Table I. New ((Dialkylamino)phosphido)hexacarbonyldiiron Derivatives

compd[a,b]	color	mp, °C	NMR $\delta(^{31}P)$[c]	IR, ν(CO),[d] cm^{-1}
(*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$	orange	114–115	225.6 s	2060 m, 2016 s, 1996 s, 1975 s, 1964 m, 1720 m[e]
(Cx$_2$NP)$_2$COFe$_2$(CO)$_6$	orange	164 dec	229.7 s	2060 m, 2016 s, 1996 s, 1973 s, 1962 m, 1721 m[e]
[(CH$_2$)$_3$(CMe$_2$)$_2$NP]$_2$COFe$_2$(CO)$_6$	orange	160	204.6 s	2058 m, 2016 s, 1992 s, 1977 s, 1962 m, 1715 m[e]
(*i*-Pr$_2$NPOMe)(*i*-Pr$_2$NPH)Fe$_2$(CO)$_6$	yellow	121	270.5 d (128), 145.7 dd (398, 128)	2050 m, 2012 s, 1987 s, 1977 m, 1962 s, 1952 m
(*i*-Pr$_2$NPOEt)(*i*-Pr$_2$NPH)Fe$_2$(CO)$_6$	yellow	114	264.4 d (127), 146.1 dd (398, 127)	2055 m, 2015 s, 1987 s, 1977 m, 1961 s, 1954 m
(*i*-Pr$_2$NPBr)(HPBr)Fe$_2$(CO)$_6$[f]	orange	119	242.1 d (136), 151.1 dd (418, 136)	2080 s, 2045 s, 2026 s, 2002 s, 1993 s
(*i*-Pr$_2$NPHCHPN-*i*-Pr$_2$)Fe$_2$(CO)$_6$	orange	97	173.7 d (100), 7.7 dd (420, 100)	2050 m, 2007 s, 1980 s, 1968 m, 1955 m
(*i*-Pr$_2$NP)$_2$CHOHFe$_2$(CO)$_6$[g]	yellow	125 dec	169.4 s	2050 m, 2007 s, 1995 s, 1959 m, 1945 m

[a] Key: *i*-Pr = isopropyl, Cx = cyclohexyl, Me = methyl, Et = ethyl. [b] All compounds listed here gave excellent C, H, N, and, where applicable, Br analyses. [c] CDCl$_3$ solutions without proton decoupling to measure $|^1J(P-H)|$; s = singlet, d = doublet, dd = double doublet. Coupling constants in Hz are given in parentheses. [d] Hexane solutions. [e] P–C(O)–P ν(CO) frequency. [f] Before the final crystallization a second stereoisomer of (*i*-Pr$_2$NPBr)(HPBr)Fe$_2$(CO)$_6$ was detected by ^{31}P NMR: δ 273.0 d (91), 167.3 dd (440, 91). [g] ν(OH) = 3450 cm^{-1} in Nujol.

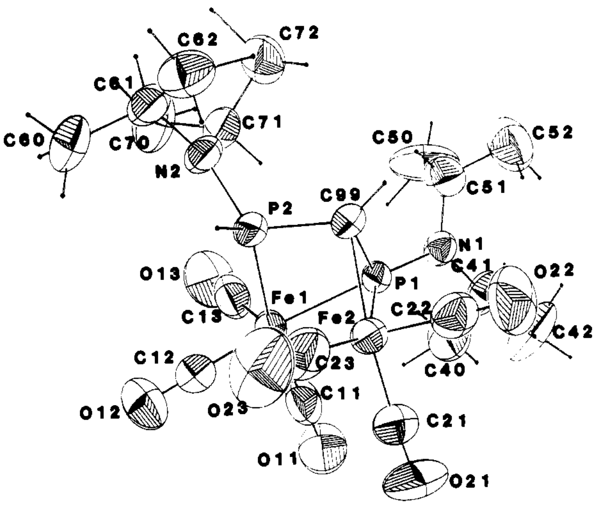
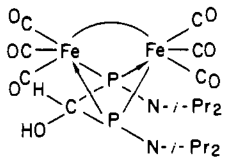


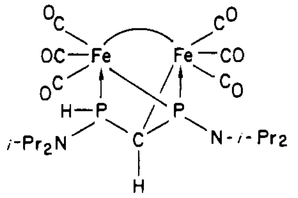
Figure 2. ORTEP diagram of (*i*-Pr$_2$NPHCHPN-*i*-Pr$_2$)Fe$_2$(CO)$_6$ (V).

hydrogen bromide in hexane follows a similar course except the more strongly acidic reagent also cleaves one of the diisopropylamino groups to give (*i*-Pr$_2$NPBr)(HPBr)Fe$_2$(CO)$_6$ (III). In this case the phosphorus-31 NMR spectrum indicates two stereoisomers in the crude product, one of which could be isolated pure by careful crystallization.

The reduction of the phosphorus-bridged carbonyl group in (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with hydridic reducing agents is of particular interest. The initial product, formed, for example, by using NaBH$_4$ in methanol, appears to be the expected alcohol (*i*-Pr$_2$NP)$_2$CHOHFe$_2$(CO)$_6$ (IV). Reduction of (*i*-Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with LiAlH$_4$ in diethyl ether forms not only this product but also (*i*-Pr$_2$NPHCHPN-*i*-Pr$_2$)Fe$_2$(CO)$_6$ (Table I), the structure of which has been determined by X-ray diffraction;[10] see Figure 2.



IV



V

In the conversion I (R = isopropyl) to V the iron–iron bond lengthens slightly (Fe–Fe = 2.726 (2) Å), an iron-phosphorus bond is broken, and an iron–carbon bond is formed. Related rearrangements have been observed in reactions of CH$_2$S$_2$Fe$_2$(CO)$_6$ with lithium diisopropylamide[11,12] and C$_6$H$_4$(CH$_2$PPh)$_2$Fe$_2$(CO)$_6$ with *n*-butyllithium.[13]

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work at the University of Georgia under Grant AFOSR-84-0050.

Supplementary Material Available: Tables of positional parameters, anisotropic thermal parameters, and bond angles and distances for Fe$_2$(CO)$_6$(*i*-Pr$_2$NP)$_2$(CO) and Fe$_2$(*i*-Pr$_2$NPH)(*i*-Pr$_2$NP)(CO)$_6$(CH) (11 pages). Ordering information is given on any current masthead page.

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(10) Crystal data for (*i*-Pr$_2$NPHCHPN-*i*-Pr$_2$)Fe$_2$(CO)$_6$ (V). Fe$_2$C$_{19}$H$_{30}$N$_2$O$_6$P$_2$, M_r 556.10, triclinic crystals, space group $P\bar{1}$; a = 14.412 (6) Å, b = 10.409 (5) Å, c = 10.014 (4) Å, α = 111.80 (3)°, β = 82.19 (3)°, γ = 106.86 (4)°, V = 1334.1 (9) Å^3, D_{calcd} = 1.384 g/cm^3, Z = 2, anisotropic least-squares refinement (Mo Kα radiation, μ(Mo Kα) = 12.37 cm^{-1}, $F(000)$ = 576, 3585 observed reflections, R = 0.057, R_w = 0.059).

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Influence of the Lone-Pair Electrons on the Stability of the Oxygenated Complex of Heme

Sir:

The remarkable stability of oxymyoglobin and oxyhemoglobin has been attributed to hydrogen bonding, a low dielectric constant, and acidity about the heme.[1-5] However, the influence of lone-pair electrons of imidazole on the stability of the oxygenated complex of heme has not been studied, though the imidazole contained in the distal histidine residue has the lone-pair electrons. In order to probe the effect of lone-pair electrons, two models of porphyrins were synthesized and the stabilities of their oxygenated complexes were examined. In consequence, it is clarified that the stability of the oxygenated complex is affected by lone-pair electrons on nitrogen atom.

The first model, bipyridine–porphyrin, includes the chain bridged between opposite meso phenyl groups, and the bipyridine moiety is inserted within this chain. The length (four atoms) of chain bridged between bipyridine and meso phenyl groups is very short. Thus, it is expected that a strong interaction between

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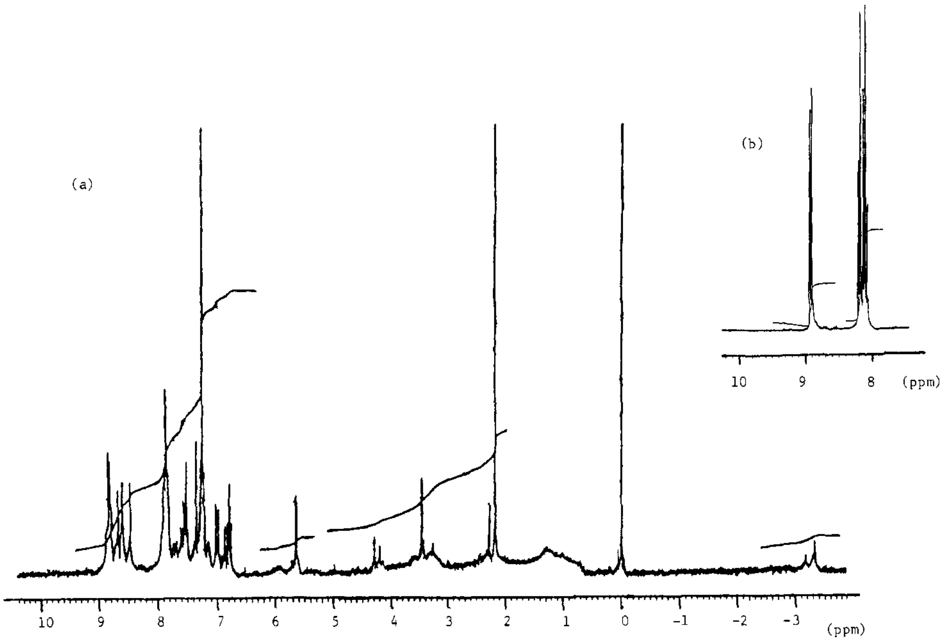
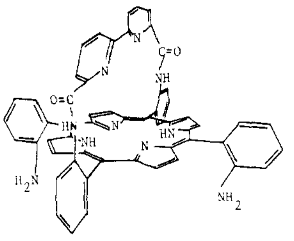
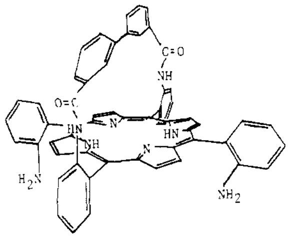


Figure 1. ^{1}H NMR spectra (270 MHz) of bipyridine–porphyrin (a) and bipyridine diacid chloride (b) in $CDCl_3$.

lone-pair electrons on nitrogen atoms of bipyridine and dioxygen atoms coordinated to the Fe atom in the porphyrin skeleton would occur. In addition, the bipyridine moiety in this model is perpendicular to the plane of the porphyrin skeleton, and the lone-pair electrons direct to the porphyrin skeleton. Then, it seems that the cavity constructed by the bipyridine moiety and the porphyrin skeleton is the smallest among the synthetic cyclophane porphyrins reported already. The structure of another model, biphenyl–porphyrin, is almost the same as that of bipyridine–porphyrin. The only difference is that bipyridine–porphyrin has N atoms at the 2,2′-positions and biphenyl–porphyrin has two C–H atoms.



bipyridine–porphyrin



biphenyl–porphyrin

Bipyridine–porphyrin was synthesized from the coupling reactions of bipyridine diacid chloride[6] with *α,β,α,β-meso*-tetrakis(*o*-aminophenyl)porphyrin under high-dilution conditions.[7,8] Three products were gained by this coupling reaction. The two main products are trans and cis isomers of bipyridine–porphyrin, because the parent peaks (882) of their FD mass spectra are the same. Another product is bis(bipyridine)–porphyrin, which was also assigned by FD mass spectroscopy. The total yield containing trans and cis isomers was 34.4%. The detailed single-crystal structure determinations of both isomers by X-ray diffraction are in progress. ^{1}H NMR (270 MHz, JEOL GX270) and FT-infrared (DIGILAB) spectra of the isomer that moves faster in TLC (silica gel) were measured. As shown in Figure 1, the protons of the bipyridine moiety were found at 4.1–4.4 ppm (2 H, neighboring C=O groups) and 2.1–2.4 ppm (4 H), shifted ($\Delta\delta$ = 4.3–5.7) upfield from the signals of the bipyridine dimethyl ester. This assignment is confirmed by the ^{1}H NMR spectrum of the bipyridine diacid chloride (8.9 ppm, 2 H, doublet; 8.05–8.3 ppm, 4 H, multiplet).[9] The inner protons of porphyrin appear at –3.1 to –3.3 ppm, this shifted upfield from those of the starting porphyrin. These pyrrolic protons show two unsymmetric peaks, probably due to the interaction between the nitrogen atoms of bipyridine and the inner hydrogen atoms or the flapping motions of the bipyridine moiety on the porphyrin skeleton. Thus, it seems that the distance between the lone-pair electrons of nitrogens atoms of bipyridine and the inner hydrogen atoms is very short. However, when the iron was inserted into this porphyrin, two kinds of complexes were formed; one of the complexes was the porphyrin–Fe complex and another was the bipyridine–Fe complex. TLC (silica gel) shows a clear single spot, indicating pure bipyridine–porphyrin. The ν(C=O) stretching band of the amide group appears at 1690 cm^{-1}, indicating the amide carbonyl of the ring structure. The NMR, IR, and mass data of the other isomer, which moves slower in TLC, are almost the same, except for the ^{1}H NMR peaks of the bipyridine moiety at 3.5–4.5 ppm. The synthesis of biphenyl–porphyrin was performed by similar coupling reaction of the biphenyl diacid chloride with the porphyrin. The data of spectroscopic measurements gave the same tendency as the case of bipyridine–porphyrin (upfield shift, $\Delta\delta$ = 4.5–5.7). However, the ^{1}H NMR spectrum of the inner protons shows a broad peak.

The structure of the CPK model of bipyridine–porphyrin suggests that the cavity between porphyrin and bipyridine moieties is small enough for lone-pair electrons of the bipyridine moiety to interact with dioxygen atoms coordinated to Fe. The Fe(III) complex of bipyridine–porphyrin that moves faster in TLC (one isomer) was reduced in purified DMF with 1 M *N*-methylimidazole by sodium dithionite under argon.[10] It was very hard to reduce this complex without *N*-methylimidazole in DMF. Thus, it seems to be firm that the unligated iron(II) complex is titrated by *N*-methylimidazole. In the presence of excess *N*-methylimidazole (1 M) in purified DMF, the Fe(II) complex of bipyridine–porphyrin exhibits peaks at 433.8 and 534.3 nm (broad), indicating it to be five-coordinate. This complex reversibly binds O_2 at 25 °C, and the electronic spectrum of this oxygenated

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(9) Assignment of other peaks: 8.4–9.00 ppm multiplet, pyrrole protons of porphyrin skeleton; 6.7–8.00 ppm multiplet, phenyl groups of porphyrin skeleton; 5.5–6.0 ppm, NH of amide of bridge; 3.1–3.7 ppm, NH_2 of phenyl group, When pivaloyl chloride was added to the methylene chloride solution of bipyridine–porphyrin, these peaks disappeared; 0.5–1.5 ppm, impurity hydrocarbon.

(10) The properties of both isomers are almost the same.

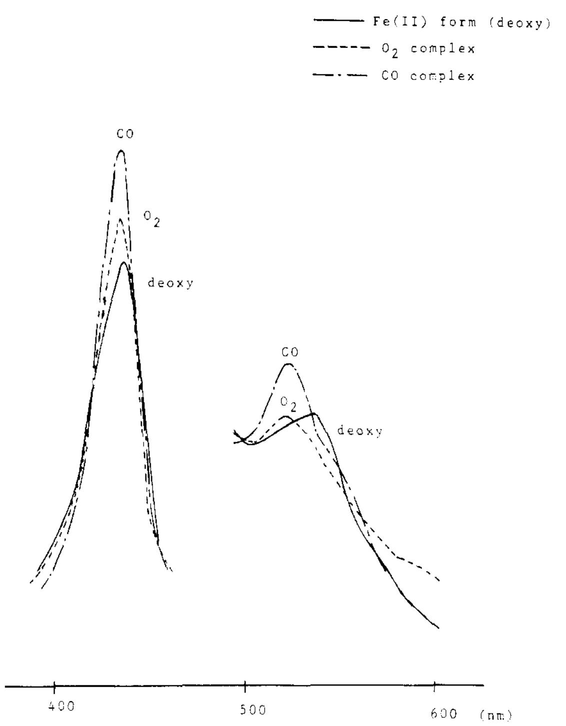

Figure 2. Absorption spectra of O_2 and CO adducts of the Fe^{II}–(bipyridine–porphyrin) complex with *N*-methylimidazole in DMF at 25 °C.

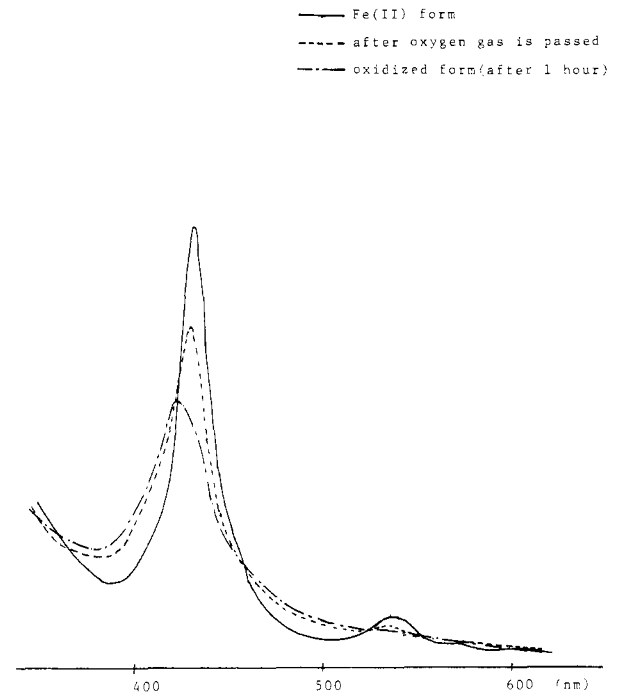

Figure 3. Absorption spectra of Fe complex of biphenyl–porphyrin with *N*-methylimidazole in DMF at 25 °C.

complex shows peaks at 430 and 520 nm. The oxygen atoms of this oxygenated complex were easily replaced by carbon monoxide, as shown in Figure 2. When oxygen gas was passed through the solution containing CO complex again, its visible spectrum is almost the same as that of the oxygenated complex, indicating the formation of the O_2 complex. This property is very similar to 7,7-anthracene cyclophane heme, which was prepared by us already.[3,7] The visible spectra of the O_2 and CO adducts are very broad. Probably, the cause of broadened peaks would come from the small cavity and the influence of lone-pair electrons. Thus, it seems that the O_2 or CO adducts of one species are formed in solution.

The ν(C=O) stretching band of the CO complex in the presence of 1 M *N*-methylimidazole was measured by using a Fourier transform infrared spectrometer, and its value in cyclohexane is 2044 cm^{-1}. We do not have any explanation for this higher frequency.[11]

The striking result is the extreme stability of the oxygenated complex at room temperature. Though there is a possibility that the lone-pair electrons of coordinated dioxygen atoms interact with those on the nitrogen atoms of the bipyridine moiety, the oxygenated species are very stable ($T_{1/2} > 6$ h). In order to confirm the effect of lone-pair electrons, the Fe(III) complex of biphenyl–porphyrin was reduced under the same conditions as in the case of (bipyridine–porphyrin)–Fe complex, and the oxygen gas was passed through the solutions of the Fe(II) complex of biphenyl–porphyrin. However, the oxygenated complex was not formed, and its Fe(II) complex was oxidized directly as shown in Figure 3. In addition, measurements of ν(C=O) stretching band of (biphenyl–porphyrin)–Fe^{II}–CO complex in cyclohexane were performed, but results were not gained due to the instability of its complex.

Though it was reported that the oxygenated complex is stabilized by hydrogen bonds between imidazole and dioxygen atoms,[12] these results suggest that the stability of the oxygenated complex is also affected by the lone-pair electrons on the nitrogen atoms.

Acknowledgment. I am grateful to Professor T. G. Traylor for helpful discussions.

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Magnetic Susceptibility as a Probe of the Solid–Discotic Phase Transition in Binuclear Copper(II) *n*-Alkanoates

Sir:

The distinctive physical properties of thermotropic mesogens (i.e. compounds that exhibit liquid crystalline behavior above a given temperature) are usually characterized by using methods such as hot-stage optical microscopy, differential scanning calorimetry, or X-ray diffraction.[1] Recent progress in the synthesis of mesogenic compounds includes the preparation of square-planar transition-metal complexes with various patterns of alkyl chain peripheral substitution. Upon heating, these give rise to nematic, smectic, or discotic mesophases, depending on chain length and core symmetry.[2–20] As yet, little attention has been paid, however,

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