilities in asymmetric catalysis resulting from the combination of their own planar chirality with that of phosphaferrocenes..

## Results and Discussion

We started from the functional phosphaferrocene (**1**) synthesized as shown in Scheme (1). The phenyl substitution is needed for improving the stability of the system. The phospholide ions resulted from the successive [1,5] shifts of phenyl and ethoxycarbonyl substituents as described in the literature.<sup>7</sup> Phosphaferrocene (**1**) was then converted into its pyrrolylmethyl derivative (**3**) as shown in scheme 3.1. The yield of the conversion of (**1**) into (**3**) was satisfactory (61%).

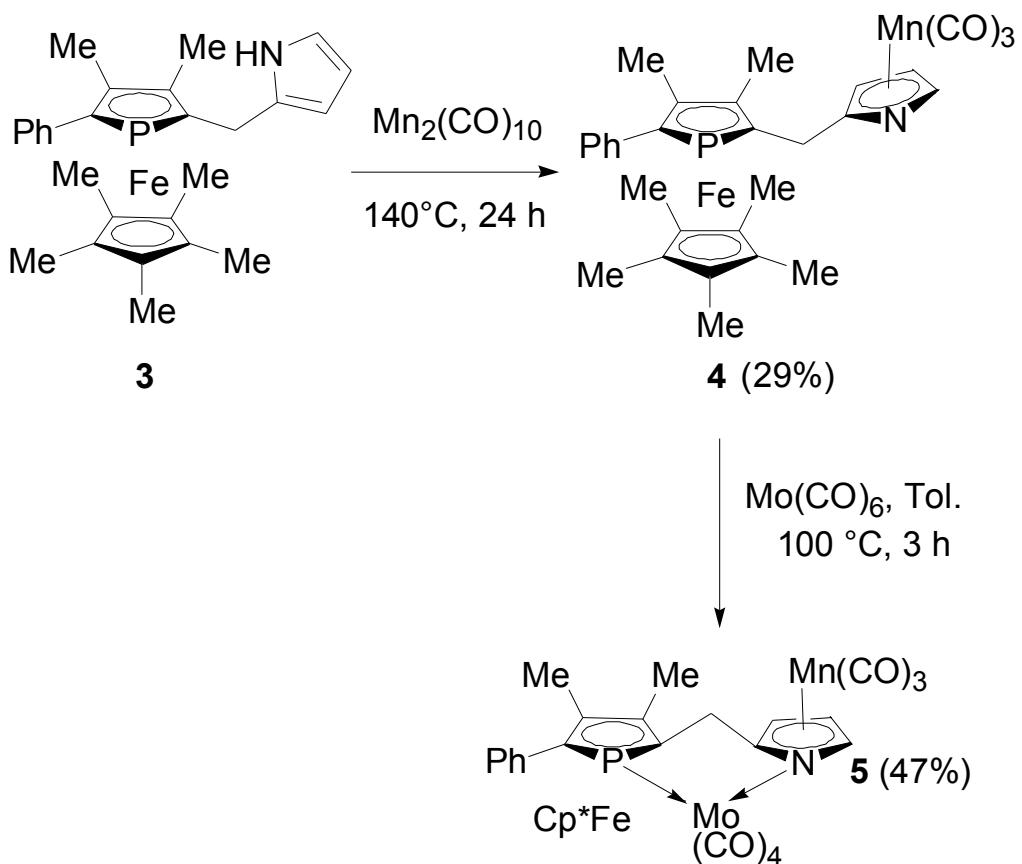


Scheme 3.1: Synthesis of the starting phosphaferrocene



Scheme 3.2: Synthesis of pyrrolylmethyl-phosphaferrocene **3**

All our attempts at synthesizing  $\eta^5$ -pyrrolyl complexes through the pyrrolide ion failed probably because the phosphaferrocene unit is poorly stable in nucleophilic media. We were finally successful when using the direct reaction of (**3**) with manganese carbonyl (scheme 3.2).



Scheme 3.3: Synthesis of azacymantrenylmethyl-phosphaferrrocene Mo complex **5**

Azacymantrenylmethyl-phosphaferrrocene (**4**) easily gives a molybdenum chelate (**5**) that was characterized by X-ray crystal structure analysis (figure 3.1). This structure gave us a lot of information on the ligating properties of (**4**). There is some strain in the chelate ring as indicated by the reduction of the tetrahedral angle at the  $\text{CH}_2$  bridge down to 106.5 deg. and the decrease of the P-Mo-N angle from 90 to 80.5 deg. This strain is accommodated by the deviation of the P-Mo bond from the P-lone pair axis by 16.5 deg. and the N-Mo bond from the N-lone pair axis by only 3.5 deg. This result clearly shows that the P-lone pair is

much less directional than the N-lone pair. A similar finding has been very recently reported in the literature for chelates derived from a 2(2-pyridyl)phosphinine.<sup>8</sup> Also noteworthy is the fact that N is planar ( $\Sigma$  angles at N 358.1 deg.) whereas P is slightly pyramidal ( $\Sigma$  angles at P 352.2 deg.). As a general rule,  $\eta^5$ -phospholyl complexes are weaker donors and better acceptors than the corresponding  $\eta^5$ -pyrrolyl complexes. But it is known that the ancillary ligands play a major role in the nucleophilicity of these complexes. For example, azacymantrene is protonated at manganese<sup>9</sup> whereas, upon replacement of one CO by one triphenylphosphine, the protonation takes place at nitrogen.<sup>10</sup> In our case, using the lengthening of the Mo-*trans*-CO bond as a criterion, it seems clear that P is a better donor than N (1.976(2) vs. 1.964(2) Å) and this is probably due to the presence of the Cp\* ligand.

It is likely that a ligand such as (4) can find some use in catalysis, but not only. The recent discovery that phosphaferrocene complexes can have interesting nonlinear optical properties<sup>11</sup> adds another possibility of application.

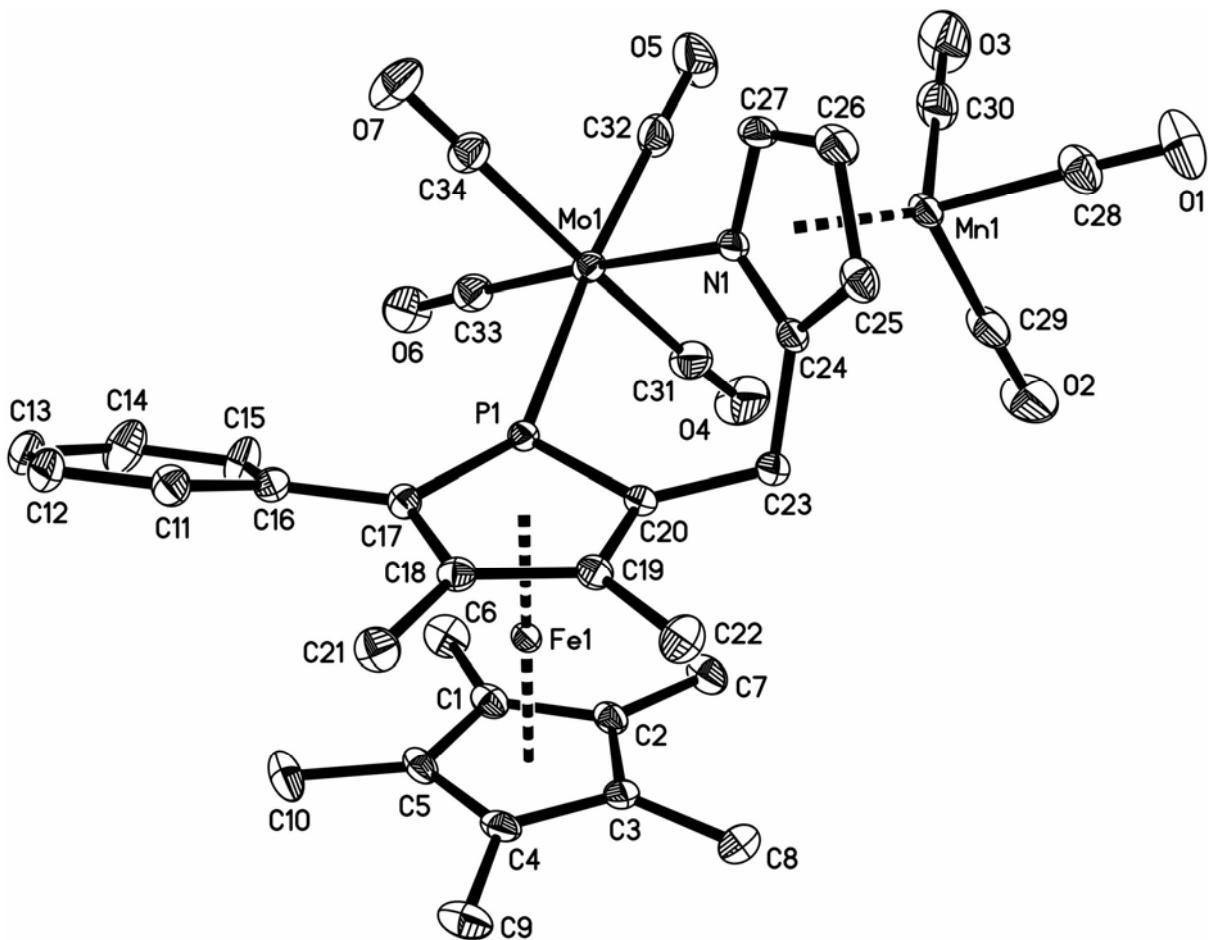


Figure 3.1: X-ray crystal structure of chelate (**5**). Selected bond lengths (Å) and angles (deg.): P1-Mo1 2.5143(5), N1-Mo1 2.3210(18), Mo1-C32 1.976(2), C32-O5 1.158(3), Mo1-C33 1.964(2), C33-O6 1.156(3); P1-Mo1-N1 80.48(4), C17-P1-C20 91.49(9), C24-N1-C27 105.85(17), C20-C23-C24 106.51(16).<sup>13</sup>

## Experimental section

All reactions were performed under nitrogen using solvents purified and dried by standard standards. Nuclear magnetic resonance spectra were obtained using JEOL ECA 400, or Bruker AV400 spectrometer operating at 400 MHz for <sup>1</sup>H,

100.56 MHz for  $^{13}\text{C}$  and 161.89 MHz for  $^{31}\text{P}$ . Chemical shifts are expressed in parts per million downfield from internal TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ). All coupling constants ( $J$  values) are reported in hertz (Hz). MS spectra were obtained in ESI mode on a Thermo Finnigan LCQ DECA XP MAX. X-ray crystallographic analyses were performed on a Bruker X8 APEX diffractometer. 3,4-dimethyl-1-phenylphosphole was prepared according to the literature<sup>12</sup>. Pyrrole was distilled before use. Other reagents were commercially available and used without further purification.

#### *Synthesis of phosphaferrocene (1)*

A mixture of 3,4-dimethyl-1-phenylphosphole (2 g, 10.6 mmol) and *t*-BuOK (1.44 g, 12.7 mmol) in THF (10 mL) were stirred in a pressure tube for 14 h at 140 °C ( $^{31}\text{P}$  NMR:  $\delta = +70.1$  ppm). The brown solution was transferred to a two-neck round bottom flask and ethyl chloroformate (1.4 g, 12.7 mmol.) was added slowly to the solution at -10 °C. The reaction mixture was stirred at room temperature for 20 min and then heated to 60 °C for 1 h. *t*-BuOK (1.49 g, 13.3 mmol.) was added to the mixture at 0 °C and the mixture was stirred at room temperature for 3 h ( $^{31}\text{P}$  NMR:  $\delta = +106.9$  ppm).  $\text{ZnCl}_2$  (1.81 g, 13.3 mmol.) was added to the phospholide solution at 0 °C. The mixture stirred at 0 °C for 5 min and then at room temperature for 30 min. In a separate flask,  $\text{Cp}^*\text{Li}$  was prepared by adding *n*-BuLi (5.2 mL, 8.2 mmol.) to 1,2,3,4,5-pentamethylcyclopentadiene (1.25 mL, 8 mmol.) in dry THF at -15 °C and stirred at -15 °C for 5 min then at room

temperature for 30 min. The suspension solution of Cp<sup>\*</sup>Li was then added quickly to the FeCl<sub>2</sub> solution in THF at -15 °C. The mixture was left to stir at room temperature for 30 minutes to obtain [Cp<sup>\*</sup>FeCl]<sub>n</sub>. The phospholide/ZnCl<sub>2</sub> solution was then added dropwise to the dark green [Cp<sup>\*</sup>FeCl]<sub>n</sub> solution at -78 °C and the resulting mixture was slowly warmed to room temperature and stirred at room temperature for 20 h. Purification was performed via cold column chromatography on silica using 2:1 hexane-dichloromethane. The orange-red band collected gives a red solid (2.44 g, 5.42 mmol.) and the yield was 51% from 3,4-dimethyl-1-phenylphosphole.

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -39.5. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.27 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.57 (s, 15H, CH<sub>3</sub>), 2.10 (s, 3H, CH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 4.04-4.18 (m, 2H, OCH<sub>2</sub>), 7.08-7.35 (m, 5H Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 9.64 (s, Cp<sup>\*</sup> Me), 12.74 (s, Me), 13.55 (s, Me), 14.43 (s, Me), 59.86 (s, O-CH<sub>2</sub>), 79.04 (d, <sup>1</sup>J<sub>CP</sub> = 55.5 Hz, =C-P), 83.51 (s, Cp<sup>\*</sup> C), 93.39 (d, <sup>2</sup>J<sub>CP</sub> = 5.8 Hz, =C-Me), 95.81 (d, <sup>2</sup>J<sub>CP</sub> = 5.0 Hz, =C-Me), 102.56 (d, <sup>1</sup>J<sub>CP</sub> = 53.5 Hz, =C-P), 125.73 (s, Ph CH para), 127.75 (s, Ph CH), 129.54 (d, <sup>3</sup>J<sub>CP</sub> = 9.5 Hz, Ph CH), 139.05 (d, <sup>2</sup>J<sub>CP</sub> = 17.8 Hz, Ph C ipso), 172.97 (d, <sup>2</sup>J<sub>CP</sub> = 17.9 Hz, C=O).

HRMS calculated for C<sub>25</sub>H<sub>32</sub>O<sub>2</sub>PFe (M+H)<sup>+</sup> 451.1498, found 451.1489.

### *Synthesis of phosphaferrocene (**3**)*

Lithium aluminium hydride (80 mg, 2 mmol.) was added to 2-phenyl-5-ethoxycarbonylphosphaferrocene **1** (450 mg, 1 mmol.) in dry THF (10 mL) at -15

°C. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. Excess LiAlH<sub>4</sub> was quenched with a little ethyl acetate and two drops of deionised water. The solvents were evaporated and the resulting precipitate was dissolved in freshly distilled pyrrole (10 mL). BF<sub>3</sub>·OEt<sub>2</sub> (0.13 mL, 1 mmol.) was added to the pyrrole solution and the mixture was stirred for 15 min and a little triethylamine was then added. Purification was performed via cold column chromatography on silica using 20:1 hexane-ethyl acetate. The dark orange band collected gives red oil (279 mg, 0.61 mmol.) and the yield was 61%.

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -53.4. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.70 (s, 15H, Me Cp\*), 1.95 (s, 3H, Me), 2.17 (s, 3H, Me), 3.31-3.47 (m, 2H, CH<sub>2</sub>), 5.89-5.90 (t, 1H, CH), 6.04-6.06 (m, 1H, CH), 6.55-6.57 (m, 1H, N-CH), 7.10-7.14 (m, 1H Ph), 7.20-7.24 (m, 2H, Ph), 7.40-7.43(t, 2H, Ph), 7.91 (s, 1H, N-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.20 (s, Cp\* Me), 11.62 (s, Me), 14.27 (s, Me), 26.59 (d, <sup>2</sup>J<sub>CP</sub> = 22.1 Hz, CH<sub>2</sub>), 82.41 (s, Cp\* C), 89.60 (d, <sup>2</sup>J<sub>CP</sub> = 4.0 Hz, =C-Me), 93.47 (d, <sup>2</sup>J<sub>CP</sub> = 5.0 Hz, =C-Me), 94.92 (d, <sup>1</sup>J<sub>CP</sub> = 54.3 Hz, =C-P), 97.01 (d, <sup>1</sup>J<sub>CP</sub> = 53.3 Hz, =C-P), 104.99 (s, Py CH), 108.02 (s, Py CH), 116.31 (s, Py CH), 125.17 (s, Ph CH *para*), 127.72 (s, Ph CH), 129.28 (d, <sup>3</sup>J<sub>CP</sub> = 10.1 Hz, Ph CH), 131.41 (s, Py C), 140.25 (d, <sup>2</sup>J<sub>CP</sub> = 17.1 Hz, Ph C *ipso*).

HRMS calcd for C<sub>27</sub>H<sub>32</sub>NPF<sub>2</sub> (M+H)<sup>+</sup> 458.1698, found 458.1700.

#### *Synthesis of phosphaferrocene (**4**)*

Phosphaferrocene **3** (338 mg, 0.74 mmol.) and Mn<sub>2</sub>(CO)<sub>10</sub> (293 mg, 0.75 mmol.) were dissolved in dry toluene in a sealed tube. The mixture was heated at 145 °C for 24 h. Purification was performed via cold column chromatography on silica using hexane and then 15:1 hexane-ethyl acetate. The pale orange band collected gives brown solid (130 mg, 0.21 mmol.) and the yield was 29 %.

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -54.2. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.70 (s, 15H, Cp\*), 2.04 (s, 3H, Me), 2.18 (s, 3H, Me), 3.27 (m, 2H, CH<sub>2</sub>), 5.00 (s, 1H Py), 5.02 (s, 1H, Py), 5.91 (1H, s, N-CH=C), 7.11-7.42 (m, 5H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.14 (s, Cp\* Me), 11.91 (s, Me), 14.23 (s, Me), 29.13 (d, <sup>2</sup>J<sub>CP</sub> = 21.7 Hz, -CH<sub>2</sub>-), 82.59 (s, Cp\* C), 89.47 (d, <sup>2</sup>J<sub>CP</sub> = 3.9 Hz, =C-Me), 93.43 (d, <sup>2</sup>J<sub>CP</sub> = 4.6 Hz, =C-Me), 94.37 (d, <sup>1</sup>J<sub>CP</sub> = 54.9 Hz, =C-P), 97.69 (d, <sup>1</sup>J<sub>CP</sub> = 53.5 Hz, =C-P), 104.88 (s, Py CH), 108.40 (s, Py CH), 116.40 (s, N-CH=C), 125.26 (s, Ph CH *para*), 127.71 (s, Ph CH), 129.26 (d, <sup>3</sup>J<sub>CP</sub> = 9.4 Hz, Ph CH), 130.90 (s, N-CR=CH), 139.90 (d, <sup>2</sup>J<sub>CP</sub> = 17.6 Hz, Ph C *ipso*), 223.17 (s, CO).

HRMS calcd for C<sub>31</sub>H<sub>35</sub>NO<sub>3</sub>P<sup>55</sup>MnFe (M+H)<sup>+</sup> 611.1084, found 611.1099.

### *Synthesis of chelate complex (**5**)*

A solution of phosphaferrocene **4** (178 mg, 029 mmol) and Mo(CO)<sub>6</sub> (80 mg, 0.3mmol) in toluene was stirred at 100 °C for 3 h. Purification was performed via cold column chromatography on silica using hexane-ethyl acetate(10:1 to 4:1). The pale orange band collected gives brown solid (111 mg, 0.135 mmol.) and the

yield was 47 %. Crystals of **5** were grown from a solution of the compound in dichloromethane/methanol.

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ -5.6. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.70 (s, 1H, Cp\*), 2.17 (s, 3H, Me), 2.28 (s, 3H, Me), 3.09-3.23 (m, 2H, CH<sub>2</sub>), 4.97 (s, 1H, Py), 5.14 (s, 1H, Py), 6.43 (s, 1H, N-CH=C), 7.15-7.43 (m, 5H, Ph).

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 10.21 (s, Cp\* Me), 11.84 (s, Me), 14.56 (s, Me), 26.16 (d, <sup>2</sup>J<sub>CP</sub> = 14.5 Hz, -CH<sub>2</sub>-), 82.53 (s, Py CH), 82.90 (d, J<sub>CP</sub> = 10.4 Hz, ), 84.04 (s, Cp\* C), 86.84 (s, Py CH), 88.02 (d, J<sub>CP</sub> = 5.2 Hz), 88.22 (d, J<sub>CP</sub> = 2.1 Hz), 91.83 (s, Py C) 112.13 (d, J<sub>CP</sub> = 4.2 Hz, Py CH), 124.02 (d, <sup>1</sup>J<sub>CP</sub> = 56.0 Hz), 125.95 (s, Ph CH *para*), 128.16 (s, Ph CH), 129.45 (d, <sup>3</sup>J<sub>CP</sub> = 4.5 Hz, Ph CH), 136.84 (d, <sup>2</sup>J<sub>CP</sub> = 14.5 Hz, Ph C *ipso*), 203.18 (d, J<sub>CP</sub> = 12.5 Hz, Mo CO), 203.18 (d, J<sub>CP</sub> = 12.5 Hz, Mo CO), 208.81 (d, J<sub>CP</sub> = 10.4 Hz, Mo CO), 214.90 (d, J<sub>CP</sub> = 41.5 Hz, Mo CO), 219.55 (d, J<sub>CP</sub> = 8.3 Hz, Mo CO), 220.60 (s, Mn CO)

HRMS calcd for C<sub>35</sub>H<sub>35</sub>NO<sub>7</sub>P<sup>55</sup>MnFe<sup>98</sup>Mo (M+H)<sup>+</sup> 820.9935, found 820.9938..

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13. X-ray crystal structure analysis of compound (**6**). This material is available free of charge via the internet at [pubs.acs.org](http://pubs.acs.org).

## Chapter 4

### Towards Phosphaferrocene Macrocycles

Macrocyclic ligands containing phosphorus have recently been the subject of much interest in coordination chemistry.<sup>1,2</sup> The incorporation of a phosphorus heteroatom allows for greater stabilization by increasing the number of available lone pairs for metal coordination. While phosphole containing macrocycles, such as calixphyrins, have recently found their way into literature, macrocycles containing phosphaferrocenes have been absent. This can be attributed to the lack of examples in literature of phosphaferrocene molecules containing handles to synthetically build macrocycles on the 2 and 5 position of the phosphole ring. Our previous work<sup>3a,b</sup> using substituted phospholide ions to make substituted phosphaferrocene and diphosphaferrocene molecules has expanded our arsenal of starting molecules on which to build upon:

1,1'-diphosphaferrocene macrocycles:

While ansa-ferrocene type bridged pyrrolic systems such as **1** have been shown to demonstrate electrochemical responsive receptor properties, it was not until 2007 when the group of Srinivasan<sup>5</sup> introduced the concept of incorporating the metallocene into the backbone of a macrocycle in an ansa-type way. The ansa-ferrocene and ruthenocene-based cyclic[2]pyrrole systems were synthesized by two different routes.

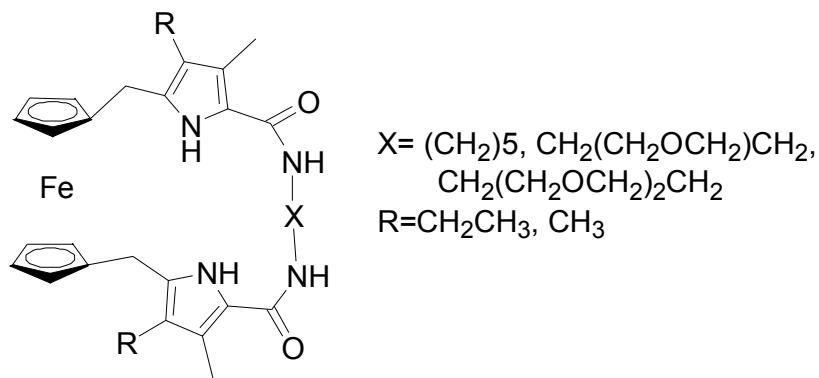
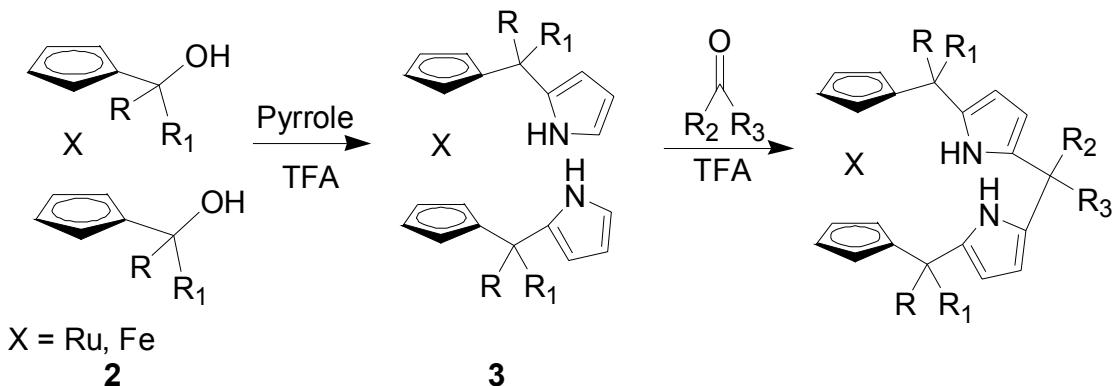
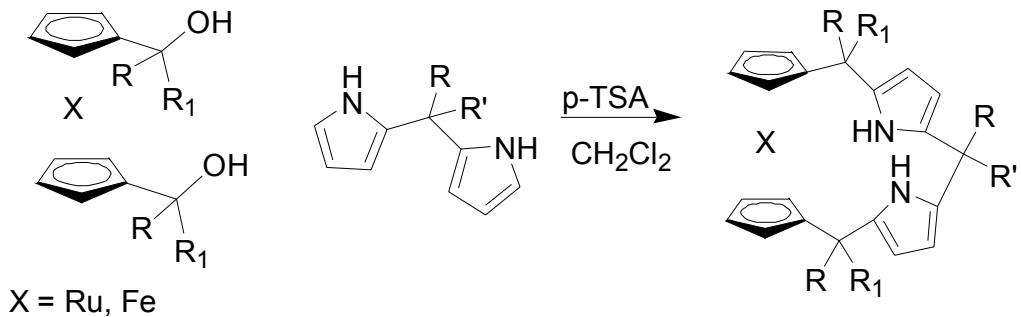


Figure 4.1: Ansa -ferrocene type bridged pyrrolic systems **1**

Route one, summarized in scheme 4.1, uses a 1,1'-bis(hydroxymethyl)metallocene (**2**), pyrrole, and an acid catalyst to make a dipyrromethane substituted metallocene **3**. The substituted metallocene **3** is then allowed to react with a variety of carbonyl containing compounds to make the desired macrocycles. Alternatively, a more straight forward route (scheme 4.2) condenses the 1,1'-bis(hydroxymethyl)metallocene **2** and a series of dipyrromethanes under acid catalyzed conditions to obtain the desired macrocycle.



Scheme 4.1: Synthesis of metallocene macrocycle from diol **2**



Scheme 4.2: Alternative route to transforming diol **2** into metallocene macrocycle

We decided that substituting a phosphaferrocene into this type of ansa-based cyclic[2]pyrrole system would be an ideal starting point for a phosphaferrocene based macrocycle. Two macrocyclic compounds were purposed: the first would be a pyrrole based phosphaferrocene (**3**) while the second would be crown ester based phosphaferrocene (**4**).

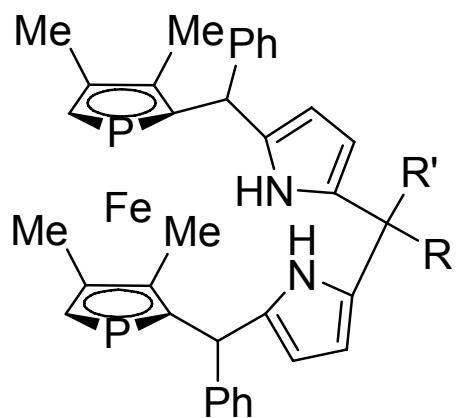


Figure 4.2: Pyrrole based phosphaferrocene macrocycle **3**

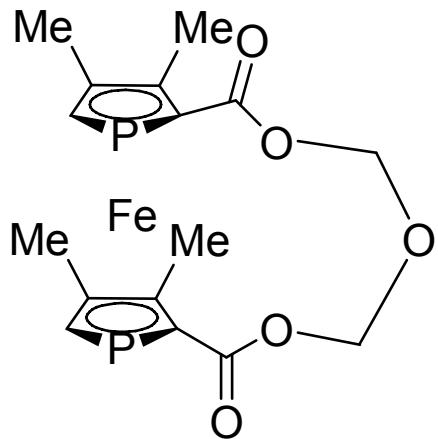
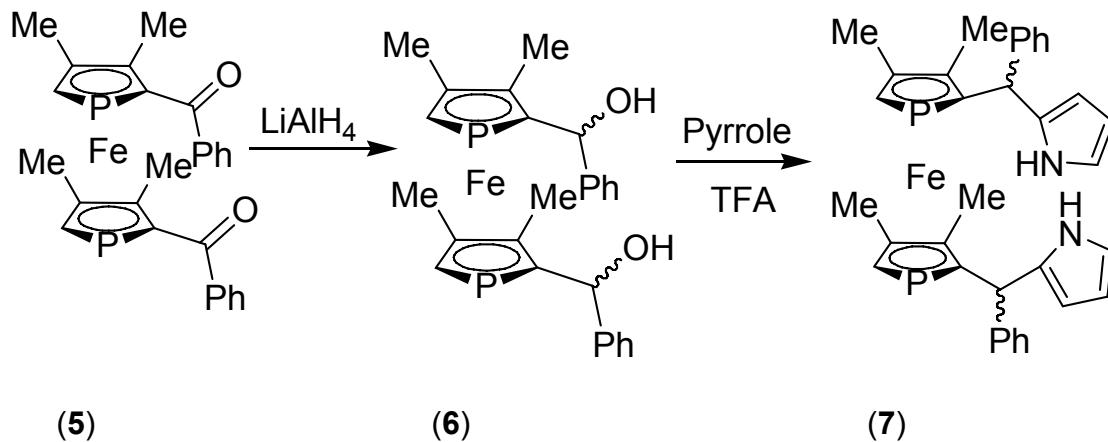


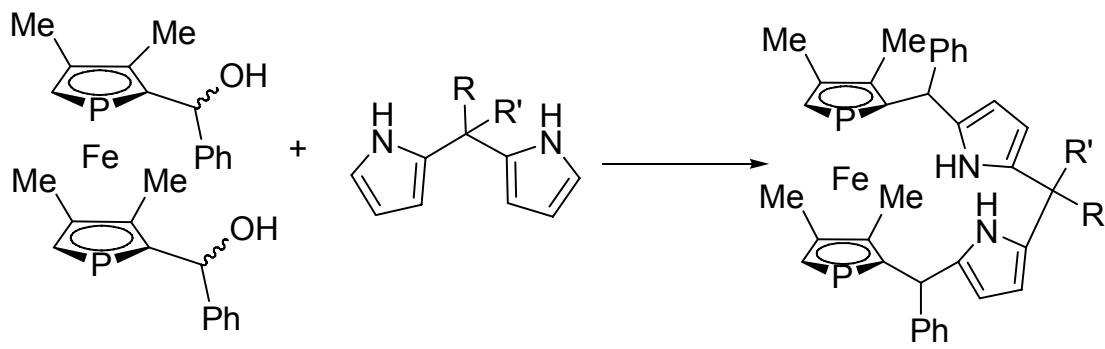
Figure 4.3: Crown ester based phosphaferrocene macrocycle **4**

The purposed synthetic scheme for synthesizing **3** starts from the meso isomer of the 3,3',4,4'-tetramethyl-2,2'-dibenzoyl-1,1'-diphosphafrocene **5**. The diketone can be reduced using lithium aluminum hydride to produce a mixture of isomeric alcohol products. The resulting mixture can be condensed with pyrrole to obtain the 2,2'-pyrrolyl(phenyl)methyl substituted phosphaferrocene **7**.



Scheme 4.3: Synthesis of 2,2'-pyrrolyl(phenyl)methyl substituted phosphaferrocene **7**.

Although we were successful at making target compound **7**, all attempts to close the ring using a ketone proved unsuccessful. We turned our focus to making the macrocycle from diol **6** using a dipyrromethane complex.

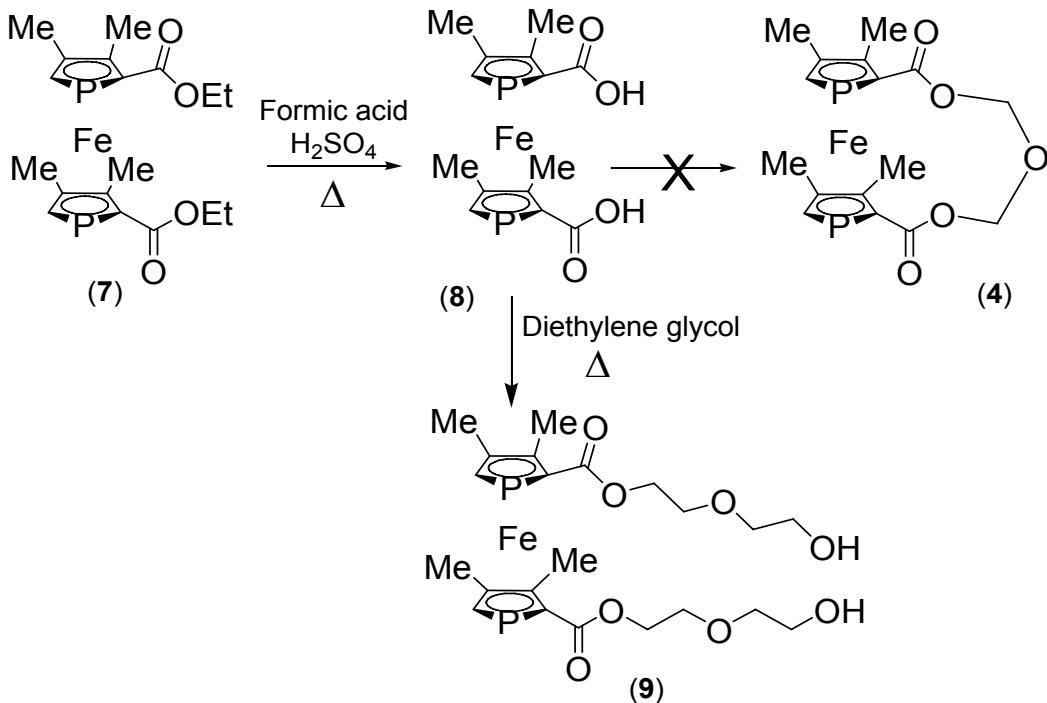


Scheme 4.4: Purposed synthesis of pyrrole based phosphaferrocene macrocycle **3** by utilizing diol **6**

Using a mixture of isomers of **6** and 5,5-dimethyl dipyrromethane<sup>6</sup>, we attempted to form the phosphaferrocene macrocycle **3** (scheme 4.4). The result was a complicated mixture of products that demonstrated extreme sensitivity towards air and acidic media. All attempts at purification failed to afford clean products. The project was refocused towards the crown ether substituted phosphaferrocene **4**. We hoped that by eliminating the pyrrole substituents, we would be able to make a lesser sensitive phosphorus containing macrocycle.

The path to obtaining **4** relied on the use of the meso isomer of 3,3',4,4'-tetramethyl-2,2'-bis(ethoxycarbonyl)-1,1'-diphosphaferrocene (**7**). Direct transesterification using diethylene glycol did not yield any products regardless of

reaction temperatures or lengthening reaction times. As an alternative approach, the bis(carboxylic acid) **8** was synthesized under acidic conditions from the bis(ethoxycarbonyl) phosphaferrocene. The bis(carboxylic acid) **8** is an orange solid with very low solubility in organic solvents. The results from the reaction of **8** with diethylene glycol were somewhat unexpected. Instead of forming the desired macrocycle **4**, the product formed was found to be a double diethylene glycol substituted diphosphapherrocene. It is worth mentioning that compound **9** was the only product recovered regardless of using less than 0.5 equivalents of diethylene glycol. The new product also demonstrated different solubility properties from the starting carboxylic acid derivative and only a slight shift in  $^{31}\text{P}$  (-43 ppm versus -50 ppm).



Scheme 4.5: Synthesis of ester based phosphaferrocene **9**

## 2, 5-diphosphapherrocene macrocycles

Our success at making the 2,5-disubstituted phosphapherrocene molecules allowed us to make our first attempts at substituting a phosphapherrocene into a planar macrocyclic ring structures such as crown ethers or porphyrin like calixpyrrole rings. The starting point for these types of molecules is the 2,5-bis(ethoxycarbonyl) phosphapherrocene **10** (figure 4.4).

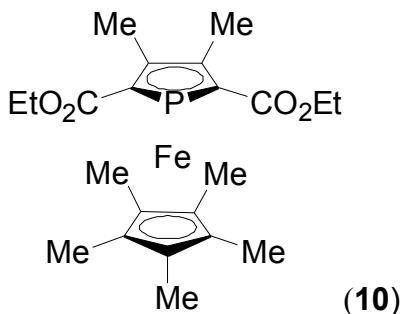
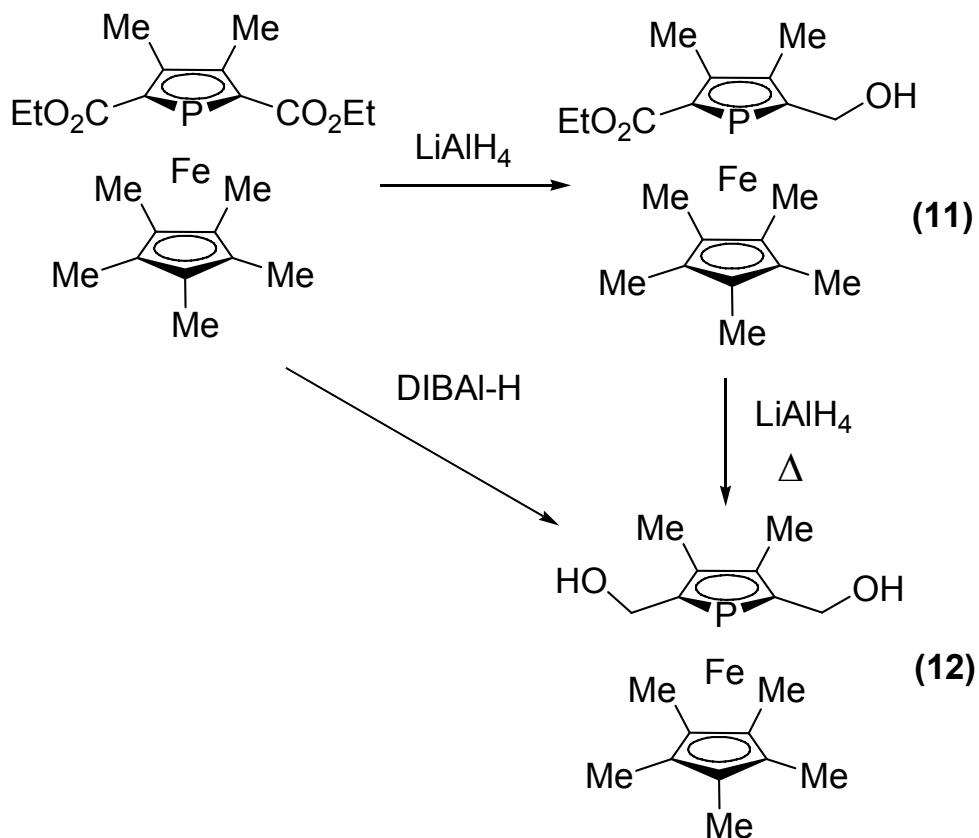


Figure 4.4: 2,5-Bis(ethoxycarbonyl) phosphapherrocene **10**

Attempts to reduce **10** into the corresponding diol revealed some information about the molecule. In contrast to the 3,3',4,4'-tetramethyl-2,2'-bis(ethoxycarbonyl)-1,1'-diphosphapherrocene (**7**) efforts to reduce using excess lithium aluminum hydride resulted in a drastic slowing in the conversion after the first carbonyl and produced stable product **11**. Forcing the reaction with longer reaction times and higher reaction temperatures affords the 2,5-bis(hydroxymethyl) product **12**, but the yield and purity of the product suffered. Product **12** was found to be much more sensitive to oxidation than the mono reduced counterpart **11**. It was later discovered that by changing the reducing

agent to diisobutylaluminium hydride, the reduction can take place under milder conditions with much short reaction times helping improve yield as well as limiting the number of side products. The 2,5-bis(hydroxymethyl) phosphaferrocene **12** could then become the starting point for two potential macrocyclic products.



Scheme 4.6: Synthesis of 2,5-bis(hydroxymethyl) phosphaferrocene **12**

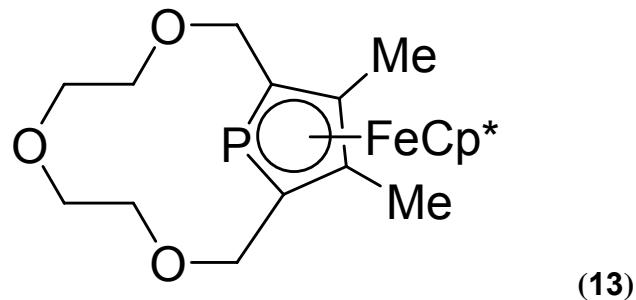


Figure 4.5: Phosphaferrocene substituted crown ether **13**

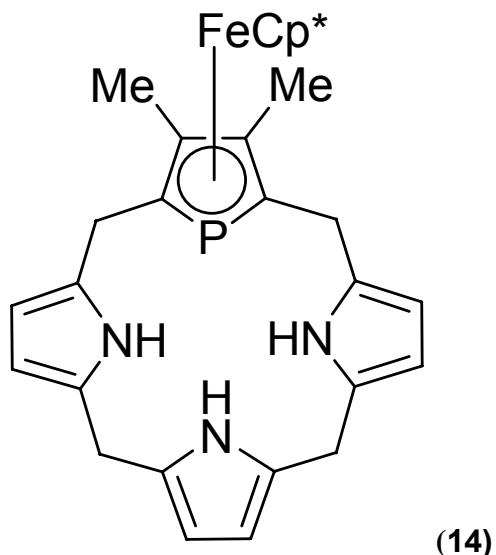
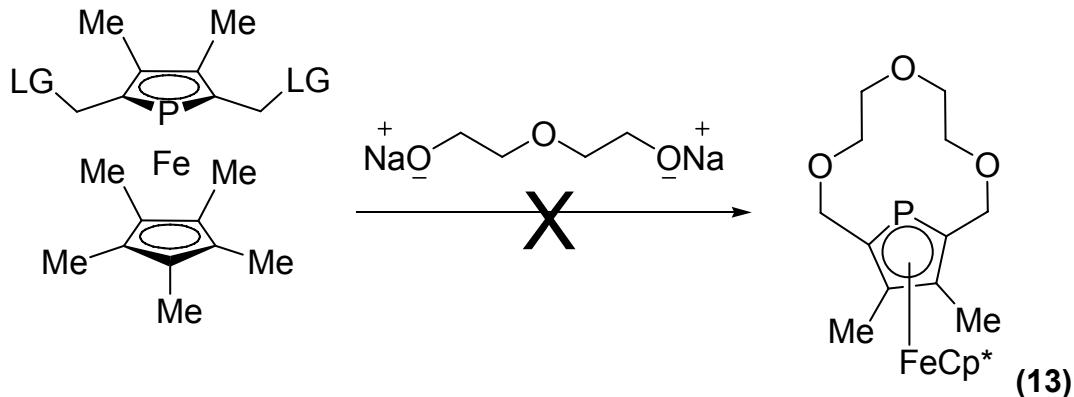


Figure 4.6: Phosphaferrocene substituted calixpyrrole **14**

Our previous work with pyrrole substitution on phosphaferrocenes led us to believe that working with the crown ether substituted phosphaferrocene **13** would be a satisfactory starting target. The strategy of making **13** was broken into two possibilities: either the alcohol groups could potentially be converted

into a leaving group or the second route would be to deprotonate the alcohol using a mild base and to react the dianion with a satisfactory electrophile.

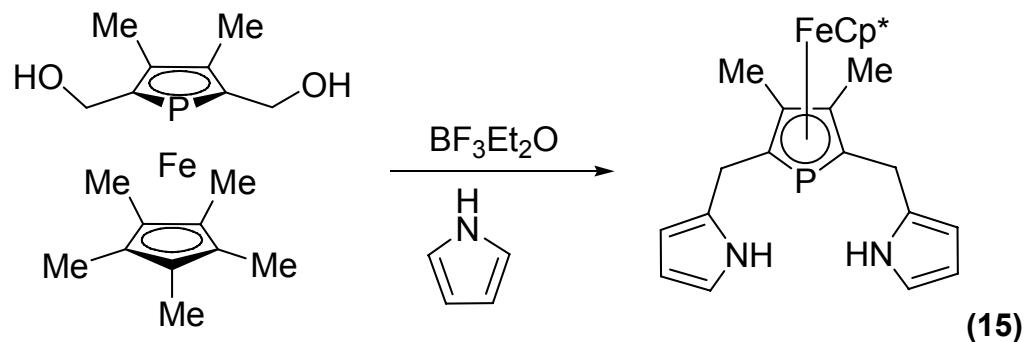
Our attempts at converting the alcohol into a better leaving group, even under mild tosylating conditions (scheme 4.7), proved to be unsuccessful. We turned our focus towards the alternative approach, deprotonation of the OH groups on the 2,5-bis(hydroxymethyl)phosphaferrocene. The phosphaferrocene's sensitivity to bases<sup>7</sup> led us to test various methods to deprotonate the alcohol group. Sodium hydride was found to be a suitable reagent for the deprotonation while not disturbing the phosphaferrocene unit but when used on the triflated derivative of diethylene glycol the result was an insoluble red polymer. Although rate of addition of the reagents, reaction time, and reaction temperatures were varied the results were consistent.



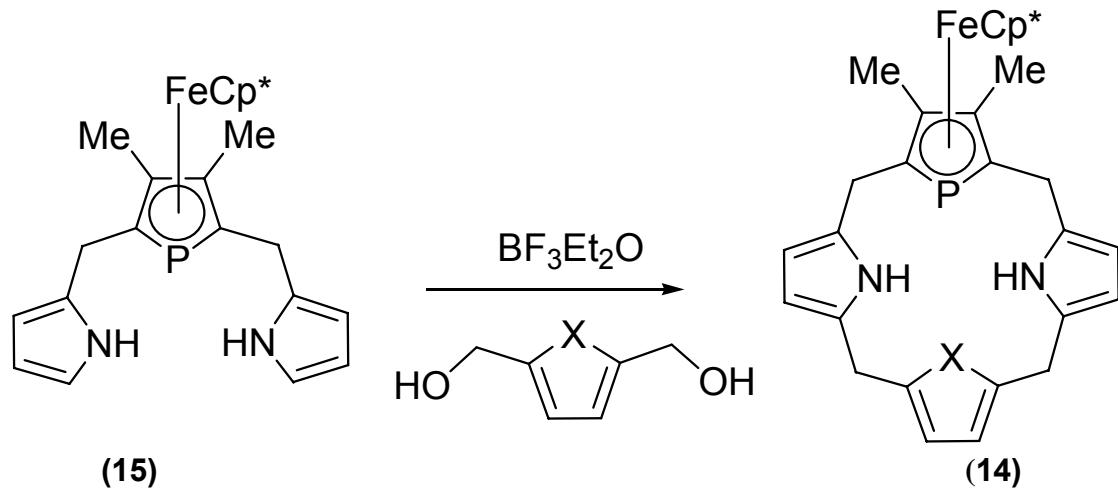
Scheme 4.7: Attempted synthesis of phosphaferrocene macrocycle **13**.

When looking toward the potential for a calixpyrrole type structure **14**, we looked to make the 2,5-bis(pyrrolylmethyl)phosphaferrocene (**15**) as an

intermediate compound. Our Intermediate compound **15** has the possibility of being incorporated into various mixed calixpyrrole systems as illustrated in scheme 4.9.



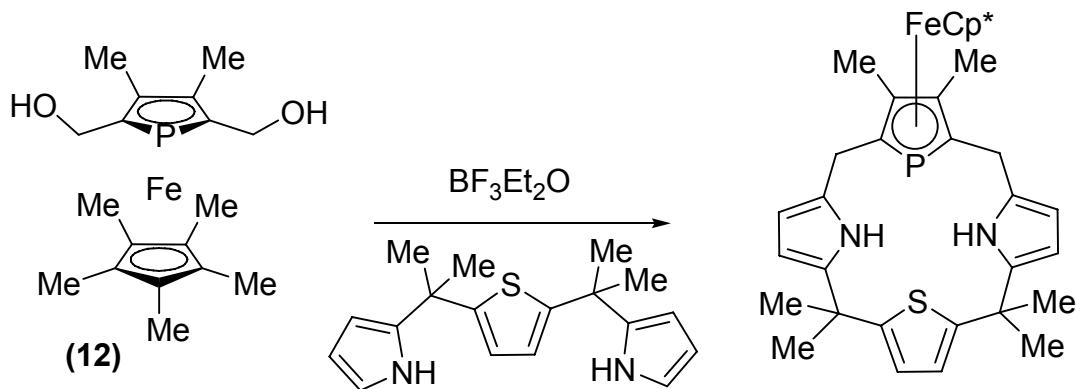
Scheme 4.8: Synthesis of 2,5-bis(pyrrolylmethyl)phosphaferrocene **15**.



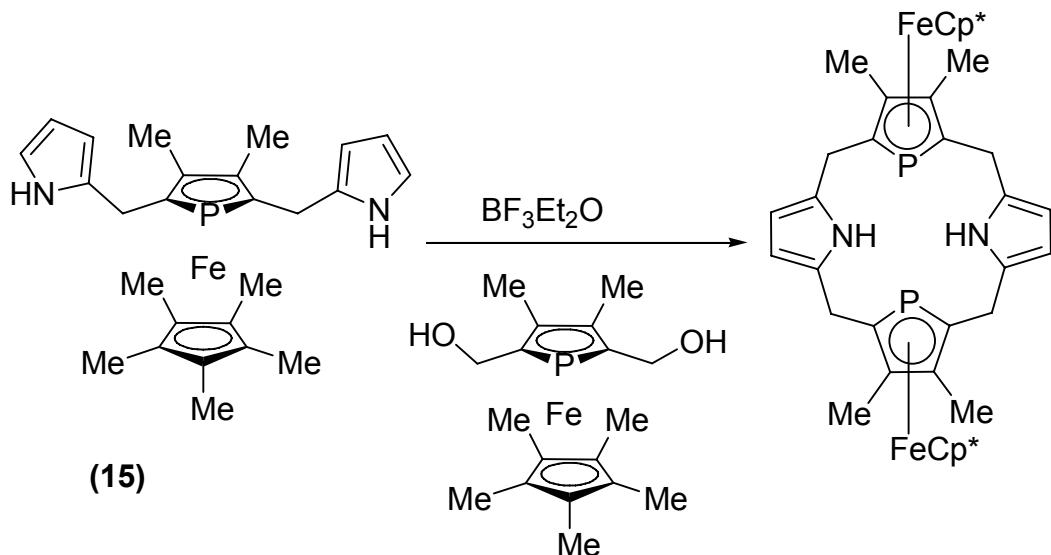
Scheme 4.9: Synthesis of phosphaferrocene substituted calixpyrrole **14**.

Current work in this field has most recently been reported by the Mathey group. In a recent publication<sup>8</sup> the use of 2,5-

bis(hydroxymethyl)phosphaferrocene (**12**) and 2,5-bis(pyrrolylmethyl)phosphaferrocene (**15**) were used to make the heteroatom substituted calixpyrroles as illustrated in figures 4.10 and 4.11 respectively. Studies of the resulting calixpyrroles are currently underway.



Scheme 4.10: Synthesis of heteroatom substituted calixpyrrole via 2,5-bis(hydroxymethyl)phosphaferrocene **12**.



Scheme 4.11: Synthesis of heteroatom substituted calixpyrrole via 2,5-bis(pyrrolylmethyl)phosphaferrocene **15**.

## Experimental Section

Nuclear magnetic resonance spectra were obtained on Bruker Avance 300 and Varian Inova spectrometers operating at 300.13 MHz for  $^1\text{H}$ , 75.45 MHz for  $^{13}\text{C}$ , and 121.496 MHz for  $^{31}\text{P}$ . A Bruker Avance 600 instrument was also used for  $^1\text{H}$  and  $^{13}\text{C}$  (150.925 MHz) spectra. Chemical shifts are expressed in parts per million downfield from external TMS ( $^1\text{H}$  and  $^{13}\text{C}$ ) and external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ).

### **3,3',4,4'-Tetramethyl-2,2'-pyrrolyl(phenyl)methyl-1,1' diphosphaferrocene 7.**

Lithium aluminum hydride (66mg, 1.7mmole) was added to the *meso* diastereomer of 3,3',4,4'-Tetramethyl-2,2'-dibenzoyl-1,1'-diphosphaferrocene **5** (0.7 mmole, 340mg) in dry THF (15 mL) at 0 °C. The mixture was warmed to room temperature and stirred for 3 hours. The solution was cooled to 0 °C, 1N HCl was added to quench excess  $\text{LiAlH}_4$ . The organic mixture was washed with brine and dried over sodium sulfate. The solvent were evaporated and the resulting precipitate was dissolved in freshly distilled pyrrole (7 mL) and allowed to stir at room temperature for 15 minutes.  $\text{BF}_3\cdot\text{OEt}_2$  (0.13 mL, 1 mmol.) was then added the pyrrole solution and the mixture was stirred for 3 hours at 60 °C. The solution was cooled to room temperature, 40 ml of methylene chloride and 40 ml of sodium bicarbonate were added. The aqueous layer was separated and extracted using methylene chloride. The organic layers were combined, washed with brine, dried over sodium sulfate, and concentrated. Purification was

performed via column chromatography on silica using 1:1 methylene chloride/petroleum ether solution. After concentration, a red oil was collected (120 mg, 0.20 mmol.), the yield was 29%.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -77.0  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.81 (s, 3H, Me), 2.13 (s, 3H, Me), 2.17 (s, 3H, Me), 3.14 ( $d, ^2J_{\text{HP}} = 36$  Hz, CH-P), 5.57 (broad s, 1H, pyrrole- $H_\beta$ ), 5.93-5.96 (m, 1H, pyrrole- $H_\beta$ ), 6.50-6.52 (m, 1H, N- $\text{CH}_\alpha$ ), 7.13-7.25(m, 5H, Ph), 7.75 (s, 1H, N-H).

### **2,5-bis(hydroxymethyl)phosphaferrrocene 12.**

DIBAL-H (0.5 mL, 20% in hexanes) was added to a solution of 2,5-bis(ethoxycarbonyl)phosphaferrrocene **10** (100 mg, 0.23 mmol) in THF (5 mL) at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 minutes. After removal of the solvent the solid was purified by cold column chromatography on silica using 3:1 ethyl acetate:hexanes. An orange solid was collected upon concentration (58 mg, 0.16 mmol.) the yield was 70%.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -61.7.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.74 (s, 15H,  $\text{CH}_3 \text{CP}^*$ ), 1.98 (s, 6H,  $\text{CH}_3$ ), 4.06-4.18 (m, 4H,  $\text{OCH}_2$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.56 (s,  $\text{Cp}^* \text{Me}$ ), 60.48 ( $d, ^2J_{\text{CP}} = 23.1$  Hz,  $\text{O-CH}_2$ ), 82.87 (s,  $\text{Cp}^* \text{C}$ ), 93.46 ( $d, ^2J_{\text{CP}} = 4.8$  Hz, =C-Me), 95.27 ( $d, ^1J_{\text{CP}} = 55.9$  Hz, =C-P).

HRMS: Calculated for  $\text{C}_{18}\text{H}_{28}\text{O}_2\text{PFe} (\text{M}+\text{H})^+$  363.1176. Found: 363.1172.

### **2,5-bis(pyrrolylmethyl)phosphaferrocene 15**

2,5-bis(hydroxylmethyl)phosphaferrocene 12 (100mg, .28mmole) was allowed to in 3 ml of freshly distilled pyrrole for 20 minutes.  $\text{BF}_3 \text{ OEt}_2$  (0.1ml) was added and the resulting solution was allowed to stir at room temperature for 30 minutes. 10 ml of methylene chloride and 10 ml of sodium bicarbonate were added. The aqueous layer was separated and extracted using methylene chloride. The organic layers were combined, washed with brine, dried over sodium sulfate, and concentrated. Purification was performed via cold column chromatography on silica using 1:2 methylene chloride/petroleum ether solution. After concentration, an orange oil was collected (51 mg, 0.11 mmol), the yield was 40 %.

$^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -63.3.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.83 (s, 15H, Me Cp\*), 1.89 (s, 6H, Me), 3.28-3.46 (m, 4H,  $\text{CH}_2$ ), 5.89 (s, 2H, CH), 6.07-6.09 (m, 2H, CH), 6.59-6.61 (m, 2H, N-CH), 7.88 (s, 2H, N-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.44 (s, Cp\* Me), 11.49 (s, Me), 26.54 (d,  $^2\text{JCP} = 22.2$  Hz,  $\text{CH}_2$ ), 82.38 (s, Cp\* C), 92.36 (d,  $^2\text{JCP} = 3.9$  Hz, =C-Me), 94.92 (d,  $^1\text{JCP} = 54.9$  Hz, =C-P), 105.01 (s, Py CH), 108.09 (s, Py CH), 116.42 (s, Py CH), 131.64 (s, Py C).

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## Appendix

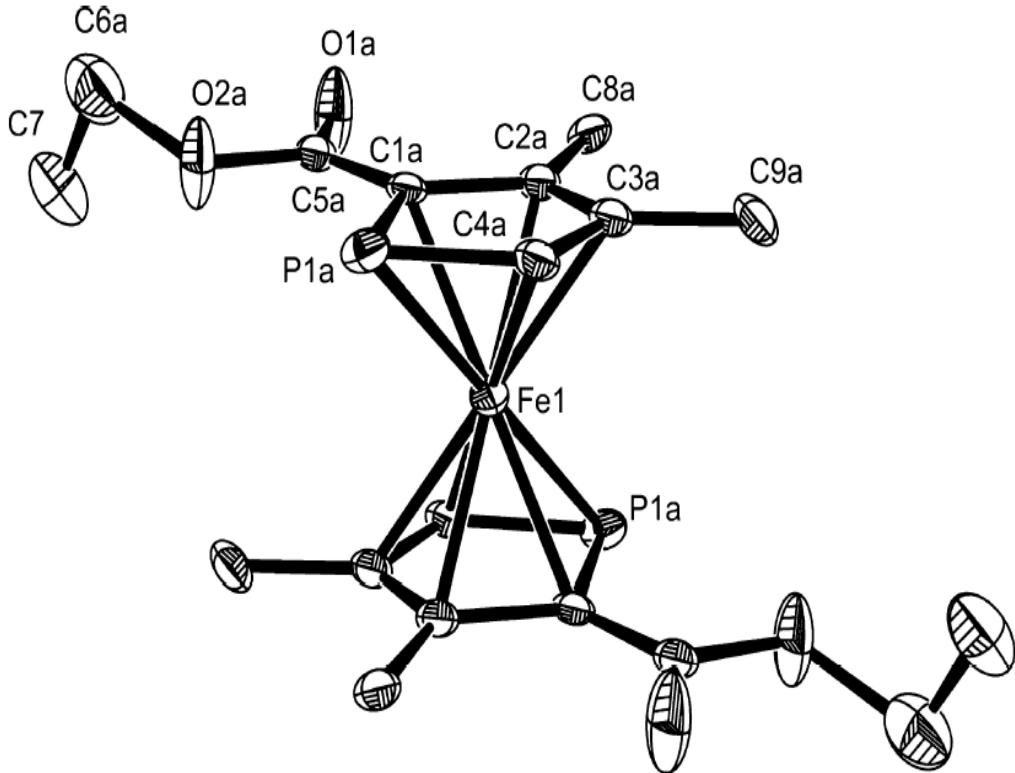


Table S1. Crystal data and structure refinement for: Compound **4a** Chapter 1.

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Empirical formula	$C_{18}H_{12}FeO_4P_2$		
Formula weight	207.05		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	$a = 6.796(5)$ Å	$\alpha = 90^\circ$	
	$b = 8.163(6)$ Å	$\beta = 96.360(9)^\circ$	
	$c = 16.939(13)$ Å	$\gamma = 90^\circ$	
Volume	$933.9(12)$ Å <sup>3</sup>		
Z	4		
Density (calculated)	1.473 Mg/m <sup>3</sup>		
Absorption coefficient	0.997 mm <sup>-1</sup>		
F(000)	424		

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Crystal size	0.12 x 0.01 x 0.01 mm3
Theta range for data collection	2.42 to 21.97°
Index ranges	-7<=h<=5, -8<=k<=8, -17<=l<=17
Reflections collected	3925
Independent reflections	1127 [R(int) = 0.0814]
Completeness to theta =	21.97° 98.5 %
Absorption correction	Sadabs
Max. and min. transmission	0.9931 and 0.8888
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	1127 / 235 / 214
Goodness-of-fit on $F^2$	1.107
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0751, wR2 = 0.1862
R indices (all data)	R1 = 0.1068, wR2 = 0.2018
Largest diff. peak and hole	0.518 and -0.519 e.Å <sup>-3</sup>

Table S2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å<sup>2</sup> x 103). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Fe(1)	10000	5000	0	28(1)
P(1A)	7510(80)	5590(50)	730(30)	26(6)
O(1A)	7070(30)	760(20)	173(10)	57(5)
O(2A)	7030(30)	2190(20)	1300(10)	55(6)
C(1A)	7420(90)	3640(30)	142(11)	24(3)
C(2A)	7550(40)	3944(19)	-694(10)	24(3)
C(3A)	7630(40)	5630(20)	-854(9)	25(3)
C(4A)	7680(50)	6590(30)	-184(11)	25(3)
C(5A)	7210(40)	2050(40)	496(19)	26(3)
C(6A)	6230(40)	600(30)	1718(14)	60(4)
C(8A)	7430(30)	2570(20)	-1310(10)	28(4)
C(9A)	7780(30)	6300(20)	-1681(9)	32(4)
P(1B)	7410(70)	5170(50)	770(30)	25(6)

O(1B)	7590(20)	881(17)	-319(9)	34(4)
O(2B)	7540(20)	1660(20)	942(12)	27(4)
C(1B)	7480(90)	3760(30)	29(11)	24(3)
C(2B)	7520(40)	4490(20)	-749(10)	25(3)
C(3B)	7700(40)	6210(20)	-685(10)	28(3)
C(4B)	7730(50)	6800(30)	63(12)	27(3)
C(5B)	7570(30)	1990(30)	151(13)	24(3)
C(6B)	7620(40)	-50(30)	1164(12)	55(4)
C(8B)	7450(30)	3500(20)	-1511(10)	29(4)
C(9B)	7800(30)	7300(20)	-1403(11)	35(4)
C(7)	7820(20)	-242(17)	2002(7)	67(3)

Table S3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

Fe(1)-C(1B)#1	2.00(5)	Fe(1)-C(1B)	2.00(5)
Fe(1)-C(2B)#1	2.04(3)	Fe(1)-C(2B)	2.04(3)
Fe(1)-C(4A)#1	2.04(3)	Fe(1)-C(4A)	2.04(3)
Fe(1)-C(3B)#1	2.09(2)	Fe(1)-C(3B)	2.09(2)
Fe(1)-C(3A)#1	2.11(2)	Fe(1)-C(3A)	2.11(2)
Fe(1)-C(1A)#1	2.11(5)	Fe(1)-C(1A)	2.11(5)
P(1A)-C(4A)	1.76(5)	P(1A)-C(1A)	1.87(5)
O(1A)-C(5A)	1.19(3)	O(2A)-C(5A)	1.39(3)
O(2A)-C(6A)	1.60(3)	C(1A)-C(5A)	1.44(4)
C(1A)-C(2A)	1.451(16)	C(2A)-C(3A)	1.407(18)
C(2A)-C(8A)	1.525(14)	C(3A)-C(4A)	1.374(18)
C(3A)-C(9A)	1.516(15)	C(6A)-C(7)	1.32(3)
P(1B)-C(1B)	1.71(6)	P(1B)-C(4B)	1.82(5)
O(1B)-C(5B)	1.21(3)	O(2B)-C(5B)	1.37(3)
O(2B)-C(6B)	1.44(3)	C(1B)-C(2B)	1.449(17)
C(1B)-C(5B)	1.45(3)	C(2B)-C(3B)	1.417(18)
C(2B)-C(8B)	1.519(14)	C(3B)-C(4B)	1.353(19)
C(3B)-C(9B)	1.515(15)	C(6B)-C(7)	1.42(2)
C(1B)#1-Fe(1)-C(1B)	180.000(2)	C(1B)#1-Fe(1)-C(2B)#1	42.1(8)

C(1B)-Fe(1)-C(2B)#1	137.9(8)	C(1B)#1-Fe(1)-C(2B)	137.9(8)
C(1B)-Fe(1)-C(2B)	42.1(8)	C(2B)#1-Fe(1)-C(2B)	180.0(9)
C(2B)-Fe(1)-C(4A)#1	122.4(9)	C(1B)#1-Fe(1)-C(4A)	108.9(15)
C(4A)#1-Fe(1)-C(4A)	180.000(2)	C(1B)#1-Fe(1)-C(3B)#1	70.3(12)
C(1B)-Fe(1)-C(3B)#1	109.7(12)	C(2B)#1-Fe(1)-C(3B)#1	40.2(6)
C(2B)-Fe(1)-C(3B)#1	139.8(6)	C(1B)#1-Fe(1)-C(3B)	109.7(12)
C(1B)-Fe(1)-C(3B)	70.3(12)	C(2B)#1-Fe(1)-C(3B)	139.8(6)
C(2B)-Fe(1)-C(3B)	40.2(6)	C(3B)#1-Fe(1)-C(3B)	180.000(2)
C(4A)#1-Fe(1)-C(3A)#1	38.7(6)	C(4A)-Fe(1)-C(3A)#1	141.3(6)
C(4A)#1-Fe(1)-C(3A)	141.3(6)	C(4A)-Fe(1)-C(3A)	38.7(6)
C(3A)#1-Fe(1)-C(3A)	180.000(1)	C(4A)#1-Fe(1)-C(1A)#1	73.3(13)
C(4A)-Fe(1)-C(1A)#1	106.7(13)	C(3A)#1-Fe(1)-C(1A)#1	68.0(11)
C(3A)-Fe(1)-C(1A)#1	112.0(11)	C(4A)#1-Fe(1)-C(1A)	106.7(13)
C(4A)-Fe(1)-C(1A)	73.3(13)	C(3A)#1-Fe(1)-C(1A)	112.0(11)
C(3A)-Fe(1)-C(1A)	68.0(11)	C(1A)#1-Fe(1)-C(1A)	180.0(10)
C(4A)-P(1A)-C(1A)	86(2)	C(4A)-P(1A)-Fe(1)	59.4(17)
C(1A)-P(1A)-Fe(1)	61(2)	C(5A)-O(2A)-C(6A)	116(2)
C(5A)-C(1A)-C(2A)	125(2)	C(5A)-C(1A)-P(1A)	123(2)
C(2A)-C(1A)-P(1A)	111.8(18)	C(5A)-C(1A)-Fe(1)	130(4)
C(2A)-C(1A)-Fe(1)	70.0(18)	P(1A)-C(1A)-Fe(1)	68.7(19)
C(3A)-C(2A)-C(1A)	111.3(12)	C(3A)-C(2A)-C(8A)	125.9(13)
C(1A)-C(2A)-C(8A)	122.6(13)	C(3A)-C(2A)-Fe(1)	70.2(12)
C(1A)-C(2A)-Fe(1)	70(2)	C(8A)-C(2A)-Fe(1)	131.2(19)
C(4A)-C(3A)-C(2A)	113.2(13)	C(4A)-C(3A)-C(9A)	124.2(14)
C(2A)-C(3A)-C(9A)	122.5(12)	C(4A)-C(3A)-Fe(1)	68.0(14)
C(2A)-C(3A)-Fe(1)	70.8(13)	C(9A)-C(3A)-Fe(1)	126.8(16)
C(3A)-C(4A)-P(1A)	117.6(19)	C(3A)-C(4A)-Fe(1)	73.3(13)
P(1A)-C(4A)-Fe(1)	72.4(19)	O(1A)-C(5A)-O(2A)	121(3)
O(1A)-C(5A)-C(1A)	128(3)	O(2A)-C(5A)-C(1A)	111(2)
C(7)-C(6A)-O(2A)	106(2)	C(1B)-P(1B)-C(4B)	90(2)
C(1B)-P(1B)-Fe(1)	57(2)	C(4B)-P(1B)-Fe(1)	61.2(17)
C(5B)-O(2B)-C(6B)	116.3(18)	C(2B)-C(1B)-C(5B)	122.1(17)
C(2B)-C(1B)-P(1B)	113.3(19)	C(5B)-C(1B)-P(1B)	124.6(19)
C(2B)-C(1B)-Fe(1)	70.5(18)	C(5B)-C(1B)-Fe(1)	119(3)

P(1B)-C(1B)-Fe(1)	77(2)	C(3B)-C(2B)-C(1B)	110.4(12)
C(3B)-C(2B)-C(8B)	126.0(12)	C(1B)-C(2B)-C(8B)	123.5(13)
C(3B)-C(2B)-Fe(1)	71.9(12)	C(1B)-C(2B)-Fe(1)	67(2)
C(8B)-C(2B)-Fe(1)	125.9(18)	C(4B)-C(3B)-C(2B)	114.6(13)
C(4B)-C(3B)-C(9B)	123.0(16)	C(2B)-C(3B)-C(9B)	122.4(14)
C(4B)-C(3B)-Fe(1)	73.4(15)	C(2B)-C(3B)-Fe(1)	67.9(12)
C(9B)-C(3B)-Fe(1)	129.0(17)	C(3B)-C(4B)-P(1B)	111(2)
C(3B)-C(4B)-Fe(1)	69.3(13)	P(1B)-C(4B)-Fe(1)	70.7(19)
O(1B)-C(5B)-O(2B)	120(2)	O(1B)-C(5B)-C(1B)	131(2)
O(2B)-C(5B)-C(1B)	109(2)	C(7)-C(6B)-O(2B)	111.5(19)
C(6A)-C(7)-C(6B)	66.2(15)		

Table S4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 103$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^* U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Fe(1) 14(1)	48(1)	22(1)	3(1)	4(1)	1(1)	
P(1A) 22(6)	31(17)	27(10)	-13(11)	7(5)	-7(11)	
O(1A) 108(16)	41(11)	25(10)	-3(9)	24(10)	-2(10)	
O(2A) 99(17)	48(13)	22(12)	2(9)	20(10)	-5(11)	
C(1A) 13(5)	38(6)	19(5)	-7(5)	-1(6)	-5(5)	
C(2A) 16(5)	35(6)	22(4)	-7(5)	2(5)	-5(6)	
C(3A) 16(5)	38(6)	22(5)	-6(5)	0(5)	-3(6)	
C(4A) 17(5)	35(7)	22(7)	-7(6)	-1(8)	-2(6)	
C(5A) 16(7)	41(7)	21(7)	-5(6)	0(7)	-4(6)	
C(6A) 60(9)	71(10)	46(8)	-9(8)	-6(7)	2(8)	
C(8A) 21(9)	40(9)	25(8)	-10(8)	7(8)	-12(10)	
C(9A) 28(9)	44(10)	21(7)	1(7)	-7(7)	5(9)	
P(1B) 16(6)	29(16)	30(5)	2(10)	5(4)	-5(10)	
O(1B) 36(9)	38(9)	24(9)	-2(8)	-9(7)	5(7)	
O(2B) 27(10)	33(11)	21(12)	-5(9)	-1(8)	-8(7)	
C(1B) 12(5)	38(5)	21(5) -	7(5)	-1(6)	-7(5)	

C(2B) 16(4)	38(6)	20(4)	-7(5)	-1(4)	-5(6)
C(3B) 19(5)	39(6)	26(6)	-4(5)	-2(6)	-2(6)
C(4B) 16(6)	39(7)	25(7)	-7(6)	-3(8)	-1(7)
C(5B) 13(6)	41(6)	19(7)	-5(6)	4(7)	-7(6)
C(6B) 56(9)	66(10)	40(7)	-5(8)	0(7)	-1(8)
C(8B) 26(8)	36(9)	24(7)	-2(7)	1(7)	-4(10)
C(9B) 23(8)	48(9)	31(8)	6(7)	-8(8)	1(9)
C(7) 70(8)	79(8)	47(6)	2(6)	-17(5)	3(6)

Table S5. Hydrogen coordinates ( x 104) and isotropic displacement parameters (Å<sup>2</sup> x 10<sup>3</sup>)

	x	y	z	U(eq)
H(6A1)	5451	926	2153	72
H(6A2)	5380	-61	1328	72
H(8A1)	7509	3045	-1838	42
H(8A2)	6169	1990	-1307	42
H(8A3)	8528	1810	-1182	42
H(9A1)	7701	5392	-2062	48
H(9A2)	9042	6873	-1690	48
H(9A3)	6685	7064	-1825	48
H(6B1)	6403	-605	930	66
H(6B2)	8764	-570	948	66
H(8B1)	7565	4235	-1960	43
H(8B2)	6193	2901	-1596	43
H(8B3)	8551	2712	-1469	43
H(9B1)	7764	6628	-1882	52
H(9B2)	9028	7941	-1337	52
H(9B3)	6662	8053	-1453	52

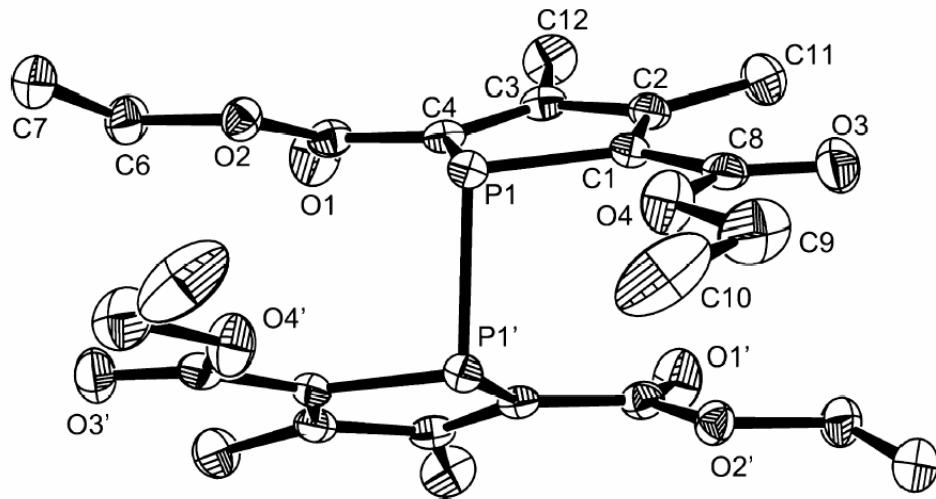


Table S1. Crystal data and structure refinement for Compound **6** Chapter 1.

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Empirical formula	$C_{12}H_{16}O_4P$	
Formula weight	255.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 20.816(5)$ Å	$\alpha = 90^\circ$
	$b = 10.489(2)$ Å	$\beta = 109.335(3)^\circ$
	$c = 12.513(3)$ Å	$\gamma = 90^\circ$
Volume	2578.2(10) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.315 Mg/m <sup>3</sup>	
Absorption coefficient	0.213 mm <sup>-1</sup>	
F(000)	1080	
Crystal size	0.59 x 0.10 x 0.06 mm <sup>3</sup>	
Theta range for data collection	2.07 to 23.25°	
Index ranges	$-21 \leq h \leq 23, -11 \leq k \leq 11, -13 \leq l \leq 13$	
Reflections collected	6858	
Independent reflections	1835 [R(int) = 0.0307]	

Completeness to theta = 23.25°	99.4 %
Absorption correction	Sadabs
Max. and min. transmission	0.9873 and 0.8844
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1835 / 0 / 158
Goodness-of-fit on F <sup>2</sup>	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.1057
R indices (all data)	R1 = 0.0461, wR2 = 0.1099
Largest diff. peak and hole	1.105 and -0.233 e.Å <sup>-3</sup>

**Table S2.** *Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.*

	x	y	z	$U(\text{eq})$
P(1)	90(1)	9700(1)	6670(1)	19(1)
O(1)	1218(1)	12857(2)	7426(2)	40(1)
O(2)	1504(1)	10802(2)	7373(1)	24(1)
O(3)	-1908(1)	9325(2)	4959(2)	38(1)
O(4)	-1069(1)	8044(2)	5994(2)	33(1)
C(1)	-762(1)	10110(2)	5775(2)	21(1)
C(2)	-794(1)	11314(2)	5361(2)	23(1)
C(3)	-146(1)	12002(2)	5806(2)	22(1)
C(4)	359(1)	11316(2)	6559(2)	19(1)
C(5)	1056(1)	11768(2)	7150(2)	24(1)
C(6)	2210(1)	11146(3)	7960(2)	32(1)
C(7)	2634(1)	9988(3)	8010(2)	36(1)
C(8)	-1317(1)	9163(3)	5508(2)	26(1)
C(9)	-1547(2)	6994(3)	5833(3)	46(1)
C(10)	-1160(2)	5895(3)	6491(4)	61(1)
C(11)	-1401(1)	11939(3)	4533(2)	35(1)
C(12)	-77(2)	13325(2)	5396(3)	36(1)

**Table S3. Bond lengths [Å] and angles [°].**

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P(1)-C(4)	1.805(2)	P(1)-C(1)	1.809(2)
P(1)-P(1)#1	2.2289(14)	O(1)-C(5)	1.209(3)
O(2)-C(5)	1.342(3)	O(2)-C(6)	1.454(3)
O(3)-C(8)	1.206(3)	O(4)-C(8)	1.343(3)
O(4)-C(9)	1.454(3)	C(1)-C(2)	1.358(4)
C(1)-C(8)	1.475(4)	C(2)-C(3)	1.466(4)
C(2)-C(11)	1.494(3)	C(3)-C(4)	1.362(3)
C(3)-C(12)	1.503(4)	C(4)-C(5)	1.472(3)
C(6)-C(7)	1.491(4)	C(9)-C(10)	1.489(5)
C(4)-P(1)-C(1)	89.66(11)	C(4)-P(1)-P(1)#1	102.95(8)
C(1)-P(1)-P(1)#1	98.29(9)	C(5)-O(2)-C(6)	115.7(2)
C(8)-O(4)-C(9)	117.1(2)	C(2)-C(1)-C(8)	127.2(2)
C(2)-C(1)-P(1)	111.75(19)	C(8)-C(1)-P(1)	120.90(19)
C(1)-C(2)-C(3)	113.0(2)	C(1)-C(2)-C(11)	126.5(2)
C(3)-C(2)-C(11)	120.5(2)	C(4)-C(3)-C(2)	113.9(2)
C(4)-C(3)-C(12)	125.7(2)	C(2)-C(3)-C(12)	120.4(2)
C(3)-C(4)-C(5)	125.8(2)	C(3)-C(4)-P(1)	111.20(18)
C(5)-C(4)-P(1)	122.83(18)	O(1)-C(5)-O(2)	123.0(2)
O(1)-C(5)-C(4)	125.7(2)	O(2)-C(5)-C(4)	111.3(2)
O(2)-C(6)-C(7)	107.7(2)	O(3)-C(8)-O(4)	123.3(2)
O(3)-C(8)-C(1)	127.4(3)	O(4)-C(8)-C(1)	109.3(2)
O(4)-C(9)-C(10)	106.8(3)		

**Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+3/2**

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^{*} b^{*} U^{12} ]$

	U11	U22	U33	U23	U13	U12
P(1)	22(1)	16(1)	19(1)	-1(1)	8(1)	-1(1)
O(1)	38(1)	22(1)	59(1)	-9(1)	14(1)	-10(1)
O(2)	22(1)	24(1)	28(1)	-2(1)	9(1)	-4(1)
O(3)	26(1)	56(1)	29(1)	5(1)	3(1)	-10(1)
O(4)	31(1)	21(1)	45(1)	-5(1)	10(1)	-9(1)
C(1)	25(1)	24(1)	17(1)	-4(1)	9(1)	-1(1)
C(2)	27(1)	27(2)	18(1)	0(1)	11(1)	4(1)
C(3)	33(1)	18(1)	21(1)	0(1)	16(1)	2(1)
C(4)	25(1)	16(1)	18(1)	-2(1)	12(1)	0(1)
C(5)	30(1)	23(2)	23(1)	-1(1)	14(1)	-3(1)
C(6)	22(1)	39(2)	31(2)	-6(1)	7(1)	-9(1)
C(7)	26(2)	47(2)	35(2)	0(1)	8(1)	0(1)
C(8)	28(2)	35(2)	17(1)	-6(1)	10(1)	-4(1)
C(9)	52(2)	38(2)	54(2)	-14(2)	25(2)	-27(2)
C(10)	74(3)	25(2)	111(3)	-3(2)	65(2)	-9(2)
C(11)	32(2)	40(2)	32(2)	8(1)	9(1)	8(1)
C(12)	45(2)	21(2)	43(2)	9(1)	19(1)	4(1)

**Table S5.** *Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )*

	x	y	z	U(eq)
H(6A)	2265	11448	8735	38
H(6B)	2352	11838	7549	38
H(7A)	2471	9292	8376	54
H(7B)	3110	10177	8447	54
H(7C)	2601	9733	7240	54
H(9A)	-1741	6772	5020	55
H(9B)	-1924	7231	6111	55
H(10A)	-763	5722	6256	92
H(10B)	-1454	5141	6349	92
H(10C)	-1007	6099	7301	92
H(11A)	-1795	11370	4373	53
H(11B)	-1308	12118	3830	53
H(11C)	-1498	12739	4855	53
H(12A)	391	13627	5759	53
H(12B)	-393	13898	5590	53
H(12C)	-182	13313	4573	53

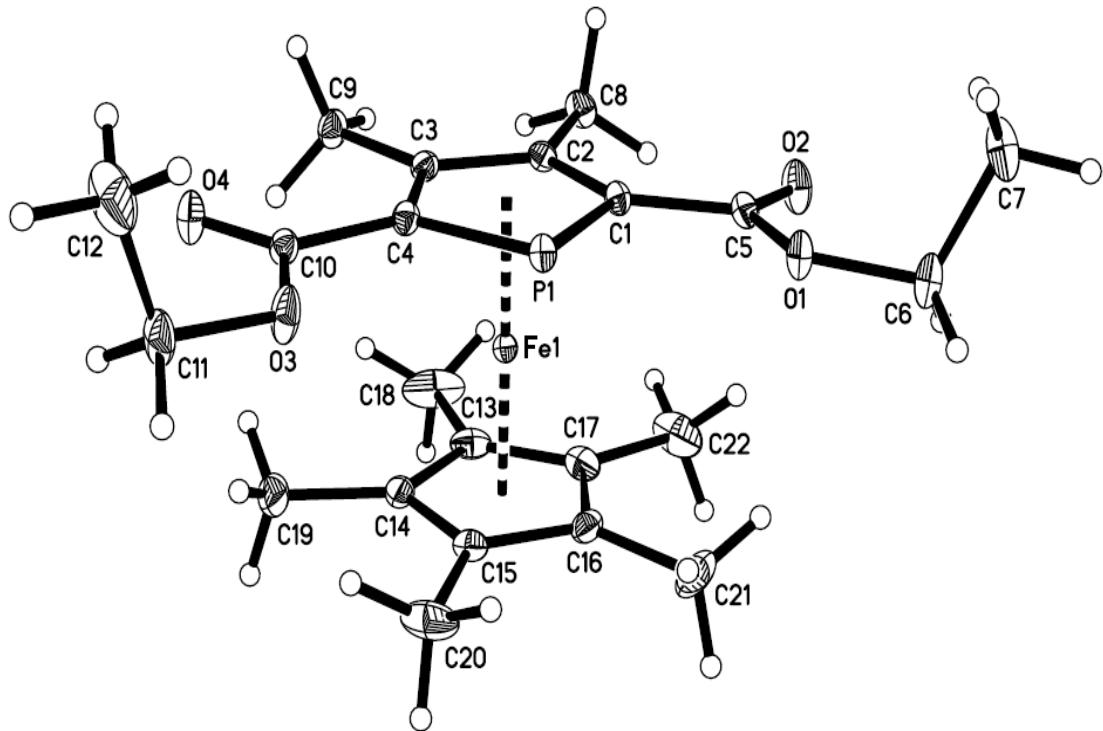


Table 7. Crystal data and structure refinement for: Compound **3** Chapter 2

Identification code:	2,5-Bis(ethoxycarbonyl)phosphaferrocene	
Empirical formula	C <sub>22</sub> H <sub>31</sub> FeO <sub>4</sub> P	
Formula weight	446.29	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 6.8549(5) Å	α = 90°.
	b = 11.1429(6) Å	β = 90.715(2)°.
	c = 28.2174(18) Å	γ = 90°.
Volume	2155.2(2) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.375 Mg/m <sup>3</sup>	
Absorption coefficient	0.799 mm <sup>-1</sup>	
F(000)	944	
Crystal size	0.16 x 0.14 x 0.06 mm <sup>3</sup>	
Theta range for data collection	1.44 to 33.62°.	

Index ranges	-10<=h<=10, -17<=k<=15, -43<=l<=43
Reflections collected	55558
Independent reflections	8467 [R(int) = 0.0371]
Completeness to theta = 33.62°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9537 and 0.8829
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	8467 / 0 / 262
Goodness-of-fit on F <sup>2</sup>	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0756
R indices (all data)	R1 = 0.0450, wR2 = 0.0798
Largest diff. peak and hole	0.593 and -0.382 e.Å <sup>-3</sup>

Table 8. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Fe(1)	1301(1)	9076(1)	1328(1)	8(1)
C(1)	-1110(2)	8178(1)	1063(1)	10(1)
C(2)	-994(2)	8039(1)	1569(1)	11(1)
C(3)	-987(2)	9172(1)	1803(1)	11(1)
C(4)	-1081(2)	10148(1)	1470(1)	11(1)
C(5)	-972(2)	7181(1)	722(1)	12(1)
C(6)	-889(2)	6717(1)	-101(1)	20(1)
C(7)	-2746(2)	6028(1)	-195(1)	26(1)
C(8)	-927(2)	6859(1)	1825(1)	15(1)
C(9)	-912(2)	9318(1)	2334(1)	15(1)
C(10)	-999(2)	11418(1)	1612(1)	12(1)
C(11)	-1049(2)	13429(1)	1334(1)	21(1)
C(12)	-3149(3)	13812(1)	1379(1)	34(1)
C(13)	3811(2)	8651(1)	1713(1)	16(1)
C(14)	3763(2)	9902(1)	1605(1)	15(1)
C(15)	3681(2)	10028(1)	1101(1)	14(1)
C(16)	3671(2)	8855(1)	898(1)	14(1)
C(17)	3755(2)	8006(1)	1276(1)	16(1)
C(18)	3945(2)	8123(2)	2199(1)	33(1)
C(19)	3868(2)	10912(2)	1953(1)	29(1)
C(20)	3700(2)	11180(1)	829(1)	27(1)
C(21)	3688(2)	8563(2)	380(1)	29(1)
C(22)	3881(2)	6670(1)	1220(1)	33(1)
O(1)	-1128(1)	7594(1)	274(1)	15(1)
O(2)	-748(2)	6125(1)	814(1)	20(1)
O(3)	-925(2)	12155(1)	1233(1)	21(1)
O(4)	-1028(2)	11794(1)	2014(1)	19(1)
P(1)	-1246(1)	9699(1)	864(1)	10(1)

Table 9. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

Fe(1)-C(15)	2.0550(12)
Fe(1)-C(16)	2.0551(12)
Fe(1)-C(1)	2.0643(11)
Fe(1)-C(4)	2.0664(11)
Fe(1)-C(14)	2.0671(12)
Fe(1)-C(17)	2.0684(12)
Fe(1)-C(2)	2.0730(11)
Fe(1)-C(13)	2.0773(12)
Fe(1)-C(3)	2.0788(11)
Fe(1)-P(1)	2.2780(3)
C(1)-C(2)	1.4384(16)
C(1)-C(5)	1.4732(16)
C(1)-P(1)	1.7868(12)
C(2)-C(3)	1.4254(16)
C(2)-C(8)	1.5014(16)
C(3)-C(4)	1.4386(16)
C(3)-C(9)	1.5058(16)
C(4)-C(10)	1.4721(17)
C(4)-P(1)	1.7832(12)
C(5)-O(2)	1.2139(15)
C(5)-O(1)	1.3497(14)
C(6)-O(1)	1.4496(15)
C(6)-C(7)	1.507(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800

C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-O(4)	1.2095(14)
C(10)-O(3)	1.3502(15)
C(11)-O(3)	1.4512(16)
C(11)-C(12)	1.509(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(17)	1.4267(19)
C(13)-C(14)	1.4270(19)
C(13)-C(18)	1.4948(18)
C(14)-C(15)	1.4281(17)
C(14)-C(19)	1.4951(18)
C(15)-C(16)	1.4270(18)
C(15)-C(20)	1.4969(18)
C(16)-C(17)	1.4268(18)
C(16)-C(21)	1.4977(18)
C(17)-C(22)	1.4998(19)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800

C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(15)-Fe(1)-C(16)	40.63(5)
C(15)-Fe(1)-C(1)	140.55(5)
C(16)-Fe(1)-C(1)	111.29(5)
C(15)-Fe(1)-C(4)	113.21(5)
C(16)-Fe(1)-C(4)	144.67(5)
C(1)-Fe(1)-C(4)	73.69(5)
C(15)-Fe(1)-C(14)	40.54(5)
C(16)-Fe(1)-C(14)	68.20(5)
C(1)-Fe(1)-C(14)	177.45(5)
C(4)-Fe(1)-C(14)	108.23(5)
C(15)-Fe(1)-C(17)	68.03(5)
C(16)-Fe(1)-C(17)	40.49(5)
C(1)-Fe(1)-C(17)	110.06(5)
C(4)-Fe(1)-C(17)	172.89(5)
C(14)-Fe(1)-C(17)	67.84(5)
C(15)-Fe(1)-C(2)	176.77(5)
C(16)-Fe(1)-C(2)	137.38(5)
C(1)-Fe(1)-C(2)	40.69(4)
C(4)-Fe(1)-C(2)	69.76(5)
C(14)-Fe(1)-C(2)	138.04(5)
C(17)-Fe(1)-C(2)	108.86(5)
C(15)-Fe(1)-C(13)	67.95(5)
C(16)-Fe(1)-C(13)	68.01(5)
C(1)-Fe(1)-C(13)	137.17(5)
C(4)-Fe(1)-C(13)	133.01(5)
C(14)-Fe(1)-C(13)	40.28(5)
C(17)-Fe(1)-C(13)	40.26(5)
C(2)-Fe(1)-C(13)	109.20(5)
C(15)-Fe(1)-C(3)	141.48(5)
C(16)-Fe(1)-C(3)	174.64(5)
C(1)-Fe(1)-C(3)	69.64(4)

C(4)-Fe(1)-C(3)	40.61(4)
C(14)-Fe(1)-C(3)	110.62(5)
C(17)-Fe(1)-C(3)	134.16(5)
C(2)-Fe(1)-C(3)	40.16(4)
C(13)-Fe(1)-C(3)	107.56(5)
C(15)-Fe(1)-P(1)	105.63(3)
C(16)-Fe(1)-P(1)	107.63(4)
C(1)-Fe(1)-P(1)	48.29(3)
C(4)-Fe(1)-P(1)	48.16(3)
C(14)-Fe(1)-P(1)	134.25(4)
C(17)-Fe(1)-P(1)	138.85(4)
C(2)-Fe(1)-P(1)	77.23(3)
C(13)-Fe(1)-P(1)	173.56(4)
C(3)-Fe(1)-P(1)	77.05(3)
C(2)-C(1)-C(5)	124.28(10)
C(2)-C(1)-P(1)	114.58(8)
C(5)-C(1)-P(1)	120.97(8)
C(2)-C(1)-Fe(1)	69.98(6)
C(5)-C(1)-Fe(1)	123.00(8)
P(1)-C(1)-Fe(1)	72.12(4)
C(3)-C(2)-C(1)	111.40(10)
C(3)-C(2)-C(8)	123.58(10)
C(1)-C(2)-C(8)	125.01(10)
C(3)-C(2)-Fe(1)	70.14(6)
C(1)-C(2)-Fe(1)	69.33(6)
C(8)-C(2)-Fe(1)	128.85(8)
C(2)-C(3)-C(4)	111.49(10)
C(2)-C(3)-C(9)	123.80(10)
C(4)-C(3)-C(9)	124.71(10)
C(2)-C(3)-Fe(1)	69.70(6)
C(4)-C(3)-Fe(1)	69.23(6)
C(9)-C(3)-Fe(1)	129.06(8)
C(3)-C(4)-C(10)	123.10(10)
C(3)-C(4)-P(1)	114.63(8)

C(10)-C(4)-P(1)	122.25(9)
C(3)-C(4)-Fe(1)	70.16(6)
C(10)-C(4)-Fe(1)	125.52(8)
P(1)-C(4)-Fe(1)	72.14(4)
O(2)-C(5)-O(1)	122.55(11)
O(2)-C(5)-C(1)	127.01(11)
O(1)-C(5)-C(1)	110.44(10)
O(1)-C(6)-C(7)	111.69(11)
O(1)-C(6)-H(6A)	109.3
C(7)-C(6)-H(6A)	109.3
O(1)-C(6)-H(6B)	109.3
C(7)-C(6)-H(6B)	109.3
H(6A)-C(6)-H(6B)	107.9
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(2)-C(8)-H(8A)	109.5
C(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(3)-C(9)-H(9A)	109.5
C(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(4)-C(10)-O(3)	122.26(11)
O(4)-C(10)-C(4)	126.05(11)
O(3)-C(10)-C(4)	111.68(10)

O(3)-C(11)-C(12)	110.62(12)
O(3)-C(11)-H(11A)	109.5
C(12)-C(11)-H(11A)	109.5
O(3)-C(11)-H(11B)	109.5
C(12)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	108.1
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(17)-C(13)-C(14)	107.93(11)
C(17)-C(13)-C(18)	126.54(14)
C(14)-C(13)-C(18)	125.52(13)
C(17)-C(13)-Fe(1)	69.53(7)
C(14)-C(13)-Fe(1)	69.48(7)
C(18)-C(13)-Fe(1)	127.59(9)
C(13)-C(14)-C(15)	107.96(11)
C(13)-C(14)-C(19)	126.48(13)
C(15)-C(14)-C(19)	125.51(13)
C(13)-C(14)-Fe(1)	70.25(7)
C(15)-C(14)-Fe(1)	69.27(7)
C(19)-C(14)-Fe(1)	128.02(9)
C(16)-C(15)-C(14)	108.09(11)
C(16)-C(15)-C(20)	125.34(12)
C(14)-C(15)-C(20)	126.51(12)
C(16)-C(15)-Fe(1)	69.69(7)
C(14)-C(15)-Fe(1)	70.19(7)
C(20)-C(15)-Fe(1)	127.94(9)
C(17)-C(16)-C(15)	107.85(11)
C(17)-C(16)-C(21)	125.76(13)
C(15)-C(16)-C(21)	126.30(13)
C(17)-C(16)-Fe(1)	70.26(7)

C(15)-C(16)-Fe(1)	69.68(7)
C(21)-C(16)-Fe(1)	128.19(9)
C(13)-C(17)-C(16)	108.18(11)
C(13)-C(17)-C(22)	126.14(13)
C(16)-C(17)-C(22)	125.59(14)
C(13)-C(17)-Fe(1)	70.21(7)
C(16)-C(17)-Fe(1)	69.26(7)
C(22)-C(17)-Fe(1)	128.87(9)
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(17)-C(22)-H(22A)	109.5
C(17)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5
C(17)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(5)-O(1)-C(6)	116.45(10)
C(10)-O(3)-C(11)	115.88(10)
C(4)-P(1)-C(1)	87.88(5)
C(4)-P(1)-Fe(1)	59.70(4)
C(1)-P(1)-Fe(1)	59.59(4)

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Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Fe(1)	9(1)	8(1)	9(1)	0(1)	0(1)	1(1)
C(1)	11(1)	9(1)	11(1)	0(1)	-1(1)	0(1)
C(2)	11(1)	10(1)	11(1)	1(1)	0(1)	-1(1)
C(3)	11(1)	12(1)	10(1)	0(1)	1(1)	0(1)
C(4)	12(1)	10(1)	12(1)	-1(1)	0(1)	1(1)
C(5)	13(1)	12(1)	13(1)	-1(1)	-2(1)	0(1)
C(6)	29(1)	17(1)	14(1)	-6(1)	-1(1)	4(1)
C(7)	35(1)	19(1)	23(1)	-7(1)	-10(1)	1(1)
C(8)	19(1)	12(1)	14(1)	3(1)	0(1)	-3(1)
C(9)	20(1)	16(1)	11(1)	-1(1)	1(1)	0(1)
C(10)	12(1)	10(1)	13(1)	-1(1)	0(1)	2(1)
C(11)	35(1)	7(1)	22(1)	-1(1)	4(1)	-1(1)
C(12)	36(1)	12(1)	54(1)	-2(1)	-11(1)	5(1)
C(13)	10(1)	23(1)	16(1)	7(1)	-2(1)	0(1)
C(14)	10(1)	19(1)	15(1)	-4(1)	0(1)	-2(1)
C(15)	11(1)	13(1)	17(1)	3(1)	1(1)	0(1)
C(16)	11(1)	19(1)	13(1)	-2(1)	1(1)	1(1)
C(17)	11(1)	11(1)	26(1)	1(1)	0(1)	2(1)
C(18)	18(1)	57(1)	24(1)	23(1)	-3(1)	0(1)
C(19)	18(1)	37(1)	33(1)	-22(1)	2(1)	-6(1)
C(20)	19(1)	19(1)	42(1)	15(1)	5(1)	0(1)
C(21)	20(1)	51(1)	15(1)	-10(1)	4(1)	2(1)
C(22)	19(1)	13(1)	68(1)	-2(1)	2(1)	4(1)
O(1)	24(1)	11(1)	11(1)	-2(1)	-2(1)	2(1)
O(2)	33(1)	9(1)	18(1)	-1(1)	-4(1)	2(1)
O(3)	40(1)	8(1)	15(1)	0(1)	5(1)	2(1)
O(4)	29(1)	14(1)	14(1)	-4(1)	-2(1)	2(1)
P(1)	13(1)	9(1)	10(1)	0(1)	-2(1)	2(1)

Table 11. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U(eq)
H(6A)	161	6149	-10	24
H(6B)	-492	7132	-394	24
H(7A)	-3076	5556	85	39
H(7B)	-2562	5490	-466	39
H(7C)	-3807	6592	-267	39
H(8A)	-277	6964	2134	23
H(8B)	-200	6275	1637	23
H(8C)	-2259	6566	1872	23
H(9A)	-2195	9572	2446	23
H(9B)	64	9926	2419	23
H(9C)	-558	8551	2481	23
H(11A)	-430	13888	1076	25
H(11B)	-333	13608	1633	25
H(12A)	-3865	13614	1087	51
H(12B)	-3207	14680	1434	51
H(12C)	-3739	13392	1647	51
H(18A)	3295	7340	2201	50
H(18B)	3308	8660	2425	50
H(18C)	5320	8024	2290	50
H(19A)	5236	11125	2013	44
H(19B)	3267	10664	2251	44
H(19C)	3170	11609	1824	44
H(20A)	5052	11415	768	40
H(20B)	3059	11809	1013	40
H(20C)	3002	11071	527	40
H(21A)	2929	9165	204	43
H(21B)	3111	7768	328	43
H(21C)	5036	8563	268	43

H(22A)	2917	6403	983	50
H(22B)	3615	6283	1525	50
H(22C)	5192	6450	1116	50

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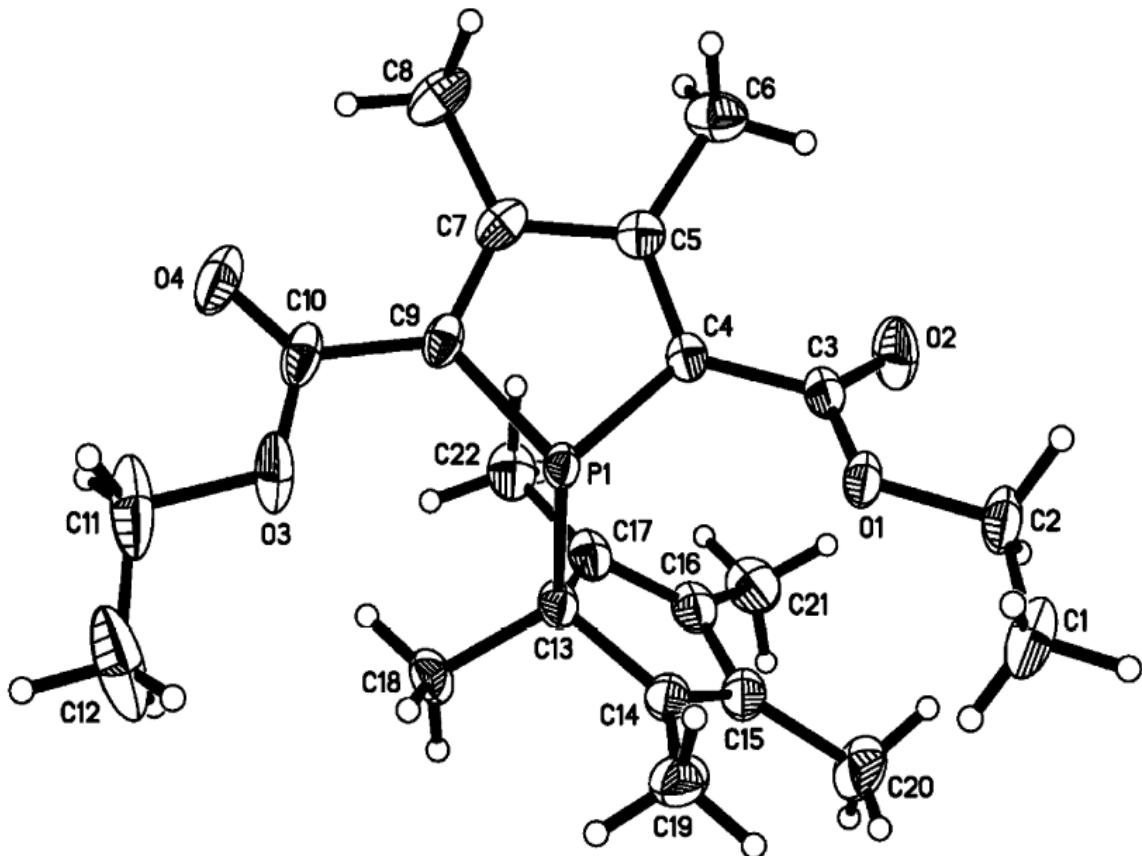


Table 1. Crystal data and structure refinement for Compound 4 Chapter 2

Identification code:	1-pentamethylcyclopentadienylphosphole		
Empirical formula	$C_{22} H_{31} O_4 P$		
Formula weight	390.44		
Temperature	103(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 9.0980(3)$ Å	$\alpha = 110.535(2)^\circ$ .	
	$b = 10.0408(3)$ Å	$\beta = 94.298(2)^\circ$ .	
	$c = 12.7079(4)$ Å	$\gamma = 99.804(2)^\circ$ .	
Volume	$1059.77(6)$ Å <sup>3</sup>		
Z	2		
Density (calculated)	1.224 Mg/m <sup>3</sup>		

Absorption coefficient	$0.153 \text{ mm}^{-1}$
F(000)	420
Crystal size	$0.34 \times 0.10 \times 0.04 \text{ mm}^3$
Theta range for data collection	1.73 to 32.06°.
Index ranges	-13≤h≤13, -14≤k≤14, -18≤l≤18
Reflections collected	24245
Independent reflections	7321 [R(int) = 0.0373]
Completeness to theta = 32.06°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9939 and 0.9497
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	7321 / 0 / 253
Goodness-of-fit on $F^2$	1.102
Final R indices [ $I > 2\sigma(I)$ ]	R1 = 0.0524, wR2 = 0.1417
R indices (all data)	R1 = 0.0944, wR2 = 0.1759
Largest diff. peak and hole	1.051 and -0.543 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
C(1)	6782(3)	10028(2)	3905(2)	44(1)
C(2)	7880(2)	9404(2)	3147(2)	34(1)
C(3)	8096(2)	7148(2)	1809(2)	23(1)
C(4)	7312(2)	5640(2)	1123(1)	20(1)
C(5)	7529(2)	4899(2)	41(1)	23(1)
C(6)	8511(2)	5487(2)	-656(2)	33(1)
C(7)	6584(2)	3432(2)	-460(1)	24(1)
C(8)	6659(2)	2502(2)	-1660(2)	35(1)
C(9)	5679(2)	3084(2)	258(1)	23(1)
C(10)	4513(2)	1734(2)	-65(2)	30(1)
C(11)	2406(3)	602(3)	534(3)	59(1)
C(12)	1892(3)	752(3)	1645(3)	69(1)
C(13)	6682(2)	4326(2)	2790(1)	24(1)
C(14)	6859(2)	5740(2)	3799(2)	28(1)
C(15)	8328(2)	6262(2)	4208(2)	33(1)
C(16)	9219(2)	5274(2)	3527(2)	31(1)
C(17)	8286(2)	4133(2)	2698(2)	27(1)
C(18)	5704(2)	3051(2)	2980(2)	31(1)
C(19)	5530(3)	6362(2)	4211(2)	37(1)
C(20)	9046(3)	7622(2)	5198(2)	47(1)
C(21)	10907(2)	5556(3)	3752(2)	42(1)
C(22)	8668(2)	2844(2)	1844(2)	33(1)
O(1)	7190(1)	7906(1)	2454(1)	25(1)
O(2)	9394(2)	7669(2)	1806(1)	40(1)
O(3)	3562(2)	1879(2)	703(1)	42(1)
O(4)	4400(2)	633(2)	-878(1)	41(1)
P(1)	5767(1)	4647(1)	1534(1)	19(1)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ]

C(1)-C(2)	1.501(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-O(1)	1.448(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-O(2)	1.208(2)
C(3)-O(1)	1.345(2)
C(3)-C(4)	1.474(2)
C(4)-C(5)	1.362(2)
C(4)-P(1)	1.8011(16)
C(5)-C(7)	1.464(2)
C(5)-C(6)	1.497(2)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-C(9)	1.367(2)
C(7)-C(8)	1.497(2)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-C(10)	1.479(2)
C(9)-P(1)	1.8033(17)
C(10)-O(4)	1.201(2)
C(10)-O(3)	1.339(3)
C(11)-O(3)	1.453(2)
C(11)-C(12)	1.485(4)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800

C(12)-H(12C)	0.9800
C(13)-C(17)	1.511(2)
C(13)-C(14)	1.517(2)
C(13)-C(18)	1.533(2)
C(13)-P(1)	1.8967(16)
C(14)-C(15)	1.341(3)
C(14)-C(19)	1.500(3)
C(15)-C(16)	1.472(3)
C(15)-C(20)	1.497(3)
C(16)-C(17)	1.353(3)
C(16)-C(21)	1.500(3)
C(17)-C(22)	1.483(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

O(1)-C(2)-C(1)	107.98(16)
O(1)-C(2)-H(2A)	110.1
C(1)-C(2)-H(2A)	110.1
O(1)-C(2)-H(2B)	110.1
C(1)-C(2)-H(2B)	110.1
H(2A)-C(2)-H(2B)	108.4
O(2)-C(3)-O(1)	122.76(16)
O(2)-C(3)-C(4)	125.24(16)
O(1)-C(3)-C(4)	112.00(13)
C(5)-C(4)-C(3)	124.16(15)
C(5)-C(4)-P(1)	111.40(12)
C(3)-C(4)-P(1)	123.90(12)
C(4)-C(5)-C(7)	113.25(15)
C(4)-C(5)-C(6)	126.31(17)
C(7)-C(5)-C(6)	120.25(16)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(9)-C(7)-C(5)	113.45(15)
C(9)-C(7)-C(8)	127.10(17)
C(5)-C(7)-C(8)	119.43(17)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-C(10)	124.63(16)
C(7)-C(9)-P(1)	110.94(13)
C(10)-C(9)-P(1)	122.90(14)
O(4)-C(10)-O(3)	122.68(17)

O(4)-C(10)-C(9)	127.15(19)
O(3)-C(10)-C(9)	110.15(15)
O(3)-C(11)-C(12)	108.1(2)
O(3)-C(11)-H(11A)	110.1
C(12)-C(11)-H(11A)	110.1
O(3)-C(11)-H(11B)	110.1
C(12)-C(11)-H(11B)	110.1
H(11A)-C(11)-H(11B)	108.4
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(17)-C(13)-C(14)	103.38(14)
C(17)-C(13)-C(18)	111.82(14)
C(14)-C(13)-C(18)	111.72(14)
C(17)-C(13)-P(1)	113.17(12)
C(14)-C(13)-P(1)	105.74(11)
C(18)-C(13)-P(1)	110.65(12)
C(15)-C(14)-C(19)	129.01(18)
C(15)-C(14)-C(13)	108.90(17)
C(19)-C(14)-C(13)	122.09(17)
C(14)-C(15)-C(16)	109.59(17)
C(14)-C(15)-C(20)	128.2(2)
C(16)-C(15)-C(20)	122.19(19)
C(17)-C(16)-C(15)	109.64(16)
C(17)-C(16)-C(21)	127.29(19)
C(15)-C(16)-C(21)	123.07(17)
C(16)-C(17)-C(22)	128.74(17)
C(16)-C(17)-C(13)	108.49(17)
C(22)-C(17)-C(13)	122.73(16)
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5

H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(14)-C(19)-H(19A)	109.5
C(14)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(14)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(15)-C(20)-H(20A)	109.5
C(15)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(15)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(16)-C(21)-H(21A)	109.5
C(16)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(16)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(17)-C(22)-H(22A)	109.5
C(17)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(17)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(3)-O(1)-C(2)	115.17(14)
C(10)-O(3)-C(11)	116.40(18)
C(4)-P(1)-C(9)	89.86(8)
C(4)-P(1)-C(13)	103.57(7)
C(9)-P(1)-C(13)	109.16(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
C(1)	50(1)	23(1)	45(1)	-1(1)	-5(1)	5(1)
C(2)	41(1)	17(1)	34(1)	5(1)	-8(1)	-3(1)
C(3)	21(1)	21(1)	26(1)	12(1)	-2(1)	0(1)
C(4)	16(1)	20(1)	23(1)	10(1)	-2(1)	2(1)
C(5)	17(1)	28(1)	23(1)	10(1)	0(1)	7(1)
C(6)	24(1)	49(1)	29(1)	17(1)	7(1)	8(1)
C(7)	21(1)	28(1)	21(1)	4(1)	-4(1)	11(1)
C(8)	31(1)	41(1)	25(1)	0(1)	0(1)	17(1)
C(9)	23(1)	18(1)	23(1)	5(1)	-6(1)	3(1)
C(10)	33(1)	18(1)	31(1)	7(1)	-16(1)	0(1)
C(11)	37(1)	36(1)	93(2)	27(1)	-20(1)	-15(1)
C(12)	34(1)	34(1)	144(3)	36(2)	34(2)	6(1)
C(13)	28(1)	20(1)	23(1)	12(1)	-4(1)	0(1)
C(14)	42(1)	23(1)	18(1)	10(1)	-3(1)	1(1)
C(15)	46(1)	26(1)	22(1)	12(1)	-9(1)	-3(1)
C(16)	33(1)	32(1)	27(1)	18(1)	-9(1)	-3(1)
C(17)	28(1)	27(1)	28(1)	17(1)	-5(1)	2(1)
C(18)	36(1)	25(1)	34(1)	18(1)	2(1)	-1(1)
C(19)	54(1)	33(1)	24(1)	12(1)	5(1)	11(1)
C(20)	62(1)	38(1)	27(1)	7(1)	-17(1)	-6(1)
C(21)	36(1)	52(1)	35(1)	23(1)	-12(1)	-6(1)
C(22)	32(1)	31(1)	38(1)	16(1)	-4(1)	7(1)
O(1)	28(1)	16(1)	26(1)	6(1)	-4(1)	0(1)
O(2)	26(1)	30(1)	56(1)	11(1)	4(1)	-6(1)
O(3)	30(1)	24(1)	58(1)	7(1)	-1(1)	-9(1)
O(4)	60(1)	19(1)	34(1)	5(1)	-18(1)	1(1)
P(1)	20(1)	16(1)	19(1)	7(1)	-3(1)	-1(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

H(1A)	5852	9983	3440	67
H(1B)	7226	11043	4385	67
H(1C)	6551	9465	4387	67
H(2A)	8122	9968	2657	41
H(2B)	8826	9451	3609	41
H(6A)	7880	5573	-1279	50
H(6B)	9182	4826	-970	50
H(6C)	9116	6448	-177	50
H(8A)	5939	1573	-1875	52
H(8B)	7680	2323	-1723	52
H(8C)	6407	3001	-2166	52
H(11A)	2820	-288	243	71
H(11B)	1547	524	-26	71
H(12A)	2729	748	2175	104
H(12B)	1057	-62	1540	104
H(12C)	1552	1670	1951	104
H(18A)	5695	2144	2347	46
H(18B)	4672	3207	3024	46
H(18C)	6119	2989	3692	46
H(19A)	5868	7206	4921	55
H(19B)	4797	5623	4344	55
H(19C)	5058	6664	3637	55
H(20A)	8261	8103	5553	71
H(20B)	9711	8278	4935	71
H(20C)	9636	7374	5753	71
H(21A)	11259	4720	3249	63
H(21B)	11230	5703	4545	63
H(21C)	11335	6429	3608	63
H(22A)	8537	2911	1093	50

H(22B)	8002	1958	1828	50
H(22C)	9718	2810	2046	50

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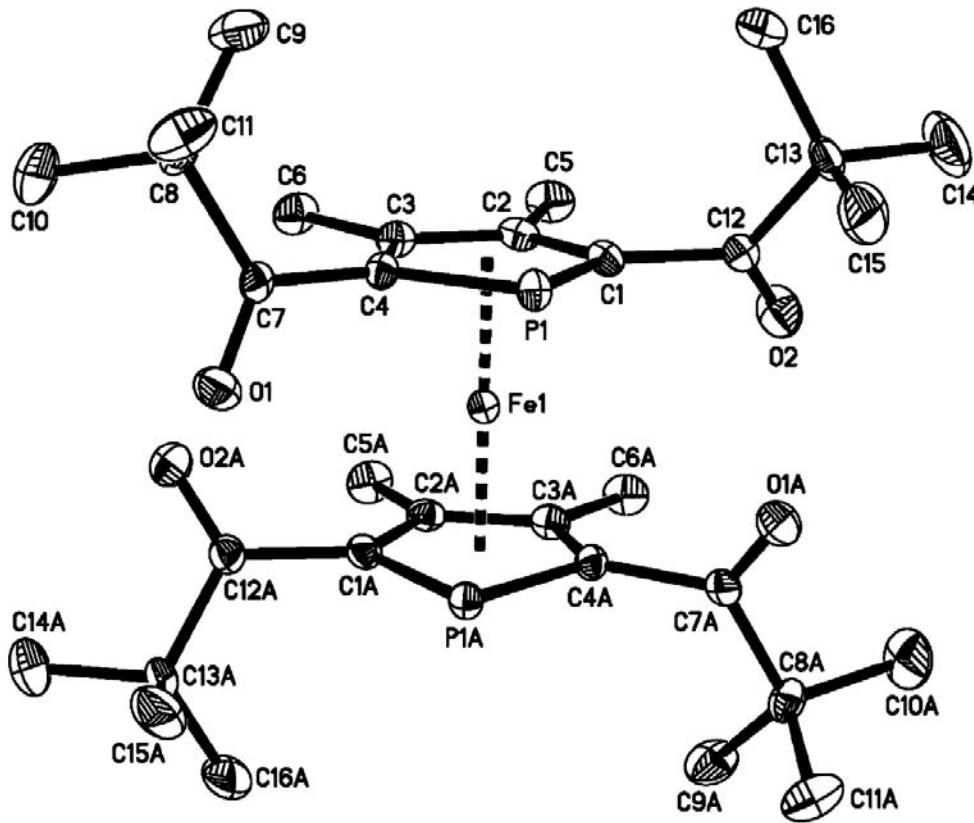


Table 1. Crystal data and structure refinement for Compound **6** Chapter 2.  
Identification code : 2,2',5,5'-Tetrapivaloyl-1,1'-diphosphaferrocene

Empirical formula	$C_{32} H_{48} Fe O_4 P_2$	
Formula weight	614.49	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(2)/n	
Unit cell dimensions	$a = 14.7385(2)$ Å	$\alpha = 90^\circ.$
	$b = 14.7385(2)$ Å	$\beta = 90^\circ.$
	$c = 14.8789(5)$ Å	$\gamma = 90^\circ.$
Volume	$3232.04(13)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.263 Mg/m <sup>3</sup>	

Absorption coefficient	0.599 mm <sup>-1</sup>
F(000)	1312
Crystal size	0.40 x 0.22 x 0.20 mm <sup>3</sup>
Theta range for data collection	1.94 to 27.99°.
Index ranges	-19<=h<=19, -19<=k<=19, -16<=l<=19
Reflections collected	44166
Independent reflections	3910 [R(int) = 0.0666]
Completeness to theta = 27.99°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8896 and 0.7957
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3910 / 0 / 185
Goodness-of-fit on F <sup>2</sup>	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0695, wR2 = 0.1751
R indices (all data)	R1 = 0.0835, wR2 = 0.1875
Largest diff. peak and hole	4.455 and -0.576 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Fe(1)	2500	7500	844(1)	12(1)
C(1)	1223(2)	6880(2)	846(2)	16(1)
C(2)	1708(2)	6649(2)	46(2)	17(1)
C(3)	2555(2)	6222(2)	235(2)	17(1)
C(4)	2718(2)	6149(2)	1174(2)	14(1)
C(5)	1361(3)	6774(3)	-900(2)	24(1)
C(6)	3180(3)	5880(2)	-490(2)	23(1)
C(7)	3512(2)	5712(2)	1640(2)	15(1)
C(8)	3585(2)	4669(2)	1635(2)	20(1)
C(9)	2876(3)	4187(3)	1047(3)	32(1)
C(10)	4551(3)	4415(3)	1357(4)	38(1)
C(11)	3427(3)	4380(3)	2616(3)	31(1)
C(12)	300(2)	7311(2)	794(2)	19(1)
C(13)	-495(2)	6814(2)	1230(3)	24(1)
C(14)	-1384(3)	7214(4)	886(4)	50(1)
C(15)	-443(3)	6972(3)	2261(3)	38(1)
C(16)	-461(3)	5799(3)	1030(4)	38(1)
O(1)	4049(2)	6160(2)	2071(2)	23(1)
O(2)	182(2)	7996(2)	356(2)	30(1)
P(1)	1803(1)	6571(1)	1852(1)	14(1)

Table 3. Bond lengths [Å] and angles [°].

Fe(1)-C(4)	2.076(3)
Fe(1)-C(4)#1	2.076(3)
Fe(1)-C(2)	2.086(3)
Fe(1)-C(2)#1	2.086(3)
Fe(1)-C(1)	2.092(3)
Fe(1)-C(1)#1	2.092(3)
Fe(1)-C(3)	2.093(3)
Fe(1)-C(3)#1	2.093(3)
Fe(1)-P(1)#1	2.2746(9)
Fe(1)-P(1)	2.2746(9)
C(1)-C(2)	1.430(5)
C(1)-C(12)	1.504(4)
C(1)-P(1)	1.782(3)
C(2)-C(3)	1.426(5)
C(2)-C(5)	1.509(5)
C(3)-C(4)	1.423(5)
C(3)-C(6)	1.505(5)
C(4)-C(7)	1.505(4)
C(4)-P(1)	1.795(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-O(1)	1.213(4)
C(7)-C(8)	1.541(4)
C(8)-C(10)	1.528(5)
C(8)-C(9)	1.538(5)
C(8)-C(11)	1.538(5)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800

C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-O(2)	1.215(4)
C(12)-C(13)	1.526(5)
C(13)-C(14)	1.524(5)
C(13)-C(16)	1.526(5)
C(13)-C(15)	1.553(6)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(4)-Fe(1)-C(4)#1	152.65(19)
C(4)-Fe(1)-C(2)	69.15(13)
C(4)#1-Fe(1)-C(2)	128.70(13)
C(4)-Fe(1)-C(2)#1	128.70(13)
C(4)#1-Fe(1)-C(2)#1	69.15(13)
C(2)-Fe(1)-C(2)#1	110.55(18)
C(4)-Fe(1)-C(1)	73.74(12)
C(4)#1-Fe(1)-C(1)	106.23(13)
C(2)-Fe(1)-C(1)	40.02(13)
C(2)#1-Fe(1)-C(1)	140.09(13)
C(4)-Fe(1)-C(1)#1	106.23(13)
C(4)#1-Fe(1)-C(1)#1	73.74(12)

C(2)-Fe(1)-C(1)#1	140.09(13)
C(2)#1-Fe(1)-C(1)#1	40.02(13)
C(1)-Fe(1)-C(1)#1	179.87(19)
C(4)-Fe(1)-C(3)	39.90(13)
C(4)#1-Fe(1)-C(3)	166.43(14)
C(2)-Fe(1)-C(3)	39.90(13)
C(2)#1-Fe(1)-C(3)	105.86(13)
C(1)-Fe(1)-C(3)	69.02(13)
C(1)#1-Fe(1)-C(3)	111.04(13)
C(4)-Fe(1)-C(3)#1	166.43(14)
C(4)#1-Fe(1)-C(3)#1	39.90(13)
C(2)-Fe(1)-C(3)#1	105.86(13)
C(2)#1-Fe(1)-C(3)#1	39.90(13)
C(1)-Fe(1)-C(3)#1	111.04(13)
C(1)#1-Fe(1)-C(3)#1	69.02(13)
C(3)-Fe(1)-C(3)#1	128.62(19)
C(4)-Fe(1)-P(1)#1	110.59(10)
C(4)#1-Fe(1)-P(1)#1	48.46(9)
C(2)-Fe(1)-P(1)#1	171.95(10)
C(2)#1-Fe(1)-P(1)#1	76.14(9)
C(1)-Fe(1)-P(1)#1	131.93(10)
C(1)#1-Fe(1)-P(1)#1	47.95(9)
C(3)-Fe(1)-P(1)#1	144.09(10)
C(3)#1-Fe(1)-P(1)#1	76.19(9)
C(4)-Fe(1)-P(1)	48.46(9)
C(4)#1-Fe(1)-P(1)	110.59(10)
C(2)-Fe(1)-P(1)	76.14(9)
C(2)#1-Fe(1)-P(1)	171.95(10)
C(1)-Fe(1)-P(1)	47.95(9)
C(1)#1-Fe(1)-P(1)	131.93(10)
C(3)-Fe(1)-P(1)	76.19(9)
C(3)#1-Fe(1)-P(1)	144.09(10)
P(1)#1-Fe(1)-P(1)	97.58(5)
C(2)-C(1)-C(12)	120.7(3)

C(2)-C(1)-P(1)	113.5(2)
C(12)-C(1)-P(1)	125.8(3)
C(2)-C(1)-Fe(1)	69.75(18)
C(12)-C(1)-Fe(1)	129.1(2)
P(1)-C(1)-Fe(1)	71.39(11)
C(3)-C(2)-C(1)	112.3(3)
C(3)-C(2)-C(5)	122.3(3)
C(1)-C(2)-C(5)	125.3(3)
C(3)-C(2)-Fe(1)	70.32(18)
C(1)-C(2)-Fe(1)	70.23(19)
C(5)-C(2)-Fe(1)	130.3(2)
C(4)-C(3)-C(2)	112.0(3)
C(4)-C(3)-C(6)	125.1(3)
C(2)-C(3)-C(6)	122.9(3)
C(4)-C(3)-Fe(1)	69.42(18)
C(2)-C(3)-Fe(1)	69.78(18)
C(6)-C(3)-Fe(1)	129.5(2)
C(3)-C(4)-C(7)	128.0(3)
C(3)-C(4)-P(1)	113.5(2)
C(7)-C(4)-P(1)	118.3(2)
C(3)-C(4)-Fe(1)	70.68(18)
C(7)-C(4)-Fe(1)	129.7(2)
P(1)-C(4)-Fe(1)	71.55(11)
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5

H(6B)-C(6)-H(6C)	109.5
O(1)-C(7)-C(4)	121.3(3)
O(1)-C(7)-C(8)	119.9(3)
C(4)-C(7)-C(8)	118.6(3)
C(10)-C(8)-C(9)	111.4(3)
C(10)-C(8)-C(11)	109.3(3)
C(9)-C(8)-C(11)	108.0(3)
C(10)-C(8)-C(7)	108.1(3)
C(9)-C(8)-C(7)	114.6(3)
C(11)-C(8)-C(7)	105.1(3)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(2)-C(12)-C(1)	120.5(3)
O(2)-C(12)-C(13)	121.2(3)
C(1)-C(12)-C(13)	118.1(3)
C(14)-C(13)-C(12)	109.4(3)
C(14)-C(13)-C(16)	110.0(4)
C(12)-C(13)-C(16)	111.2(3)

C(14)-C(13)-C(15)	108.4(4)
C(12)-C(13)-C(15)	108.1(3)
C(16)-C(13)-C(15)	109.8(4)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(1)-P(1)-C(4)	88.72(15)
C(1)-P(1)-Fe(1)	60.65(11)
C(4)-P(1)-Fe(1)	59.99(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+3/2,z

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^* a^* U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Fe(1)	12(1)	14(1)	9(1)	0	0	0(1)
C(1)	14(1)	17(2)	16(2)	1(1)	-2(1)	-2(1)
C(2)	18(2)	17(1)	16(2)	2(1)	-3(1)	-5(1)
C(3)	19(2)	17(2)	14(2)	-2(1)	3(1)	-2(1)
C(4)	14(1)	14(1)	15(2)	0(1)	1(1)	2(1)
C(5)	30(2)	27(2)	15(2)	0(1)	-8(1)	-2(2)
C(6)	28(2)	24(2)	16(2)	-5(1)	6(1)	-1(1)
C(7)	14(1)	17(2)	14(2)	-2(1)	6(1)	1(1)
C(8)	22(2)	15(2)	22(2)	-4(1)	-2(1)	5(1)
C(9)	40(2)	19(2)	36(2)	-3(2)	-8(2)	-4(2)
C(10)	30(2)	34(2)	50(3)	-10(2)	10(2)	13(2)
C(11)	50(2)	19(2)	25(2)	2(2)	0(2)	1(2)
C(12)	15(2)	18(2)	23(2)	-2(1)	-1(1)	0(1)
C(13)	10(1)	22(2)	40(2)	4(2)	0(1)	0(1)
C(14)	16(2)	48(3)	84(4)	15(3)	-3(2)	3(2)
C(15)	30(2)	40(2)	44(3)	1(2)	19(2)	-2(2)
C(16)	25(2)	22(2)	68(3)	-3(2)	6(2)	-8(2)
O(1)	21(1)	24(1)	26(1)	-2(1)	-5(1)	-4(1)
O(2)	24(1)	29(1)	36(2)	13(1)	-3(1)	3(1)
P(1)	14(1)	18(1)	12(1)	2(1)	1(1)	2(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U(eq)
H(5A)	1864	6953	-1293	36
H(5B)	895	7248	-906	36
H(5C)	1099	6203	-1116	36
H(6A)	3778	5753	-231	34
H(6B)	3238	6341	-961	34
H(6C)	2930	5322	-750	34
H(9A)	2896	3533	1163	47
H(9B)	3009	4301	411	47
H(9C)	2270	4419	1191	47
H(10A)	4986	4737	1739	57
H(10B)	4649	4585	728	57
H(10C)	4636	3759	1426	57
H(11A)	2833	4599	2816	47
H(11B)	3902	4640	2998	47
H(11C)	3445	3717	2658	47
H(14A)	-1394	7868	1005	74
H(14B)	-1894	6923	1195	74
H(14C)	-1434	7107	238	74
H(15A)	118	6707	2495	57
H(15B)	-966	6685	2552	57
H(15C)	-450	7625	2385	57
H(16A)	-516	5702	381	57
H(16B)	-962	5494	1340	57
H(16C)	118	5550	1241	57

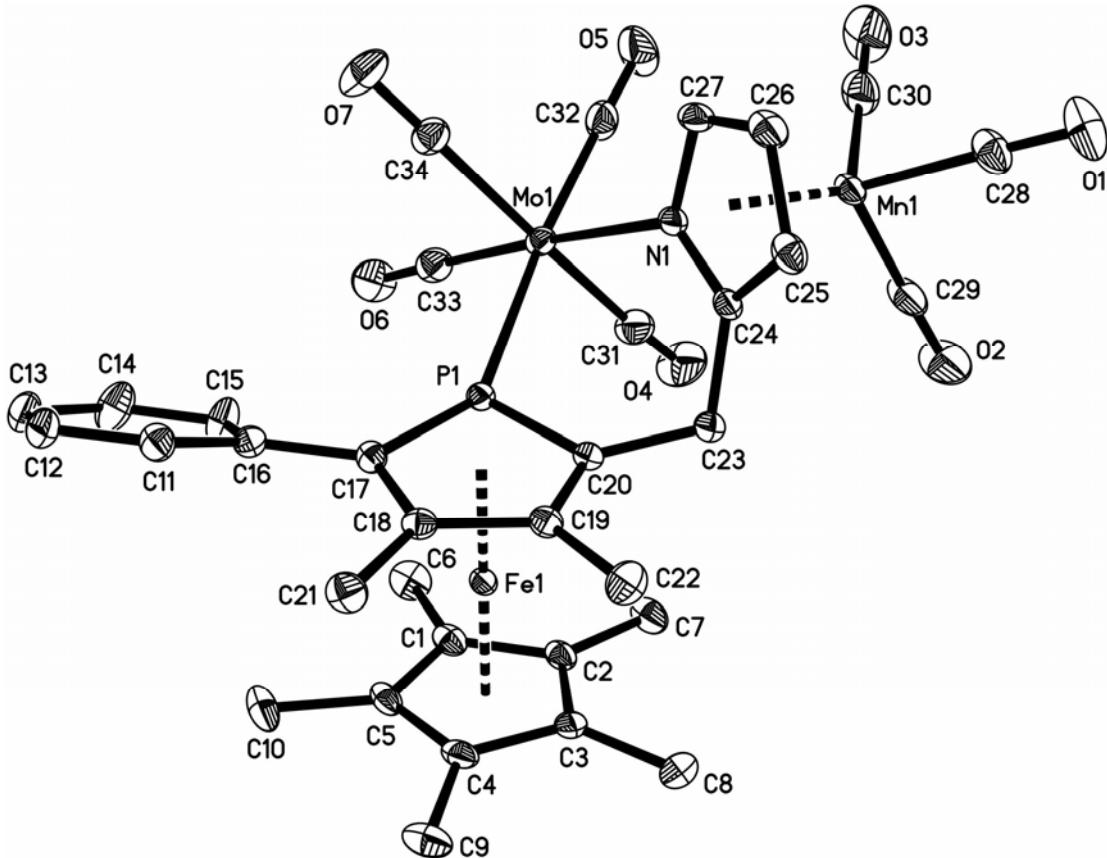


Table 1. Crystal data and structure refinement for: Compound **5** Chapter **3**

Identification code: Azacymanthrenylmethyl-phosphaferrrocene Mo complex

Empirical formula	$C_{34} H_{31} Fe Mn Mo N O_7 P$	
Formula weight	803.30	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	$a = 20.6389(19)$ Å	$\alpha = 90^\circ$ .
	$b = 7.6989(7)$ Å	$\beta = 93.509(5)^\circ$ .
	$c = 42.255(4)$ Å	$\gamma = 90^\circ$ .
Volume	$6701.6(10)$ Å <sup>3</sup>	
Z	8	
Density (calculated)	1.592 Mg/m <sup>3</sup>	

Absorption coefficient	1.263 mm <sup>-1</sup>
F(000)	3248
Crystal size	0.40 x 0.22 x 0.20 mm <sup>3</sup>
Theta range for data collection	1.93 to 34.99°.
Index ranges	-33<=h<=33, -12<=k<=10, -68<=l<=68
Reflections collected	149076
Independent reflections	29371 [R(int) = 0.0583]
Completeness to theta = 34.99°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7863 and 0.6321
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	29371 / 0 / 843
Goodness-of-fit on F <sup>2</sup>	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.0924
R indices (all data)	R1 = 0.0716, wR2 = 0.1049
Largest diff. peak and hole	1.149 and -1.352 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
C(1)	878(1)	7649(3)	1737(1)	17(1)
C(2)	515(1)	8018(3)	1444(1)	17(1)
C(3)	-150(1)	7618(3)	1482(1)	18(1)
C(4)	-203(1)	7000(3)	1799(1)	18(1)
C(5)	431(1)	7020(3)	1956(1)	17(1)
C(6)	1590(1)	7961(3)	1801(1)	25(1)
C(7)	780(1)	8817(3)	1156(1)	23(1)
C(8)	-701(1)	7906(3)	1242(1)	26(1)
C(9)	-823(1)	6542(3)	1946(1)	26(1)
C(10)	588(1)	6505(3)	2295(1)	25(1)
C(11)	947(1)	1313(3)	2224(1)	18(1)
C(12)	1292(1)	943(3)	2508(1)	22(1)
C(13)	1867(1)	1784(3)	2592(1)	24(1)
C(14)	2107(1)	2973(3)	2384(1)	29(1)
C(15)	1763(1)	3373(3)	2100(1)	24(1)
C(16)	1168(1)	2574(3)	2016(1)	16(1)
C(17)	812(1)	3009(2)	1712(1)	14(1)
C(18)	122(1)	2907(3)	1642(1)	15(1)
C(19)	-71(1)	3426(3)	1325(1)	14(1)
C(20)	466(1)	3961(2)	1153(1)	13(1)
C(21)	-366(1)	2287(3)	1868(1)	20(1)
C(22)	-757(1)	3357(3)	1186(1)	22(1)
C(23)	463(1)	4449(3)	806(1)	16(1)
C(24)	737(1)	2926(3)	639(1)	15(1)
C(25)	399(1)	1647(3)	455(1)	19(1)
C(26)	864(1)	360(3)	386(1)	22(1)
C(27)	1459(1)	909(3)	528(1)	20(1)
C(28)	752(1)	2297(3)	-190(1)	26(1)

C(29)	1016(1)	5069(3)	116(1)	27(1)
C(30)	1930(1)	2857(3)	17(1)	28(1)
C(31)	2124(1)	6016(3)	869(1)	26(1)
C(32)	2838(1)	3181(3)	733(1)	24(1)
C(33)	2800(1)	4508(3)	1374(1)	22(1)
C(34)	2431(1)	1201(3)	1234(1)	22(1)
C(35)	5224(1)	11777(3)	8584(1)	23(1)
C(36)	5210(1)	11207(3)	8260(1)	21(1)
C(37)	4562(1)	11384(3)	8127(1)	21(1)
C(38)	4169(1)	12062(3)	8367(1)	21(1)
C(39)	4582(1)	12306(3)	8648(1)	22(1)
C(40)	5815(1)	11909(4)	8806(1)	33(1)
C(41)	5792(1)	10656(3)	8088(1)	28(1)
C(42)	4348(1)	10989(3)	7789(1)	27(1)
C(43)	3464(1)	12520(3)	8331(1)	28(1)
C(44)	4389(1)	13145(3)	8949(1)	30(1)
C(45)	3228(1)	7865(3)	7956(1)	27(1)
C(46)	2882(1)	7508(4)	7671(1)	33(1)
C(47)	3107(1)	6275(3)	7465(1)	27(1)
C(48)	3661(1)	5366(3)	7552(1)	24(1)
C(49)	4007(1)	5706(3)	7838(1)	20(1)
C(50)	3805(1)	6994(3)	8045(1)	16(1)
C(51)	4156(1)	7375(3)	8352(1)	15(1)
C(52)	4839(1)	7173(3)	8431(1)	17(1)
C(53)	5024(1)	7641(3)	8752(1)	18(1)
C(54)	4487(1)	8239(3)	8917(1)	16(1)
C(55)	5328(1)	6491(3)	8210(1)	22(1)
C(56)	5697(1)	7451(3)	8902(1)	26(1)
C(57)	4475(1)	8743(3)	9262(1)	19(1)
C(58)	4121(1)	7335(3)	9428(1)	17(1)
C(59)	4380(1)	5995(3)	9626(1)	23(1)
C(60)	3854(1)	4889(3)	9693(1)	26(1)
C(61)	3297(1)	5611(3)	9536(1)	22(1)
C(62)	3998(1)	9593(3)	9949(1)	26(1)

C(63)	3945(1)	6741(3)	10259(1)	30(1)
C(64)	2887(1)	8081(4)	9998(1)	30(1)
C(65)	2858(1)	10716(3)	9143(1)	23(1)
C(66)	2190(1)	9167(3)	8625(1)	22(1)
C(67)	2013(1)	8184(4)	9266(1)	27(1)
C(68)	2472(1)	5845(3)	8810(1)	22(1)
Fe(1)	422(1)	5437(1)	1560(1)	12(1)
Fe(2)	4584(1)	9733(1)	8515(1)	14(1)
Mn(1)	1148(1)	2795(1)	188(1)	16(1)
Mn(2)	3676(1)	7458(1)	9870(1)	18(1)
Mo(1)	2180(1)	3571(1)	1046(1)	15(1)
Mo(2)	2741(1)	8247(1)	8982(1)	15(1)
N(1)	1390(1)	2484(2)	684(1)	15(1)
N(2)	3457(1)	7104(2)	9371(1)	17(1)
O(1)	477(1)	1963(3)	-426(1)	40(1)
O(2)	903(1)	6498(2)	65(1)	45(1)
O(3)	2424(1)	2891(3)	-92(1)	44(1)
O(4)	2168(1)	7381(2)	767(1)	41(1)
O(5)	3211(1)	2941(3)	544(1)	42(1)
O(6)	3151(1)	5067(3)	1572(1)	32(1)
O(7)	2638(1)	-40(2)	1346(1)	35(1)
O(8)	4224(1)	10932(2)	10001(1)	39(1)
O(9)	4143(1)	6215(3)	10500(1)	48(1)
O(10)	2391(1)	8491(3)	10078(1)	48(1)
O(11)	2858(1)	12104(3)	9235(1)	40(1)
O(12)	1877(1)	9682(3)	8409(1)	33(1)
O(13)	1590(1)	8180(3)	9433(1)	46(1)
O(14)	2266(1)	4592(2)	8702(1)	35(1)
P(1)	1208(1)	3778(1)	1375(1)	12(1)
P(2)	3754(1)	8177(1)	8684(1)	14(1)

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Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ].

C(1)-C(5)	1.432(3)
C(1)-C(2)	1.435(3)
C(1)-C(6)	1.497(3)
C(1)-Fe(1)	2.064(2)
C(2)-C(3)	1.425(3)
C(2)-C(7)	1.499(3)
C(2)-Fe(1)	2.058(2)
C(3)-C(4)	1.431(3)
C(3)-C(8)	1.494(3)
C(3)-Fe(1)	2.067(2)
C(4)-C(5)	1.431(3)
C(4)-C(9)	1.497(3)
C(4)-Fe(1)	2.0727(19)
C(5)-C(10)	1.504(3)
C(5)-Fe(1)	2.0697(19)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(12)	1.389(3)
C(11)-C(16)	1.403(3)

C(11)-H(11)	0.9500
C(12)-C(13)	1.380(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.383(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.390(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.399(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.479(3)
C(17)-C(18)	1.439(3)
C(17)-P(1)	1.7866(19)
C(17)-Fe(1)	2.1194(19)
C(18)-C(19)	1.431(3)
C(18)-C(21)	1.506(3)
C(18)-Fe(1)	2.080(2)
C(19)-C(20)	1.423(3)
C(19)-C(22)	1.499(3)
C(19)-Fe(1)	2.0732(19)
C(20)-C(23)	1.511(3)
C(20)-P(1)	1.754(2)
C(20)-Fe(1)	2.0687(18)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.499(3)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-N(1)	1.392(3)
C(24)-C(25)	1.411(3)
C(24)-Mn(1)	2.1355(19)

C(25)-C(26)	1.423(3)
C(25)-Mn(1)	2.160(2)
C(25)-H(25)	1.0000
C(26)-C(27)	1.400(3)
C(26)-Mn(1)	2.149(2)
C(26)-H(26)	1.0000
C(27)-N(1)	1.391(3)
C(27)-Mn(1)	2.117(2)
C(27)-H(27)	1.0000
C(28)-O(1)	1.145(3)
C(28)-Mn(1)	1.789(2)
C(29)-O(2)	1.143(3)
C(29)-Mn(1)	1.795(2)
C(30)-O(3)	1.144(3)
C(30)-Mn(1)	1.808(3)
C(31)-O(4)	1.142(3)
C(31)-Mo(1)	2.026(2)
C(32)-O(5)	1.158(3)
C(32)-Mo(1)	1.976(2)
C(33)-O(6)	1.156(3)
C(33)-Mo(1)	1.964(2)
C(34)-O(7)	1.137(3)
C(34)-Mo(1)	2.044(2)
C(35)-C(39)	1.428(3)
C(35)-C(36)	1.435(3)
C(35)-C(40)	1.495(4)
C(35)-Fe(2)	2.065(2)
C(36)-C(37)	1.427(3)
C(36)-C(41)	1.502(3)
C(36)-Fe(2)	2.070(2)
C(37)-C(38)	1.435(3)
C(37)-C(42)	1.499(3)
C(37)-Fe(2)	2.072(2)
C(38)-C(39)	1.433(3)

C(38)-C(43)	1.496(3)
C(38)-Fe(2)	2.067(2)
C(39)-C(44)	1.501(3)
C(39)-Fe(2)	2.060(2)
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(45)-C(46)	1.390(3)
C(45)-C(50)	1.398(3)
C(45)-H(45)	0.9500
C(46)-C(47)	1.385(4)
C(46)-H(46)	0.9500
C(47)-C(48)	1.372(4)
C(47)-H(47)	0.9500
C(48)-C(49)	1.390(3)
C(48)-H(48)	0.9500
C(49)-C(50)	1.403(3)
C(49)-H(49)	0.9500
C(50)-C(51)	1.478(3)
C(51)-C(52)	1.436(3)
C(51)-P(2)	1.7814(19)
C(51)-Fe(2)	2.114(2)

C(52)-C(53)	1.430(3)
C(52)-C(55)	1.511(3)
C(52)-Fe(2)	2.076(2)
C(53)-C(54)	1.422(3)
C(53)-C(56)	1.500(3)
C(53)-Fe(2)	2.077(2)
C(54)-C(57)	1.513(3)
C(54)-P(2)	1.754(2)
C(54)-Fe(2)	2.072(2)
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800
C(57)-C(58)	1.502(3)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(58)-N(2)	1.389(3)
C(58)-C(59)	1.412(3)
C(58)-Mn(2)	2.1341(19)
C(59)-C(60)	1.423(4)
C(59)-Mn(2)	2.152(2)
C(59)-H(59)	1.0000
C(60)-C(61)	1.404(4)
C(60)-Mn(2)	2.154(2)
C(60)-H(60)	1.0000
C(61)-N(2)	1.394(3)
C(61)-Mn(2)	2.118(2)
C(61)-H(61)	1.0000
C(62)-O(8)	1.147(3)
C(62)-Mn(2)	1.797(2)
C(63)-O(9)	1.146(3)
C(63)-Mn(2)	1.789(3)

C(64)-O(10)	1.143(3)
C(64)-Mn(2)	1.813(3)
C(65)-O(11)	1.138(3)
C(65)-Mo(2)	2.028(2)
C(66)-O(12)	1.155(3)
C(66)-Mo(2)	1.964(2)
C(67)-O(13)	1.158(3)
C(67)-Mo(2)	1.980(2)
C(68)-O(14)	1.139(3)
C(68)-Mo(2)	2.050(2)
Fe(1)-P(1)	2.2428(6)
Fe(2)-P(2)	2.2423(6)
Mn(1)-N(1)	2.1421(17)
Mn(2)-N(2)	2.1453(17)
Mo(1)-N(1)	2.3210(18)
Mo(1)-P(1)	2.5143(5)
Mo(2)-N(2)	2.3169(18)
Mo(2)-P(2)	2.5060(6)
C(5)-C(1)-C(2)	107.47(19)
C(5)-C(1)-C(6)	126.9(2)
C(2)-C(1)-C(6)	125.53(19)
C(5)-C(1)-Fe(1)	69.96(11)
C(2)-C(1)-Fe(1)	69.43(12)
C(6)-C(1)-Fe(1)	128.26(15)
C(3)-C(2)-C(1)	108.43(17)
C(3)-C(2)-C(7)	125.7(2)
C(1)-C(2)-C(7)	125.7(2)
C(3)-C(2)-Fe(1)	70.14(11)
C(1)-C(2)-Fe(1)	69.83(11)
C(7)-C(2)-Fe(1)	129.30(14)
C(2)-C(3)-C(4)	107.93(19)
C(2)-C(3)-C(8)	126.09(19)
C(4)-C(3)-C(8)	125.9(2)

C(2)-C(3)-Fe(1)	69.46(11)
C(4)-C(3)-Fe(1)	69.98(11)
C(8)-C(3)-Fe(1)	129.20(16)
C(3)-C(4)-C(5)	108.00(18)
C(3)-C(4)-C(9)	125.7(2)
C(5)-C(4)-C(9)	126.20(19)
C(3)-C(4)-Fe(1)	69.58(11)
C(5)-C(4)-Fe(1)	69.68(11)
C(9)-C(4)-Fe(1)	129.70(16)
C(4)-C(5)-C(1)	108.17(18)
C(4)-C(5)-C(10)	125.20(19)
C(1)-C(5)-C(10)	126.6(2)
C(4)-C(5)-Fe(1)	69.91(11)
C(1)-C(5)-Fe(1)	69.50(11)
C(10)-C(5)-Fe(1)	127.32(15)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5

C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(12)-C(11)-C(16)	120.9(2)
C(12)-C(11)-H(11)	119.5
C(16)-C(11)-H(11)	119.5
C(13)-C(12)-C(11)	120.9(2)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	118.9(2)
C(12)-C(13)-H(13)	120.6
C(14)-C(13)-H(13)	120.6
C(13)-C(14)-C(15)	120.8(2)
C(13)-C(14)-H(14)	119.6
C(15)-C(14)-H(14)	119.6
C(14)-C(15)-C(16)	121.1(2)
C(14)-C(15)-H(15)	119.5
C(16)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	117.30(19)
C(15)-C(16)-C(17)	120.21(18)
C(11)-C(16)-C(17)	122.43(19)
C(18)-C(17)-C(16)	126.87(17)
C(18)-C(17)-P(1)	110.42(14)
C(16)-C(17)-P(1)	122.71(15)
C(18)-C(17)-Fe(1)	68.47(11)
C(16)-C(17)-Fe(1)	128.49(14)

P(1)-C(17)-Fe(1)	69.49(7)
C(19)-C(18)-C(17)	113.19(17)
C(19)-C(18)-C(21)	121.53(18)
C(17)-C(18)-C(21)	125.26(18)
C(19)-C(18)-Fe(1)	69.61(11)
C(17)-C(18)-Fe(1)	71.45(11)
C(21)-C(18)-Fe(1)	128.28(14)
C(20)-C(19)-C(18)	112.21(17)
C(20)-C(19)-C(22)	123.80(18)
C(18)-C(19)-C(22)	123.96(18)
C(20)-C(19)-Fe(1)	69.73(11)
C(18)-C(19)-Fe(1)	70.08(11)
C(22)-C(19)-Fe(1)	129.64(15)
C(19)-C(20)-C(23)	127.61(18)
C(19)-C(20)-P(1)	112.67(14)
C(23)-C(20)-P(1)	119.34(14)
C(19)-C(20)-Fe(1)	70.07(11)
C(23)-C(20)-Fe(1)	132.18(14)
P(1)-C(20)-Fe(1)	71.31(7)
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-C(20)	106.51(16)
C(24)-C(23)-H(23A)	110.4
C(20)-C(23)-H(23A)	110.4

C(24)-C(23)-H(23B)	110.4
C(20)-C(23)-H(23B)	110.4
H(23A)-C(23)-H(23B)	108.6
N(1)-C(24)-C(25)	110.38(17)
N(1)-C(24)-C(23)	121.04(18)
C(25)-C(24)-C(23)	128.10(19)
N(1)-C(24)-Mn(1)	71.26(10)
C(25)-C(24)-Mn(1)	71.78(11)
C(23)-C(24)-Mn(1)	129.87(14)
C(24)-C(25)-C(26)	106.4(2)
C(24)-C(25)-Mn(1)	69.88(12)
C(26)-C(25)-Mn(1)	70.28(12)
C(24)-C(25)-H(25)	126.8
C(26)-C(25)-H(25)	126.8
Mn(1)-C(25)-H(25)	126.8
C(27)-C(26)-C(25)	106.58(19)
C(27)-C(26)-Mn(1)	69.61(12)
C(25)-C(26)-Mn(1)	71.15(12)
C(27)-C(26)-H(26)	126.7
C(25)-C(26)-H(26)	126.7
Mn(1)-C(26)-H(26)	126.7
N(1)-C(27)-C(26)	110.81(19)
N(1)-C(27)-Mn(1)	71.91(11)
C(26)-C(27)-Mn(1)	72.08(13)
N(1)-C(27)-H(27)	124.6
C(26)-C(27)-H(27)	124.6
Mn(1)-C(27)-H(27)	124.6
O(1)-C(28)-Mn(1)	177.4(2)
O(2)-C(29)-Mn(1)	176.8(3)
O(3)-C(30)-Mn(1)	179.7(3)
O(4)-C(31)-Mo(1)	172.1(2)
O(5)-C(32)-Mo(1)	178.3(2)
O(6)-C(33)-Mo(1)	178.1(2)
O(7)-C(34)-Mo(1)	172.3(2)

C(39)-C(35)-C(36)	107.6(2)
C(39)-C(35)-C(40)	126.3(2)
C(36)-C(35)-C(40)	126.0(2)
C(39)-C(35)-Fe(2)	69.55(13)
C(36)-C(35)-Fe(2)	69.88(12)
C(40)-C(35)-Fe(2)	129.16(18)
C(37)-C(36)-C(35)	108.19(19)
C(37)-C(36)-C(41)	126.4(2)
C(35)-C(36)-C(41)	125.3(2)
C(37)-C(36)-Fe(2)	69.95(12)
C(35)-C(36)-Fe(2)	69.50(12)
C(41)-C(36)-Fe(2)	129.76(17)
C(36)-C(37)-C(38)	108.2(2)
C(36)-C(37)-C(42)	124.9(2)
C(38)-C(37)-C(42)	126.9(2)
C(36)-C(37)-Fe(2)	69.76(12)
C(38)-C(37)-Fe(2)	69.50(12)
C(42)-C(37)-Fe(2)	128.29(16)
C(39)-C(38)-C(37)	107.5(2)
C(39)-C(38)-C(43)	125.3(2)
C(37)-C(38)-C(43)	127.1(2)
C(39)-C(38)-Fe(2)	69.41(13)
C(37)-C(38)-Fe(2)	69.93(12)
C(43)-C(38)-Fe(2)	128.09(16)
C(35)-C(39)-C(38)	108.53(19)
C(35)-C(39)-C(44)	125.5(2)
C(38)-C(39)-C(44)	125.7(2)
C(35)-C(39)-Fe(2)	69.94(13)
C(38)-C(39)-Fe(2)	69.94(12)
C(44)-C(39)-Fe(2)	130.54(16)
C(35)-C(40)-H(40A)	109.5
C(35)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(35)-C(40)-H(40C)	109.5

H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(36)-C(41)-H(41A)	109.5
C(36)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(36)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(37)-C(42)-H(42A)	109.5
C(37)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(37)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(38)-C(43)-H(43A)	109.5
C(38)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(38)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(39)-C(44)-H(44A)	109.5
C(39)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(39)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(46)-C(45)-C(50)	121.4(2)
C(46)-C(45)-H(45)	119.3
C(50)-C(45)-H(45)	119.3
C(47)-C(46)-C(45)	120.4(2)
C(47)-C(46)-H(46)	119.8
C(45)-C(46)-H(46)	119.8
C(48)-C(47)-C(46)	119.2(2)
C(48)-C(47)-H(47)	120.4

C(46)-C(47)-H(47)	120.4
C(47)-C(48)-C(49)	120.8(2)
C(47)-C(48)-H(48)	119.6
C(49)-C(48)-H(48)	119.6
C(48)-C(49)-C(50)	121.3(2)
C(48)-C(49)-H(49)	119.4
C(50)-C(49)-H(49)	119.4
C(45)-C(50)-C(49)	116.9(2)
C(45)-C(50)-C(51)	120.31(18)
C(49)-C(50)-C(51)	122.70(19)
C(52)-C(51)-C(50)	127.15(17)
C(52)-C(51)-P(2)	110.67(15)
C(50)-C(51)-P(2)	122.18(15)
C(52)-C(51)-Fe(2)	68.54(12)
C(50)-C(51)-Fe(2)	128.88(14)
P(2)-C(51)-Fe(2)	69.68(7)
C(53)-C(52)-C(51)	113.21(17)
C(53)-C(52)-C(55)	121.51(19)
C(51)-C(52)-C(55)	125.26(19)
C(53)-C(52)-Fe(2)	69.88(12)
C(51)-C(52)-Fe(2)	71.40(11)
C(55)-C(52)-Fe(2)	128.37(15)
C(54)-C(53)-C(52)	111.97(18)
C(54)-C(53)-C(56)	123.62(19)
C(52)-C(53)-C(56)	124.35(19)
C(54)-C(53)-Fe(2)	69.75(12)
C(52)-C(53)-Fe(2)	69.83(12)
C(56)-C(53)-Fe(2)	130.32(16)
C(53)-C(54)-C(57)	128.01(19)
C(53)-C(54)-P(2)	112.80(15)
C(57)-C(54)-P(2)	118.95(15)
C(53)-C(54)-Fe(2)	70.15(12)
C(57)-C(54)-Fe(2)	131.10(15)
P(2)-C(54)-Fe(2)	71.22(7)

C(52)-C(55)-H(55A)	109.5
C(52)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(52)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(53)-C(56)-H(56A)	109.5
C(53)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(53)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(58)-C(57)-C(54)	107.51(17)
C(58)-C(57)-H(57A)	110.2
C(54)-C(57)-H(57A)	110.2
C(58)-C(57)-H(57B)	110.2
C(54)-C(57)-H(57B)	110.2
H(57A)-C(57)-H(57B)	108.5
N(2)-C(58)-C(59)	110.03(19)
N(2)-C(58)-C(57)	121.00(18)
C(59)-C(58)-C(57)	128.7(2)
N(2)-C(58)-Mn(2)	71.49(11)
C(59)-C(58)-Mn(2)	71.43(12)
C(57)-C(58)-Mn(2)	128.46(14)
C(58)-C(59)-C(60)	106.8(2)
C(58)-C(59)-Mn(2)	70.09(12)
C(60)-C(59)-Mn(2)	70.79(13)
C(58)-C(59)-H(59)	126.6
C(60)-C(59)-H(59)	126.6
Mn(2)-C(59)-H(59)	126.6
C(61)-C(60)-C(59)	106.4(2)
C(61)-C(60)-Mn(2)	69.44(13)
C(59)-C(60)-Mn(2)	70.61(13)
C(61)-C(60)-H(60)	126.8

C(59)-C(60)-H(60)	126.8
Mn(2)-C(60)-H(60)	126.8
N(2)-C(61)-C(60)	110.5(2)
N(2)-C(61)-Mn(2)	71.97(12)
C(60)-C(61)-Mn(2)	72.19(14)
N(2)-C(61)-H(61)	124.7
C(60)-C(61)-H(61)	124.7
Mn(2)-C(61)-H(61)	124.7
O(8)-C(62)-Mn(2)	177.6(3)
O(9)-C(63)-Mn(2)	175.9(2)
O(10)-C(64)-Mn(2)	179.3(3)
O(11)-C(65)-Mo(2)	173.1(2)
O(12)-C(66)-Mo(2)	177.9(2)
O(13)-C(67)-Mo(2)	178.7(2)
O(14)-C(68)-Mo(2)	172.9(2)
C(2)-Fe(1)-C(1)	40.74(8)
C(2)-Fe(1)-C(3)	40.40(8)
C(1)-Fe(1)-C(3)	68.32(9)
C(2)-Fe(1)-C(20)	108.87(8)
C(1)-Fe(1)-C(20)	135.43(8)
C(3)-Fe(1)-C(20)	111.58(8)
C(2)-Fe(1)-C(5)	68.10(8)
C(1)-Fe(1)-C(5)	40.54(8)
C(3)-Fe(1)-C(5)	68.06(8)
C(20)-Fe(1)-C(5)	175.95(8)
C(2)-Fe(1)-C(4)	67.96(8)
C(1)-Fe(1)-C(4)	68.19(8)
C(3)-Fe(1)-C(4)	40.43(8)
C(20)-Fe(1)-C(4)	141.68(8)
C(5)-Fe(1)-C(4)	40.42(9)
C(2)-Fe(1)-C(19)	131.09(8)
C(1)-Fe(1)-C(19)	171.76(8)
C(3)-Fe(1)-C(19)	105.76(8)
C(20)-Fe(1)-C(19)	40.20(7)

C(5)-Fe(1)-C(19)	143.81(8)
C(4)-Fe(1)-C(19)	111.39(8)
C(2)-Fe(1)-C(18)	167.65(9)
C(1)-Fe(1)-C(18)	147.88(8)
C(3)-Fe(1)-C(18)	127.88(8)
C(20)-Fe(1)-C(18)	69.65(8)
C(5)-Fe(1)-C(18)	113.91(8)
C(4)-Fe(1)-C(18)	105.18(8)
C(19)-Fe(1)-C(18)	40.30(8)
C(2)-Fe(1)-C(17)	152.22(8)
C(1)-Fe(1)-C(17)	117.50(8)
C(3)-Fe(1)-C(17)	165.24(8)
C(20)-Fe(1)-C(17)	74.51(7)
C(5)-Fe(1)-C(17)	106.85(8)
C(4)-Fe(1)-C(17)	126.90(8)
C(19)-Fe(1)-C(17)	69.69(8)
C(18)-Fe(1)-C(17)	40.07(8)
C(2)-Fe(1)-P(1)	112.81(6)
C(1)-Fe(1)-P(1)	105.81(6)
C(3)-Fe(1)-P(1)	145.67(6)
C(20)-Fe(1)-P(1)	47.79(6)
C(5)-Fe(1)-P(1)	130.29(7)
C(4)-Fe(1)-P(1)	170.43(6)
C(19)-Fe(1)-P(1)	75.66(6)
C(18)-Fe(1)-P(1)	75.74(6)
C(17)-Fe(1)-P(1)	48.25(5)
C(39)-Fe(2)-C(35)	40.51(9)
C(39)-Fe(2)-C(38)	40.65(10)
C(35)-Fe(2)-C(38)	68.41(10)
C(39)-Fe(2)-C(36)	68.04(8)
C(35)-Fe(2)-C(36)	40.62(8)
C(38)-Fe(2)-C(36)	68.15(9)
C(39)-Fe(2)-C(54)	107.94(8)
C(35)-Fe(2)-C(54)	113.56(9)

C(38)-Fe(2)-C(54)	132.15(8)
C(36)-Fe(2)-C(54)	145.57(9)
C(39)-Fe(2)-C(37)	68.06(9)
C(35)-Fe(2)-C(37)	68.15(10)
C(38)-Fe(2)-C(37)	40.56(8)
C(36)-Fe(2)-C(37)	40.29(9)
C(54)-Fe(2)-C(37)	172.20(9)
C(39)-Fe(2)-C(52)	164.63(10)
C(35)-Fe(2)-C(52)	125.49(9)
C(38)-Fe(2)-C(52)	151.26(9)
C(36)-Fe(2)-C(52)	105.02(8)
C(54)-Fe(2)-C(52)	69.51(8)
C(37)-Fe(2)-C(52)	116.19(8)
C(39)-Fe(2)-C(53)	128.45(9)
C(35)-Fe(2)-C(53)	105.35(10)
C(38)-Fe(2)-C(53)	168.43(9)
C(36)-Fe(2)-C(53)	113.98(9)
C(54)-Fe(2)-C(53)	40.10(8)
C(37)-Fe(2)-C(53)	147.63(8)
C(52)-Fe(2)-C(53)	40.29(8)
C(39)-Fe(2)-C(51)	155.13(9)
C(35)-Fe(2)-C(51)	162.03(8)
C(38)-Fe(2)-C(51)	119.33(9)
C(36)-Fe(2)-C(51)	124.32(8)
C(54)-Fe(2)-C(51)	74.32(8)
C(37)-Fe(2)-C(51)	106.36(9)
C(52)-Fe(2)-C(51)	40.06(8)
C(53)-Fe(2)-C(51)	69.63(8)
C(39)-Fe(2)-P(2)	114.41(6)
C(35)-Fe(2)-P(2)	148.98(6)
C(38)-Fe(2)-P(2)	104.47(7)
C(36)-Fe(2)-P(2)	166.39(7)
C(54)-Fe(2)-P(2)	47.78(6)
C(37)-Fe(2)-P(2)	126.86(7)

C(52)-Fe(2)-P(2)	75.71(6)
C(53)-Fe(2)-P(2)	75.65(6)
C(51)-Fe(2)-P(2)	48.16(5)
C(28)-Mn(1)-C(29)	90.14(11)
C(28)-Mn(1)-C(30)	91.21(12)
C(29)-Mn(1)-C(30)	92.13(12)
C(28)-Mn(1)-C(27)	124.25(10)
C(29)-Mn(1)-C(27)	145.10(10)
C(30)-Mn(1)-C(27)	92.78(10)
C(28)-Mn(1)-C(24)	128.39(10)
C(29)-Mn(1)-C(24)	92.27(9)
C(30)-Mn(1)-C(24)	140.12(10)
C(27)-Mn(1)-C(24)	62.96(8)
C(28)-Mn(1)-N(1)	156.44(9)
C(29)-Mn(1)-N(1)	107.34(9)
C(30)-Mn(1)-N(1)	103.48(9)
C(27)-Mn(1)-N(1)	38.13(7)
C(24)-Mn(1)-N(1)	37.99(7)
C(28)-Mn(1)-C(26)	92.27(10)
C(29)-Mn(1)-C(26)	150.96(10)
C(30)-Mn(1)-C(26)	116.73(10)
C(27)-Mn(1)-C(26)	38.31(9)
C(24)-Mn(1)-C(26)	63.96(8)
N(1)-Mn(1)-C(26)	64.76(8)
C(28)-Mn(1)-C(25)	94.39(10)
C(29)-Mn(1)-C(25)	112.39(10)
C(30)-Mn(1)-C(25)	154.79(10)
C(27)-Mn(1)-C(25)	63.89(9)
C(24)-Mn(1)-C(25)	38.34(8)
N(1)-Mn(1)-C(25)	64.67(8)
C(26)-Mn(1)-C(25)	38.58(8)
C(63)-Mn(2)-C(62)	91.18(12)
C(63)-Mn(2)-C(64)	92.43(12)
C(62)-Mn(2)-C(64)	91.75(12)

C(63)-Mn(2)-C(61)	119.03(11)
C(62)-Mn(2)-C(61)	148.84(10)
C(64)-Mn(2)-C(61)	94.21(11)
C(63)-Mn(2)-C(58)	131.65(11)
C(62)-Mn(2)-C(58)	91.76(10)
C(64)-Mn(2)-C(58)	135.66(10)
C(61)-Mn(2)-C(58)	63.15(8)
C(63)-Mn(2)-N(2)	153.87(10)
C(62)-Mn(2)-N(2)	110.69(9)
C(64)-Mn(2)-N(2)	100.71(9)
C(61)-Mn(2)-N(2)	38.16(7)
C(58)-Mn(2)-N(2)	37.89(7)
C(63)-Mn(2)-C(59)	95.66(10)
C(62)-Mn(2)-C(59)	108.44(11)
C(64)-Mn(2)-C(59)	158.02(11)
C(61)-Mn(2)-C(59)	64.02(9)
C(58)-Mn(2)-C(59)	38.47(8)
N(2)-Mn(2)-C(59)	64.57(8)
C(63)-Mn(2)-C(60)	89.20(10)
C(62)-Mn(2)-C(60)	146.77(11)
C(64)-Mn(2)-C(60)	121.43(12)
C(61)-Mn(2)-C(60)	38.37(9)
C(58)-Mn(2)-C(60)	64.12(8)
N(2)-Mn(2)-C(60)	64.68(8)
C(59)-Mn(2)-C(60)	38.60(9)
C(33)-Mo(1)-C(32)	94.77(10)
C(33)-Mo(1)-C(31)	86.53(10)
C(32)-Mo(1)-C(31)	85.41(10)
C(33)-Mo(1)-C(34)	85.12(10)
C(32)-Mo(1)-C(34)	87.52(9)
C(31)-Mo(1)-C(34)	168.57(10)
C(33)-Mo(1)-N(1)	175.90(7)
C(32)-Mo(1)-N(1)	89.33(8)
C(31)-Mo(1)-N(1)	94.00(9)

C(34)-Mo(1)-N(1)	94.89(8)
C(33)-Mo(1)-P(1)	95.41(6)
C(32)-Mo(1)-P(1)	169.71(7)
C(31)-Mo(1)-P(1)	96.67(7)
C(34)-Mo(1)-P(1)	91.88(6)
N(1)-Mo(1)-P(1)	80.48(4)
C(66)-Mo(2)-C(67)	92.76(10)
C(66)-Mo(2)-C(65)	88.34(10)
C(67)-Mo(2)-C(65)	84.18(10)
C(66)-Mo(2)-C(68)	85.55(10)
C(67)-Mo(2)-C(68)	89.59(10)
C(65)-Mo(2)-C(68)	171.06(9)
C(66)-Mo(2)-N(2)	175.09(8)
C(67)-Mo(2)-N(2)	91.98(9)
C(65)-Mo(2)-N(2)	93.45(8)
C(68)-Mo(2)-N(2)	93.17(8)
C(66)-Mo(2)-P(2)	94.84(6)
C(67)-Mo(2)-P(2)	172.41(8)
C(65)-Mo(2)-P(2)	95.92(6)
C(68)-Mo(2)-P(2)	91.10(6)
N(2)-Mo(2)-P(2)	80.43(4)
C(27)-N(1)-C(24)	105.85(17)
C(27)-N(1)-Mn(1)	69.96(11)
C(24)-N(1)-Mn(1)	70.75(10)
C(27)-N(1)-Mo(1)	122.55(14)
C(24)-N(1)-Mo(1)	129.68(13)
Mn(1)-N(1)-Mo(1)	135.82(8)
C(58)-N(2)-C(61)	106.28(18)
C(58)-N(2)-Mn(2)	70.62(11)
C(61)-N(2)-Mn(2)	69.87(11)
C(58)-N(2)-Mo(2)	130.76(13)
C(61)-N(2)-Mo(2)	120.61(15)
Mn(2)-N(2)-Mo(2)	137.46(8)
C(20)-P(1)-C(17)	91.49(9)

C(20)-P(1)-Fe(1)	60.90(6)
C(17)-P(1)-Fe(1)	62.26(6)
C(20)-P(1)-Mo(1)	114.18(6)
C(17)-P(1)-Mo(1)	147.09(7)
Fe(1)-P(1)-Mo(1)	147.92(2)
C(54)-P(2)-C(51)	91.33(10)
C(54)-P(2)-Fe(2)	61.01(7)
C(51)-P(2)-Fe(2)	62.16(7)
C(54)-P(2)-Mo(2)	115.76(7)
C(51)-P(2)-Mo(2)	147.74(7)
Fe(2)-P(2)-Mo(2)	145.61(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\alpha^2 [ h^2 a^*{}^2 U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
C(1)	24(1)	12(1)	17(1)	-2(1)	5(1)	-2(1)
C(2)	25(1)	12(1)	14(1)	0(1)	6(1)	2(1)
C(3)	23(1)	14(1)	16(1)	0(1)	4(1)	8(1)
C(4)	22(1)	14(1)	17(1)	-3(1)	7(1)	3(1)
C(5)	26(1)	13(1)	12(1)	-2(1)	5(1)	-1(1)
C(6)	26(1)	20(1)	29(1)	-3(1)	4(1)	-7(1)
C(7)	38(1)	14(1)	19(1)	3(1)	10(1)	0(1)
C(8)	27(1)	25(1)	24(1)	2(1)	0(1)	11(1)
C(9)	24(1)	28(1)	29(1)	-4(1)	13(1)	1(1)
C(10)	37(1)	25(1)	13(1)	0(1)	2(1)	-5(1)
C(11)	23(1)	15(1)	18(1)	1(1)	2(1)	-1(1)
C(12)	28(1)	18(1)	18(1)	4(1)	2(1)	3(1)
C(13)	30(1)	23(1)	19(1)	3(1)	-4(1)	6(1)
C(14)	23(1)	28(1)	34(1)	8(1)	-9(1)	-4(1)
C(15)	21(1)	24(1)	25(1)	10(1)	-6(1)	-4(1)
C(16)	19(1)	13(1)	16(1)	0(1)	2(1)	2(1)
C(17)	16(1)	11(1)	14(1)	1(1)	2(1)	-1(1)
C(18)	14(1)	13(1)	17(1)	0(1)	2(1)	0(1)
C(19)	15(1)	13(1)	14(1)	-2(1)	1(1)	-1(1)
C(20)	15(1)	13(1)	12(1)	-2(1)	1(1)	2(1)
C(21)	18(1)	21(1)	22(1)	2(1)	5(1)	-2(1)
C(22)	16(1)	24(1)	24(1)	0(1)	-3(1)	-2(1)
C(23)	19(1)	14(1)	14(1)	0(1)	2(1)	3(1)
C(24)	21(1)	14(1)	10(1)	0(1)	2(1)	2(1)
C(25)	26(1)	17(1)	15(1)	1(1)	3(1)	-4(1)
C(26)	36(1)	12(1)	17(1)	0(1)	5(1)	-2(1)
C(27)	31(1)	13(1)	16(1)	1(1)	7(1)	6(1)
C(28)	40(1)	20(1)	17(1)	0(1)	4(1)	-5(1)

C(29)	48(2)	18(1)	16(1)	-1(1)	9(1)	1(1)
C(30)	36(1)	29(1)	19(1)	6(1)	5(1)	0(1)
C(31)	28(1)	23(1)	27(1)	4(1)	8(1)	4(1)
C(32)	19(1)	34(1)	20(1)	4(1)	0(1)	4(1)
C(33)	20(1)	23(1)	25(1)	4(1)	6(1)	2(1)
C(34)	21(1)	22(1)	25(1)	5(1)	4(1)	2(1)
C(35)	28(1)	21(1)	23(1)	-4(1)	9(1)	-10(1)
C(36)	26(1)	17(1)	20(1)	-2(1)	10(1)	-5(1)
C(37)	29(1)	14(1)	19(1)	2(1)	9(1)	1(1)
C(38)	28(1)	13(1)	23(1)	2(1)	11(1)	1(1)
C(39)	31(1)	14(1)	23(1)	-4(1)	13(1)	-5(1)
C(40)	30(1)	39(2)	30(1)	-11(1)	4(1)	-16(1)
C(41)	27(1)	30(1)	28(1)	-2(1)	14(1)	-3(1)
C(42)	40(1)	24(1)	19(1)	3(1)	5(1)	5(1)
C(43)	33(1)	18(1)	34(1)	5(1)	12(1)	8(1)
C(44)	44(2)	20(1)	27(1)	-9(1)	17(1)	-8(1)
C(45)	27(1)	25(1)	29(1)	-10(1)	-5(1)	7(1)
C(46)	30(1)	30(1)	37(1)	-10(1)	-15(1)	7(1)
C(47)	34(1)	25(1)	21(1)	-1(1)	-7(1)	-5(1)
C(48)	35(1)	20(1)	16(1)	-3(1)	2(1)	-3(1)
C(49)	26(1)	16(1)	17(1)	-1(1)	4(1)	2(1)
C(50)	19(1)	13(1)	17(1)	-1(1)	1(1)	-1(1)
C(51)	17(1)	13(1)	16(1)	-1(1)	4(1)	2(1)
C(52)	17(1)	15(1)	18(1)	0(1)	5(1)	1(1)
C(53)	17(1)	21(1)	18(1)	2(1)	2(1)	0(1)
C(54)	16(1)	19(1)	13(1)	0(1)	2(1)	0(1)
C(55)	22(1)	24(1)	22(1)	-1(1)	6(1)	5(1)
C(56)	17(1)	35(1)	26(1)	-1(1)	-1(1)	3(1)
C(57)	17(1)	25(1)	14(1)	-1(1)	2(1)	-3(1)
C(58)	20(1)	19(1)	11(1)	-3(1)	1(1)	2(1)
C(59)	30(1)	23(1)	16(1)	-1(1)	1(1)	8(1)
C(60)	44(1)	15(1)	21(1)	0(1)	5(1)	5(1)
C(61)	33(1)	16(1)	17(1)	-1(1)	6(1)	-5(1)
C(62)	35(1)	22(1)	20(1)	0(1)	3(1)	2(1)

C(63)	46(2)	25(1)	19(1)	-2(1)	1(1)	4(1)
C(64)	37(1)	36(1)	16(1)	-4(1)	6(1)	2(1)
C(65)	24(1)	22(1)	22(1)	-2(1)	6(1)	-2(1)
C(66)	17(1)	24(1)	24(1)	-3(1)	3(1)	1(1)
C(67)	21(1)	38(1)	21(1)	-6(1)	0(1)	-5(1)
C(68)	17(1)	23(1)	26(1)	-2(1)	3(1)	0(1)
Fe(1)	14(1)	11(1)	10(1)	0(1)	2(1)	0(1)
Fe(2)	16(1)	14(1)	13(1)	-1(1)	4(1)	-1(1)
Mn(1)	27(1)	11(1)	11(1)	0(1)	4(1)	1(1)
Mn(2)	27(1)	16(1)	12(1)	0(1)	3(1)	2(1)
Mo(1)	14(1)	15(1)	16(1)	3(1)	3(1)	2(1)
Mo(2)	14(1)	16(1)	16(1)	-2(1)	3(1)	-1(1)
N(1)	22(1)	12(1)	12(1)	1(1)	3(1)	3(1)
N(2)	22(1)	15(1)	13(1)	0(1)	3(1)	-2(1)
O(1)	54(1)	45(1)	20(1)	-3(1)	-2(1)	-13(1)
O(2)	86(2)	17(1)	34(1)	6(1)	16(1)	12(1)
O(3)	36(1)	63(2)	33(1)	13(1)	15(1)	-1(1)
O(4)	51(1)	24(1)	49(1)	15(1)	14(1)	4(1)
O(5)	24(1)	80(2)	24(1)	-1(1)	7(1)	10(1)
O(6)	22(1)	39(1)	35(1)	-7(1)	-3(1)	-2(1)
O(7)	31(1)	28(1)	48(1)	16(1)	5(1)	8(1)
O(8)	57(1)	22(1)	39(1)	-5(1)	2(1)	-6(1)
O(9)	84(2)	39(1)	20(1)	-1(1)	-11(1)	10(1)
O(10)	37(1)	76(2)	33(1)	-16(1)	12(1)	9(1)
O(11)	52(1)	26(1)	45(1)	-14(1)	13(1)	-3(1)
O(12)	25(1)	42(1)	31(1)	2(1)	-3(1)	8(1)
O(13)	25(1)	87(2)	26(1)	-12(1)	9(1)	-11(1)
O(14)	25(1)	25(1)	54(1)	-15(1)	1(1)	-2(1)
P(1)	13(1)	12(1)	12(1)	0(1)	2(1)	1(1)
P(2)	14(1)	14(1)	13(1)	-1(1)	2(1)	0(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U(eq)
H(6A)	1826	7517	1624	37
H(6B)	1740	7360	1997	37
H(6C)	1670	9210	1825	37
H(7A)	526	8419	966	35
H(7B)	1234	8470	1143	35
H(7C)	753	10085	1170	35
H(8A)	-833	9129	1246	38
H(8B)	-1068	7170	1293	38
H(8C)	-563	7609	1031	38
H(9A)	-728	5776	2128	40
H(9B)	-1114	5945	1789	40
H(9C)	-1032	7604	2017	40
H(10A)	425	7394	2436	38
H(10B)	1059	6395	2334	38
H(10C)	381	5389	2337	38
H(11)	556	703	2169	22
H(12)	1129	100	2647	26
H(13)	2094	1551	2790	29
H(14)	2512	3522	2435	34
H(15)	1934	4202	1961	28
H(21A)	-792	2788	1807	30
H(21B)	-228	2653	2084	30
H(21C)	-393	1017	1859	30
H(22A)	-809	4178	1009	33
H(22B)	-1054	3671	1349	33
H(22C)	-856	2179	1110	33
H(23A)	15	4697	721	19
H(23B)	733	5495	778	19

H(25)	-77	1622	395	23
H(26)	778	-751	268	26
H(27)	1874	241	525	24
H(40A)	5982	13100	8804	49
H(40B)	6148	11107	8738	49
H(40C)	5701	11607	9021	49
H(41A)	5655	9854	7917	42
H(41B)	6104	10074	8237	42
H(41C)	5995	11680	7999	42
H(42A)	4523	11869	7650	41
H(42B)	3873	11000	7764	41
H(42C)	4509	9840	7732	41
H(43A)	3245	12091	8516	42
H(43B)	3268	11984	8138	42
H(43C)	3416	13784	8317	42
H(44A)	4461	14400	8938	45
H(44B)	4651	12663	9129	45
H(44C)	3928	12918	8976	45
H(45)	3068	8720	8094	33
H(46)	2490	8113	7616	40
H(47)	2879	6061	7267	33
H(48)	3810	4494	7415	28
H(49)	4388	5054	7894	24
H(55A)	5339	5220	8221	33
H(55B)	5758	6955	8274	33
H(55C)	5203	6857	7993	33
H(56A)	5746	8193	9091	39
H(56B)	6014	7798	8750	39
H(56C)	5773	6237	8964	39
H(57A)	4923	8860	9358	23
H(57B)	4249	9867	9283	23
H(59)	4848	5822	9695	27
H(60)	3879	3787	9818	31
H(61)	2852	5097	9536	27