The $g_y$ and $g_x$ values found for the spectrum in Figure 7 are close to the $g_\perp$ range, but the $g_z$ is seemingly way out of the $g_\parallel$ range. It must be remembered, however, that the unpaired electron in $Fe_2(C_5H_4)_4^+$ is rapidly exchanging between the two iron centers, which is a unique situation compared to all other ferricenium systems. The room-temperature spectrum of the solid, as well as the acetonitrile solution spectra (300 and 77°K), is very similar to that reproduced in Figure 7, except the resolution is somewhat poorer.[27]

**Registry No.** $[Fe(C_5H_5)(C_5H_4)]_2Hg$, 1274-09-5; $[Fe(C_5H_5)(C_5H_4)]_2[(CH_3)_2CC(CH_3)_2]$, 12610-01-4; $[Fe(C_5H_5)(C_5H_4)]_2[CHCHC_6H_4CHCH]$, 12094-51-8; $[Fe(C_5H_5)(C_5H_4)]_2[C_2H_4]$, 12156-05-7; $[Fe(C_5H_5)(C_5H_4)]_2[CH_2]$, 1317-11-9; $[Fe(C_5H_5)(C_5H_4)]_2$, 1287-38-3; $[Fe(C_5H_4)_2]_2$, 11105-90-1; $[Fe(C_5H_5)(C_5H_4)(C_6H_5)]$, 1287-25-8; $Fe(C_5H_5)_2$, 102-54-5; $[1,1\text{-}(CH_2)Fe(C_2H_5)_2(C_5H_4)_2][PF_6]_2$, 39291-61-7; $[1,1\text{-}[(CH_3)_2CC(CH_3)_2]Fe_2(C_5H_5)_2(C_5H_4)_2][PF_6]_2$, 39291-62-8; $Fe(C_5H_5)_2I_3$, 1291-35-6; $[Co(C_5H_5)_2](DDQH)$, 39291-56-0; $[Fe(C_5H_5)_2](DDQH)$, 39291-57-1; $[Fe_2(C_5H_5)_2(C_5H_4)_2](DDQH)_2$, 39291-60-6; $[Fe_2(C_5H_4)_4](DDQH)_2$, 39291-59-3.

**Acknowledgment.** We are grateful for support from NIH Grant HL 13652.

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[27] Note Added in Proof. Professor W. E. Watts has pointed out to us (and we have verified this by proton nmr) that the compound labeled as $-C(CH_3)_2C(CH_3)_2-$ bridged biferrocene is (for our sample) a mixture of 80% $-C(CH_3)_2CH{=}C(CH_3)-$ bridged and 20% $-C(CH_3)CH_2C({=}CH_2)-$ bridged biferrocene, a fact that in no way detracts from the conclusions of our work.

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# Mono- and Disubstituted Derivatives of Benzo[*c*]cinnolinebis(tricarbonyliron)

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The preparations of benzo[*c*]cinnolinebis(tricarbonyliron) derivatives containing phosphine, phosphite, cyclohexyl isocyanide, triphenylarsine, or triphenylstibine ligands are reported. Depending upon both the ligand and the reaction conditions, mono- or disubstituted products are obtained. Trisubstitution has not been observed. Infrared, mass spectroscopic, pmr, and cmr data indicate that the preferred substitution site is that trans to the metal–metal bond. A close similarity is noted between these complexes and the corresponding derivatives of bis-$\mu$-mercapto-bis(tricarbonyliron) complexes.

## Introduction

A variety of ligand-bridged hexacarbonyldiiron complexes is known. Bridging ligands include sulfur[1] and halogens[2] as well as phosphorus-,[3,4] arsenic-,[4] sulfur-,[5] selenium-,[6] tellurium-,[6] and nitrogen-donor[7] moieties. Although carbon monoxide displacement from mercapto-bridged complexes by phosphines and other soft ligands has been extensively studied,[8] only scattered observations of such substitutions have been made for complexes in which the bridging moiety involves a phosphorus-,[9] arsenic-,[9] or nitrogen-donor[10,11] ligand. This paper reports the preparation and characterization of a number of mono- and disubstituted derivatives of benzo[*c*]cinnolinebis(tricarbonyliron) containing phosphine, phosphite, cyclohexyl isocyanide, and triphenylarsine ligands. A triphenylstibine derivative was identified by infrared spectroscopy but was not isolated.

## Experimental Section

Benzo[*c*]cinnolinebis(tricarbonyliron) and its substituted derivatives are remarkably air-stable, even in solution. Nevertheless, all reactions were carried out under a nitrogen atmosphere, and subsequent work-up procedures involved only short periods of exposure to atmospheric oxygen. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

**Materials.** Phosphines, phosphites, and iron pentacarbonyl were obtained from commercial sources and were used as received. Commercially obtained triphenylarsine was recrystallized from methanol before use. Cyclohexyl isocyanide was prepared by dehydration of *N*-cyclohexylformamide according to the procedure of Hertler and Corey.[12] Benzo[*c*]cinnoline was prepared by $LiAlH_4$ reduction of 2,2′-dinitrobiphenyl following the description of Badger,[13] and benzo[*c*]cinnolinebis(tricarbonyliron) was prepared from iron pentacarbonyl and benzo[*c*]cinnoline as described by Bennett.[11]

**Preparation of Derivatives of Benzo[*c*]cinnolinebis(tricarbonyliron). General Procedure.** Disubstituted derivatives were formed with smooth evolution of 2 equiv of carbon monoxide when a slight excess of tri-*n*-butylphosphine, diphenylphosphine, trimethyl phosphite, or cyclohexyl isocyanide was allowed to react with $Fe_2(CO)_6(C_{12}H_8N_2)$ in toluene solution at ambient temperatures. With ethyldiphenylphosphine, triphenyl phosphite, and triphenylphosphine the monosubstituted derivatives were formed under these conditions. The monosubstituted tri-*n*-butylphosphine derivative, $Fe_2(CO)_5(C_{12}H_8N_2)P(n\text{-}C_4H_9)_3$, was obtained from reactions involving equimolar reagents. The disubstituted triphenylphosphine derivative, $Fe_2(CO)_4(C_{12}H_8N_2)[P(C_6H_5)_3]_2$, was produced under more vigorous reaction conditions (100° for 48 hr). Similar conditions (100° for 72 hr) were required to achieve complete monosubstitution with triphenylarsine. Infrared spectra of crude products clearly demonstrated the formation of the monosubstituted triphenylstibine derivative, $Fe_2(CO)_5(C_{12}H_8N_2)Sb(C_6H_5)_3$. However, this substitution was less than 50% complete after 100 hr at 100°. This product was not obtained in a pure state.

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Table I. Analytical Data

| Compound | % calcd C | % calcd H | % calcd Fe | % found C | % found H | % found Fe | Mp, °C[a] |
|---|---|---|---|---|---|---|---|
| $Fe_2(CO)_5C_{12}H_8N_2P(OC_6H_5)_3$ | 56.64 | 3.12 | 15.05 | 56.74 | 3.14 | 15.23 | 144-145[b] |
| $Fe_2(CO)_5C_{12}H_8N_2As(C_6H_5)_3$ | 56.95 | 3.14 | 15.13 | 56.79 | 3.30 | 14.95 | 218-220 |
| $Fe_2(CO)_5C_{12}H_8N_2P(n\text{-}C_4H_9)_3$ | 54.92 | 5.56 | 17.61 | 54.78 | 5.39 | 17.32 | 173-176[b] |
| $Fe_2(CO)_5C_{12}H_8N_2P(C_6H_5)_3$ | 60.55 | 3.34 | 16.09 | 60.33 | 3.27 | 16.17 | 247-249 |
| $Fe_2(CO)_5C_{12}H_8N_2P(C_2H_5)(C_6H_5)_2$ | 57.62 | 3.59 | 17.28 | 57.83 | 3.64 | 17.35 | 160-162[b] |
| $Fe_2(CO)_4C_{12}H_8N_2[P(n\text{-}C_4H_9)_3]_2$ | 59.42 | 7.73 | 12.81 | 59.19 | 7.68 | 13.68 | 185-187 |
| $Fe_2(CO)_4C_{12}H_8N_2[PH(C_6H_5)_2]_2$ | 61.89 | 3.90 | 14.39 | 61.59 | 3.68 | 14.19 | 188-190[b] |
| $Fe_2(CO)_4C_{12}H_8N_2[P(C_6H_5)_3]_2$ | 67.27 | 4.12 | 12.03 | 67.40 | 4.12 | 12.22 | *b, c* |
| $Fe_2(CO)_4C_{12}H_8N_2[P(OCH_3)_3]_2$ | 40.52 | 4.02 | 17.13 | 40.47 | 4.08 | 17.10 | 191-194 |
| $Fe_2(CO)_4C_{12}H_8N_2[CNC_6H_{11}]_2$ | 57.90 | 4.86 | 17.95 | 58.01 | 4.85 | 17.68 | 115-119 |

[a] All melting points are corrected; all complexes melt with decomposition. [b] Gas evolution accompanies decomposition at the melting point. [c] Irreproducible.

Crude products were recrystallized to analytical purity from hot toluene or toluene-hexane mixtures. Analytical data are reported in Table I. The preparation of the bis(tri-*n*-butylphosphine) derivative was typical and is described to illustrate the general procedure.

**Preparation of $Fe_2(CO)_4(C_{12}H_8N_2)[P(n\text{-}C_4H_9)_3]_2$.** Tri-*n*-butylphosphine (0.42 g, 2.1 mmol) was added to a toluene (35 ml) solution of $Fe_2(CO)_6(C_{12}H_8N_2)$ (0.33 g, 0.72 mmol) in an atmosphere of pure nitrogen. The reaction mixture was allowed to stand at room temperature, and carbon monoxide evolution was monitored. When gas evolution was complete (12 hr), the solution was concentrated to dryness under vacuum. The solid, red residue was extracted with a minimum of warm toluene, and the resulting toluene solution was diluted approximately threefold with warm hexane. This solution was then filtered hot and slowly cooled to *ca.* −10°. Large, red, needle-like crystals were deposited. These were recovered, washed with hexane, and vacuum dried (0.1 Torr), giving 0.53 g (90%) of the bis(tri-*n*-butylphosphine) derivative.

**Instrumentation.** Infrared spectra were obtained on a Perkin-Elmer Model 621 grating spectrometer and calibrated with polystyrene and indene.[14] Proton nmr spectra were recorded on Varian A-60 and A-60D spectrometers. Mass spectra were obtained on a Hitachi Model RMU-6D spectrometer. Melting points were determined in sealed, evacuated, capillary tubes.

Carbon-13 nmr spectra were obtained at 63.1 MHz by the Fourier transform technique on a saturated solution (*ca.* 0.3 *M*) of $Fe_2(CO)_5C_{12}H_8N_2P(OC_6H_5)_3$ in THF.[15] A good signal to noise ratio was obtained with 1000 scans in *ca.* 2 hr.

## Results and Discussion

Benzo[*c*]cinnolinebis(tricarbonyliron) reacts readily with phosphines and other soft Lewis bases with displacement of 1 or 2 equiv of carbon monoxide. Qualitatively, the reactivities of the entering ligands vary in the way usual for SN2 displacements on metal carbonyl substrates: alkylphosphines > alkyl phosphites ~ arylphosphines > aryl phosphites > arylarsines > arylstibines.[16] It is noteworthy that tri-*o*-tolylphosphine undergoes no observable reaction in 60 hr at 100°. In view of the facile reaction with triphenylphosphine, this can only be attributed to a large, inhibitory, steric effect for nucleophilic attack by tri-*o*-tolylphosphine.[17] Hence, both the electronic and steric properties of the incoming group have substantial effects on its observed reactivity.

Doedens[18] has determined the crystal and molecular structure of the parent benzo[*c*]cinnolinebis(tricarbonyliron). Doubtless the derivatives obtained here are structurally analogous not only to the parent complex but also to the corresponding derivatives in the extensively studied *μ*-mercapto series of hexacarbonyldiiron complexes. Figure 1 indicates the isomers possible for the substitution products.

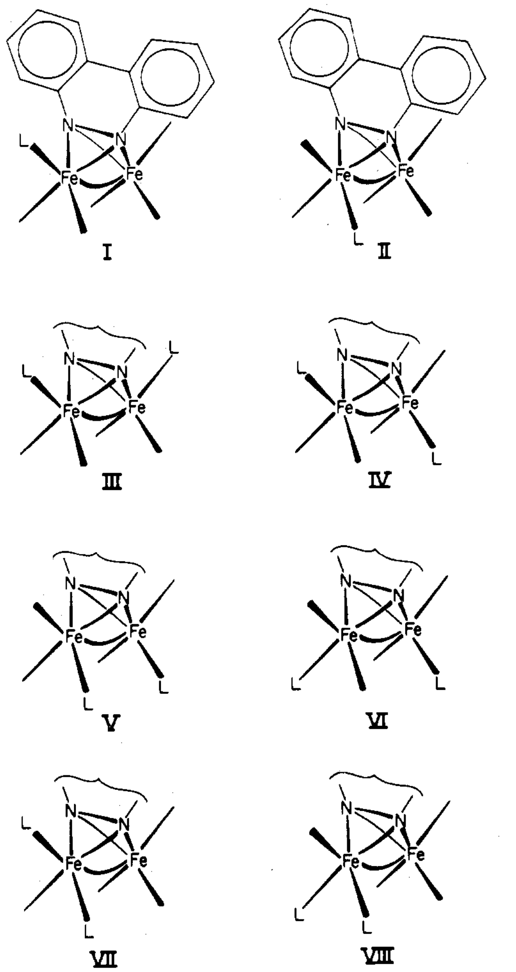

Figure 1. Isomers possible for mono- and disubstituted derivatives of benzo[*c*]cinnolinebis(tricarbonyliron). Carbonyl groups have been omitted for clarity.

Mass spectra of the disubstituted derivatives $Fe_2(CO)_4C_{12}H_8N_2[P(OCH)_3]_2$ and $Fe(CO)_4C_{12}H_8N_2(CNC_6H_{11})_2$ show the expected pattern of peaks from the parent ion and from ions derived from it by losses of successive carbon monoxide ligands. Numerous other mass peaks can be ascribed to fragments containing one or two iron atoms. However, in no case is a peak ascribable to a fragment containing a *single* iron atom and portions of *two* $P(OCH_3)_3$ or $CNC_6H_{11}$ ligands. This suggests that isomers VII and VIII are not important species.

The infrared spectrum of a substitution product appears to be diagnostic of the derivative's structure. Table II presents spectroscopic data for the complexes reported here. Data for analogous mercapto-bridged derivatives are included for

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**Table II.** Spectroscopic Data

| Complex | | Infrared, $\nu_{CO}$, cm$^{-1}$ [a] | | | | | | Ir[a] solvent | Pmr, ppm[b] | Pmr[a] solvent |
|---|---|---|---|---|---|---|---|---|---|---|
| $Fe_2(CO)_5C_{12}H_8N_2P(OC_6H_5)_3$ | | 2052 vs | 1999 vs | 1980 vs | | 1970 m | 1948 w | H | 7.9, 7.2, 6.8 | T |
| $Fe_2(CO)_5C_{12}H_8N_2As(C_6H_5)_3$ | | 2046 s | 1987 vs | 1977 s | | 1967 vw | 1933 w | H | 7.3, 7.0 | T |
| $Fe_2(CO)_5C_{12}H_8N_2P(n\text{-}C_4H_9)_3$ | | 2042 s | 1981 vs | 1970 s | | 1960 w | 1926 m | H | 7.7, 7.2, 1.0 | M |
| $Fe_2(CO)_5C_{12}H_8N_2P(C_6H_5)_3$ | | 2039 vs | 1980 vs | 1965 s | | 1956 sh | 1923 w | D | 7.5, 7.1 | T |
| $Fe_2(CO)_5C_{12}H_8N_2P(C_2H_5)(C_6H_5)_2$ | | 2044 s | 1983 vs | 1973 s | | 1963 w | 1928 m | H | 7.4, 7.0, 6.7, 1.7, 0.8 | D |
| $Fe_2(CO)_5(SCH_3)_2P(n\text{-}C_4H_9)_3$[c,d] | | 2041 s | 1981 vs | 1967 m | | 1960 sh | 1924 w | H | | |
| $Fe_2(CO)_5(SCH_3)_2P(C_6H_5)_3$[c,d] | | 2044 s | 1987 vs | 1972 mw | | 1965 sh | 1930 w | H | | |
| $Fe_2(CO)_5(SC_6H_5)_2P(C_6H_5)_3$[c] | | 2052 s | 1991 s | 1975 w | | 1944 w | | H | | |
| $Fe_2(CO)_5(SC_6F_5)_2P(C_6H_5)_3$[c] | | 2058 m | 2009 s | 1992 ms | | 1976 mw | 1944 w | H | | |
| $Fe_2(CO)_5(SCH_3)_2As(C_6H_5)_3$[e] | | 2047 s | 1986 s | 1972 m | | 1934 w | 1927 sh | B | | |
| $Fe_2(CO)_4C_{12}H_8N_2[P(n\text{-}C_4H_9)_3]_2$ | | 1993 vs | | 1944 m | 1927 vs | | | H | 7.5, 7.0, 1.0 | D |
| $Fe_2(CO)_4C_{12}H_8N_2[PH(C_6H_5)_2]_2$ | α | 1966 vs | | 1953 } s | 1943 | | | } D | g | |
| | β | | 1988 m | 1953 } | | 1907 m | 1901 w | | | |
| $Fe_2(CO)_4C_{12}H_8N_2[P(C_6H_5)_3]_2$ | α | 1993 vs | | 1948 } m | 1926 vs | | | } D | 7.5, 7.0 | T |
| | β | | 1984 w | 1948 } | | 1915 w | 1897 vw | | | |
| $Fe_2(CO)_4C_{12}H_8N_2[P(OCH_3)_3]_2$ | α | 2006 s | | 1967 vs | 1944 s | | | } H | 7.7, 7.1, 3.3[h] | F |
| | β | | 1999 s | 1962 sh | | 1933 s | 1917 w | | | |
| $Fe_2(CO)_4C_{12}H_8N_2[CNC_6H_{11}]_2$[f] | α | 2004 m | | 1976 w | 1953 m | | | } H | 7.6, 7.1, 3.7, 1.5 | D |
| | β | | 1997 s | 1971 vs | | 1940 s | 1927 m | | | |
| $Fe_2(CO)_4(SCH_3)_2[P(C_2H_5)_3]_2$[e] | | | 1985 s | 1948 m | | 1941 ms | 1922 s | C | | |
| $Fe_2(CO)_4(SCH_3)_2[P(C_6H_5)_3]_2$[e] | | 1989 s | | 1948 m | 1931 s | | | B | | |
| $Fe_2(CO)_4(SCH_3)_2[As(C_6H_5)_3]_2$[e] | | 1991 s | | 1949 m | 1931 s | | | B | | |
| $Fe_2(CO)_4(SCH_3)_2[Sb(C_6H_5)_3]_2$[e] | | 1991 s | | 1951 m | 1933 s | | | B | | |
| $Fe_2(CO)_4(SCH_3)_2[P(OCH_3)_3]_2$[e] | | 2006 s | | 1966 ms | 1943 s | | | B | | |

[a] Abbreviations: v, very; s, strong; m, medium; w, weak; sh, shoulder; br, broad; H = hexane; D = carbon disulfide; B = benzene; C = cyclohexane; T = tetrahydrofuran; M = dichloromethane; F = chloroform. [b] Centers of complex multiplets except as noted. [c] Reference 18. [d] Syn isomer; frequencies are slightly different for the anti isomer. [e] Reference 19. [f] A strong, broad band at 2121 cm$^{-1}$ is assigned as the C≡N stretching vibration(s). [g] Solubility insufficient for pmr. [h] Center of doublet; $J(P\text{-}CH_3) = 11$ Hz.

comparison. It can be noted that the monosubstituted derivatives have carbonyl-region infrared spectra which are very similar to one another. Moreover, these spectra are very similar to those of the corresponding mercapto-bridged species. The monosubstituted derivatives in the mercapto-bridged series have been assigned structures in which the unique ligand occupies a coordination site trans to the metal-metal bond.[19,20] Therefore, in view of the close similarity of the infrared spectra, structure I is assigned to the monosubstituted derivatives obtained in this work.

This conclusion is supported by the $^{13}C$ nmr spectrum of $Fe_2(CO)_5C_{12}H_8N_2P(OC_6H_5)_3$. Four observed resonances are assignable to the four different carbons of the triphenyl phosphite ligand. As expected for structure I, six observed absorptions are assignable to the carbons in two equivalent rings of the benzo[*c*]cinnoline ligand, and three carbonyl-carbon resonances are observed. However, two of the latter are only partially resolved and may represent phosphorus splitting of the resonance from two, equivalent carbonyl carbons on the same iron atom. The remaining peak would then result from the accidental overlap of resonances from two, nonequivalent, carbonyl-carbon environments on the second iron atom. The relative intensities of the observed peaks support the latter assignment. In any event, five carbonyl-carbon resonances are expected for II; therefore, the cmr spectrum is negative evidence which supports structure I over structure II.

A somewhat more complex situation obtains for the disubstituted derivatives of the benzo[*c*]cinnoline complex. As can be seen from Table II, most of these derivatives exhibit six or seven absorptions in the carbonyl-stretching region. This doubtless arises from the coexistence of two isomers. (Chromatographic attempts to separate these isomers have been unsuccessful.)

For $Fe_2(CO)_4C_{12}H_8N_2[P(n\text{-}C_4H_9)_3]_2$, only three infrared bands are observed. As is again evident from Table II, this spectrum is strikingly similar to the spectra of a number of disubstituted derivatives in the mercapto-bridged family whose structures have been shown to result from substitution at each iron in the position trans to the metal-metal bond.[19] Again, on the basis of the close similarity of infrared spectra, structure III can be assigned to $Fe_2(CO)_4C_{12}H_8N_2$-$[P(n\text{-}C_4H_9)_3]_2$.

For each of the other disubstituted derivatives, it is possible to identify a set of three bands which are very similar in both position and intensity to those observed for the bis(tri-*n*-butyl)phosphine derivative. Hence, structure III also appears to be an important one for the disubstituted products given by each of the other ligands investigated. When these three peaks are deleted, the remaining four peaks ascribable to the second isomer again have similar positions and intensities for all of the derivatives obtained. Presumably this reflects the fact that the second isomer has the same structure in each case. Although the available data do not permit a distinction among structures IV, V, or VI, the apparent preference for substitution trans to the metal-metal bond favors structure IV. Since three infrared active bands are allowed for III while four are allowed for each of IV, V, and VI, this interpretation assumes that all symmetry-allowed absorptions are observed.

The pmr spectra obtained (Table II) are consistent with, but not diagnostic of, the proposed structural assignments. For example, the predominant methyl resonance of $Fe_2(CO)_4$-$C_{12}H_8N_2[P(OCH_3)_2]_2$ is a doublet, implying that the two phosphite ligands occupy equivalent coordination sites and give rise to a single doublet by coupling to phosphorus. Only structure IV is inconsistent with this feature. Consistent with the interpretation offered for the infrared spectrum, additional methyl pmr absorptions are present. However, these are broad and unresolved.

**Registry No.** $Fe_2(CO)_5C_{12}H_8N_2P(OC_6H_5)_3$, 40583-27-5; $Fe_2(CO)_5C_{12}H_8N_2As(C_6H_5)_3$, 40583-28-6; $Fe_2(CO)_5C_{12}H_8$-

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$N_2P(n\text{-}C_4H_9)_3$, 40620-73-3; $Fe_2(CO)_5C_{12}H_8N_2P(C_6H_5)_3$, 40583-29-7; $Fe_2(CO)_5C_{12}H_8N_2P(C_2H_5)(C_6H_5)_2$, 40583-30-0; $Fe_2(CO)_4C_{12}H_8N_2[P(n\text{-}C_4H_9)_3]_2$, 40583-31-1; $Fe_2(CO)_4C_{12}H_8N_2[PH(C_6H_5)_2]_2$, 40583-32-2; $Fe_2(CO)_4C_{12}H_8N_2[P(C_6H_5)_3]_2$, 40620-74-4; $Fe_2(CO)_4C_{12}H_8N_2[P(OCH_3)_3]_2$, 40583-33-3; $Fe_2(CO)_4C_{12}H_8N_2[CNC_6H_{11}]_2$, 40583-34-4; $Fe_2(CO)_6(C_{12}H_8N_2)$, 40583-35-5; $P(OPh)_3$, 101-02-0; $P(Ph)_3$, 603-35-0; $P(OMe)_3$, 121-45-9.

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# Equilibria of Imidazole with Iron(III) Tetraphenylporphine

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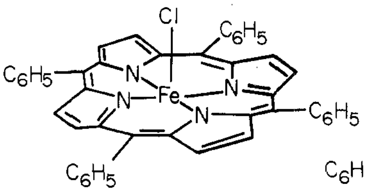
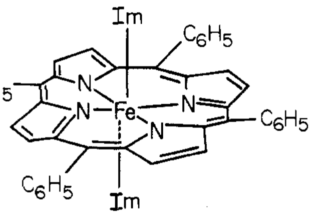
The equilibrium of imidazole with chlorotetraphenylporphinatoiron(III) has been investigated in nonpolar media. The reaction is shown to proceed by the displacement of the chloride ion by two imidazoles to give tetraphenylporphinatobis(imidazole)iron(III) chloride as a tightly bound ion pair. No evidence could be found for an intermediate six-coordinate monochloromonoimidazole complex or for an intermediate five-coordinate monoimidazole complex. The spin of the iron(III) is seen to decrease from $S = {}^5/_2$ to $S = {}^1/_2$ during the reaction and the absence of intermediate complexes is attributed to the high stability of the low-spin product. In all solvent studies, isosbestic points were observed indicating that only two different absorbing species are present; however, in some solvents, computed equilibrium constants showed strong dependences on imidazole concentration. In aromatic solvents computed equilibrium constants become larger with increasing solvent dielectric constant and they also depend more and more strongly on imidazole concentration. The consequences of these effects are considered.

## Introduction

Iron porphyrin coordination compounds are essential constituents of a number of important biological systems including hemoglobin, the cytochromes, and the peroxidase enzymes. Many bioinorganic problems remain to be solved in these systems. Of the structural changes which may occur in the region of the iron, there is particular interest in the motion of the iron into the plane of the porphyrin as its spin state changes from high to low during a reaction. In the simplest of the iron(III) porphines, this situation is exemplified by the structures FeTPPCl,[3] I, and $FeTPPIm_2Cl$, II.[4,5] In FeTPPCl, the iron is in a high-spin, square-pyramidal state about 0.3 Å above the porphine nitrogens[4] while in $FeTPPIm_2Cl$ the iron is low spin and is in an elongated tetragonal environment.[5]



I



II

Spin change and the dropping of the iron into the porphine plane occur in the binding of oxygen by hemoglobin and in cytochrome reactions. As part of a program to elucidate the features of macrocyclic complexes which may influence the reactivity of their metal ions, we have been investigating the factors governing the equilibria of FeTPPCl with Im to give $FeTPPIm_2Cl$. The original work in this area is that of Davies[6] and of Cowgill and Clark.[7] These workers examined equilibria in aqueous systems of natural porphyrins; however, the presence of $\mu$-oxo-bisiron(III) species[8] and other complexities have made it difficult to interpret their results. The work reported herein was done entirely in nonaqueous media to simplify the equilibria.

## Experimental Section

**Materials.** $TPPH_2$ and FeTPPCl were prepared by methods developed by Adler.[9,10] The FeTPPCl was purified by converting it to $\mu$-oxo-bis(tetraphenylporphinatoiron(III)) which was chromatographed on alumina. When samples of FeTPPCl were required, a few milligrams of the $\mu$-oxo compound was dissolved in 100 ml of methylene chloride and a stream of dry HCl was passed through for 30 sec. After the solvent was removed, the chloro complex was dried and used within a few days.

Tetraphenylporphinatobis(imidazole)iron(III) chloride was prepared as follows. A 300-mg sample of imidazole and 60 mg of FeTPPCl were dissolved in 1000 ml of benzene. The absorption spectrum showed about a 50% conversion to $FeTPPClIm_2$. The solution was left at room temperature in the dark for several days during which lustrous purple needles formed. *Anal.* Calcd for $C_{50}H_{36}N_8FeCl \cdot 2H_2O$: C, 69.0; H, 4.56; N, 12.9; Cl, 4.05. Found: C, 69.76; H, 4.51; N, 12.58; Cl, 3.82.

Other reagents were of the highest purity readily obtainable. Solvents were stored over molecular sieves and distilled just prior to use.

**Measurements.** Absorption spectra were obtained with a Cary 14

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[2] Abstracted, in part, from work performed in the partial fulfillment of the City University of New York B.A. degree.

[3] Abbreviations: TPP, tetraphenylporphine dianion; Im, imidazole; FeTPPCl, chlorotetraphenylporphinatoiron(III); $FeTPPIm_2Cl$, tetraphenylporphinatobis(imidazole)iron(III) chloride.

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