

Using Phosphohydrazides as Building Blocks to Multiredox Polymetallic Compounds Containing Ferrocenyl Groups. Electrochemical and NMR Behaviors in Solution

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The condensation of phosphodi- or phosphotrihydrazides $\text{Ph}_{3-n}\text{P}(\text{X})[\text{N}(\text{CH}_3)\text{NH}_2]_n$ (**1a** ($n = 2$; $\text{X} = \text{S}$); **1b** ($n = 2$; $\text{X} = \text{O}$); **2a**; ($n = 3$; $\text{X} = \text{S}$); **2b** ($n = 3$; $\text{X} = \text{O}$)) with ferrocenecarbaldehyde is a high-yield synthetic route to new ferrocenyl phosphohydrazone ligands $\text{Ph}_n\text{P}(\text{X})[\text{N}(\text{CH}_3)\text{N}=\text{CHC}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)]_{3-n}$ (**3a**, **3b**, **4a**, **4b**). The structure of **3b** has been solved by X-ray crystallography. Crystal data at room temperature are $a = 15.176(1)\text{Å}$, $b = 15.170(2)\text{Å}$, $c = 12.533(2)\text{Å}$, $\beta = 106.582(8)^\circ$, $Z = 4$ for a monoclinic system, space group $P2_1/c$, $V = 2765.5(5)\text{Å}^3$, $Z = 4$; $R = 0.049$, $R_w = 0.056$ for 2104 observations and 361 variable parameters. Similar phenyl thiophosphodi- and trihydrazones **6** and **7** were obtained by condensation with benzaldehyde. Depending on the ligand/copper(I) ratio **1a**, **3a**, or **6** led to $[\text{LCu}]_2[\text{SO}_3\text{CF}_3]_2$ or $[\text{L}_2\text{Cu}][\text{SO}_3\text{CF}_3]$ complexes. For the 1/1 adducts the sulfur atom of the PS group bridges the two copper centers and the P-N-N arms of each ligand are coordinated to two different copper atoms. For the 2/1 adducts each ligand is bonded by the sulfur and one P-N-N arm, and in solution, NMR gives evidence of an exchange phenomenon between the free and complexed P-N-N arms. The ligand **4a** is a bidentate ligand through the sulfur atom with one of the P-N-N arms toward CuCl and a tridentate one through the P-N-N arms toward CuSO_3CF_3 . Condensation reactions between ferrocenecarbaldehyde and the complexes of **1a** led to the similar complexes containing the ligand **3a**. Electrochemical studies of the ligands containing the ferrocenyl moieties and their complexes show that complexation induces, as expected, a shift toward more anodic potential. For the $[(\text{3a})_2\text{Cu}][\text{SO}_3\text{CF}_3]$ complex, two waves corresponding to the two different ferrocene environments have been observed.

Introduction

After the important work of Lehn and his group concerning the design of receptors for small organic molecules,¹ Constable explained in a recent paper how metallic sandwiches could bring a new element to molecular recognition.² The use of appropriate acyclic ferrocene derivatives in this field could have many advantages and a wide field of applications in chemistry, physics, and biology. For instance in an approach toward new technologies, they can be used for the constitution of membranes, micellars, or other supramolecular assemblies, for the design of molecular switches or sensors, in which a change in the redox potential of the ferrocene unit is triggered by an alkali metal ion binding for instance. Specifically, Beer *et al.* have been interested in the design of such molecules and have extended this study to macrocyclic compounds³ and recently to anion acyclic receptors containing cobaltocenium moieties.⁴

Recently one of us has shown that phosphohydrazides $\text{RP}(\text{X})[\text{N}(\text{CH}_3)\text{NH}_2]_2$ ($\text{X} = \text{O}, \text{S}$; $\text{R} = \text{Ph}$) are well adapted to the building of macrocycles by condensation with various functionalized dialdehydes.⁵ With the aim of synthesizing, according to the same strategy, phosphorus-containing macrocycles possessing some of the afore mentioned properties, we have chosen in a first approach to condense ferrocenecarbaldehyde with phosphohydrazides and to check their coordination properties. Indeed these

ligands contain several binding sites due to the presence of two types of nitrogen donor sites and the heteroatom X. Surprisingly, results about complexing properties of phosphorus hydrazides are sparse.⁶ Recently Engelhardt *et al.* have studied the formation of complexes between phosphoric acid hydrazides and $\text{Cd}(\text{II})$ or $\text{Ni}(\text{II})$ salts. Dimeric and polymeric structures have been obtained⁷ in which the chelating ligands are N-bonded or N- and S-bonded. Katti *et al.* also reported on the potentialities of functionalized phosphorus hydrazides as novel chelating ligands for $\text{Co}(\text{I})$, $\text{Cu}(\text{I})$, and $\text{Pd}(\text{II})$ complexation.⁸

In a previous paper, we described the synthesis and characterization of the first example of a derivative possessing ferrocenylhydrazone and thiophosphanyl moieties⁹ which shows a remarkable ability to give a dicopper complex. In this paper we

- * Abstract published in *Advance ACS Abstracts*, December 15, 1993.
- (1) See, for example: Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89.
 - (2) Constable, E. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 407 and references therein.
 - (3) See, for example: (a) Beer, P. D. *Chem. Soc. Rev.* **1989**, 409 and references therein. (b) Beer, P. D.; Keefe, A. D.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3675. (c) Beer, P. D.; Tite, E. L.; Ibboston, A. J. *J. Chem. Soc., Dalton Trans.* **1991**, 1691. (d) Beer, P. D.; Kocian, O.; Mortimer, J. R.; Spencer, P. J. *J. Chem. Soc., Chem. Commun.* **1992**, 602.
 - (4) Beer, P. D.; Heseck, D.; Kodacova, J.; Stokes, S. E. *J. Chem. Soc., Chem. Commun.* **1992**, 270.

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- (6) (a) Casteran-Baumassy, J.; Dagnac, P.; Gleizes, A. *J. Chem. Res. Synop.* **1979**, 164; *J. Chem. Res. Miniprint* **1979**, 2129-2166. (b) Dagnac, P.; Casteran-Baumassy, J. *J. Mol. Struct.* **1980**, *62*, 157. (c) Turpin, R.; Casteran-Baumassy, J.; Dagnac, P. *J. Chem. Res. Synop.* **1980**, 138; *J. Chem. Res. Miniprint* **1980**, 2074. (d) Engelhardt, U.; Friedrich, B.; Stronburg, B. *Acta Crystallogr.* **1982**, *B38*, 753. (e) Engelhardt, U.; Friedrich, B.; Kirner, I. *Z. Naturforsch.* **1981**, *36B*, 791. (f) Engelhardt, U.; Renz-Kreikebohn, C. *Acta Crystallogr.* **1989**, *C45*, 1679.
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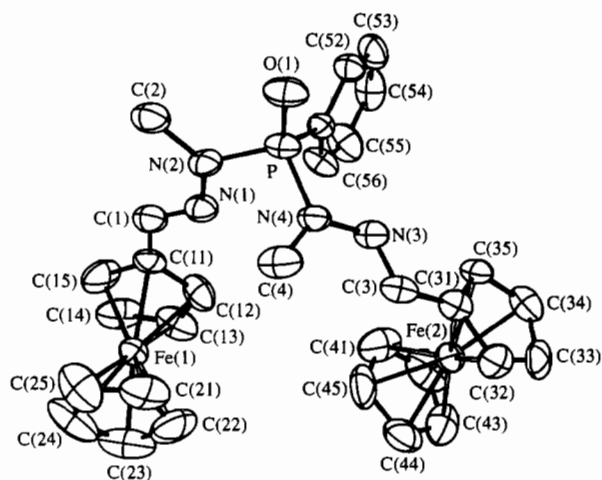


Figure 1. Perspective view of the complex $\text{PhP}(\text{O})[\text{N}(\text{CH}_3)\text{N}=\text{CHC}_5\text{H}_4\text{Fe}(\text{C}_5\text{H}_5)_2]$ (**3b**). Thermal ellipsoids are shown at the 50% probability level.

describe the synthesis and characterization of other phosphorus ferrocenyl ligands¹⁰ $\text{Ph}_{(3-n)}\text{P}(\text{X})[\text{N}(\text{CH}_3)\text{N}=\text{CH}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)]_n$ ($\text{X} = \text{O}$ or S , $n = 2$; $\text{X} = \text{O}$, S , $n = 3$) and of the non-ferrocenylhydrazones $\text{Ph}_{(3-n)}\text{P}(\text{S})[\text{N}(\text{CH}_3)\text{N}=\text{CHPh}]_n$ ($n = 2, 3$). Some of their complexation reactions toward $\text{Cu}(\text{I})$ salts are also reported. The new heteropolymetallic iron-copper complexes can alternatively be obtained by condensation of ferrocenecarbaldehyde with the preformed copper complexes of the related phosphohydrazides. We detail some NMR characterization of the complexes in solution as well as their electrochemical behavior.

Results and Discussion

1. Syntheses of New Ferrocenyl- or Phenyl-Phosphohydrazide Ligands. Phosphodihydrazides $\text{PhP}(\text{X})(\text{NMeNH}_2)_2$ ($\text{X} = \text{S}$, **1a**; $\text{X} = \text{O}$, **1b**) or phosphotrihydrazides $\text{P}(\text{X})(\text{NMeNH}_2)_3$ ($\text{X} = \text{S}$, **2a**; $\text{X} = \text{O}$, **2b**) react respectively with 2 or 3 equiv of ferrocene carboxaldehyde in ethanol at room temperature to give after purification the compounds **3a,b** and **4a,b** in high yield (74–88%) (Scheme 1). The structure of these new molecules were first deduced from spectroscopic data and microanalysis (see Experimental Section). The condensation reaction was confirmed in the ^1H NMR spectra by the disappearance of the NH_2 signal and the appearance of a new signal corresponding to the protons of the imino group (from $\delta = 7.3$ to $\delta = 7.5$ ppm in CDCl_3 or C_6D_6). In the solid state weak $\nu(\text{C}=\text{N})$ absorptions are located between 1586 and 1596 cm^{-1} .

Suitable crystals for X-ray analysis were obtained for **3b** ($\text{X} = \text{O}$) by recrystallization from a mixture of EtOH and pentane (1/1). A perspective view of the molecule is shown in Figure 1. Selected bond lengths and interatomic distances are listed in Table 1. $\text{P}=\text{O}$, $\text{N}-\text{N}$, $\text{N}=\text{C}$, and $\text{P}-\text{C}$ distances are within the normal range^{5a,8,9} as well as the $\text{N}(2)-\text{P}-\text{N}(4)$, $\text{O}(1)-\text{P}-\text{N}(2)$, $\text{O}(1)-\text{P}-\text{N}(4)$, and $\text{O}(1)-\text{P}-\text{C}(51)$ angles.^{8,9} The geometry of the organometallic part is similar to that observed for ferrocene itself, the two rings being nearly parallel to each other (dihedral angles: $\text{Fe}(1)$, ca. 2.5° ; $\text{Fe}(2)$, ca. 1.8°). In the ferrocene $\text{Fe}(1)$ moiety the two cyclopentadienyl rings are more staggered than in the $\text{Fe}(2)$ part (deviation from eclipsed conformation: $27.7(9)$ and $8.8(9)^\circ$, respectively). This structure does not deserve any further comment.

Even though some examples of condensation of metallocene-carboxaldehyde with hydrazines have been described,¹¹ these

Table 1. Interatomic Distances (Å) and Angles (deg) for $\text{PhP}(\text{O})(\text{NMeNCH}=\text{Fc})_2$ (**3b**), with Esd's in Parentheses

| | | | |
|--|----------|--|----------|
| $\text{P}-\text{O}(1)$ | 1.466(6) | $\text{P}-\text{C}(51)$ | 1.791(9) |
| $\text{P}-\text{N}(2)$ | 1.680(7) | $\text{P}-\text{N}(4)$ | 1.664(7) |
| $\text{N}(1)-\text{N}(2)$ | 1.380(9) | $\text{N}(3)-\text{N}(4)$ | 1.367(8) |
| $\text{N}(1)-\text{C}(1)$ | 1.27(1) | $\text{N}(3)-\text{C}(3)$ | 1.27(1) |
| $\text{N}(2)-\text{C}(2)$ | 1.47(1) | $\text{N}(4)-\text{C}(4)$ | 1.45(1) |
| $\text{C}(1)-\text{C}(11)$ | 1.47(1) | $\text{C}(3)-\text{C}(31)$ | 1.45(1) |
| Fe-Cp Linkage | | | |
| $\text{Fe}(1)-\text{C}(11)$ | 2.045(8) | $\text{Fe}(2)-\text{C}(31)$ | 2.046(9) |
| $\text{Fe}(1)-\text{C}(12)$ | 2.024(9) | $\text{Fe}(2)-\text{C}(32)$ | 2.04(1) |
| $\text{Fe}(1)-\text{C}(13)$ | 2.01(1) | $\text{Fe}(2)-\text{C}(33)$ | 2.02(1) |
| $\text{Fe}(1)-\text{C}(14)$ | 2.02(1) | $\text{Fe}(2)-\text{C}(34)$ | 2.033(8) |
| $\text{Fe}(1)-\text{C}(15)$ | 2.02(1) | $\text{Fe}(2)-\text{C}(35)$ | 2.036(7) |
| $\text{Fe}(1)-\text{C}(21)$ | 2.03(1) | $\text{Fe}(2)-\text{C}(41)$ | 2.02(1) |
| $\text{Fe}(1)-\text{C}(22)$ | 2.01(1) | $\text{Fe}(2)-\text{C}(42)$ | 2.02(1) |
| $\text{Fe}(1)-\text{C}(23)$ | 2.02(1) | $\text{Fe}(2)-\text{C}(43)$ | 2.03(1) |
| $\text{Fe}(1)-\text{C}(24)$ | 2.01(1) | $\text{Fe}(2)-\text{C}(44)$ | 2.033(9) |
| $\text{Fe}(1)-\text{C}(25)$ | 2.04(1) | $\text{Fe}(2)-\text{C}(45)$ | 2.04(1) |
| Cyclopentadienyl Rings | | | |
| $\text{C}(11)-\text{C}(12)$ | 1.43(1) | $\text{C}(31)-\text{C}(32)$ | 1.41(1) |
| $\text{C}(12)-\text{C}(13)$ | 1.43(1) | $\text{C}(32)-\text{C}(33)$ | 1.39(1) |
| $\text{C}(13)-\text{C}(14)$ | 1.38(1) | $\text{C}(33)-\text{C}(34)$ | 1.42(1) |
| $\text{C}(14)-\text{C}(15)$ | 1.40(2) | $\text{C}(34)-\text{C}(35)$ | 1.39(1) |
| $\text{C}(15)-\text{C}(11)$ | 1.41(1) | $\text{C}(35)-\text{C}(31)$ | 1.43(1) |
| $\text{C}(21)-\text{C}(22)$ | 1.41(2) | $\text{C}(41)-\text{C}(42)$ | 1.42(2) |
| $\text{C}(22)-\text{C}(23)$ | 1.41(2) | $\text{C}(42)-\text{C}(43)$ | 1.39(2) |
| $\text{C}(23)-\text{C}(24)$ | 1.36(2) | $\text{C}(43)-\text{C}(44)$ | 1.36(2) |
| $\text{C}(24)-\text{C}(25)$ | 1.37(2) | $\text{C}(44)-\text{C}(45)$ | 1.37(2) |
| $\text{C}(25)-\text{C}(21)$ | 1.38(2) | $\text{C}(45)-\text{C}(41)$ | 1.40(2) |
| $\text{O}(1)-\text{P}-\text{C}(51)$ | 112.9(3) | $\text{N}(2)-\text{P}-\text{N}(4)$ | 102.6(3) |
| $\text{O}(1)-\text{P}-\text{N}(2)$ | 109.1(3) | $\text{O}(1)-\text{P}-\text{N}(4)$ | 116.4(4) |
| $\text{C}(51)-\text{P}-\text{N}(2)$ | 108.8(4) | $\text{C}(51)-\text{P}-\text{N}(4)$ | 106.4(3) |
| $\text{P}-\text{N}(2)-\text{N}(1)$ | 113.1(4) | $\text{P}-\text{N}(4)-\text{N}(3)$ | 116.3(5) |
| $\text{P}-\text{N}(2)-\text{C}(2)$ | 123.2(6) | $\text{P}-\text{N}(4)-\text{C}(4)$ | 121.0(5) |
| $\text{N}(1)-\text{N}(2)-\text{C}(2)$ | 120.1(7) | $\text{N}(3)-\text{N}(4)-\text{C}(4)$ | 122.6(7) |
| $\text{N}(2)-\text{N}(1)-\text{C}(1)$ | 120.4(6) | $\text{N}(4)-\text{N}(3)-\text{C}(3)$ | 119.4(7) |
| $\text{N}(1)-\text{C}(1)-\text{C}(11)$ | 119.3(7) | $\text{N}(3)-\text{C}(3)-\text{C}(31)$ | 118.5(8) |
| $\text{C}(1)-\text{C}(11)-\text{C}(12)$ | 126.4(8) | $\text{C}(3)-\text{C}(31)-\text{C}(35)$ | 127.5(8) |
| $\text{C}(1)-\text{C}(11)-\text{C}(15)$ | 126.5(8) | $\text{C}(3)-\text{C}(31)-\text{C}(32)$ | 125.4(8) |
| $\text{C}(12)-\text{C}(11)-\text{C}(15)$ | 107.0(8) | $\text{C}(32)-\text{C}(31)-\text{C}(35)$ | 107.0(7) |
| $\text{C}(11)-\text{C}(12)-\text{C}(13)$ | 106.3(8) | $\text{C}(11)-\text{C}(12)-\text{C}(33)$ | 108.7(9) |
| $\text{C}(12)-\text{C}(13)-\text{C}(14)$ | 109.3(9) | $\text{C}(32)-\text{C}(33)-\text{C}(34)$ | 108.1(8) |
| $\text{C}(13)-\text{C}(14)-\text{C}(15)$ | 107.9(9) | $\text{C}(33)-\text{C}(34)-\text{C}(35)$ | 108.2(8) |
| $\text{C}(14)-\text{C}(15)-\text{C}(11)$ | 109.4(8) | $\text{C}(34)-\text{C}(35)-\text{C}(31)$ | 108.0(8) |

ligands constitute the first examples of condensation of such metallocenes with phosphohydrazides.

The imino group in complex **3a** can be reduced with lithium aluminium hydride in refluxing THF. After hydrolysis, compound **5** is the only product observed by NMR in solution. A slight deshielding effect is observed in $^{31}\text{P}\{^1\text{H}\}$ NMR from 77.9 to 81.4 ppm. ^1H NMR spectra are consistent with the reduction of the imino group.^{5b,12} This compound exhibits characteristic new ^{13}C NMR features such as, for example, doublet of triplet with a $^3J_{\text{C}-\text{P}} = 7.0$ Hz and $^1J_{\text{C}-\text{H}} = 137.7$ Hz for the CH_2 groups at 47.7 ppm^{5b,12} and, for the C_{ipso} ¹³ of the substituted rings, a multiplet due to the $^2J_{\text{C}-\text{H}}$ couplings.

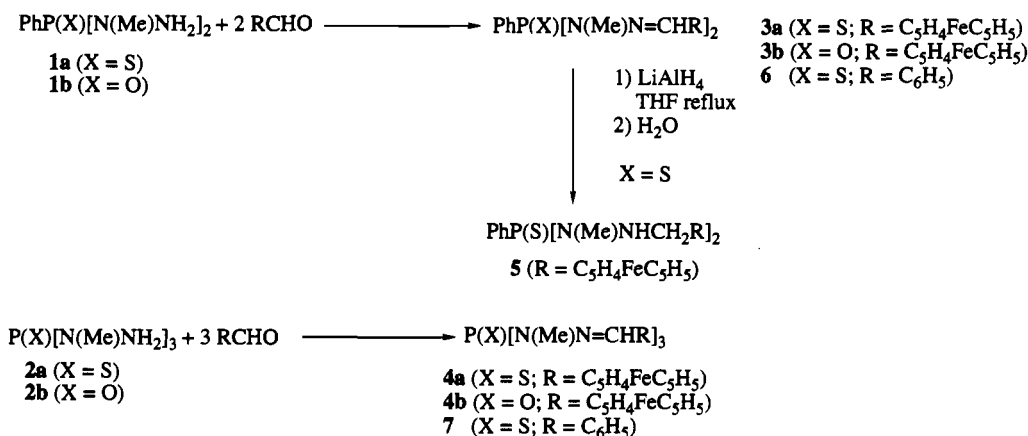
To have a good insight into the influence of ferrocenyl moieties on the binding properties of these ligands and on the electrochemical properties of the isolated complexes we have also developed the synthesis of the organic phosphohydrazones $\text{PhP}(\text{S})(\text{NMeN}=\text{CHPh})_2$ (**6**) and $\text{P}(\text{S})(\text{NMeN}=\text{CHPh})_3$ (**7**). These ligands are obtained in good yield (87–75%) in THF as white powders, as described in Scheme 1, and microanalyses are in agreement with their formulation. Synthesis of compound **6** was

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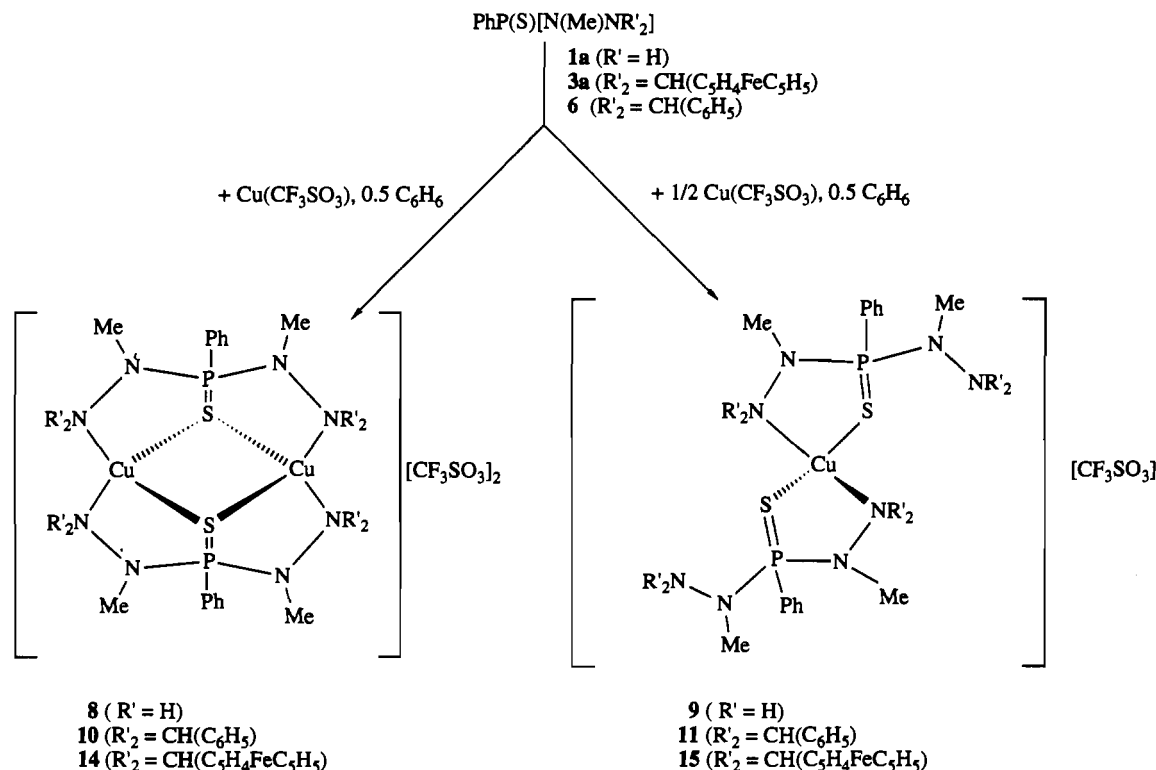
(9) Delavaux-Nicot, B.; Luga, N.; Mathieu, R.; Majoral, J.-P. *Inorg. Chem.* **1992**, *31*, 334.

(10) Part of this work was presented at the XXIIth International Conference on Phosphorus Chemistry, Toulouse, France, July 6–10, 1992: *Phosphorus, Sulfur Silicon* **1993**, *77*, 323.

Scheme 1



Scheme 2



previously described in chloroform.¹⁴ As observed for **3** and **4**, the ³¹P{¹H} NMR chemical shifts are higher for the phosphodi- and phosphotrihydrazones than for the hydrazines. The IR spectra show two bands at 1592, 1563 cm⁻¹ and 1593, 1564 cm⁻¹, respectively, but the assignment of ν(C=N) is not straightforward because of the phenyl absorption in the same region.

2. Synthesis of Copper Complexes. To check the bonding ability of these ligands we have investigated their reactivity toward copper(I) triflate and in some cases with copper(I) chloride as this metal is known to bind to tertiary phosphine chalcogenides or imine ligands.¹⁵

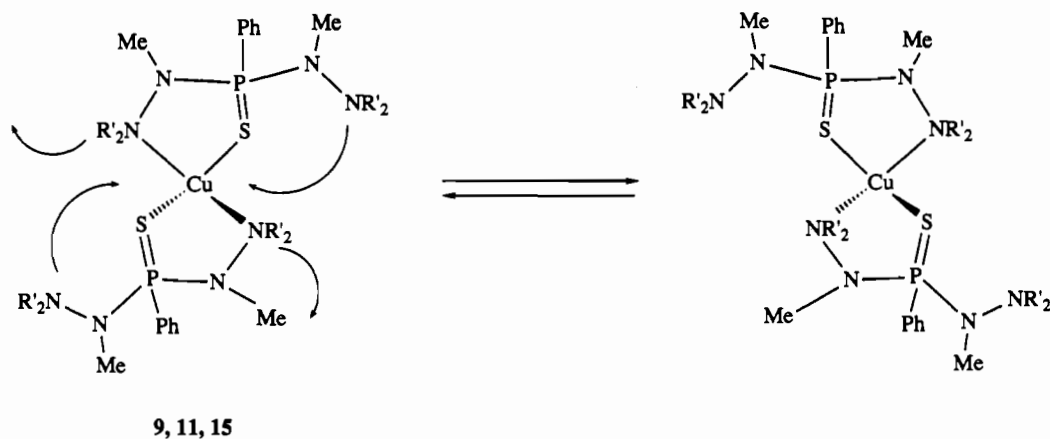
Reactivity of the Thiophosphodihydrazide 1a with Cu(CF₃SO₃)₂·0.5C₆H₆. Cu(CF₃SO₃)₂·0.5C₆H₆ reacts with **1a** in a 1/1 or a 1/2 stoichiometry to afford adduct **8** or **9** in good yield (92 or 86%) as a pale yellow powder. The low solubility of complex **8** prevents any NMR characterization, but since **8** reacts with ferrocenecarboxaldehyde to give complex **14** (*vide infra*),⁹ we propose for **8** the same type of structure shown in Scheme 2.

9 is soluble enough to be identified by its NMR spectra in deuterated tetrahydrofuran. The ³¹P{¹H} NMR spectrum indicates a shift from 84.8 to 79.4 ppm. At 294 K, the ¹H NMR spectrum reveals that the NCH₃ groups (doublet) are equivalent and the NH₂ groups (broad singlet), as well. The ¹³C NMR spectrum confirms the equivalence of the NCH₃ groups at this temperature. At 183 K the NH₂ signal is split into a set of three signals of relative intensity 1/1/2 at 6.45, 5.6, and 4.5 ppm, respectively, revealing the inequivalence of the NH₂ groups. The first two signals of the NH₂ groups are attributed to the inequivalent hydrogen atoms of the coordinated NH₂ groups, and the last broad one is attributed to uncoordinated NH₂ groups. Two doublets of equal intensity are observed at 3.37 and 3.16 ppm for the NCH₃ groups. At the same temperature in the ³¹P{¹H} NMR spectrum a singlet is observed at δ 79.5 ppm confirming the presence of only one product in solution. These observations are in agreement with the tetrahedral structure shown in Scheme 2 in which the ligand would be coordinated to copper through the sulfur atom and one of the two NH₂ ends of the ligand **1a**. In this situation the hydrogens of the bonded NH₂ groups are not equivalent. The fluxionality of the molecule would occur through

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Scheme 3



exchange between bonded and free hydrazide arms of the ligand (Scheme 3).

A careful comparison of the infrared spectra of **9** and **1a** in the solid state shows that the $\nu(\text{NH}_2)$ bands are broader in compound **9** than in the free ligand, with a small shift to higher frequency of 13 and 18 cm^{-1} for the two bands, respectively. A third and discreet band emerges at 3306 cm^{-1} (shoulder). Easy attribution of the $\nu(\text{P}=\text{S})$ vibration is not obvious because of the presence of CF_3SO_3^- anion¹⁶ vibrations in the same region.

In a recent paper⁸ Katti *et al.* reported the synthesis by a different way, starting from a copper(II) salt, of a cationic copper(I) complex analyzing for $[\text{Cu}(\mathbf{1a})_2][\text{ClO}_4]$ and for which they proposed a structure in which each ligand would be bonded through sulfur and the NH_2 end of its two hydrazido groups. This complex was only characterized by IR spectroscopy studies and microanalysis, and its structure was proposed by analogy to the structure of the related $[\text{Co}(\mathbf{1a})_2]^+$ cation, which was established by an X-ray diffraction study. This proposal seems unrealistic from two points of view: (i) the octahedral geometry is not common for mononuclear copper(I) complexes, and (ii) in this configuration this complex would be a 22-valence electron compound. Furthermore, our infrared data have to be contrasted with those reported by Katti *et al.*: only one band at 3055 cm^{-1} attributed to the coordinated $\text{N}-\text{NH}_2$ groups has been observed. This shows that the two complexes are different and that Katti's compound may be polymeric. (The absence of NMR study suggests a low solubility of the $[\text{Cu}(\mathbf{1a})_2][\text{ClO}_4]$ compound and prevents any further comparison with **9**.)

Reactivity of the Thiophosphodihydrazone 6 toward $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{C}_6\text{H}_6$. The thiophosphodihydrazone **6**, when treated with copper(I) in 1/1 and 2/1 stoichiometries affords the two adducts **10** and **11**, respectively. The poor solubility of the 1/1 complex prevents ^1H and ^{31}P NMR studies, and we propose either the same structure as **8** or a polymeric one. For the 2/1 adduct, the ^1H NMR spectra at 294 K shows only one doublet for the NCH_3 . The singlet observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a shift from 79.1 to 74.8 ppm, suggesting coordination of the sulfur atom of the $\text{P}=\text{S}$ group.⁹ In ^{13}C NMR experiments a characteristic deshielding of the imino carbon from 137.1 to 143.4 ppm is observed, also suggesting the bonding of the imino group.

At 183K, the ^1H NMR signal of the NCH_3 groups is split into two broad signals at 3.61 and 3.05 ppm of equal intensity even in the ^{31}P -decoupled spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is unchanged. This behavior is reminiscent to that of **9**. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 173K resonances attributed to the NCH_3 and $\text{CH}=\text{N}$ groups are split into two broad signals of

equal intensity at 36.8 and 33.1 ppm and 144.7 and 139.7 ppm, respectively. These experiments clearly demonstrate the existence of two kinds of exchanging $\text{CH}=\text{N}$ and NCH_3 groups in the molecule in agreement with Scheme 3.

Reactivity of the Thiophosphotrihydrazone 2a and of the Thiophosphotrihydrazone 7 toward $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{C}_6\text{H}_6$. Compounds **12** and **13** precipitate, respectively, from equimolar THF solutions of the trihydrazone ligand **2a** and the trihydrazone **7** and copper triflate. The characterization of these 1/1 adducts by NMR was prevented by their low solubility in most of the solvents. Moreover we have observed that in acetonitrile, pyridine, or dimethyl sulfoxide, only the spectrum of the free ligand was observed, suggesting that decomplexation reaction had occurred. The same phenomenon has been observed with complexes **8** and **10**. In the absence of enough spectroscopic data no structure is proposed for these complexes. Attempts to prepare $(\mathbf{2a})\text{CuCl}$ failed.

Reactivity of the Functionalized Ferrocene-Thiophosphohydrazone 3a toward $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{C}_6\text{H}_6$. The complexing properties of several functionalized ferrocenes are now well established, in particular toward copper(II).¹⁷ One original trimeric phosphorus iron-copper(I) complex with $\text{P}-\text{Cu}$ and $\text{S}-\text{Cu}$ bonds has been mentioned.¹⁸ Moreover, recent reports reveal interesting properties concerning ferrocenyl copper derivatives: for example, irreversible one-electron transfer from iron(II) to copper(II) leading to a $\text{Fe}(\text{III})-\text{Cu}(\text{I})$ complex.¹⁹

Our study has been carried out through two approaches: by the direct reaction of the ferrocenyl ligands with copper(I) trifluoromethane sulfonate or by the reaction of ferrocenecarbaldehyde with the preformed copper(I) thiophosphohydrazone complexes.²⁰

As described in Scheme 2, compound **15** is the unique product of the reaction in 2/1 stoichiometry between **3a** and $\text{Cu}(\text{I})$. The $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of **15**, similar to that found for **14**, suggests the coordination of the sulfur atom. According to ^1H NMR data, all the chemical groups of the same nature are equivalent and microanalyses are in agreement with a 2/1 stoichiometry, but some of the ^1H NMR signals are broad at

(16) For this compound and all those containing the CF_3SO_3^- anion, characteristic vibrations near 1260 (s, br), 1030 (s, f), and 640 (s, f) cm^{-1} in IR solid spectra are observed. The presence of a vibration near 1270 cm^{-1} is characteristic of anionic SO_3^- : Straus, D. A.; Zhang, C.; Quimbata, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673 and references therein.

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(20) Delavaux-Nicot, B.; Lavigne, G.; Mathieu, R. Unpublished results. During the course of our study we have observed that **14** in THF affords crystals which belong to another space group than that previously published.⁹ The new structure determination will be reported separately as the two structures differ only by a small rotation of the ferrocenyl groups around the $\text{N}=\text{C}-\text{C}$ arms and by the presence of one molecule of THF in the cell.

room temperature, suggesting a possible fluxional phenomenon in the molecule. This was confirmed by a variable-temperature experiment in CD_2Cl_2 , which shows a broadening of the signals when the temperature is lowered. At 183 K whereas phenyl and $\text{CH}=\text{N}$ signals remain broad, Cp signals split into numerous signals from 5.68 to 3.71 ppm, and the doublet of the NCH_3 groups (3.26 ppm) splits into four broad doublets of relative intensities 0.4, 0.4, 1, and 0.3 at δ 3.46, 3.37, 3.20, and 3.12. Relative intensities of the different groups remain constant in several different experiments. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra the singlet observed at 233 K (δ 72.1 ppm) splits into three singlets at 183 K (δ 72.8, 72.7, 70.5 ppm) of relative intensity 1/2/0.9. In the variable temperature $^{13}\text{C}\{^1\text{H}\}$ NMR experiments, three singlets characteristic of $\text{CH}=\text{N}$, C_{ipso} of the substituted Cp rings, and $\text{N}(\text{CH}_3)_2$ groups broaden at 228 K (140.9, 78.1, 34.4 ppm) in CD_2Cl_2 , and at 198 K, each one splits into two broad but well-identified singlets at 146.5 and 138.9, 79.1 and 76.0, and 36.9 and 32.0 ppm, respectively, thus confirming the existence of two types of $\text{CH}=\text{N}$, Cp, and NCH_3 groups in the molecule. So we observe for **15** the same phenomenon as for **9** and **11**, i.e. an exchange between free and complexed hydrazone arms of the ligand. The three resonances which appear in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in 1/2/0.9 ratio at 183 K are attributed to the fact that when the exchange is frozen, the molecule is chiral and has three centers of chirality: the two phosphorus atoms and the copper atom.

The difference in the ^{31}P NMR results between **15**, **9**, and **11** is attributed to the presence of the bulky ferrocene groups which would induce larger chemical shift differences between the diastereoisomers.

A similar phenomenon concerning ligand coordination-decoordination processes has been proposed in $[\text{N},\text{N}'\text{-bis}\{2\text{-}((\text{phenylmethyl})\text{thio})\text{phenyl}\}\text{methylene}\text{ethane-1,2-diamine}\}]_{\text{Cu}}$ compounds which imply $\text{Cu}-\text{S}$ bonds,²¹ and an elegant chirality problem has recently been discussed for aza copper complexes.²²

Finally it has to be mentioned that acetonitrile displaces ligand **3a** when complexes **14** and **15** are dissolved in this solvent.

Reactivity of the Thiophosphotrihydrazone 4a toward CuCl and $\text{Cu}(\text{CF}_3\text{SO}_3)\cdot 0.5\text{C}_6\text{H}_6$. After solubilization of CuCl in a solution of 1 equiv of **4a**, the product **16** precipitates partially in THF, and no other intermediate or byproduct is detected in solution. Slight modifications are induced by complexation in the ^1H NMR spectrum when compared to the parent compound. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the deshielding of the $\text{CH}=\text{N}$ group resonance suggests the complexation of this group whereas in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum the singlet moves to higher field (+4.75 ppm), consistent with the complexation of the $\text{P}=\text{S}$ group. In the solid state, the IR spectra show an increase of the intensity of the $\nu(\text{C}=\text{N})$ vibration at 1590 cm^{-1} and the shift of the $\text{P}=\text{S}$ band from 737 to 727 cm^{-1} in accordance with NMR observations.

Examination of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 193 K shows that each signal characteristic of the $\text{CH}=\text{N}$ and $\text{N}-\text{CH}_3$ groups (143.2 and 33.6 ppm at 298 K) splits into two broad singlets (146.8 and 140.0 ppm and 36.3 and 32.6 ppm) of relative intensity 1/2. The singlet of the C_{ipso} (79.1 ppm) splits into two singlets at 193 K (80.4 and 76.7 ppm; 2/1 ratio) while several new signals appear for the ferrocene part. The ^1H NMR spectra confirm this observation: the $\text{CH}=\text{N}$ signal at 7.67 ppm at 296 K splits into two signals at 7.81 and 7.49 ppm at 198 K of relative intensities 1/2. These observations show that there is an exchange process between one bound and two free imino groups at room temperature. Similar exchanges have already been detected,²³ and we propose (Figure 2) for **16** a structure in which the ligand **4a** is

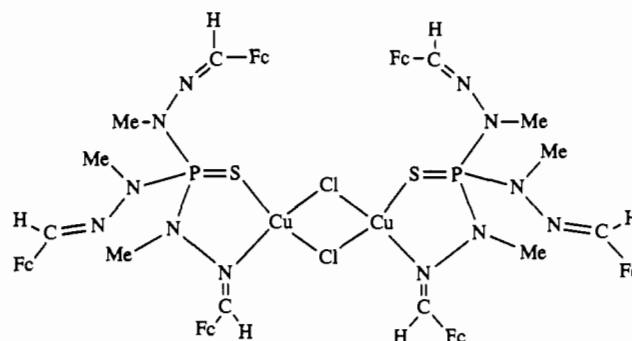


Figure 2. Proposed structure for complex **16**.

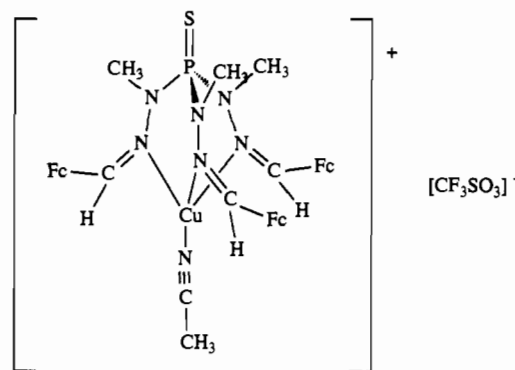


Figure 3. Proposed structure for complex **17**.

bonded through the sulfur atom and one of its three imino groups. A dimeric formulation with two chloride bridges leads to an 18-electron configuration for the copper centers.^{6f,7} Attempts to get crystals for an X-ray investigation failed.

With copper(I) triflate, 1 equiv of **4a** rapidly gave compound **17**. As opposed to **4a** this new complex is soluble in CH_3CN but not in CH_2Cl_2 . In deuterated acetonitrile ^1H and ^{13}C NMR data at room temperature are similar to those for **16** in deuterated dichloromethane, but in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra the shift of the signal is only 0.75 ppm to higher field, suggesting that the sulfur atom is not bound to copper. So we propose, in solution, the $[(\eta^3\text{-4a})\text{Cu}(\text{CH}_3\text{CN})][\text{CF}_3\text{SO}_3]$ structure shown in Figure 3, analogous to the structure of the recently reported $[(\text{tris-pyrazole})\text{Cu}(\text{CH}_3\text{CN})]^+$ ^{23b} or $[(\text{tris-pyrazole})\text{Cu}(\text{CO})]^+$ ²⁴ the bonding occurring only by the imino arms of the ligand. It has to be pointed out that on standing only **4a** crystallizes from the solution (**4a** is not soluble in acetonitrile), which is not surprising taking into account the good propensity of acetonitrile to bind copper centers.²⁵

In the solid state, the IR spectrum indicates that the CF_3SO_3 group is non coordinating.¹⁶ A characteristic increase of the $\nu(\text{C}=\text{N})$ vibration intensity (1579 cm^{-1}) due to coordination of this group and a significant shift of the $\nu(\text{P}=\text{S})$ from 737 to 715 cm^{-1} consistent with an interaction of the $\text{P}=\text{S}$ bond with copper atom are observed. This shows that, in the absence of acetonitrile in the solid state, the structure is different and may be polymeric. Note that compound **17** can be synthesized by reacting **12** with 3 equiv of ferrocenecarbaldehyde at 65°C in THF.

Reactivity of the Functionalized Ferrocenylphosphodihydrazone and trihydrazone Oxides 3b and 4b toward $\text{Cu}(\text{CF}_3\text{SO}_3)\cdot 0.5\text{C}_6\text{H}_6$. These ligands also react with copper triflate to produce the insoluble 1/1 adducts **18** and **19**. Their IR spectra in the solid state also reveal an enhancement of the intensity of the $\nu(\text{C}=\text{N})$ vibration by complexation, but the $\nu(\text{P}=\text{O})$ absorption cannot be securely attributed. **3b** and **4b** are recovered after dissolution of **18** and **19** in pyridine.

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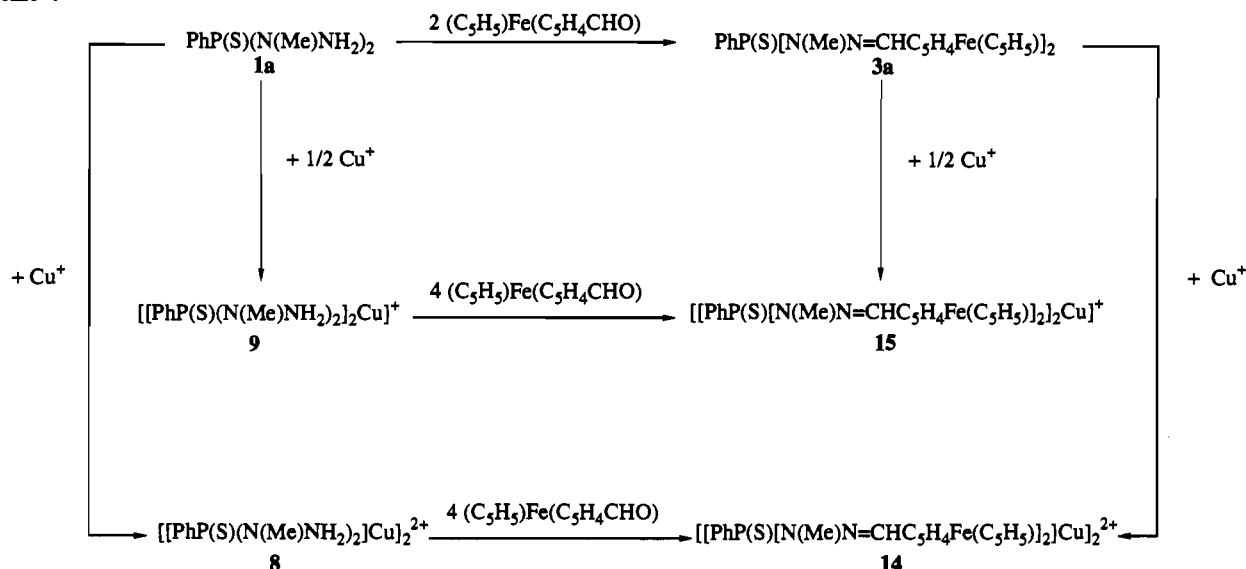
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Scheme 4

**Table 2.** Electrochemical Characteristics of $(C_5H_5)_2Fe$ and $[FcCH=NN(Me)]_n(Ph)_{3-n}PX$ ($X = O, S; n = 2, 3$)

| compounds | $E_{1/2}$ (V) | P (mV) | n | E_p (V) | ΔE_p (mV) | RI_p |
|----------------|---------------|----------|-----|-----------|-------------------|--------|
| $(C_5H_5)_2Fe$ | 0.42 | 58 | 1 | 0.45 | 60 | 1 |
| 3a | 0.42 | 58 | 2 | 0.46 | 87 | 1 |
| 3b | 0.41 | 60 | 2 | 0.44 | 77 | 1 |
| 4a | 0.44 | 70 | 3 | 0.49 | 100 | 1 |
| 4b | 0.44 | 67 | 3 | 0.49 | 100 | 1 |

^a $\Delta E_p = E_p(\text{backward}) - E_p(\text{forward})$. $RI_p = |I_p(\text{backward})/I_p(\text{forward})|$. $n = \text{number of exchanged electrons in the electrochemical process}$. $P = \text{slope of the linear regression of } E = f(\log |i/i_d - i|)$. Conditions: [ligands], 1 mmol L^{-1} ; Pt electrode; rotating electrode 1000 *t*/min; potential scan speed in cyclic voltammetry 0.1 V s^{-1} ; solvent, CH_2Cl_2 , containing Bu_4NPF_6 (0.1 mol L^{-1}).

3. Electrochemical Studies. According to the reactivity of some of the complexes toward CH_3CN , we have retained CH_2Cl_2 as solvent for electrochemical experiments. We have focused our attention to the [Fe–Cu] compounds **14** and **15** and for comparison to their related phosphohydrazide and phosphohydrazone complexes, the synthesis of which is summarized in Scheme 4.

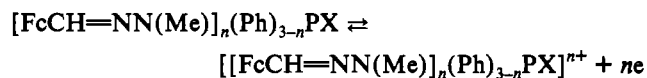
Case of the Functionalized Ferrocenyl Phosphorus Ligands. The electrochemical properties of the ligands **3a,b** and **4a,b** were investigated in a medium of CH_2Cl_2 containing $0.1 \text{ M } Bu_4NPF_6$. In stationary voltammetry at a platinum disk electrode, all studied compounds exhibit one oxidation wave at *ca.* 0.40 V vs SCE . The results obtained for the four compounds (in comparison with the ferrocene $FeCp_2$) are gathered in Table 2. The limiting currents obey the Levich law. They are proportional to the square root of the electrode rotation speed (from 500 to 4000 rpm) as for a diffusion-controlled process. Limiting currents are proportional to the concentration in the usual domain (up to 5 mmol L^{-1}). When compared with the ferrocene oxidation wave in the same conditions, the limiting current magnitudes are consistent with a two-electron exchange (**3a,b**) or a three-electron exchange processes (**4a,b**). Cyclic voltammograms indicate that the electrochemical processes are reversible. The constant value of $I_p/v^{1/2}$ ($I_p = \text{peak current}$, $v = \text{potential scan rate}$) is consistent with the diffusion-controlled process observed in stationary voltammetry. The current peak ratio I_{p_2}/I_{p_1} is 1 in the $0.1 \leq v \leq 1 \text{ V s}^{-1}$ scan rate range. The number of electrons involved in the electrochemical oxidation process was confirmed by exhaustive electrolysis of solutions of compounds on a platinum gauze as electrode. The initial orange solution turned red during the electrolysis. The ESR spectra of the resulting frozen solutions (helium, 4 K) exhibit signals which seem similar to analogous frozen solutions of ferrocenium salt²⁶ (for example **3a** in acetone,

Table 3. Electrochemical Characteristics of Complexes **8–11**, **14**, and **15** (1 mmol L^{-1})

| compounds | $E_{1/2}$ (V) | P (mV) | n | E_p (V) | ΔE_p (mV) | RI_p |
|-----------------------|-------------------|----------|-----|-------------------|-------------------|-------------------|
| 14 | 0.62 | 56 | 4 | 0.65 | 59 | 0.9 |
| 15^b | 0.50 | 55 | 2 | 0.54 | 87 | 1 |
| | 0.61 | 52 | 2 | 0.66 | 99 | 1 |
| 8^c | 0.70 | 102 | | 0.74 | 120 | 0.96 |
| 10 | 0.88 ^d | | | 1.11 ^e | 404 | 0.70 ^d |
| 9 | 0.50 | 70 | 1 | 0.57 | 95 | 1 |
| 11 | 1.05 | 89 | | 1.14 | 108 | 0.82 |
| 1a | | | | 0.87 | | |
| 6 | | | | 1.39 | | |

^a Conditions: Pt electrode in CH_2Cl_2 containing Bu_4NPF_6 (0.1 mmol L^{-1}); rotating electrode 1000 *t*/min; potential scan speed in cyclic voltammetry, 0.1 V s^{-1} . ^b An ill-defined additional wave at *ca.* 1.20 V was also observed. ΔE_p , RI_p , n and P have the same meaning as in Table 2. ^c Second oxidation wave $E_{1/2} = 0.96 \text{ V}$, $P = 106 \text{ mV}$. ^d At 1 V s^{-1} . ^e Preabsorption peak at 0.72 V .

$g_{\parallel} = 4.50$, $g_{\perp} = 2.08$, $\Delta G = 2.42$). Hence these observations suggest that the electron transfers exchange take place on the ferrocene part of the molecule. Significantly the two redox centers are independent, whereas in some other biferrrocene molecules the bridging ligands allow some degree of interaction between the ferrocenyl centers.²⁷ Electrochemical reduction of the oxidized forms regenerates the initial compounds, and several oxidation–reduction cycles can be carried out without any change in the composition of the solution. So the electrochemical oxidation of these ligands *L* can be written according to



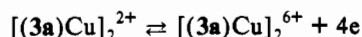
where $n = 2, 3$ and $X = O, S$.

Case of the Complexes **14 and **15**.** We have investigated the electrochemical behavior of complex **14** resulting from the complexation of copper(I) with **3a**. For a 1/1 stoichiometry as previously described, complex **14** is electrochemically oxidized to $[(\mathbf{3a})Cu]_2^{6+}$.⁹ In stationary voltammetry at a platinum disk electrode, a freshly prepared solution of **14** in CH_2Cl_2 containing Bu_4NPF_6 (0.1 M) exhibits one well-defined, diffusion-controlled, oxidizing wave at $E_{1/2} = 0.62 \text{ V vs SCE}$ (Table 3) which follows a Nernstian shape (the linear regression of $i/i_d - i = 56 \text{ mV}$).

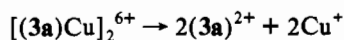
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By limitation of the scan to a 0–0.75 V scale, only a quasi-reversible oxidation peak centered at 0.62 V is observed under nonstationary conditions (at a 0.2 V s⁻¹ rate, $\Delta E_p = 59$ mV and $I_{pc}/I_{pa} = 0.9$; ΔE_p increases to 92 mV by increasing the scan rate to 3 V s⁻¹). Up to 0.75 V, we did not observe any well-defined wave which could be due to a Cu(I) → Cu(II) oxidation step. As previously observed for ligand **3a**, we attributed this oxidation step to the ferrocene part of the molecule, and as expected the complexation has induced a 0.2-V shift of the oxidation potential of the ferrocene part of the molecule toward a more anodic value. Controlled-potential coulometry at 0.7 V indicates that four electrons are exchanged, in agreement with the oxidation of the four ferrocene parts of the molecule. The initial orange solution turns red. (When electrolysis is carried out at potential values higher than 0.7 V, the number of electrons is higher than 4 faradays/mol of complex suggesting a copper(I) co-oxidation (*vide infra*) and the solution turns maroon.) Neither under potentiostatic nor under galvanostatic conditions is a paramagnetic signal detected, even though the electrolysis is carried out in the cavity of the ESR spectrometer at liquid N₂ temperature. In the potentiostatic mode a weak signal was observed corresponding to a Cu²⁺ species, showing that electrolysis did not lead to the expected species.²⁸

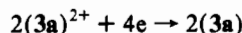
After electrolysis, reduction of the oxidized form did not give back the initial solution [(**3a**)₂Cu]₂²⁺. The red solution turned orange, during which time four electrons were exchanged. The resulting solution exhibited a well-developed reversible wave centered at 0.44 V characteristic of the free ligand. The following reaction scheme may be proposed:



The [(**3a**)₂Cu]₂⁶⁺ species is not stable on the electrolysis time scale leading to a decomposition according to



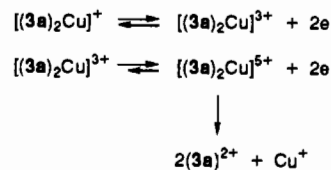
the (**3a**²⁺) species being rereduced at 0.1 V:



To summarize, the complexation of the ligand **3a** has induced an anodic shift of the oxidation potential of the ferrocene part. Other reported bis(ferrocene)copper(II) compounds have the same electrochemical behavior as **14** when compared to their free ferrocene ligands: they exhibit more anodic oxidation potentials but the shifts observed are lower (20 to 80 mV).^{17a,c}

The complex **15** undergoes two well-defined reversible oxidations at $E_{1/2} = 0.50$ V and $E_{1/2} = 0.61$ V vs SCE (Table 3) which follows a Nernstian shape. Controlled-potential coulometry on the first wave involves two electrons per mole of complex, and the initial orange solution turns red. A voltammogram recorded just after the electrolysis presents a cathodic wave and an anodic wave of the same intensity with the same potentials as the monooxidized species. This indicates that only two ferrocene parts of the molecule were involved, and the oxidized form is relatively stable. At room temperature this solution decomposes in a few minutes to give the ligand **3a** as confirmed by a cyclic voltammogram and ¹H NMR spectra. Only if the oxidized form is immediately reduced at 0.1 V is the initial complex **15** regenerated. Because of this weak stability, neither RPE nor NMR spectra of [(**3a**)₂Cu]³⁺ have been observed.

Electrolysis on the second wave involves 4 faraday/mol of complex. The dark red solution turns deep orange. At the end of the electrolysis only one well-developed reversible wave centered at 0.42 V persisted, which can be ascribed to **3a**²⁺. This hypothesis was confirmed by coulometry at 0.1 V which involves four electrons for two (**3a**²⁺) leading to the original **3a** ligand as ascertained by ¹H NMR spectra. The preceding results can be rationalized by the following oxidation scheme:



Extension of the scan up to 1.6 V gives evidence of an additional ill-defined wave at 1.2 V which is compatible with a one-electron process and could be attributed to the oxidation of Cu(I) to Cu(II). Unfortunately, the instability of [(**3a**)₂Cu]⁵⁺ precludes further insights.

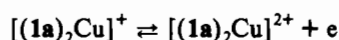
The two oxidation wave phenomenon can have two origins: the creation of a mixed-valence system or the presence of two different chemical environments for the ferrocene groups. In the first case bridged biferrrocene systems and their derivatives are well-known to play a central role in this type of phenomenon.²⁹ In the second case, to our knowledge, there is only one example of a compound structurally characterized containing four pendant ferrocene parts and presenting an electrochemical double wave due to two different ferrocenyl environments^{3c,30} each occupied by two groups of ferrocene. For complex **15**, even if an iron–iron electronic interaction through the ligand itself or through the metal atom³¹ can be considered, considering the electrochemical behavior of **3a** and **14**, it seems difficult to assume the occurrence of a mixed valence system. Indeed the second oxidation wave is at a potential close to that of **14** and the first oxidation wave is at an intermediate potential between the free ligand and the totally complexed one. Therefore the different electronic environments for the ferrocene parts of the molecule are more surely related to the proposed structure for **15**.

Case of the Complexes 9 and 11. At a rotating Pt disk electrode, the voltammograms show a diffusion-controlled wave for the oxidation of Cu(I) into Cu(II) at $E_{1/2} = 0.50$ V and $E_{1/2} = 1.05$ V vs SCE, respectively. We observed some passivation phenomena, attributed to nonconducting deposits, especially when the potential sweeps the whole electroactivity domain. In the CH₂Cl₂ containing 0.1 M Bu₄NPF₆ medium, the limiting currents obey the Levich law. As expected, decreasing the basicity of the ligand increases the oxidation potential of the Cu complex. Considering the electrochemical oxidation of complex **15** and owing to the basicity of the ligand, an oxidation wave for copper at a potential value nearer to that of **11** than to that of **9** can be expected. This confirms that the additional wave previously observed at 1.2 V for complex **15** (*vide supra*) is compatible with the one-electron oxidation of Cu(I) to Cu(II).

For **9** and **11** under non stationary conditions, the voltammograms present the shape of reversible systems. Exhaustive electrolysis of a saturated solution in CH₂Cl₂ of **9** at 0.6 V confirms a single electron transfer. The initially colorless solution becomes green and simultaneously all the product dissolves, giving an homogeneous solution. The ESR spectra parameters ($g_{\text{iso}} = 2.09$; $A_{\text{iso}} = 82$ G; $g_{\parallel} = 2.26$; $g_{\perp} = 2.05$; $A_{\parallel} = 165$ G) obtained on a frozen (110 K) oxidized solution are typical of Cu(II) species.^{25a,32} Rereduction of the solution gives back the initial colorless solution

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of Cu(I). The following oxidation reaction may thus be proposed:



During the electrolysis of **11** at 1.25 V the solution turned green with a 0.5-electron exchange.

Case of the Complexes 8 and 10. Compound **8** undergoes two oxidation steps of the same intensity at $E_{1/2} = 0.70$ V and $E_{1/2} = 0.96$ V vs SCE, respectively. Furthermore, the wave obtained by RDE voltammetry for the second step is distorted by electrode passivation probably owing to compound decomposition since it is in the region of the ligand oxidation (Table 3). Because of the low solubility of the complex the number of electrons exchanged in the electrochemical oxidation could not be determined. In the case of compound **10**, a quasi-reversible oxidation wave is observed at $E_{1/2} = 0.88$ V for a scan rate of 1 V s⁻¹ in cyclic voltammetry.

To summarize, we have observed that for similar complexes, the coordination of organic phosphohydrazone instead of -hydrazide increases the oxidation potential of the Cu(I) compounds, which is expected considering the greater basicity of the hydrazide ligands. All the oxidation potentials of these complexes are in a normal range for copper(I) complexes.^{22,33} In the case of copper complexes with ligands containing ferrocenylhydrazone substituents, the oxidation potential of the ferrocenyl moieties increases to higher anodic potential traducing a through-space interaction of copper(I) with equivalent or nonequivalent ferrocenyl moieties, and the oxidation wave of Cu(I) becomes more discreet.

Conclusion

The condensation of ferrocene carbaldehyde with phosphohydrazides XP[N(CH₃)NH₂]_nPh_{3-n} ($n = 2, 3$; X = O, S) leads to a new class of ligands XP[N(CH₃)N=CHFc]_nPh_{3-n} containing an electroactive iron center. Evaluation of the complexing properties of these ligands toward Cu(I) salts has highlighted their versatility since they can act as chelating or bridging ligands. When $n = 2$ and X = S, we have shown that in the 2/1 complex the ligand is chelating through its S atom and one of its two hydrazone arms and that there is an exchange between coordinated and free hydrazone arms of the ligands. When $n = 2$, in the 1/1 complex, the sulfur atom of the PS group is able to bridge two copper atoms, and each arm of the dihydrazone ligand is bonded to a different metal center. When $n = 3$ (compound **16**), the ligation through sulfur is involved and exchanges between the coordinated and the two other free hydrazone arms have been observed. This versatility is due to the phosphohydrazide skeleton of the ligand since the same complexes have been obtained by condensation of ferrocenecarbaldehyde with the preformed copper phosphohydrazide complexes.

Electrochemical studies have shown that, as expected, the electronic properties of the ferrocene centers are very sensitive to the complexation of the ligand but also to their mode of complexation. Furthermore, the electrochemical oxidation of these iron centers can lead to elimination of the complexed copper. This should be of interest for cation recycling.

Extension of the study of the chemical and complexation properties of the new phosphohydrazide and -hydrazone ligands toward other metals will be described separately. The synthesis of phosphorus macrocycles compounds containing metallocenes starting from phosphohydrazide ligands is under way.

Experimental Section

All the syntheses have been performed under nitrogen or argon atmosphere using standard Schlenk tube techniques.

¹H and ¹³C NMR spectra have been performed on a Bruker AC 200 spectrometer, and the ³¹P spectra were obtained on a Bruker AC 80 instrument. ¹H and ¹³C NMR spectra are referenced to external tetramethylsilane. ³¹P values are referenced to external 85% H₃PO₄ in D₂O. Variable-temperature and selective decoupling experiments were carried out on a Bruker WM 250 machine equipped with multinuclear attachment. ESR spectra were obtained with a Bruker ER 200 in the X-band mode at room temperature, equipped at 4 K with an Oxford ESR cryostat. IR spectra have been performed on a Perkin-Elmer 983 instrument in KBr pellets. Microanalyses have been performed by the Centre de Microanalyse du CNRS or in the lab. Tetrahydrofuran and diethyl ether were freshly distilled over sodium/benzophenone, dichloromethane was freshly distilled over P₂O₅, and pentane was freshly distilled over CaH₂ and stored under argon. Absolute ethanol and acetonitrile were stored over molecular sieves. Cu(CF₃SO₃)·0.5C₆H₆ (Fluka) and (C₅H₅)Fe(C₅H₄CHO) (Aldrich) were used without further purification. **1a**, **b** and **2a**, **b** have been prepared by a published procedure.³⁴

Synthesis of 3b. A mixture of 2.00 g of CpFe(C₅H₄CHO) (9.34 mmol) and 1.00 g of **1b** (4.67 mmol) in 120 mL of ethanol was stirred under argon for 18 h. The orange solution was evaporated to dryness and the powder washed with 2 × 60 mL of pentane. The precipitate was filtered and dried under vacuum (88.4% yield). Anal. Calcd for C₃₀H₃₁N₄OPFe₂: C, 59.43; H, 5.12; N, 9.25; P, 5.12; Fe, 18.44. Found: 59.37; H, 5.32; N, 9.24; P, 5.08; Fe, 18.60. ¹H NMR (CDCl₃), δ: [7.98 (m), 7.51 (m)] (5 H, C₆H₅); 7.38 (m, 2H, CH=N); [4.20 (m), 4.41 (m)] (4H, C₅H₄); 4.04 (s, 5H, C₅H₅); 3.12 (d, 6H, J = 7 Hz, N-CH₃). ³¹P{¹H} NMR (CDCl₃), δ: 24.2 ppm. ¹³C NMR (CDCl₃), δ: 136.1 (dd, J_{PC} = 14.6 Hz, J_{CH} = 161 Hz, CH=N); 133.1 (dd, J_{PC} = 8.6 Hz, J_{CH} = 156 Hz), 131.5 (d, J_{CH} = 161 Hz), 129.8 (d, J_{PC} = 155 Hz), 127.3 (dd, J_{PC} = 14.3 Hz, J_{CH} = 166 Hz)] (C₆H₅P); 81.2 (s), 68.9 (d, J_{CH} = 176 Hz), 67.0 (d, J_{CH} = 171 Hz), 66.9 (d, J_{CH} = 171 Hz) (C₅H₅ and C₅H₄). 30.7 (dq, J_{PC} = 8.0 Hz, J_{CH} = 138 Hz, N-CH₃). IR (KBr): 1588 (w, ν(C=N)) cm⁻¹.

Synthesis of Compounds 4a and 4b. A mixture of 3 equiv of CpFe(C₅H₄CHO) and 1 equiv of **2a** (0.86 g, 4.34 mmol) or **2b** (4.40 mmol) in 140 mL of ethanol was stirred under nitrogen for 18 h. **4a** was treated in a similar manner to **3a** and obtained as an orange brown powder in 74% yield. **4b** was treated in a similar manner to **3b** and obtained as an orange powder in 79% yield. **4a.** Anal. Calcd. for C₃₆H₃₉N₆SPFe₂: C, 55.0; H, 4.96; N, 10.69; P, 3.95; S, 4.07; Fe, 21.33. Found: C, 54.84; H, 4.95; N, 10.66; P, 3.91; S, 4.37; Fe, 20.96. ¹H NMR (CD₂Cl₂), δ: 7.50 (d, 1H, J_{HP} = 1.8 Hz, CH=N); [4.28 (t), 4.53 (t)] (4H, C₅H₄); 4.11 (s, 5H, C₅H₅); 3.23 (d, 3H, J_{HP} = 8.8 Hz, N-CH₃). ³¹P{¹H} NMR (CD₂Cl₂), δ: 72.4. ¹³C NMR (CDCl₃), δ: 136.8 (dd, J_{PC} = 14.7 Hz, J_{CH} = 161 Hz, CH=N); 81.4 (s), 69.0 (br d, J_{CH} = 176 Hz), 67.3 (d, J_{CH} = 177 Hz) (C₅H₅, C₅H₄); 32.6 (dq, J_{PC} = 8.0 Hz, J_{CH} = 138.5 Hz, N-CH₃). IR (KBr): 1596 (w, ν(C=N)) cm⁻¹. **4b.** Anal. Calcd for C₃₆H₃₉N₆OPFe₂: C, 56.4; H, 5.07; N, 10.92; P, 4.03; Fe, 21.77. Found: C, 56.02; H, 5.17; N, 10.71; P, 4.18; Fe, 21.55. ¹H NMR (C₆D₆), δ: 7.3 (s, 1H, CH=N); [4.07 (t), 4.53 (t)] (4H, C₅H₄); 4.05 (s, 5H, C₅H₅); 3.05 (d, 3H, J_{HP} = 7.3 Hz). ³¹P{¹H} NMR (C₆D₆), δ: 11.6. ¹³C NMR (CDCl₃), δ: 136.9 (dd, J_{PC} = 14.9 Hz, J_{CH} = 160 Hz, CH=N); 81.2 (s); 69.0 (d, J_{CH} = 176 Hz), 68.9 (d, J_{CH} = 176 Hz), 67.0 (d, J_{CH} = 177 Hz) (C₅H₅, C₅H₄); 32.32 (dq, J_{CP} = 7.4 Hz, J_{CH} = 138.5 Hz). IR (KBr): 1596 (w, ν(C=N)) cm⁻¹.

Synthesis of Compound 5. To a solution of 183 mg (4.8 mmol) of LiAlH₄ in 40 mL of THF was added dropwise a solution of **3a** (250 mg (0.4 mmol)) in 10 mL of THF. The mixture was stirred for 20 h at 65 °C. Excess LiAlH₄ was decomposed by addition of 1.5 mL of water at 0 °C. After filtration, the yellow organic layer was evaporated to dryness for 2 h. The residue was diluted in 5 mL of toluene and purified by a new filtration and evaporation of the solvent. ¹H NMR (C₆D₆), δ: [8.38 (m), 7.15 (m)] (5 H, C₆H₅); [3.97 (m), 3.92 (m)] (8H, C₅H₄); 4.01 (m, 10H, C₅H₅); 3.45 (m, 4H, CH₂N); 3.20 (m, 2H, NH); 2.78 (d, 6H, J_{PH} = 11.7 Hz). ³¹P{¹H} NMR (C₆D₆), δ: 81.2. ¹³C NMR (CDCl₃), δ: 132.6 (m, J_{PC} = 10.2 Hz, J_{CH} = 164 Hz), 132.5 (d, J_{PC} = 107.5 Hz), 131.0 (m, J_{PC} = 2.5 Hz, J_{CH} = 160 Hz); 127.4 (ddd, J_{CP} = 13.2 Hz, J_{CH} = 161 Hz, J_{CH} = 6.8 Hz) (C₆H₅P); 83.7 (m); 68.8 (m, J_{CH} = 174 Hz), 68.4 (m, J_{CH} = 175 Hz), 68.2 (m, J_{CH} = 176 Hz); 67.8 (m, J_{CH} = 176 Hz), 67.7 (m, J_{CH} = 176 Hz), (C₅H₄, C₅H₅); 47.7 (dt, J_{CP} = 7.0 Hz, J_{CH} = 137 Hz, CH₂) 35.5 (dq, J_{PC} = 8.4 Hz, J_{CH} = 137 Hz, N-CH₃).

Synthesis of Compounds 6 and 7. Preparation of 6. To a solution of **1a** (0.3 g (1.3 mmol)) in 15 mL of absolute ethanol was added benzaldehyde (0.266 mL, 2.6 mmol). The mixture was stirred for 15 h, and a white powder precipitated. The solvent was evaporated to dryness and the

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white powder washed with 30 mL of pentane. After filtration the product was dried under vacuum: 87% yield. Anal. Calcd for $C_{22}H_{23}N_4PS$: C, 65.02; H, 5.66; N, 13.79; Found: C, 64.98; H, 5.85; N, 13.69. 1H NMR ($CDCl_3$); δ : [8.10 (m), 7.46 (m), 7.22 (m)] (17H, C_6H_5 , $CH=N$); 3.28 (d, $J_{PH} = 10.6$ Hz, 6H, $N-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ : 79.1. ^{13}C NMR ($CDCl_3$), δ : 137.1 (dd, $J_{PC} = 13.1$ Hz, $J_{CH} = 161$ Hz) ($CH=N$); 135.5 (s), 133.2 (dd, $J_{PC} = 10.9$ Hz, $J_{CH} = 165$ Hz), 131.6 (m, $J_{CH} = 153$ Hz), 127.5 (ddd, $J_{CP} = 14.7$ Hz, $J_{CH} = 6.4$ Hz, $J_{CH} = 165$ Hz) (C_6H_5-PS); 128.4 (d, $J_{CH} = 161$ Hz), 128.3 (d, $J_{CH} = 162$ Hz), 126.4 (d, $J_{CH} = 159$ Hz) ($C_6H_5-CH=N$); 31.0 (dq, $J_{PC} = 9.8$ Hz, $J_{CH} = 139$ Hz) ($N-CH_3$).

Preparation of 7. This was prepared as for 6 but with 3 equiv of benzaldehyde and 4 h of stirring: white powder; 75% yield. Anal. Calcd for $C_{24}H_{27}N_6SP$: C, 62.33; H, 5.84; N, 18.1; Found: C, 62.40; H, 6.07; N, 18.12. 1H NMR ($CDCl_3$), δ : 7.61 (d), $J_{PH} = 1.9$ Hz, $CH=N$; [7.52 (m), 7.16 (m)] (5H, C_6H_5); 3.34 (d, 3H, $J_{PH} = 9.4$ Hz, $N-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ : 73.7. ^{13}C NMR ($CDCl_3$), δ : 136.8 (dd, $J_{CP} = 14.7$ Hz, $J_{CH} = 160$ Hz, $CH=N$); 135.6 (m), 128.3 (d, $J_{CH} = 162$ Hz), 128.2 (d, $J_{CH} = 161$ Hz), 126.5 (d, $J_{CH} = 160$ Hz) (C_6H_5); 32.26 (dq, $J_{PC} = 9.1$ Hz, $J_{CH} = 139$ Hz, $N-CH_3$).

Synthesis of Compound 8. To a solution of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ (158 mg, 0.63 mmol) in 10 mL of THF was rapidly added a solution of **1a** (0.145 g, 0.63 mmol) in 10 mL of THF, dropwise with a cannula under argon. The mixture was stirred for 18 h. This mixture turned deep green then clearer after 45 min and finally clear yellow. The solvent was evaporated to dryness under vacuum and the yellow product washed with 15 mL of diethyl ether and 15 mL of pentane. The clear powder was dried under vacuum (92% yield). Anal. Calcd for $C_{18}H_{30}N_8O_6F_6P_2S_4Cu_2$: C, 24.39; H, 3.39; N, 12.65; Found: C, 25.30; H, 3.39; N, 12.42. IR (KBr): 3267 (m), 3169 (m) ($\nu(NH_2)$) cm^{-1} .

Synthesis of Compound 9. A 131.7-mg (0.5-mmol) sample of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ was dissolved in 10 mL of THF and added with a cannula under argon to a solution of **1a** (240.7 mg (1 mmol)) in 10 mL of THF. The mixture turned green and orange and then gave after 5 h of stirring a colorless solution. The mixture was evaporated to dryness under vacuum. The white powder was washed with diethyl ether and pentane and then dried under vacuum (86% yield). Anal. Calcd for $C_{17}H_{30}N_8O_3F_3P_2S_3Cu$: C, 30.33; H, 4.46; N, 16.65; F, 8.47; P, 9.22; S, 14.30; Cu, 9.44. Found: C, 30.31; H, 4.53; N, 16.47; F, 8.01; P, 8.70; S, 13.70; Cu, 9.13. 1H NMR (THF-*d*), δ : [8.05 (m), 7.67 (m)] (5H, C_6H_5); 5.07 (s, 4H, NH_2); 3.19 (d, 6H, $J_{PH} = 11.6$ Hz, $N-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ : 79.4. ^{13}C NMR (THF-*d*), δ : 133.6 ($J_{PC} = 10.2$ Hz, $J_{CH} = 163$ Hz), 133.1 (m, $J_{PC} = 2.0$ Hz, $J_{CH} = 145$ Hz), 132.2 (d, $J_{PC} = 133$ Hz), 129.7 (m, $J_{PC} = 13.3$ Hz, $J_{CH} = 163$ Hz) (C_6H_5); 42.0 (dq, $J_{PC} = 7.8$ Hz, $J_{CH} = 138$ Hz) ($N-CH_3$). IR (KBr): 3306 (sh), 3273 (m), 3178 (m) ($\nu(NH_2)$) cm^{-1} . IR (Nujol): 3276 (m), 3182 (m) cm^{-1} .

Synthesis of Compound 10. To a solution of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ (234.9 mg, 0.93 mmol) in 10 mL of THF was syringed under argon a solution of **6** (341 mg, 0.84 mmol) in 20 mL of THF. The mixture turned green, and a white powder precipitated within a few minutes. The reaction was stirred for 14 h. The powder was washed with THF and then with 2×15 mL of diethyl ether and dried under vacuum: 82% yield. Anal. Calcd for **10**-2THF, $C_{50}H_{54}N_8O_7F_6P_2S_4Cu_2$: C, 45.85; H, 4.13; N, 8.56; F, 8.71; P, 4.74; S, 9.78; Cu, 9.71; Found: C, 45.78; H, 4.01; N, 8.64; F, 8.54; P, 4.76; S, 9.86; Cu, 10.17.

Synthesis of Compound 11. A 409.3-mg (1-mmol) sample of **6** was dissolved in 15 mL of THF. A 127.3-mg (0.5-mmol) sample of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ was dissolved in 15 mL of THF and added rapidly to the first solution under argon. The yellow mixture was stirred for 18 h and then evaporated to dryness. The product was obtained by recrystallization from dichloromethane/diethyl ether or dichloromethane/pentane mixtures (65% yield) as yellow crystals. Anal. Calcd for $C_{45}H_{46}N_8O_3F_3P_2S_3Cu$: C, 52.70; H, 4.49; N, 10.93; F, 5.56; P, 6.05; S, 9.37; Cu, 6.20; Found: 52.83; H, 4.44; N, 10.90; F, 5.52; P, 5.90; S, 9.34; Cu, 6.20. 1H NMR ($CDCl_3$), δ : [8.75 (m), 7.53 (m), 7.25 (m)] (17H, C_6H_5 and $CH=N$); 3.25 (d, 6H, $J_{PH} = 8.9$ Hz, $N-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ : 74.8. ^{13}C NMR ($CDCl_3$) (297 K), δ : 143.4 (dd, $J_{PC} = 13.3$ Hz, $J_{CH} = 164$ Hz, $CH=N$); 133.4 (m, $J_{CH} = 160$ Hz, $J_{CP} = 3.0$ Hz), 133.2 (m, $J_{PC} = 11.3$ Hz, $J_{CH} = 137$ Hz), 130.0 (d, $J_{PC} = 134$ Hz), 129.2 (m, $J_{PC} = 14.8$ Hz, $J_{CH} = 157$ Hz) (C_6H_5-PS); 133.5 (m), 130.1 (m, $J_{CH} = 129$ Hz), 128.5 (dd, $J_{CH} = 162$ Hz, $J_{CH} = 7.0$ Hz), 127.7 (m, $J_{CH} = 147$ Hz) ($C_6H_5-CH=N$); 34.14 (qd, $J_{PC} = 7.2$ Hz, $J_{CH} = 140$ Hz, $N-CH_3$).

Synthesis of Compound 12. A 301.6-mg (1.2-mmol) sample of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ was rapidly added under argon to a solution of **2a** (237 mg, 1.2 mmol) in 20 mL of THF. The mixture was green and then lightened. The mixture was stirred for 16 h. The product was obtained

as a white powder after filtration, washed with 15 mL of THF and 15 mL of diethyl ether, and then dried under vacuum: 72% yield. Anal. Calcd for $C_8H_{15}N_6O_3F_3P_2S_3Cu$: C, 11.63; H, 3.65; N, 20.45. Found: C, 13.19; H, 3.66; N, 19.48. IR (KBr): 3319 (m), 3257 (s), 3234 (s), 3170 (s), 3129 (s) ($\nu(NH_2)$) cm^{-1} .

Synthesis of Compound 13. A solution of 142.9 mg (0.57 mmol) of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ in 15 mL of THF was added under argon to a solution of **7** (262.4 mg, 0.57 mmol) in 15 mL of THF. A white product precipitated immediately. The mixture was stirred for 4 h. The moisture sensitive powder was washed with 20 mL of diethyl ether and then dried under vacuum: 76% yield. Anal. Calcd for $C_{25}H_{27}N_6O_3F_3P_2S_3Cu$: C, 44.46; H, 4.00; N, 12.45; P, 4.60; S, 9.49; Cu, 9.42. Found: C, 44.57; H, 4.06; N, 12.13; P, 4.95; S, 9.46; Cu, 8.90.

Synthesis of Compound 14 Starting from Complex 8. A mixture of 245 mg (0.28 mmol) of **8** and 1.12 mmol of $(C_5H_5)FeC_5H_4CHO$ was stirred in 35 mL of THF under nitrogen. After 1 h of stirring, solubilization was achieved, and after 16 h of stirring, a clear orange powder was isolated after filtration. The product was washed with 40 mL of diethyl ether and dried under vacuum (69% yield). ^{13}C NMR (CD_2Cl_2), δ : 161.7 (dd, $J_{PC} = 8$ Hz, $J_{CH} = 173$ Hz, $CH=N$); 134.9 (br d, $J_{CH} = 157$ Hz), 132.7 (dd, $J_{PC} = 11.5$ Hz, $J_{CH} = 159$ Hz), 130.1 (dd, $J_{PC} = 11.6$ Hz, $J_{CH} = 159$ Hz) (C_6H_5); 75.0 (br), 73.2 (m, $J_{CH} = 180$ Hz), 70.5 (m, $J_{CH} = 175$ Hz), 69.8 (m, $J_{CH} = 177$ Hz), 64.8 (s) (C_5H_5 , C_5H_4), 37.5 (br q, $J_{CH} = 144$ Hz) ($N-CH_3$). IR (KBr): 1583 (s, $\nu(C=N)$) cm^{-1} .

Synthesis of Compound 15. Method A. To a solution of **3a** (563.3 mg, 0.86 mmol) in 20 mL of THF was rapidly added a solution of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ (108.5 mg, 0.43 mmol) in 4 mL of THF dropwise. After 20 min, an orange powder precipitated at room temperature. The mixture was stirred for 4 h. The product after filtration was washed with 30 mL of diethyl ether and dried under vacuum: 72.5% yield. Anal. Calcd for **15**-2THF, $C_{69}H_{78}N_8O_3F_3P_2S_3Fe_4Cu$: C, 51.75; H, 4.88; N, 7.00; F, 3.56; P, 3.88; S, 6.01; Fe, 13.96; Cu, 3.97. Found: C, 52.01; H, 5.01; N, 6.90; F, 3.88; S, 6.21; Fe, 6.10; Cu, 4.11.

Method B. A mixture of 210 mg (0.31 mmol) of **9** and 267.3 mg (1.25 mmol) of $C_5H_5FeC_5H_4COH$ was stirred in 20 mL of THF for 24 h at room temperature. An orange powder was isolated after filtration. This product was washed with diethyl ether and dried under vacuum. The product could be recrystallized from a 2/1 mixture of $CHCl_3$ /diethyl ether 1H NMR ($CDCl_3$), δ : 7.65 (m, 7H, C_6H_5 and $CH=N$); [4.72 (br), 4.41 (br)] (8H, C_5H_4); 4.16 (s, 10H, C_5H_5); 3.20 (d, 6H, $J_{PH} = 9.3$ Hz, $N-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ : 72.1. ^{13}C NMR ($CDCl_3$) 144.0 (br d, $J_{CH} = 157$ Hz, $CH=N$); 132.7 (br d, $J_{CH} = 162$ Hz), 132.0 (br d, $J_{CH} = 173$ Hz), 128.8 (br d, $J_{CH} = 162$ Hz) (C_6H_5); 79.2 (br), 71.1 (br d, $J_{CH} = 175$ Hz), 70.2 (br d, $J_{CH} = 175$ Hz), 68.8 (br d, $J_{CH} = 170$ Hz) (C_5H_5 and C_5H_4); 34.1 (br q, $J_{CH} = 137$ Hz, $N-CH_3$). ^{13}C NMR (CD_2Cl_2 , 198 K), δ : 146.5 (br d, $J_{CH} = 174$ Hz), 138.9 (br d, $J_{CH} = 163$ Hz), 132.7 (br d, $J_{CH} = 143$ Hz), 131.7 (br), 131.0 (br d, $J_{CH} = 164$ Hz), 129.6 (br), 128.8 (br d, $J_{CH} = 162$ Hz) (C_6H_5); 79.1 (br), 76.0 (br), 70.7 (br), 68.9 (m), 65.5 (br) (C_5H_5 and C_5H_4); 36.9 (br q, $J_{CH} = 142$ Hz), 32.0 (br q, $J_{CH} = 143$ Hz) ($N-CH_3$). IR (KBr): 1585 (m, $\nu(C=N)$) cm^{-1} .

Synthesis of Compound 16. A 400-mg (0.5-mmol) sample of **4a** was dissolved in 35 mL of THF, and 50 mg (0.5 mmol) of $CuCl$ was added to the orange solution. The mixture was stirred for 24 h. The solution turned deep red whereas $CuCl$ solubilized. A red-brown precipitate appeared. The mixture was evaporated off under vacuum, washed with pentane (20 mL), and then filtered off. The red microcrystalline powder was dried under vacuum. Anal. Calcd for $C_{36}H_{39}N_6PSClFe_3Cu$: C, 48.84; H, 4.41; N, 9.50; P, 3.50; S, 3.62; Fe, 18.94; Cu, 7.18; Found: C, 48.59; H, 4.44; N, 9.19; P, 3.55; S, 3.39; Fe, 17.93; Cu, 7.24. 1H NMR (CD_2Cl_2), δ : 7.67 (d, 1H, $J_{PH} = 2$ Hz, $CH=N$); [4.73 (t), 4.39 (t)] (4H, C_5H_4); 4.15 (s, 5H, C_5H_5); 3.27 (d, 1H, $J_{PH} = 9$ Hz, $N-CH_3$). $^{31}P\{^1H\}$ (CD_2Cl_2), δ : 67.7. ^{13}C NMR (CD_2Cl_2), δ : 142.8 (dd, $J_{PC} = 14.0$ Hz, $J_{CH} = 163$ Hz, $CH=N$); 79.3 (br d, $J_{PC} = 5$ Hz), 70.4 (d, $J_{CH} = 177$ Hz), 69.6 (d, $J_{CH} = 176$ Hz), 68.2 (d, $J_{CH} = 177$ Hz) (C_5H_5 and C_5H_4); 33.6 (dq, $J_{PC} = 6.0$ Hz, $J_{CH} = 140$ Hz, $N-CH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) (193 K), δ : (146.7 (br), 140.0 (br)) (1/2 ratio, $CH=N$); (80.4 (br), 76.7 (br) (2/1 ratio C_{ipso}); 71.7 (s), 70.2 (s), 69.7 (s), 68.2 (s), 67 (s), 66.4 (s) (C_5H_5 , C_5H_4); 36.3 (br), 32.6 (br) (1/2 ratio, $N-CH_3$). IR (KBr): 1590 (m, $\nu(C=N)$) cm^{-1} .

Synthesis of Compound 17. Method A. To an orange solution of **4a** (278 mg, 0.35 mmol) in 15 mL of THF was rapidly added a solution of $Cu(CF_3SO_3) \cdot 0.5C_6H_6$ (89.3 mg, 0.35 mmol) in 5 mL of THF dropwise. The mixture immediately darkened. Then 5 mL of THF were added. After 7 h of stirring, the orange-pink precipitate was washed with diethyl ether and the product was dried under vacuum after filtration: 85% yield. When the product was dissolved in CH_3CN for a long time (>24

Table 4. Crystal and Intensity Data for $\text{PhP(O)(NMeNCH=Fe)}_2$ (3b)

| | |
|---|---|
| chemical formula: $\text{C}_{30}\text{H}_{31}\text{N}_4\text{O}_1\text{P}_1\text{Fe}_2$ | fw: 606.27 amu |
| $a = 15.176(1) \text{ \AA}$ | space group: $P2_1/c$ |
| $b = 15.170(2) \text{ \AA}$ | $T = 23 \text{ }^\circ\text{C}$ |
| $c = 12.533(2) \text{ \AA}$ | $\lambda(\text{Mo K}\alpha_1) = 0.7093 \text{ \AA}$ |
| $\beta = 106.582(8)^\circ$ | $\rho_{\text{calcd}} = 1.455 \text{ g, cm}^{-3}$ |
| $V = 2765.5(5) \text{ \AA}^3$ | $\mu = 11.35 \text{ cm}^{-1}$ |
| $Z = 4$ | transm coeff: 0.515–0.936 |
| | $R^a = 0.049$ |
| | $R_w^a = 0.056$ |

$$^a R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|; R_w = [\sum w(|F_o| - |F_c|)^2 / (\sum w|F_o|^2)]^{1/2}.$$

h), orange crystals appeared. After a washing with diethyl ether this product was soluble in CH_2Cl_2 and analyzed as 4a.

Method B. A mixture of 100 mg (0.24 mmol) of **12** and 3 equiv of $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{CHO})$ (156 mg, 0.73 mmol) was dissolved in 30 mL of THF. The mixture was stirred for 17 h at $80 \text{ }^\circ\text{C}$. A deep orange powder precipitated. After filtration the product was washed with THF (15 mL) and diethyl ether (15 mL) and obtained in a 58% yield. No other new product was obtained in the corresponding solution. Anal. Calcd for $\text{C}_{37}\text{H}_{39}\text{N}_6\text{O}_3\text{F}_3\text{PS}_2\text{Fe}_3\text{Cu}$: C, 44.48; H, 3.91; N, 8.42; F, 5.70; P, 3.10; S, 6.41; Fe, 16.78; Cu, 6.37. Found: C, 44.47; H, 4.01; N, 8.05; F, 5.91; P, 2.76; S, 6.44; Fe, 16.09; Cu, 6.26. $^1\text{H NMR}$ (CD_3CN), δ : 7.75 (d, 1H, $J_{\text{PH}} \sim 1.5 \text{ Hz CH=N}$); [(4.73 (t), 4.40 (t))] (4H, C_5H_4); 4.20 (s, 5H, C_5H_5); 3.26 (d, 3H, $J_{\text{PH}} = 9.0 \text{ Hz, N-CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN), δ : 71.7. $^{13}\text{C NMR}$ (CD_3CN), δ : 143.5 (dd, $J_{\text{PC}} = 14 \text{ Hz, } J_{\text{CH}} = 163.0 \text{ Hz, CH=N}$); 80.7 (br s), 71.1 (d, $J_{\text{CH}} = 177 \text{ Hz}$), 70.4 (d, $J_{\text{CH}} = 176 \text{ Hz}$), 69.0 (d, $J_{\text{CH}} = 177 \text{ Hz}$) (C_5H_5 and C_5H_4); 3.42 (dq, $J_{\text{CH}} = 140 \text{ Hz, } J_{\text{CH}} = 7.0 \text{ Hz, N-CH}_3$). IR (KBr): 1579 (s, $\nu(\text{C=N})$), 715 (s, $\nu(\text{P=S})$) cm^{-1} .

Synthesis of Compound 18. Into a stirred solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{C}_6\text{H}_6$ (105 mg, 0.4 mmol) in 10 mL of THF was syringed a solution of **3b** (252.7 mg, 0.42 mmol) in 15 mL of THF. The mixture was degassed and stirred under argon for 20 h. The orange brown powder was filtered and washed with 10 mL of THF and then with 20 mL of ether and finally dried under vacuum: 89% yield. Anal. Calcd for $\text{C}_{31}\text{H}_{31}\text{N}_4\text{O}_4\text{F}_3\text{PSFe}_2\text{Cu}$: C, 45.45; H, 3.79; N, 6.84; F, 6.96; P, 3.80; S, 3.91; Fe, 13.64; Cu, 7.76. Found: C, 45.37; H, 3.79; N, 6.64; F, 6.90; P, 3.46; S, 3.95; Fe, 13.43; Cu, 7.77. IR (KBr): 1583 (m, $\nu(\text{C=N})$) cm^{-1} .

Synthesis of Compound 19. A solution of 154.6 mg (0.61 mmol) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2 \cdot 0.5\text{C}_6\text{H}_6$ in 10 mL of THF was added to a solution of **4b** (472.7 mg, 0.61 mmol) in 30 mL of THF. A deep red precipitate appeared. The mixture was stirred for 4 h, and after filtration the powder was washed with $2 \times 20 \text{ mL}$ of diethylether then dried under vacuum: 92% yield. Anal. Calcd for $\text{C}_{37}\text{H}_{39}\text{N}_6\text{O}_4\text{PSFe}_3\text{Cu}$: C, 45.20; H, 3.97; N, 8.55; F, 5.80; P, 3.16; S, 3.26; Fe, 17.04; Cu, 6.46. Found: C, 44.90; H, 3.96; N, 8.23; F, 6.02; P, 2.94; S, 3.19; Fe, 17.00; Cu, 6.56. IR (KBr): 1589 (m, $\nu(\text{C=N})$) cm^{-1} .

Electrochemical Studies. Electrochemical measurements were carried out with a homemade potentiostat using an interfacing hardware with microcomputer PC compatible. Positive feedback or interrupt methods were used to compensate for IR drop. The electrochemical cell was a conventional one with three electrodes. The working electrode was a Pt disk (diameter 2 mm, EDI, Tacussel) for analytical purposes and a Pt foil for electrolysis. The counter electrode was a Pt wire. The reference electrode consisted of an SCE separated from the solution by a bridge compartment filled with the same solvent and supporting electrolyte solution as used in the cell. The supporting electrolyte Bu_4NPF_6 (TBAHFP, Aldrich analytical grade) was used as received. Dichloromethane CH_2Cl_2 (SDS, Purex) was passed over alumina (neutral, Merck) prior to use and degassed by bubbling argon during the experiments. With the above reference and bridge system, $E^\circ = 0.42 \text{ V}$ was obtained for 1 mM ferrocene. Electrochemical studies were done in 0.1 M dichloromethane solutions of Bu_4NPF_6 containing the sample to be used at $\sim 10^{-3} \text{ M}$ concentration.

Crystallographic Study of 3b. Crystals of the ligand **3b** suitable for X-ray diffraction were obtained by slow evaporation of a pentane/ethanol solution at $18 \text{ }^\circ\text{C}$. Intensity data were recorded on an Enraf-Nonius CAD4 diffractometer at $23 \text{ }^\circ\text{C}$. Cell constants were obtained from a least-squares fit to the setting angles of 25 randomly selected reflections in the range $12^\circ < \theta (\text{Mo K}\alpha_1) < 14^\circ$. The space group was determined by careful examination of systematic extinctions in the listing of measured reflections. Data reductions were carried out using the MOLEN crystallographic computing package.³⁵ Intensities were corrected for

Table 5. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors ($\text{\AA} \times 100$) with Esd's in Parentheses ($U_{\text{eq}} = 1/3 \text{ Tr } U$).

| atom | x/a | y/b | z/c | $U_{\text{eq}}/U_{\text{iso}}$ |
|--------|-------------|------------|-----------|--------------------------------|
| Fe(1) | 0.39562(8) | 0.82954(7) | 0.4530(1) | 4.27(7) |
| Fe(2) | -0.02531(8) | 0.64729(7) | 0.1459(1) | 4.51(8) |
| P | 0.2651(2) | 0.4467(1) | 0.5235(2) | 4.2(1) |
| O(1) | 0.2662(4) | 0.3746(3) | 0.6018(5) | 5.8(4) |
| N(1) | 0.3609(5) | 0.5823(4) | 0.5080(6) | 4.5(5) |
| N(2) | 0.3568(5) | 0.5118(4) | 0.5760(5) | 4.3(4) |
| N(3) | 0.1129(5) | 0.5119(4) | 0.4008(6) | 4.3(5) |
| N(4) | 0.1778(4) | 0.5172(4) | 0.5019(6) | 4.1(4) |
| C(1) | 0.4327(7) | 0.6304(5) | 0.5283(7) | 5.1(6) |
| C(2) | 0.4401(8) | 0.4821(7) | 0.6604(9) | 5.8(7) |
| H(201) | 0.454(5) | 0.530(5) | 0.715(7) | 7.00(0) |
| H(202) | 0.423(6) | 0.435(5) | 0.694(7) | 7.00(0) |
| H(203) | 0.471(6) | 0.458(6) | 0.620(7) | 7.00(0) |
| C(3) | 0.0430(6) | 0.5622(5) | 0.3803(7) | 4.6(6) |
| C(4) | 0.1694(8) | 0.5771(7) | 0.5890(9) | 6.0(7) |
| H(401) | 0.166(6) | 0.635(5) | 0.554(7) | 7.00(0) |
| H(402) | 0.217(6) | 0.568(6) | 0.644(8) | 7.00(0) |
| H(403) | 0.108(6) | 0.565(5) | 0.621(7) | 7.00(0) |
| C(11) | 0.4375(6) | 0.7016(5) | 0.4505(8) | 4.8(6) |
| C(12) | 0.3683(7) | 0.7238(6) | 0.3503(7) | 6.0(7) |
| C(13) | 0.4045(9) | 0.7955(6) | 0.3012(9) | 7.6(8) |
| C(14) | 0.4904(8) | 0.8173(7) | 0.369(1) | 9.0(9) |
| C(15) | 0.5110(7) | 0.7605(7) | 0.460(1) | 7.6(8) |
| C(21) | 0.3081(9) | 0.8403(7) | 0.548(1) | 8.2(8) |
| C(22) | 0.2759(8) | 0.8880(9) | 0.448(1) | 9.1(1) |
| C(23) | 0.343(1) | 0.9521(8) | 0.449(1) | 10.1(1) |
| C(24) | 0.412(1) | 0.9401(7) | 0.545(1) | 10.1(1) |
| C(25) | 0.393(1) | 0.8722(7) | 0.6066(9) | 8.7(9) |
| C(31) | -0.0226(6) | 0.5590(5) | 0.2702(7) | 4.5(6) |
| C(32) | -0.1077(6) | 0.6037(6) | 0.2377(8) | 5.3(6) |
| C(33) | -0.1488(6) | 0.5884(6) | 0.1250(9) | 5.8(7) |
| C(34) | -0.0900(7) | 0.5327(6) | 0.0853(8) | 5.6(6) |
| C(35) | -0.0122(6) | 0.5150(5) | 0.1735(7) | 4.4(6) |
| C(41) | 0.0959(8) | 0.6893(8) | 0.127(2) | 10.1(1) |
| C(42) | 0.024(1) | 0.7031(8) | 0.028(1) | 10.1(1) |
| C(43) | -0.0413(8) | 0.7579(8) | 0.051(1) | 7.3(8) |
| C(44) | -0.0099(8) | 0.7803(6) | 0.161(1) | 7.6(9) |
| C(45) | 0.0728(8) | 0.7402(8) | 0.209(1) | 7.2(8) |
| C(51) | 0.2674(5) | 0.4086(5) | 0.3891(7) | 3.5(5) |
| C(52) | 0.2684(6) | 0.3178(5) | 0.3733(8) | 4.7(6) |
| C(53) | 0.2753(6) | 0.2845(6) | 0.2745(9) | 6.1(7) |
| C(54) | 0.2807(6) | 0.3393(7) | 0.1915(8) | 6.8(7) |
| C(55) | 0.2792(7) | 0.4293(7) | 0.2048(8) | 7.2(8) |
| C(56) | 0.2724(6) | 0.4633(6) | 0.3034(8) | 5.5(6) |

absorption, using a numerical method based on Gaussian integration. Table 4 summarizes crystal and intensity data.

The structure was solved by using the SHELXS package³⁶ and refined with the SHELX-76 package.³⁷ The position of Fe and P atoms was determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses.

Atomic scattering factors were taken from the usual tabulations.³⁸ All non-hydrogen atoms were allowed to vibrate anisotropically. Hydrogen atoms were entered in idealized positions ($\text{C-H} = 0.97 \text{ \AA}$) riding the carbon atoms.

Final atomic coordinates and $U_{\text{eq}} \times 100$ (or $U_{\text{iso}} \times 100$) for non-hydrogen atoms are given in Table 5.

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Supplementary Material Available: Table S1, anisotropic thermal parameters, Table S2, hydrogen positions, and Table S3, complete crystal and intensity data (3 pages). Ordering information is given on any current masthead page.

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