properties of these complexes are in progress. In particular, the availability of Fe(III)Zn(II) and Ga(III)Fe(II) analogues of the Fe(III)Fe(II) complex will allow us to study in detail the electronic properties of the individual paramagnetic centers and then apply the information toward a better understanding of the spin-coupled mixed-valence Fe(III)Fe(II) complexes.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $[FeZnBPMP(OAc)_2](BPh_4)_2 \cdot CH_3CN$ (5 pages). Ordering information is given on any current masthead page.

Metazidohemerythrin Models Featuring a Bis-Benzimidazole Tripod Ligand. Structure and Spectroscopy of (μ-Oxo)bis(μ-benzoato)bis(bis(2-benzimidazolylmethyl)amine)diiron(III)†

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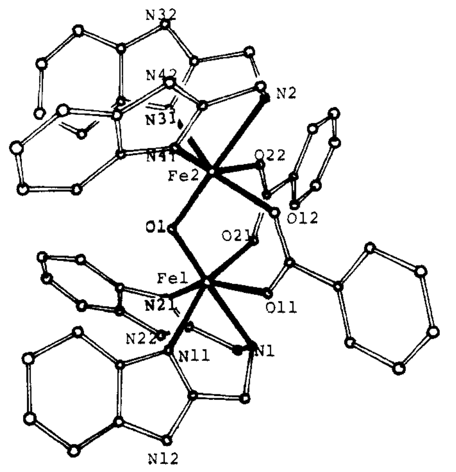
There is increasing interest in non-heme single iron and diiron proteins.[1-6] In this respect, the characterization of low molecular weight models has proved to be of crucial importance.[7-13]



$[\,N3\ Fe\ C_6H_5COO\,]_2O\ (ClO_4)_2 \cdot 2C_2H_5OH \cdot 0.5(Et_3NH\ ClO_4)$

Fe1-O1	1.777(5)	Fe2-O1	1.802(6)
Fe1-O11	2.047(5)	Fe2-O12	2.028(4)
Fe1-O21	2.035(5)	Fe2-O22	2.034(5)
Fe1-N1	2.284(6)	Fe2-N2	2.289(8)
Fe1-N11	2.108(7)	Fe2-N31	2.091(5)
Fe1-N21	2.131(7)	Fe2-N41	2.116(6)

Fe1..Fe2	3.079(2)
Fe1-O1-Fe2	118.7(3)

Figure 1. ORTEP diagram of **4** with selected bond distances in Å and angles in deg. Numbers in parentheses are estimated standard deviations.

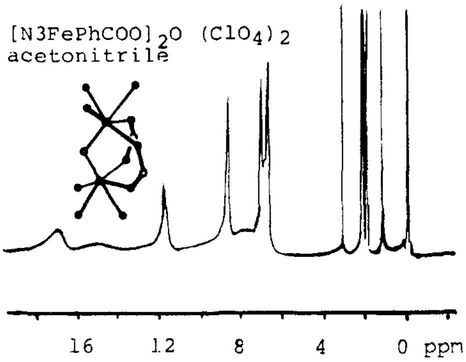


Figure 2. ^1H NMR (300 MHz) of **4** in CD_3CN. The peak at 17 ppm is the only one disappearing upon exchange with D_2O (imidazole N-H). No other peaks were observed from −20 to 100 ppm.

Hemerythrin,[1-3,4b-d] ribonucleotide reductase,[5] and several purple acid phosphatases[4a,6] are diiron proteins that in their fully oxidized forms contain the Fe(III)-O-Fe(III) motif. In hemerythrin the protein also provides μ-carboxylato bridges and imidazole ligands. Several synthetic models for metazidohemerythrin have been reported recently (**1**,[7a] **2**,[8a,b] **3**[9]). These models feature amine tripod ligands,[14] in addition to oxo and carboxylato bridges.

$[HBpz_3CH_3COOFe]_2O$ **1** $[tacnCH_3COOFe]_2O\ I_2$ **2**

$[tpbn(CH_3COO)_2Fe_2O]_2(NO_3)_4$ **3**

We sought to prepare models with imidazole-based tripod ligands that would allow us to examine the N-H resonance and

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(1) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; *J. Am. Chem. Soc.* **1984**, *106*, 618-22. (b) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; McCallum, J. D.; Sanders-Loehr, J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 713-6.

(2) (a) Richardson, D. E.; Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 7780-1. (b) Reem, R. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 8323-5.

(3) (a) Shienke, A. K.; Loehr, T. M.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1984**, *106*, 4951-6. (b) Shienke, A. K.;Loehr, T. M.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1986**, *108*, 2437-43.

(4) (a) Lauffer, R. B.; Antanaitis, B. C.; Aisen, P.; Que, L., Jr. *J. Biol. Chem.* **1983**, *258(23)*, 14212-8. (b) Maroney, M. J.; Lauffer, R. B.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6445-6. (c) Nocek, J. M.; Kurtz, D. M., Jr.; Sage, J. T.; Debrunner, P.; Maroney, M. J.; Que, L., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 3382-4. (d) Maroney, M. J.; Kurtz, D. M., Jr.; Nocek, J. M.; Pearce, L. L.; Que, L., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 6871-9.

(5) (a) Sjoberg, B.-M.; Graslund, A.; Sanders-Loehr, J.; Loehr, T. M. *Biochem. Biophys. Res. Commun.* **1980**, *94(3)*, 793-9. (b) Sahlin, M.; Ehrenberg, A.; Graslund, A.; Sjoberg, B.-M. *J. Biol. Chem.* **1986**, *261*, 2778-80. (c) Bunker, G.; Petersson, L.; Sjoberg, B.-M.; Sahlin, M.; Chance, M.; Ehrenberg, A. *Biochemistry* **1987**, *26*, 4708-16. (d) Sjoberg, B.-M.; Sanders-Loehr, J.; Loehr, T. M. *Biochemistry* **1987**, *26*, 4242-7.

(6) (a) Debrunner, P. G.; Hendrich, M. P.; De Jersey, J.; Keough, D. T.; Sage, J. T.; Zerner, B. *Biochim. Biophys. Acta* **1983**, *745*, 103-6. (b) Kauzlarich, S. M.; Teo, B. K.; Zirino, T.; Burman, S.; Davis, J. C.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 2781-5. (c) Averill, B. A.; Davis, J. C.; Burman, S.; Zirino, T.; Sanders-Loehr, J.; Loehr, T. M.; Sage, J. T.; Debrunner, P. G. *J. Am. Chem. Soc.* **1987**, *109*, 3760-7. (d) Antanaitis, B. C.; Aisen, P. *Adv. Inorg. Biochem.* **1983**, *5*, 111-36.

(7) (a) Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653-67. (b) Armstrong, W. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 4632-3. (c) Gorun, S. G.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337-48.

(8) (a) Wieghardt, K.; Pohl, K.; Gebert, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 727. (b) Wieghardt, K.; Pohl, K.; Ventur, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 392-3. (c) Chaudhuri, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, 778-9. (d) Wieghardt, K.; Tolksdorf, I.; Herrman, W. *Inorg. Chem.* **1985**, *24*, 1230-5.

(9) Toftlund, H.; Murray, K.; Zwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191-3.

(10) Mockler, G. M.; de Jersey, J.; Zerner, B.; O'Connor, C.; Sinn, E. **1983**, *105*, 1891-3.

(11) (a) Pyrz, J. W.; Roe, L.; Stern, L. J.; Que, L., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 614-20. (b) Murch, B. P.; Boyle, P. D.; Que, L., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6728-9.

(12) Davis, J. C.; Kung, W.-J.; Averill, B. A. *Inorg. Chem.* **1986**, *25*, 394-6.

(13) Czernuszewicz, R. S.; Sheats, J. E.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 2063-7.

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Table I. Summary of Structural and Spectroscopic Properties of Hr Models

complex	1	2	3	4	MetN$_3$Hr
Fe–O[a]	1.780 (2)	1.77 (2)	1.794 (3)	1.777 (5)	1.64 (1)[b]
	1.788 (2)	1.80 (2)		1.802 (6)	1.89 (3)
Fe–O–Fe, deg	123.6 (1)	118.3 (5)	121.3 (3)	118.7 (3)	135 (2)
Fe–Neq	2.153 (5)	2.17 (1)	2.136 (8)	2.112 (16)	2.22 (7)
Fe–Ntr	2.188 (17)	2.21 (1)	2.307 (5)	2.287 (4)	2.26 (5)
J, cm^{-1}	−121 (1)	−115[c]	−120[d]	−117 (1)	−134[e]
	995 (3.5)	1020 (3.2)			
λ_{max} (nm)	695 (70)	743 (33)	730 (78.5)	620 (50)[f]	680 (95)
(ext coeff	528 sh	543 sh		560 (50) sh	
cm^{-1} mol Fe^{-1} L)	492 (460)	506 (199)	505 (493)	525 (110)	446 (1850)
	457 (505)	464 (269)	470 (554)	485 (310) sh	
	339 (4635)	335 (1840)	348 (3678)	355 (4000)	326 (3375)
	262 (3375)				
ν_{as} (Fe–O–Fe) (cm^{-1})	751	730	725	745	770
ν_s (Fe–O–Fe) (cm^{-1})	528			545	507
^{1}H NMR δ (ppm) imidazole N–H				17	23, 19, 16, 13
ref	7a	8	9	this work	1a, 19, 7a, 4d

[a] Distances in Å. Standard deviations in parentheses are from least-squares refinements or from the scatter of values about their mean, as appropriate. [b] The big difference in Fe–O distances is probably a refinement artefact (see ref 17). [c] Reference 8c. A value of −84 cm^{-1} has also been reported (ref 8b). [d] Value corresponding to the 1,3-propanediamine analogue. [e] Value for MetHr (ref 19), having hexa- and pentacoordinated Fe atoms (ref 1a). That asymmetry may be responsible for the apparently significantly stronger coupling (see ref 17). [f] Acetonitrile solution, from 300 to 800 nm.

to establish correlations between NMR spectra and structure in both dimeric and monomeric species. We report here the facile synthesis, structure, and the spectroscopic and magnetic properties of triply bridged Fe(III) dimers **4** and **5** that feature a bis-benzimidazole tripod ligand (N3).[15a]

$$\underset{\mathbf{4}}{[N3C_6H_5COOFe]_2O(ClO_4)_2} \qquad \underset{\mathbf{5}}{[N3CH_3COOFe]_2O(ClO_4)_2}$$

Complex **4** was assembled by adding 1 equiv of Fe(ClO$_4$)$_3$ to a 1:1 solution of ligand N3 and benzoic acid in ethanol. The resulting dark red solution turned green as 2 equiv of base (Et$_3$N, 2,6-lutidine, or KOH in ethanol) were added. A green crystalline solid was obtained *in high yield* (ca. 70%).[15b] The solid can be recrystallized from ethanol. An analogous dimer containing acetate **5** was prepared in a similar way by using acetic acid instead of benzoic acid.

Table I summarizes the relevant structural and spectroscopic features of these models for hemerythrin. Magnetic susceptibility data in the range 40–300 K are well fit to an antiferromagnetically coupled Fe dimer model[16] assuming $g = 2$ and no TIP, yielding values for J ($H = -2JS_1S_2$) of −117 (1) cm^{-1} (**4**) and −118 (1) cm^{-1} (**5**), after correction for very small amounts (0.01 and 0.02%, respectively) of Fe(III) $S = 5/2$ paramagnetic impurities, determined from data in the range 7–40 K.

As shown in Figure 1, the stereochemistry of the dimer is generally similar to other models reported previously (**1**, **2**, and **3**). Notably, the Fe–N bond trans to the μ-oxo is much longer than the other Fe–N bonds, as we have found for N5 species.[17] The Fe–O–Fe angle is more acute than in the tris-pyrazolylborate model.[7]

The proton NMR of **4** in acetonitrile (Figure 2) shows a peak at 16.9 ppm that disappears upon exchange with D$_2$O, and we assign this to the imidazole N-H resonances. An analogous peak is also found at 16.5 ppm for **5**. For the unsymmetrical singly bridged diiron(III) complex [N5FeOFeCl$_3$]$^+$, where in the solid state J = −122 (1) cm^{-1}, and a 4% of paramagnetic ($S = 5/2$) impurity was detected, the N-H protons are observed at 17.5 ppm.[17b,c] Peaks at 11.7, 6.8 (br), and 6.7 ppm of **4** are also present in the spectrum of **5** and therefore must be assigned to other N3 ligand protons; on the other hand, peaks at 8.6, 7.0, and possibly a broad feature at 8 ppm, assigned to benzoate, do not show for **5**, for which CH$_3$ protons appear at 9.8 ppm.

The imidazole N-H peaks at 17 ppm for Fe(III) dimers are shifted downfield much less than those of high spin Fe(III) monomers; for example, δ (imidazole N-H) = 73 ppm for [N5FeOC$_2$H$_5$](ClO$_4$)$_2$.[17b,c] In addition, these studies should allow the elucidation of subtle structural features, such as the effect of coordination of histidine cis or trans to a μ-oxo group on the N-H resonances[18] and on the resonance Raman enhancement of the Fe–O–Fe symmetric stretch mode. For **1** and metazidohemerythrin a strong enhancement has been attributed[19] to the coordination of an aromatic amine trans to the oxo group. On the other hand, **2**, which lacks aromatic amines, shows weak enhancement,[19] as does [N5FeOFeCl$_3$]$^+$.[17b,c] The title compound and **3**, as triply bridged species that have only aromatic amines coordinated cis to the μ-oxo, will provide a good point of reference for the testing of that hypothesis.

In conclusion, compounds **4** and **5**, together with the mononuclear species [N5FeOC$_2$H$_5$]$^{2+}$, provide data correlating imidazole N-H proton resonances with structure. As such, they provide useful reference points for assigning the basic stereochemistry in histidine-containing non-heme Fe proteins.

Note Added in Proof. We have confirmed the assignment of the Fe-O-Fe vibrational modes[15b] by means of ^{18}O exchange experiments.

Acknowledgment. We gratefully acknowledge the support of the National Institute of Diabetes and Digestive and Kidney Diseases through Grant 5ROI DK37702-02. We thank Professor

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(14) HBpz$_3$, tri-1-pyrazolylborate; tacn, 1,4,7-triazacyclononane; tpbn, tetrakis(2-pyridylmethyl)-1,4-butanediamine.

(15) (a) N3 (bis(2-benzimidazolylmethyl)amine) was prepared by refluxing iminodiacetic acid and *o*-phenylenediamine (1:1) in ethylene glycol for 18 h, precipitated with water and recrystallized from acetone–water. Chemical analysis satisfactory for $C_{16}H_{15}N_5 \cdot {}^1/_2H_2O$. (b) Chemical analysis: satisfactory for (**4**)·0.5[(C$_2$H$_5$)$_3$NH$^+$][ClO$_4^-$]. Crystal and refinement data: space group $P\bar{1}$, a = 15.263 (4) Å, b = 18.623 (3) Å, c = 13.024 (2) Å, α = 105.84 (1)°, β = 108.87 (2)°, γ = 69.65 (2)°, $Z = 2$, d_{calcd} = 1.35, d_{obsd} = 1.42; Mo Kα radiation (λ = 0.7107Å), 4151 data with $I > 3\sigma(I)$, 747 variables; final R = 0.063, R_w = 0.076; IR spectra major peaks at 1545, 1400 cm^{-1} (COO ν_{as}, ν_s, respectively); 1100, 650 cm^{-1} (ClO$_4^-$); 725 cm^{-1} (benzoate monosubstituted benzene, absent for the acetato analogue), and 750 cm^{-1} (*o*-substituted benzene from benzimidazole. A shoulder at 745 cm^{-1} and a peak at 545 cm^{-1} are tentatively assigned to the asymmetric and symmetric Fe–O–Fe stretch modes, respectively. Magnetic susceptibility: An S.H.E. Corp. SQUID magnetometer with diamagnetic corrections estimated from Pascal's constants. NMR spectra: Bruker-300 MHz spectrometer; CD$_3$CN solutions of the complexes (TMS internal standard).

(16) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203–283.

(17) (a) Gomez-Romero, P.; DeFotis, G. C.; Jameson, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 851–3. (b) Gomez-Romero, P.; Jameson, G. B., results to be published. N5 denotes *N*,*N*,*N'*-tris[(2-benzimidazolyl)methyl]-*N'*-(2-hydroxyethyl)-1,2-ethanediamine. (c) Gomez-Romero, P. Doctoral dissertation, Georgetown University, 1987.

(18) A report of an Fe tetramer containing imidazole coordinated trans to a μ-oxo will appear soon: Chen, Q.; Lynch, J. B.; Gomez-Romero, P.; Ben-Hussein, A.; Jameson, G. B.; O'Connor, C. J.; Que, L., Jr., submitted to *Inorg. Chem.*

(19) Sanders-Loehr, J. 194th National Meeting of the American Chemical Society, Fall 1987, Division of Inorganic Chemistry, no. 7 (Tutorial on Metal Clusters in Proteins).

Ekkehardt Sinn for facilitating the use of the SQUID susceptometer and Thitinant Thanyasiri for the collection of the magnetic susceptibility data. P.G.-R. gratefully acknowledges the award of a fellowship from the Comite Conjunto Hispano-Norteamericano para la Cooperacion Cultural y Educativa.

Supplementary Material Available: Table SI consists of final positional parameters with estimated standard deviations and B_{eq} (4 pages). Ordering information is given on any current masthead page.

Unprecedented Rearrangement of a Diphosphene $\eta^1\eta^2$-Bonded to Iron. Synthesis and X-ray Structure of Fe_4 Complexes Containing Either a μ_4 Spiro Phosphorus Atom or a 1,1,2-Trimetalladiphosphorus Ligand >P═P—

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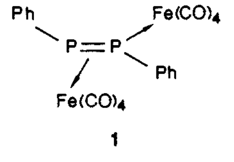
Free and complexed diphosphenes exhibit an interesting and diversified reactivity which has been the subject of numerous articles.[1] In contrast very few papers deal with their thermal behavior. Indeed thermolysis of the dinuclear $\eta^1\eta^1$-$[(CO)_5M]_2$-$(Me_3Si)_2CH$—P═P—$CH(SiMe_3)_2$ (M = Cr, W) or trinuclear $\eta^1\eta^2\eta^1$-$[(CO)_5Cr]_3Ph$—P═P—Ph complexes proceeds only with partial decomplexation and leads to the corresponding mononuclear η^1- or dinuclear $\eta^1\eta^1$-diphosphene complexes, $[(CO)_5M]$-$(Me_3Si)_2CH$—P═P—$CH(SiMe_3)_2$ (M = Cr, W)[2] or $[(CO)_5Cr]_2Ph$—P═P—Ph,[3] respectively.

Because of the better tendency of group 8 complexes to form clusters, we investigated the thermolytic behavior of the $\eta^1\eta^2$-diiron diphosphene **1**,[4] expecting unusual rearrangements of the diphosphene ligands assisted by cluster formation.



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We report here (i) the preparation and X-ray structure of the original, and unique so far, complex **3** in which one P atom acts as a spiro center between three cyclic fragments, (ii) the synthesis of a tetrairon cluster **4** possessing four phosphorus atoms in four different coordination modes, and (iii) the first structural information on a P═P unit $\mu_4\eta^2$ bonded.

Compound **1** was refluxed in benzene for 1 h, infrared monitoring showing the disappearance of **1**. The solvent then was removed, and a chromatography on Florisil (eluent hexane/toluene, 1/1) was allowed to separate the derivative $Fe_3(CO)_9(\mu$-$PPh)_2$, **2**,[5] isolated as traces from the major product $[Fe_4(CO)_{12}(PPh)_4]$, **3**. **3** was isolated in 70% yield as air-stable yellow crystals.[6] The first indication of an unusual structure came from the $^{31}P\{^1H\}$ NMR spectrum which appeared as an ABCX system. Computer simulation by routine methods afforded the following parameters: P_X δ 440.5, P_A δ 138.6, P_B δ 136.5, P_C δ 122.7 ppm ($J_{P_XP_A} = 95.7$, $J_{P_XP_B} = 249.5$, $J_{P_CP_X} = 175.7$, $J_{P_AP_B} = 1.7$, $J_{P_AP_C} = 41.4$, $J_{P_BP_C} = 99.8$ Hz). The structure of the complex was solved by single-crystal X-ray diffraction,[7] and one of the two independent molecules is shown in Figure 1. It consists of a spiranic molecule with one of the four phosphorus atoms P(1) acting as a μ_2 spiro center linked to two $Fe(CO)_3$ moieties and two phosphorus atoms, P(3) and P(4). This is the first example of such a derivative in which a P atom is the joining center between one three-membered P(1)Fe(1)Fe(2) and two four-membered P(1)P(4)Fe(4)P(3) and P(1)P(3)Fe(3)P(4) rings.[8] All the phosphorus atoms occupy a conventional phosphido bridging position between $Fe(CO)_3$ groups. The phosphorus–phosphorus distances are in the range expected for P-P single bonds: P(1)–P(3) = 2.250 (2) and 2.300 (2) Å, P(1)–P(4) = 2.245 (2) and 2.247 (2) Å. These data suggest the following attributions for the ^{31}P NMR spectrum; P_X = P(1), P_A = P(2), P_B or P_C = P(3), P_C or P_B = P(4).

Heating compound **3** at a higher temperature in refluxing xylene or direct heating of **1** in the same solvent for 1 h afforded a new complex **4**. After removal of the volatile products followed by chromatography on Florisil (eluent hexane/toluene, 1/1), **4** is obtained as air-stable black crystals by crystallization in CH_2Cl_2/C_5H_{12} at -20 °C (yield, 30% in each case). The IR spectrum of **4** in the ν_{CO} stretching region gives evidence of terminal carbonyl groups only. Mass spectrometry (m/z = 936 with successive loss of 10 CO groups) and chemical analysis[10] are in good agreement with a $(CO)_{10}Fe_4(PPh)_4\cdot{}^1/_2C_5H_{12}$ formulation.

The structure of **4** was determined by single-crystal X-ray diffraction[11] and is illustrated in Figure 2. **4** consists of a metallic slightly distorted square containing four iron atoms, two of them being surrounded by two terminal carbonyl groups and the other two by three terminal carbonyl groups. To this square is coordinated a phosphanediyl group PhP(1) acting as a four-electron donor. All four P(1)–Fe bond lengths are virtually the same. The phosphorus atom P(2) is bonded to two phenyl groups and to the two adjacent $Fe(CO)_2$ groups.

The main feature of interest in the molecule involves the P(3)P(4) fragment. Each of the two phosphorus atoms is coordinated to an $Fe(CO)_2$ and an $Fe(CO)_3$ moieties. Furthermore the phosphorus atom P(3) is linked to a phenyl group. The

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(1) For a general review, see: (a) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (b) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924.

(2) Lang, H.; Orama, D.; Huttner, G. *J. Organomet. Chem.* **1985**, *291*, 293.

(3) Born, J.; Huttner, G.; Orama, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *282*, 53.

(4) (a) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; Sanchez, M. *Organometallics* **1986**, *5*, 1914 and references therein. (b) Caminade, A.-M.; Majoral, J.-P.; Sanchez, M.; Mathieu, R.; Attali, S.; Grand, A. *Organometallics* **1987**, *6*, 1459.

(5) Cook, S. L.; Evans, J.; Gray, L. R.; Weboter, M. *J. Organomet. Chem.* **1982**, *236*, 367.

(6) $Fe_4(CO)_{12}[PPh]_4$, **3**: IR ν_{CO} (hexane solution) 2067 (m), 2049 (s), 2027 (vs), 2002 (s), 1990 (m), 1972 (s) cm^{-1}, Ms, m/z = 992 with successive loss of 12 CO. Anal. Calcd for $C_{36}H_{20}Fe_4O_{12}P_4$: C, 43.55; H, 2.01. Found: C, 43.74; H, 1.77.

(7) Crystal data for **3**: $C_{36}Fe_4H_{20}O_{12}P_4$, Fw = 991.4, orthorhombic, space group $Pna2_1$, a = 20.781 (2) Å, b = 37.222 (3) Å, c = 10.378 (1) Å, V = 8027 (2) Å^3, D_x = 1.641 g·cm^{-3}, Z = 8. X-ray diffraction data were measured on a CAD4 Enraf-Nonius diffractometer by using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Reflections (5941) were collected up to 2θ = 47° by the θ–2θ scan technique. The crystal structure was solved by direct methods (SHELXS-86) (Sheldrick, G. M. SHELXS-86. *Program for Crystal Structure Solution*; University of Göttingen, FRG, 1986) and refined by full-matrix least-squares (SHELX 76) (Sheldrick, G. M. SHELX 76. *Program for Crystal Structure Determination*; University of Cambridge, England, 1976) by using the 5139 observed reflections $[F_o^2 > 2\sigma(F_o^2)]$ to the R factor of 0.024 including anisotropic temperature factors, except for phenyl rings refined as isotropic rigid groups (hydrogen atoms included but not refined).

(8) To our knowledge, only one other spiranic phosphorus species has been reported;[9] in this case phosphorus is included in two three-membered rings.

(9) Huttner, G.; Mohr, G.; Pritzlaff, B.; von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1982**, *115*, 2044.

(10) $Fe_4(CO)_{10}(PPh)_4\cdot{}^1/_2C_5H_{12}$, **4**: IR ν_{CO} (CH_2Cl_2 solution) 2057 (m), 2021 (s), 2011 (s), 1992 (m), 1962 (w). Anal. Calcd for $C_{36.5}H_{26}Fe_4O_{10}P_4$: C, 45.06; H, 2.67. Found: C, 44.92; H, 2.63.

(11) Crystal data for **4**: $(C_{34}Fe_4H_{20}O_{10}P_4)\cdot{}^1/_2C_5H_{12}$, Fw = 971.4, monoclinic, space group $P2_1/c$, a = 11.926 (1) Å, b = 16.631 (2) Å, c = 21.900 (3) Å, β = 103.09 (2)°, V = 4230.8 (9) Å^3, D_x = 1.525 g·cm^{-3}, Z = 4. The 6240 reflections were collected up to 2θ = 47° by the θ–2θ scan technique as for **3**. Same programs were used. Full-matrix refinement using 3332 reflections $[F_o^2 > 3\sigma(F_o^2)]$ led to the R factor of 0.025 (anisotropic temperature factors, isotropic phenyl rigid groups with hydrogen atoms not refined, isotropic solvent molecule).

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