4256 *Inorg. Chem.* **1995,** *34,* 4256−4261

# $[PhP(S)(NMeNH_2)_2]ZnCl_2$: A Reagent for the Synthesis of Polymetallic Complexes. X-ray Structure of the Electroactive Compound $[PhP(S)(NMeN{=}CHC_5H_4FeCp)_2]ZnCl_2$

**Béatrice Delavaux-Nicot,* Bénédicte Douziech, René Mathieu,* and Guy Lavigne**

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, lié par conventions à l'Université Paul
Sabatier et à l'Institut National Polytechnique de Toulouse, 205 route de Narbonne,
Toulouse Cedex, France

*Received April 14, 1995*[⊗]

The zinc complex $[PhP(S)(NMeNH_2)_2]ZnCl_2$ (**2**), cleanly obtained by reaction of the phosphodihydrazide $PhP(S)(NMeNH_2)_2$ (**1**) with $ZnCl_2$, is a good reagent in producing new polymetallic compounds by condensation reaction with aldehydes. The reaction of **2** with terephthalaldehyde (**3**) in a 2/1 or 1/1 stoichiometry leads selectively to the acyclic zinc compound $[C_6H_4\text{-}1,4\text{-}(CH{=}NNMePhP(S)NMeNH_2)_2][ZnCl_2]_2$ (**6**) or to the macrocyclic zinc complex $[PhP(S)C_6H_4\text{-}1,4\text{-}(CH{=}NNMe)_2]_2[ZnCl_2]_2$ (**7**). Reaction of compound **2** with 2 equiv of ferrocenecarbaldehyde affords the zinc−iron phosphodihydrazone complex $[PhP(S)(NMeN{=}CHC_5H_4FeCp)_2]ZnCl_2$ (**8**) whose structure has been determined by X-ray crystallography. Crystal data: triclinic $P\bar{1}$, with $a = 12.798(1)$ Å, $b = 14.639(2)$ Å, $c = 11.744(2)$ Å, $\alpha = 111.74(1)°$, $\beta = 115.92(1)°$, $\gamma = 68.36(1)°$, $V = 1780.9$ Å$^3$, $Z = 2$; $R = 0.037$, $Rw = 0.044$ for 3345 observations and 448 variable parameters. In this neutral trimetallic complex, the Zn(II) center adopts a pseudotetrahedral geometry. This structure is characterized by a five-membered ring with the Zn(II) bonded to the S atom and to one of the N atoms of the phosphodihydrazone ligand $PhP(S)(NMeN{=}CHC_5H_4FeCp)_2$ (**9**). Variable-temperature NMR investigations of **8** show that **9** can act as a hemilabile ligand toward $ZnCl_2$ through an exchange process between the two hydrazone arms in solution. Electrochemical study of complex **8**, when compared to the ferrocenyl ligand **9**, shows that $ZnCl_2$ complexation induces a shift of 80 mV toward a more anodic potential. Reaction of **2** with the ferrocene-1,1′-dicarbaldehyde also produces the bisferrocenyl dizinc macrocycle $[Fe(C_5H_4CH{=}NNMePhP(S)NMeN{=}CHC_5H_4)_2Fe][ZnCl_2]_2$ (**10**).

## Introduction

Pursuing the goal of synthesizing phosphorus-containing bisferrocene macrocycles, we decided in a parallel approach to develop the study of the coordination properties of phosphohydrazides $Ph_{3-n}P(X)(NMeNH_2)_n$ ($n = 2, 3$; X = O, S). The ability of these ligands to give macrocycles by a condensation reaction with organic aldehydes is well established,[1] but examples concerning their complexing properties are sparse.[2] In previous papers, we have described the first examples of the acyclic phosphorus-containing ferrocenyl ligands $Ph_{3-n}P(X)(NMeN{=}CHC_5H_4FeCp)_n$ (X = O, S; $n = 2, 3$).[3] They exhibit good ability to give electroactive complexes with copper (I) triflate. At the same time, the coordination chemistry of the phosphohydrazides toward Pd, Cd, and Ni salts was developed by others.[4]

In order to complete our studies concerning the coordination properties of phosphohydrazides, herein we describe the synthesis of the complex $[PhP(S)(NMeNH_2)_2]ZnCl_2$ (**2**) and we demonstrate how the $NH_2$ functionalities can produce a varied number of acyclic and macrocyclic zinc compounds, starting from **2** and terephthalaldehyde (**3**), ferrocenecarbaldehyde (**4**), or ferrocene-1,1′-dicarbaldehyde (**5**). An X-ray structure of the first example of a derivative possessing a ferrocenyl phosphodihydrazone moiety and a zinc unit is reported.

## Results and Discussion

**Synthesis of 2.** The phosphohydrazide **1** reacts in THF at room temperature with 1 equiv of $ZnCl_2$ to give white $[PhP(S)(NMeNH_2)_2]ZnCl_2$ (**2**) isolated in 85% yield (Scheme 1). The $\nu(NH_2)$ stretching vibrations observed at 3310, 3200 (broad), and 3120 cm$^{-1}$ (3260 and 3160 cm$^{-1}$ for the free ligand **1**) suggest the presence of free and coordinated $NH_2$ groups.[5] Contrary to the palladium homologue, there is no significant difference in the $\nu(P{=}S)$ region.[4a,b] In solution the $^1H$ and $^{31}P$ NMR spectra (DMSO) are very similar to those of the free ligand except for a $^3J_{HP}$ coupling constant (8.8 Hz) at $\delta = 4.01$ attributable to the $NH_2$ groups. This is consistent either with the coordination of the two $NH_2$ groups to Zn or like in the case of similar Cu(I) complexes[3c] with a ligand **1** N and S bound

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) See for example: (a) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1988**, *27*, 3873. (b) Badri, M.; Majoral, J.-P.; Caminade, A.-M.; Delmas, M.; Gaset, A.; Gorgues, A.; Jaud, J. *J. Am. Chem. Soc.* **1990**, *112*, 5618. (c) Majoral, J.-P.; Badri, M.; Caminade, A.-M.; Delmas, M.; Gaset, A. *Inorg. Chem.* **1991**, *30*, 334.

(2) (a) Casteran-Baumassy, J.; Dagnac, P.; Gleizes, A. *J. Chem. Res.* **1979**, *Synop.* 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.* **1980**, *Synop.* 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.

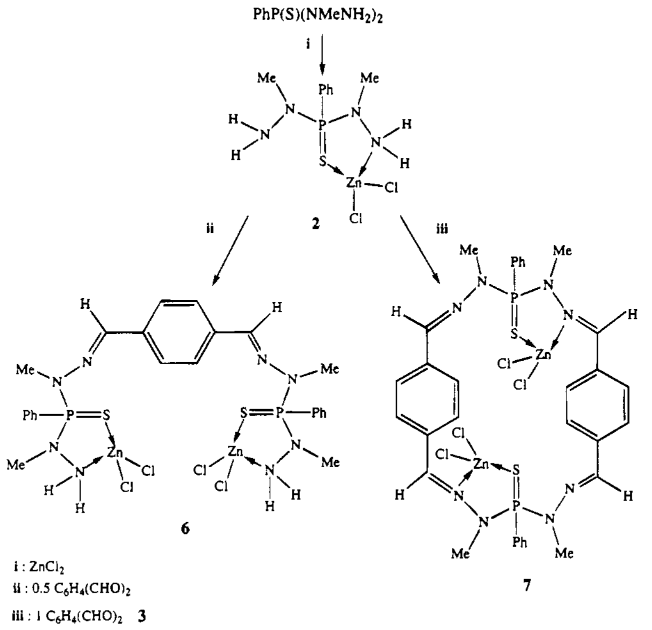
(3) (a) Delavaux-Nicot, B.; Lugan, N.; Mathieu, R.; Majoral, J.-P. *Inorg. Chem.* **1992**, *31*, 334. (b) Delavaux-Nicot, B.; Mathieu, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *77*, 323. (c) Delavaux-Nicot, B.; Mathieu, R.; de Montauzon, D.; Lavigne, G.; Majoral, J.-P. *Inorg. Chem.* **1994**, *33*, 434.

(4) (a) Katti, K. V.; Singh, P. R.; Barnes, C. L. *Inorg. Chem.* **1992**, *31*, 4588. (b) Singh, P. R.; Jimenez, H.; Katti, K. V.; Volkert, W. A.; Barnes, C. L. *Inorg. Chem.* **1994**, *33*, 736. (c) Katti, K. V.; Ge, Y. W.; Singh, P. R.; Date, S. V.; Barnes, C. L. *Organometallics* **1994**, *13*, 541. (d) Engelhardt, U.; Renz-Kreikebohn, C.; Stromburg, B. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *77*, 266. (e) Colombo-Khater, D.; Caminade, A.-M.; Kraemer, R.; Raynaud, B.; Jaud, J.; Majoral, J.-P. *Bull. Soc. Chim. Fr.* **1994**, 131, 733.

(5) Gonce, F.; Caminade, A.-M.; Boutonnet, F.; Majoral, J.-P. *J. Org. Chem.* **1992**, *57*, 970.

0020-1669/95/1334-4256$09.00/0

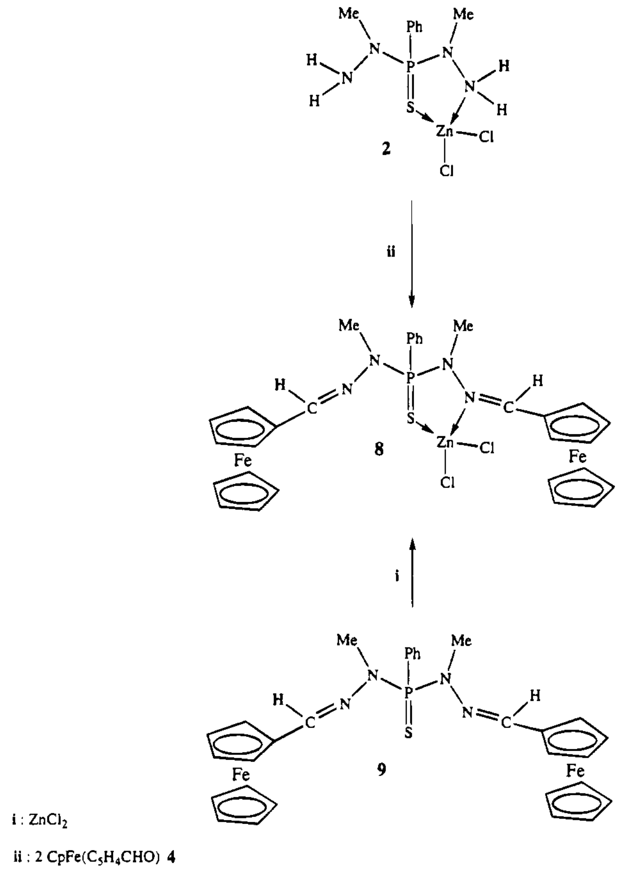
**Scheme 1**



and presenting an exchange phenomenon between free and complexed hydrazide arms. Unfortunately the low solubility of this compound prevents any further low-temperature NMR characterization, but as compound **2** reacts at 60 °C with ferrocene carbaldehyde to afford **8**, which has been fully characterized (vide infra), we propose for **2** the same coordination mode in which the ligand is bound to zinc through its sulfur atom and one of its two NH$_2$ groups (Scheme 1).

**Reactivity of 2 toward Terephthalaldehyde (3).** The presence of free and coordinated NH$_2$ functions in the molecule prompted us to check if it was possible to achieve selective condensation reactions with aldehydes, and in a first approach, we have chosen terephthalaldehyde (**3**). Reaction of **2** with **3** in a 2/1 stoichiometry at 55 °C in THF produces as a major product [C$_6$H$_4$-1,4-(CH=NNMePhP(S)NMeNH$_2$)$_2$][ZnCl$_2$]$_2$ (**6**) (Scheme 1). This can be isolated as a white powder whose microanalyses are in agreement with its proposed formula. IR stretching frequencies were observed at 3200 and 3110 cm$^{-1}$, indicating the presence of coordinated NH$_2$ groups. Characterization of compound **6** was achieved by NMR in THF-$d_8$ and of note is the CH=N signal at $\delta = 137.9$ in the $^{13}$C NMR spectra. In the $^1$H NMR spectra, two doublets show that two types of NMe groups are present at $\delta = 3.07$ ($^3J_{PH} = 11.6$ Hz), which can be attributed to methyl groups belonging to the complexed hydrazido arm NMeNH$_2$, and a doublet centered at 3.49 ppm ($^3J_{PH} = 9.0$ Hz), which belongs to the methyl groups of the NMeN=CH fragments.[3a,b,5] In the $^{31}$P{$^1$H} NMR spectrum, two singlets of equal intensity at $\delta = 87.06$ and 87.01 are detected. This observation is in agreement with the existence of two different asymmetric phosphorus centers involved in the Zn complexation leading to the existence of diastereoisomers. When dissolved in DMSO, compound **6** presents a unique singlet at $\delta = 79.7$, which is consistent with a decomplexation process induced by the solvent. Indeed, when the phosphohydrazide **1** and the dialdehyde **3** react under the same conditions as for the synthesis of **6**, a major compound possessing identical $^1$H and $^{31}$P NMR spectra is observed in DMSO-$d_6$. The transient formation of the free ligand has already been detected by low-temperature NMR experiments,[1b,c,5] but attempts to isolate it have failed. Thus, complexation with ZnCl$_2$ is an indirect way to stabilize such a type of ligand and to complete its characterization.

**Scheme 2**

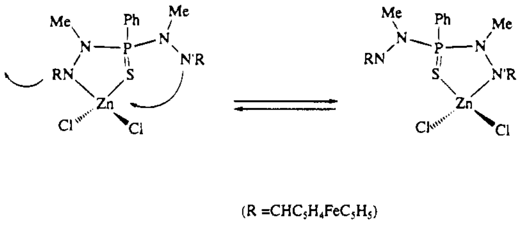


Reaction of **3** with 1 equiv of **2** leads to the product [PhP(S)C$_6$H$_4$-1,4-(CH=NNMe)$_2$]$_2$[ZnCl$_2$]$_2$ (**7**) (90%, NMR), which was isolated as an orange powder in 12% yield (first recrystallization in CH$_2$Cl$_2$). Its spectral data and microanalyses are in agreement with a product resulting from a [2 + 2] cyclocondensation and containing two ZnCl$_2$ units. In the solid state, the IR spectra show the absence of the NH$_2$ vibration and the appearance of a new band at 1586 cm$^{-1}$ which is attributed to the $\nu$(C=N) vibration. Unlike the corresponding free zinc macrocycle,[1a] complex **7** is not soluble in CHCl$_3$. Spectral NMR data in DMSO are the same as the free macrocycle, suggesting again a decomplexation process in this solvent. The complex **7** is also a minor product in the synthesis of **6**.

**Reactivity of 2 toward 4 and 5.** In order to explore the electroactive properties of derivatives of compound **2**, its reactivity toward organometallic aldehydes Fc(CHO) (**4**) and Fc(CHO)$_2$ (**5**) was investigated.

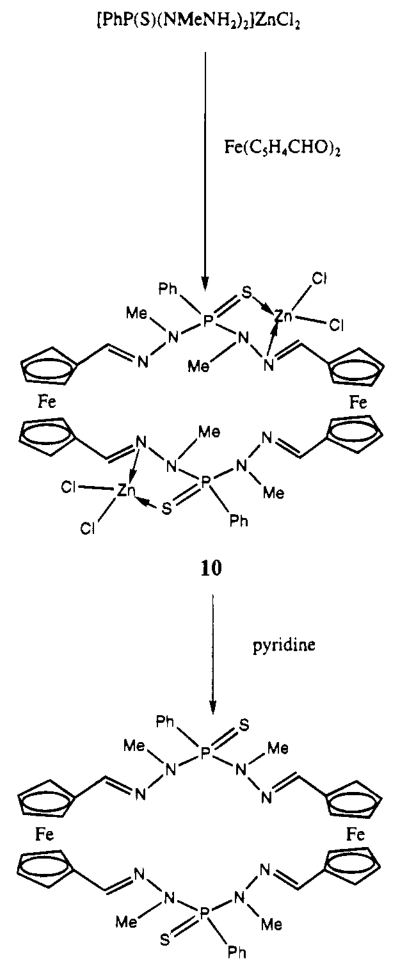
Compound **2** reacts with 2 equiv of **4** (Scheme 2) in THF at 60 °C to give [PhP(S)(NMeN=CHC$_5$H$_4$FeCp)$_2$]ZnCl$_2$ (**8**) as a microanalytically pure solid in 85–90% yield. This compound is also obtained from the reaction of PhP(S)(NMeN=CHC$_5$H$_4$FeCp)$_2$ (**9**)[3a] with 1 equiv of ZnCl$_2$. The IR spectrum of **8** reveals stretches due to the coordinated C=N groups at 1587 cm$^{-1}$. In the $^1$H NMR spectrum, the unique doublet observed for the methyl of the NMe groups is found at $\delta = 3.22$ ($^3J_{PH} = 10.9$ Hz) and suggests a symmetrical involvement of both of the C=N functional groups. $^{13}$C{$^1$H} NMR (297 K) spectra show a very broad signal centered at $\delta = 150$ due to the C=N groups and a broad signal centered at 35.6 ppm for the NMe groups. At 193 K, in the $^{13}$C{$^1$H}{$^{31}$P} NMR spectra, these resonances split into two sets of two signals at $\delta = 140.9$, 154.7 and 32.5, 37.1, respectively. These observations prove that there is an exchange process between a bound and a free imino group at room temperature (Scheme 3) involving alternative SN and

**Scheme 3**



(R =CHC$_5$H$_4$FeC$_5$H$_5$)

**Scheme 4**



**10**

**11**

SN′ coordination modes to the Zn center. Similar exchanges have already been detected in solution in the case of iron–copper compounds [Cu(**9**)$_2$]$^+$, but no X-ray structural characterization establishing the existence of a P=S—M bond was obtained.[3c]

The easy synthesis of the zinc macrocycle **7** and the selectivity of the last reaction suggested to us to check the reactivity of **2** toward **5**. This could lead to the macrocycle [Fe(C$_5$H$_4$-CH=NNMePhP(S)NMeN=CHC$_5$H$_4$)$_2$Fe][ZnCl$_2$]$_2$ (**10**) (Scheme 4). When **2** is added to **5** at 60 °C in THF in a 1/1 stoichiometric ratio, a red product is obtained in 44% yield. Microanalyses are in agreement with the proposed formula for **10**. Addition of pyridine to **10** induces a zinc decomplexation process: when a sample of **10** is dissolved in pyridine, after evaporation, the residue becomes soluble in CHCl$_3$ and spectral characteristics of the zinc-free corresponding macrocycle Fe(C$_5$H$_4$CH=NNMe-PhP(S)NMeN=CHC$_5$H$_4$)$_2$Fe (**11**) are obtained. This macrocycle can also be synthesized by direct reaction between the phosphodihydrazide and **5** and, unlike **10**, is soluble in CHCl$_3$.[6]

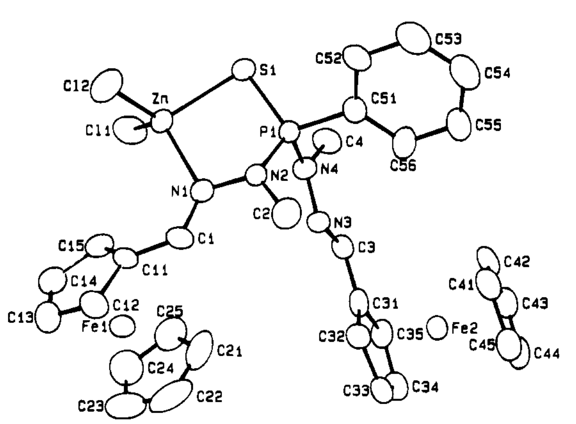


**Figure 1.** ORTEP drawing of the molecular structure of compound **8** with 50% thermal ellipsoids.

**Table 1.** Crystal and Intensity Data for the Complex (C$_6$H$_5$)P(S){(NCH$_3$N=CH(C$_5$H$_4$)Fe(C$_5$H$_5$)}$_2$·CHCl$_3$ (**8**·CHCl$_3$)

| | |
|---|---|
| chem form, C$_{31}$H$_{32}$N$_4$S$_1$P$_1$Cl$_5$Fe$_2$Zn | form wt, 877.99 amu |
| $a = 12.798(1)$ Å | space group, *triclinic* $P\bar{1}$ |
| $b = 14.639(2)$ Å | $T = 23$ °C |
| $c = 11.744(2)$ Å | $\lambda$(Mo K$\alpha$) = 0.710 73 Å |
| $\alpha = 111.74(1)°$ | $\varrho_{calcd} = 1.637$ g·cm$^{-3}$ |
| $\beta = 115.92(1)°$ | $\mu = 19.98$ cm$^{-1}$ |
| $\gamma = 68.36(1)°$ | transmission coeffs, |
| $V = 1780.9(7)$ Å$^3$ | 0.631–0.832 |
| $Z = 2$ | $R(F_o)^a = 0.038$ |
| | $R_w(F_o)^b = 0.043$ |

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/(\Sigma w|F_o|^2)]^{1/2}$. Weighting scheme: $w = 1/(\sigma_{(F_o)}^2 + p^2F_o^2)$; $p = 0.019$ (refined value).

**Molecular Structure of [PhPS(NMeN=CHC$_5$H$_4$FeCp)$_2$]-ZnCl$_2$ (8).** Crystals suitable for an X-ray structure determination of **8** were obtained by slow crystallization in CHCl$_3$. A perspective view of the molecule is shown in Figure 1. Crystallographic data are listed in Table 1, and selected bond lengths and angles are listed in Table 2. The ligand **9** is coordinated to the ZnCl$_2$ unit via a nitrogen atom of one of its imino groups (N(1)–Zn = 2.144(6) Å) and via the sulfur atom (S(1)–Zn = 2.402(2) Å) as suggested by low-temperature NMR data. The zinc atom displays a pseudotetrahedral environment. Complexation of the nitrogen of the imino group does not induce significant changes in the C=N bond lengths C(1)–N(1) = 1.286(8) Å, compared to 1.28(1) Å for either PhP(S)(NMeN=CH-(C$_6$H$_4$-2-OH))$_3$ (**12**)[7] or [PhP(S)(NMeN=CHC$_5$H$_4$FeCp)$_2$Cu]$_2$-[CF$_3$SO$_3$]$_2$ (**13**),[3a] and 1.27(1) Å for PhP(O)(NMeNCH=C$_5$H$_4$-FeCp)$_2$ (**14**).[3c] The most important change concerns bond length of the PS group: a lengthening from 1.921(1) Å in **12** to 1.964(3) Å in **8** is observed. This is comparable to the lengthening observed for the copper compound **13** (1.979(4) Å) even though the sulfur atom is involved in a bridging mode. This value is also close to that found in the [(C$_6$H$_5$O)P(S)(NMeNMeH)$_2$-CdCl$_2$]$_2$[2f] complex (1.957(2) Å), in which the sulfur atom is terminally bound to the metal. Nevertheless this lengthening is less important than for the two Pd structurally characterized complexes with an N, S bond linking: PhP(S)(NMeN=CHC$_6$H$_4$O)(NMeN=CHN=CHC$_6$H$_4$OH)PdCl[4a] (1.982(2)Å) and PhP(S)(NMeNH$_2$)(NMeC$_6$H$_4$CH=CHCOOH)PdCl$_2$[4b] (1.993(3) Å). This greater lengthening could be attributed to the fact that in these two complexes the palladium center is bound to more basic ligands like a phenoxy or a hydrazine group. The N–N

---

(6) Delavaux-Nicot, B.; Guari, Y; Douziech, B.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 585.

(7) Colombo-Khater, D.; He, Z.; Caminade, A.-M.; Dahan, F.; Kramer, R.; Majoral, J.-P. *Synthesis* **1993**, *11*, 1147.

**Table 2.** Selected Bond Lengths (Å) and Selected Bond Angles (deg) for **8**·CHCl$_3$ with Esd's in Parentheses

| | | | |
|---|---|---|---|
| | Bond Lengths (Å) | | |
| Zn−N(1) | 2.144(6) | P(1)−C(51) | 1.782(5) |
| Zn−Cl(1) | 2.192(2) | N(1)−N(2) | 1.409(6) |
| Zn−Cl(2) | 2.215(3) | N(3)−N(4) | 1.398(9) |
| Zn−S(1) | 2.402(2) | N(1)−C(1) | 1.286(8) |
| P(1)−S(1) | 1.964(3) | N(3)−C(3) | 1.28(1) |
| P(1)−N(2) | 1.667(4) | C(1)−C(11) | 1.449(8) |
| P(1)−N(4) | 1.672(7) | C(3)−C(31) | 1.45(1) |
| | Fe−Cp Linkage | | |
| Fe(1)−C(11) | 2.035(9) | Fe(2)−C(31) | 2.041(6) |
| Fe(1)−C(12) | 2.017(9) | Fe(2)−C(32) | 2.043(6) |
| Fe(1)−C(13) | 2.04(1) | Fe(2)−C(33) | 2.050(6) |
| Fe(1)−C(14) | 2.05(1) | Fe(2)−C(34) | 2.022(8) |
| Fe(1)−C(15) | 2.04(1) | Fe(2)−C(35) | 2.036(6) |
| Fe(1)−C(21) | 2.02(1) | Fe(2)−C(41) | 2.048(7) |
| Fe(1)−C(22) | 2.03(1) | Fe(2)−C(42) | 2.035(6) |
| Fe(1)−C(23) | 2.03(2) | Fe(2)−C(43) | 2.038(7) |
| Fe(1)−C(24) | 2.04(1) | Fe(2)−C(44) | 2.029(8) |
| Fe(1)−C(25) | 2.031(9) | Fe(2)−C(45) | 2.040(6) |
| | Cyclopentadienyl Rings | | |
| C(11)−C(12) | 1.428(9) | C(31)−C(32) | 1.426(8) |
| C(12)−C(13) | 1.402(9) | C(32)−C(33) | 1.41(1) |
| C(13)−C(14) | 1.41(1) | C(33)−C(34) | 1.41(1) |
| C(14)−C(15) | 1.408(1) | C(34)−C(35) | 1.42(1) |
| C(15)−C(11) | 1.413(8) | C(35)−C(31) | 1.44(1) |
| C(21)−C(22) | 1.38(1) | C(41)−C(42) | 1.40(1) |
| C(22)−C(23) | 1.37(1) | C(42)−C(43) | 1.40(2) |
| C(23)−C(24) | 1.39(1) | C(43)−C(44) | 1.41(1) |
| C(24)−C(25) | 1.38(1) | C(44)−C(45) | 1.40(1) |
| C(25)−C(21) | 1.39(1) | C(44)−C(41) | 1.42(1) |
| | Bond Angles (deg) | | |
| Cl(1)−Zn−Cl(2) | 119.53(9) | S(1)−P(1)−N(4) | 110.6(2) |
| Cl(1)−Zn−N(1) | 120.3(2) | S(1)−P(1)−N(2) | 112.0(2) |
| Cl(1)−Zn−S(1) | 108.81(7) | S(1)−P(1)−C(51) | 112.0(3) |
| Cl(2)−Zn−N(1) | 102.6(2) | N(2)−P(1)−N(4) | 107.4(3) |
| Cl(2)−Zn−S(1) | 109.27(9) | N(2)−P(1)−C(51) | 106.1(2) |
| Zn−S(1)−P(1) | 91.38(8) | N(4)−P(1)−C(51) | 108.6(3) |
| Zn−N(1)−N(2) | 110.6(4) | N(2)−N(1)−C(1) | 117.9(5) |
| P(1)−N(4)−N(3) | 112.6(3) | N(4)−N(3)−C(3) | 118.7(5) |
| P(1)−N(2)−N(1) | 113.9(3) | N(1)−N(2)−C(2) | 119.0(5) |
| P(1)−N(2)−C(2) | 123.1(4) | N(1)−C(1)−C(11) | 123.9(6) |
| P(1)−N(4)−C(4) | 118.8(6) | N(3)−N(4)−C(4) | 121.1(7) |
| C(1)−C(11)−C(12) | 121.7(6) | N(3)−C(3)−C(31) | 119.8(6) |
| C(1)−C(11)−C(15) | 130.6(5) | C(14)−C(15)−C(11) | 108.1(6) |
| C(3)−C(31)−C(32) | 127.5(8) | C(31)−C(32)−C(33) | 108.6(7) |
| C(3)−C(31)−C(35) | 124.9(6) | C(32)−C(31)−C(35) | 107.5(7) |
| C(11)−C(12)−C(13) | 108.4(6) | C(32)−C(33)−C(34) | 129.7(5) |
| C(12)−C(11)−C(15) | 107.2(5) | C(33)−C(34)−C(35) | 109.3(8) |
| C(12)−C(13)−C(14) | 107.8(6) | C(34)−C(35)−C(31) | 106.7(6) |
| C(13)−C(14)−C(15) | 108.4(6) | | |

and P−C distances are within the normal range,[1a,e,3,4a] as are the Zn−Cl[8] and Zn−S distances.[9] Considering the ligand modifications induced by complexation, comparison with **12** and **13** shows that the geometry around the phosphorus is not significantly modified (internal angle N(2)−P(1)−N(4) = 107.7° compared to 105.4° for **12** and 106.9° for **13**).

**Electrochemical Study of Compound 8.** Preceding electrochemical studies on [Fe−Cu] complexes have shown that the variation of the electrochemical properties of the ferrocene centers is a sensitive probe for evaluating the complexation of the ligand **9**.[3c] Furthermore, the electrochemical oxidation of the iron centers can lead to elimination of the complexed copper, and this should be of interest for cation recovery. For solubility reasons, we focused our attention on the structurally characterized compound **8**, and for comparison to our previous studies, the experiments were performed in 0.1 M CH$_2$Cl$_2$ solutions of NBu$_4$PF$_6$.

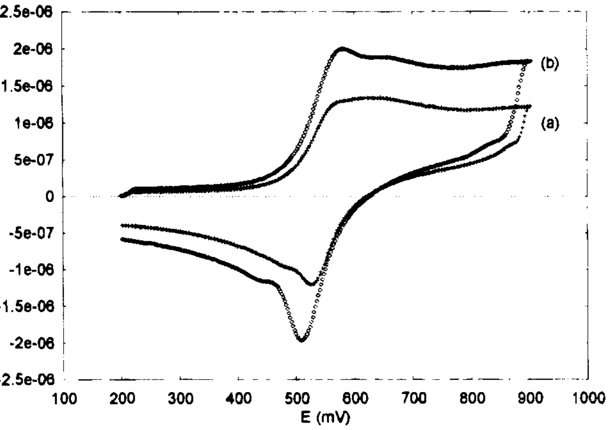


**Figure 2.** Cyclic voltammograms of compound **8** at (a) 100 V s$^{-1}$ and (b) 200 V s$^{-1}$. Experimental conditions: Pt electrode in 0.1 mol L$^{-1}$ solution of NBu$^n{}_4$PF$_6$ in CH$_2$Cl$_2$, complex concentration 10$^{-3}$ M.

In cyclic voltammetry, moving first to anodic potential and then to cathodic potential, two waves are observed, one at 0.5 V and a more discrete one at −1 V vs SCE. The wave at 0.5 V, due to the oxidation of the ferrocene part of the molecule, corresponds to a quasi-reversible oxidation process ($\Delta E_p = E_{pa} - E_{pc}$ = 80 mV, $R_{ip}$ = 1 at 0.1 V s$^{-1}$). Under the same conditions, ferrocene has a reversible oxidation peak at 0.42 V vs SCE ($\Delta E_p$ = 58 mV, $R_{ip}$ = 1), and for the free ligand **9**, this wave is observed at 0.42 ($\Delta E_p$ = 87mV, $R_{ip}$ = 1 at 0.1 V s$^{-1}$). These results are in contrast with those obtained for the iron−copper complex [(PhP(S)(NMeN=CHC$_5$H$_4$FeCp)$_2$)$_2$Cu][CF$_3$SO$_3$],[3c] which has two well-defined oxidation waves at 0.50 and 0.61 V vs SCE. In this complex the two ligands **9** are chelating through the S atoms and one of the two hydrazone arms and there is an exchange as for **8** between the coordinated and the free hydrazone arms. The first oxidation wave at 0.5 V was attributed to the free ferrocenyl hydrazone arm and the second at 0.61 V to the complexed one. So the different behavior of **8** could be attributed to a higher frequency for the exchange phenomenon, and for this reason cyclic voltammetry was performed at higher speeds until 300 V s$^{-1}$. At 100 V s$^{-1}$, the shape of the anodic wave appears broader ($E_{pa} - E_{p1/2}$ = 157 mV) than that at 0.1 V s$^{-1}$ (77 mV). This suggests that there are two Fe(II)/Fe(III) systems with two close $E_{pa}$ values and approximatively the same $E_{pr}$ value. At 200 V s$^{-1}$ and 30 °C, the two redox systems appear (see Figure 2), and this is reminiscent of the results observed for the copper compound. This difference of behavior can be rationalized if we recall that during the electrochemical oxidation the first ferrocenyl molecule oxidized is that associated with the free hydrazone arm. Moreover, the cationic nature of the copper center prevents, through electrostatic repulsion, the coordination of the free oxidized hydrazone arm and suppresses the exchange phenomenon. This explains the observation of two well-defined oxidation waves. In the case of the neutral Zn(II) complex, this affinity for binding the oxidized hydrazone arm still remains and the exchange phenomenon persists: a minimum speed of 200 V s$^{-1}$ is necessary to observed two ill-defined oxidation waves.

Coming back to the electrochemical study of compound **8**, in the oxidation zone (0−1500 mV), limiting currents obey the

---

(8) Tokar, J. C.; Kettler, P. B.; Tolman, W. B. *Organometallics* **1992**, *11*, 2737.

(9) (a) Mathew, M.; Palenik, G. J. *Inorg. Chim. Acta* **1971**, *5*, 349. (b) Antolini, L.; Fabretti, A. C.; Franchini, G.; Menabre, L.; Pellacani, G. C.; Desseyn, H. O.; Dommisse, R.; Hofmans, H. C. *J. Chem. Soc. Dalton Trans.* **1987**, 1921.

(10) Levich,V. G. In *Physico Chemical Hydrodynamics*; Prentice Hall: Englewood Cliffs, NJ, 1962.

Levich law.[10] They are proportionnal to the square root of the electrode rotation speed (from 1000 to 3000 rpm) and to the concentration (from $2.4 \times 10^{-1}$ to 1.1 mmol $L^{-1}$). The thorough electrochemical study is consistent with a diffusion-controlled process with $D = 3.0 \times 10^{6}$ $cm^2$ $s^{-1}$. Exhaustive electrolysis of solutions of compound **8** on a platinum gauze as electrode confirms that two electrons are involved in the electrochemical oxidation process. When this oxidation is followed by an electrochemical reduction at 0.3 V vs SCE, the $E_{1/2}$ value moves to that of the free ligand **9**. Moreover, NMR data of the electrochemical solution after extraction with toluene are those of **9**.

The ill-defined wave at −1 V vs SCE could be consistent with zinc reduction.[11] Electrolysis at −1.5 V confirms a two-electron exchange, with the solution turning clear. Simultaneously on the cathode, a dark deposit is observed. After electrode cleaning, cyclic voltammograms are those of **9**, and the zinc wave has disappeared. After toluene extraction, compound **9** is identified by NMR. Moreover, voltammograms of compounds **2** and **7** present a similar discreet and ill-defined reduction wave at −1.3 V vs SCE, and the same phenomenon has been detected during their electrolysis. The free corresponding ligands have also been characterized by NMR in $CDCl_3$ according to an identical procedure.

To summarize, as in the case of copper complexes, the oxidation potential of the ferrocenyl moieties moves to a higher anodic potential (+80 mV), reflecting the electron-withdrawing effect of the $ZnCl_2$ complexation. A similar anodic shift of +110 mV in acetonitrile has been reported for $Fe(C_5H_4CH_2NH(CH_2)_2)_2NH$ in the presence of $Zn(ClO_4)_2$.[12]

## Conclusion

As earlier demonstrated for iron−copper chemistry,[3] the phosphohydrazide $PhP(S)(NMeNH_2)_2$ appears to be a very versatile building block for the synthesis of polymetallic complexes due to the presence of complexation sites with different bonding abilities (P(X), NMe, and $NH_2$ groups) which can be stimulated differently depending on the metal. We have exploited this versatility to build in an easy, selective, one-step procedure acyclic and macrocyclic polymetallic compounds by the condensation reaction between **2** and organic or organometallic aldehydes. Variations of stoichiometric conditions appear to be an easy way to control the number and the nature of the metallic centers in the new molecules. Moreover, full characterization of compound **8** clearly establishes that the ferrocenyl phosphohydrazone **9** can act as a hemilabile ligand. The electrochemical properties of the complex **8** confirm that the ligand **9** is a good sensor for electrochemical recognition. Moreover, the free ligand can be recovered from the complex by successive controlled electrochemical oxidation/reduction processes.

## Experimental Section

All the syntheses have been performed under a nitrogen or argon atmosphere using standard Schlenk tube techniques. 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. $^{1}H$, $^{13}C$, and $^{31}P$ NMR spectra have been performed on Bruker AC 80, AC 200, and AM 250 spectrometers. $^{31}P$ are referenced to external 85% $H_3PO_4$ in $D_2O$, and other spectra are referenced to external tetramethylsilane. Variable-temperature and selective-decoupling experiments were carried out on an AM 250 machine equipped with multinuclear attachment. The observation and decoupling frequencies were in the ranges of 250.13 MHz for $^{1}H$, 101.27 MHz for $^{31}P$, and 62.89 MHz for $^{13}C$. All these spectrometers operate in the Fourier transform mode. Tetrahydrofuran and diethyl ether were distilled over sodium/benzophenone, dichloromethane over $P_2O_5$, and pentane over $CaH_2$ and stored under argon. $MeNHNH_2$, $C_6H_4$-1,4-$(CHO)_2$, Fc(CHO) (Aldrich), $PhP(S)Cl_2$, and anhydrous $ZnCl_2$ 98% (Prolabo) were used without further purification. $PhP(S)(NMeNH_2)_2$ (**1**),[13] $PhP(S)(NMeN{=}CHC_5H_4FeCp)_2$ (**9**),[3a] and $Fc(CHO)_2$ (**5**)[14] were prepared by published procedures.

**Electrochemical Studies.** Electrochemical measurements were carried out with a homemade potentiostat using interfacing hardware with a PC-compatible microcomputer. The positive feedback or interrupt method was 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 was used in the cell. The supporting electrolyte $Bu_4NPF_6$ (Aldrich analytical grade) was used as received. Dichloromethane (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 V was obtained for 1 mM ferrocene. Electrochemical studies have been done in 0.1 M dichloromethane solutions of $Bu_4NPF_6$ containing the sample to be used at $\sim 10^{-3}$ M concentration, and electrolysis was performed at a constant potential.

**$[PhP(S)(NMeNH_2)_2]ZnCl_2$ (2).** A 0.72 g (5.3 mmol) sample of $ZnCl_2$ was added to a solution of 1.22 g (5.3 mmol) of **1** in 60 mL of THF. After the solution was stirred for 12 h, the white precipitate formed was filtered, washed with THF and $Et_2O$, and dried in vacuum to obtain the title compound in 85% yield. $^{1}H$ NMR (200 MHz, DMSO-$d_6$): $\delta$ 2.86 (d, $^{3}J_{HP}$ = 11.4 Hz, 6H, $CH_3$), 4.02 (d, $^{3}J_{HP}$ = 8.8 Hz, 4H, $NH_2$), 7.59, 8.12 (each m, 5H, $C_6H_5$). $^{31}P\{^{1}H\}$ NMR (32.4 MHz, DMSO-$d_6$): $\delta$ 81.7 (s). Anal. Calcd for $C_8H_{15}N_4PSCl_2Zn$: C, 26.21; H, 4.10; N, 15.29; P, 8.46; Cl, 19.36; Zn, 17.85. Found: C, 26.38; H, 4.43; N, 15.13; P, 8.45; Cl, 20.01; Zn, 18.09. IR (KBr, $\nu$, $cm^{-1}$): 3310, 3200 (br), 3120 (s, $\nu(NH_2)$).

**$[C_6H_4\text{-}1,4\text{-}(CH{=}NNMePhP(S)NMeNH_2)_2][ZnCl_2]_2$ (6).** A mixture of 0.60 g (1.6 mmol) of **2** in 45 mL of THF and of 0.11 g (0.8 mmol) of **3** was stirred at 55 °C for 24 h, giving a colorless solution. After 4 days, a white powder was obtained and washed with THF (3 mL) and two 10 mL portions of ether and dried in vacuum: 30% yield. $^{1}H$ NMR (250 MHz, THF-$d_8$): $\delta$ 3.07 (d, $^{3}J_{HP}$ = 11.6 Hz, 6H, $CH_3NNH_2$), 3.49 (d, $^{3}J_{HP}$ = 9.0 Hz, 6H, $CH_3NN{=}C$), 4.58 (br s, 4H, $NH_2$), 7.62 (m), 7.66 (br s)), 7.78 (br s), 8.20 (m) (16H, $C_5H_5$, $C_6H_4$, CH=N). $^{1}H$ NMR (90 MHz, DMSO-$d_6$): $\delta$ 2.96 (d, $^{3}J_{HP}$ = 12 Hz, 6H, $CH_3NNH_2$), 3.27 (d, $^{3}J_{HP}$ = 8.8 Hz, 6H, $CH_3NN{=}C$), 4.11 (d, $^{3}J_{HP}$ = 10.6 Hz, 4H, $NH_2$), 7.62 (m), 7.69 (br s), 7.83 (s), 8.13 (m) (16H, $C_5H_5$, $C_6H_4$, CH=N). $^{31}P\{^{1}H\}$ NMR (101.3 MHz, THF-$d_8$): $\delta$ 87.06 (s), 87.01 (s). $^{13}C\{^{1}H\}$ NMR (62.9 MHz, THF-$d_8$): $\delta$ 32.8 (d, $J_{CP}$ = 10 Hz, $CH_3$-$NCH{=}NC_6H_4$), 41.10 (d, $J_{CP}$ = 8 Hz, $CH_3NNH_2$) 127.9 (s), 128.0 (s), 129.3 d, $J_{CP}$ = 14 Hz), 133.17 (d, $J_{CP}$ = 2 Hz), 134.3 (d, $J_{CP}$ = 10 Hz), ($C_6H_5$, $C_6H_4$), 139.3 (d, $J_{CP}$ = 12 Hz, CH=N). Anal. Calcd for **5**·1 THF, $C_{28}H_{40}N_8OP_2S_2Cl_4Zn_2$: C, 37.23; H, 4.43; N, 12.40; P, 6.47; Cl, 15.70; Zn, 14.49. Found: C, 36.90; H, 4.40; N, 12.30; P, 6.70; Cl, 16.08; Zn, 14.70. IR (KBr, $\nu$, $cm^{-1}$): 3200, 3110 (m, $\nu(NH_2)$); 1585 ($\nu$ (C=N)).

**$[PhP(S)C_6H_4\text{-}1,4\text{-}(CH{=}NNMe)_2]_2[ZnCl_2]_2$ (7).** To a suspension of 0.50 g (1.3 mmol) of **2** was added 0.18 g (1.3 mmol) of **3** and stirred at 55 °C for 4 days. The solvent was evaporated under vacuum, and the product was recrystallized as an orange powder from a 1/1 mixture of $CH_2Cl_2/Et_2O$: 12% yield (first recrystallization). $^{1}H$ NMR (200 MHz, DMSO-$d_6$): $\delta$ 3.23 (d, $^{3}J_{HP}$ = 8.4 Hz, 12H, $CH_3$), 7.45 (s), 7.59 (s), 7.78 (s), 8.06 (m) (22H, $C_6H_5$, $C_6H_4$, and CH=N). $^{31}P\{^{1}H\}$ NMR (32.4 MHz, DMSO-$d_6$): $\delta$ 77.4. $^{13}C\{^{1}H\}$ NMR (50.3 MHz, DMSO-

---

(11) Paratian, J. M.; Labbé, E.; Sibille, S.; Nédélec, J. Y.; Périchon, J. *J. Organomet. Chem.* **1995**, *487*, 61.

(12) Beer, P. D.; Kocian, O.; Mortimer, J. P.; Spencer, P. *J. Chem. Soc., Chem. Commun.* **1992**, 602.

(13) Majoral, J.-P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633.

(14) Balavoine, G. G. A.; Doisneau, G.; Fillebeen-Khan, T. *J. Organomet. Chem.* **1991**, *412*, 381.

$d_6$): $\delta$ 31.3 (d, $J_{CP}$ = 9 Hz, $CH_3$), 127.8 (d, $J_{CP}$ = 14 Hz), 130.3 (s), 133.1 (d, $J_{CP}$ = 10 Hz), 132.0 (br s) ($C_6H_5$), 126.5, 135.7 (each br s, $C_6H_4$), 137.9 (d, $J_{CP}$ = 12 Hz, CH=N). Anal. Calcd for **6**·THF·1.5$CH_2Cl_2$, $C_{37.5}H_{45}N_8OP_2Cl_7S_2Zn_2$: C, 39.39; H, 3.99; N, 9.93; P, 5.49. Found: C, 39.85; H, 4.23; N, 10.37; P, 5.82.

**$PhP(S)(NMeN{=}CHC_5H_4FeCp)_2ZnCl_2$ (8). Method A.** A sample of 0.41 g (1.8 mmol) of **4** was added to a 0.33 g (0.9 mmol) solution of **2** at 60 °C in 30 mL of THF and was stirred for 15 h. The solvent was evaporated to dryness, and the product was recrystallized as a red powder in a 1/1 mixture of $CH_2Cl_2/Et_2O$ (85% yield). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ 3.22 (d, $^3J_{HP}$ = 10.9 Hz, 6H, $CH_3$), 4.18 (s, 10H, $C_5H_5$), 4.52 (m), 4.78 (s), 4.93 (s) (8H, $C_5H_4$), 7.62 (m), 7.88 (s) 8.02 (m) (7H, $C_6H_5$, CH=N). $^{31}P\{^1H\}$ NMR (32.4 MHz, $CDCl_3$): $\delta$ 77.9. $^{13}C\{^1H\}$ NMR (62.9 MHz, $CD_2Cl_2$, 302 K): $\delta$ 35.6 (br s, $CH_3$), 69.6, 70.0, 70.7, 70.9, 72.2, 75.8 (each br s, $C_5H_5$, $C_5H_4$), 129.3 (d, $J_{CP}$ = 15 Hz), 132.9 (d, $J_{CP}$ = 12 Hz), 134.3 (d, $J_{CP}$ = 3 Hz) ($C_6H_5$), 150.0 (very broad, CH=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.0 MHz): $\delta$ 77.8 (s). $^{13}C\{^1H\}\{^{31}P\}$ NMR (62.9 MHz, $CD_2Cl_2$, 194 K): $\delta$ 32.5, 37.1 (s, $CH_3$), 68.6, 69.6, 72.6, 77.3, 78.4 (each br s, $C_5H_5$, $C_5H_4$), 126.7, 128.2, 131.7, 133.8 ($C_6H_5$), 140.9, 154.7 (CH=N). Anal. Calcd for $C_{30}H_{31}N_4PSCl_2Fe_2Zn$: C, 47.49; H, 4.09; N, 7.39. Found: C, 47.15; H, 4.15; N, 7.30. IR (KBr, $\nu$, $cm^{-1}$): 1587 (w, $\nu$(C=N)).

**Method B.** A 0.06 g (0.44 mmol) sample of anhydrous $ZnCl_2$ was added to a solution of 0.24 g (0.39 mmol) of **8** in 20 mL of THF. The mixture was stirred for 16 h at 60 °C in THF. An orange powder was isolated after pentane addition (15 mL). The powder was washed with $Et_2O$ and pentane and dried in vacuum (89%, yield).

**$[Fe(C_5H_4CH{=}NNMePhP(S)NMeN{=}CHC_5H_4)_2Fe][ZnCl_2]_2$ (10).** A sample of 0.2 g (0.82 mmol) of **9** was added to a stirred suspension of 0.3 g (0.82 mmol) of **2** in 30 mL of THF at 60 °C, giving a red solution which was stirred for 2 days. After addition of pentane (15 mL), a red powder was obtained. Recrystallization from a $CH_2Cl_2/Et_2O$ 1/1 solution yielded a red precipitate (44% yield). $^1H$ NMR (90 MHz, DMSO-$d_6$): $\delta$ 3.08 (br, $^3J_{HP}$ = 10.0 Hz, 12H, $CH_3$), 4.25 (s, 8H, $C_5H_4$), 4.44 (m, 8H, $C_5H_4$), 7.42, 7.69, 8.19 (each m, 14H, $C_6H_5$, CH=N). $^{31}P\{^1H\}$ NMR (32.4 MHz, DMSO-$d_6$): $\delta$ 76.0. $^{13}C\{^1H\}$ NMR (50.3 MHz, pyridine-$d_5$): $\delta$ 31.3 (br s, $CH_3$), 67.5, 67.1, 68.4, 68.8, 70.3, 70.6, 82.4 ($C_5H_4$), 127.6, 130.9, 133.8, 137.3 ($C_6H_5$) 131.9 (s, CH=N). Anal. Calcd for $C_{40}H_{42}N_8P_2S_2Cl_2Fe_2Zn_2$: C, 41.94; H, 3.67; N, 9.79; P, 5.42. Found, C, 41.67; H, 3.78; N, 9.62, P, 5.50. IR (KBr, $\nu$, $cm^{-1}$): 1584 (s, $\nu$(C=N)).

After zinc decomplexation: $[FeC_5H_4CH{=}NNMePhP(S)NMeN{=}CHC_5H_4Fe]_2$ (**11**). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 3.00 (m, 12H, $CH_3$), 4.06, 4.25, 4.32, 4.37 (each br s, 16 H, $C_5H_4$), 7.06 (br s), 7.17 (br s), 7.50 (br s), 8.16 (m) (14H, $C_6H_5$ and CH=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.0 MHz): $\delta$ 77.8 (s). $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$): $\delta$ 31.2 (d, $J_{CP}$ = 8.5 Hz, $CH_3$), 67.1, 67.6, 68.3, 68.6, 69.0, 69.8, 70.1, 82.1, 82.2 (each s, $C_5H_4$), 127.3 (d, $J_{CP}$ = 14 Hz), 131.8 ($^1J_{CP}$ = 136 Hz), 133.6 (d, $J_{CP}$ = 10 Hz), 137.1 (d, $J_{CP}$ = 14 Hz) ($C_6H_5$), 131.6 (br s, CH=N).

**Crystallogaphic Study of 8·$CHCl_3$.** Crystals of $PhP(S)(NMeN{=}CH(C_5H_4)FeCp)_2{\cdot}CHCl_3$ suitable for X-ray diffraction were obtained by slow crystallization in a $CHCl_3$ solution at 18 °C. Intensity data were recorded on an Enraf-Nonius CAD4 diffractometer at 23 °C. Cell constants were obtained from a least-squares fit to the setting angles of 25 randomly selected reflections in the range $12° < \theta(\mathrm{Mo}\ K\alpha_1) < 14°$. Data reduction was carried out using the MOLEN crystallographic computing package.[15] Intensities were corrected for absorption using a numerical method based on Gaussian integration. Table 1 summarizes crystal and intensity data.

The structure was solved by using the SHELXS package[16] and refined with the SHELX-76 package.[17] The positions of the Fe, Zn, and P atoms were determined by direct methods. All remaining nonhydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. A free molecule of chloroform solvent was located in the lattice and refined. All hydrogen atoms could be located in a final Fourier difference map. The atomic coordinates of those belonging to phenyl, methyl, and methine groups were refined independently. In order to reduce the number of variable parameters, the hydrogen atoms belonging to cyclopentadienyl rings were entered in idealized positions riding the carbon atoms.

Atomic scattering factors were taken from the usual tabulations.[18] All nonhydrogen atoms were allowed to vibrate anisotropically.

**Supporting Information Available:** Final anisotropic thermal parameters (Table S1), hydrogen positions (Table S2), fractional atomic coordinates and isotropic or equivalent temperature factors (Table S3), complete crystal and intensity data (Table S4) (4 pages). Ordering information is given on any current masthead page.

IC950446U

---

(15) *MOLEN. Package for Crystal Structure Analysis*; Enraf Nonius: Delft, The Netherlands, 1990.

(16) Sheldrick, G. M. *SHELXS-86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

(17) Sheldrick, G. M. *SHELX-76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

(18) (a) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4, Table 2.2B, pp 99–101. (b) See also: Cromer, D. T., ref 18a, Table 2.3.1, p 149.