value of K, from eq 20, for each experiment by an iterative procedure that minimizes the expression (experimental $[Co^{3+}]_0$ − calculated $[Co^{3+}]_0$). The results are listed in Table III, and the values of K are reasonably constant over a moderately extensive range of experimental conditions. For comparison, the values of calculated $[VO^{2+}]_\infty$ computed from eq 21 and the best value of K are listed also. The calculated values are systematically high. Much of the discrepancy can be attributed to experimental error in the determination of $[VO^{2+}]_\infty$, but also the uncertainty in the determination of K is probably larger than the indicated average uncertainty.

The kinetic results allow an independent estimate of k_6/k_5, and the results are summarized in the last column of Table V. The value of 0.13_6 obtained in 1.0 M $HClO_4$ at 20.0 °C compares favorably with the value of 0.12 obtained in the stoichiometric experiments under the same conditions.

The rate constants for the oxidation of VO_3^+ and H_2O_2[2d] by cobalt(III) are 10.3 and 11.5 $M^{-1}\ s^{-1}$, respectively, in 3.0 M $HClO_4$ at 20.0 °C. However, the H_2O_2 reaction is carried almost exclusively by $CoOH^{2+}$, whereas both Co^{3+} and $CoOH^{2+}$ appear to be reactive toward VO_3^+.[15] The composite activation parameters in 1.0 M $HClO_4$ for the VO_3^+ system are $\Delta H^{\ddagger} = 17._6$ kcal/mol and $\Delta S^{\ddagger} = 6$ cal/(deg mol).

It should be noted that the only fate of the $VO_3^{2+}\cdot$ intermediate in the proposed schemes is an internal oxidation–reduction reaction. It is important to consider the validity of this assumption since the major theme of this study is to utilize the subsequent formation of VO^{2+} as a diagnostic probe in future studies for a distinction between one- and two-electron oxidations of the complexed peroxide moiety. One alternative reaction of $VO_3^{2+}\cdot$ is dissociation to form uncomplexed $HO_2\cdot$. If this did occur, then disproportionation of the HO_2 or oxidation by HSO_5^-, Co^{3+}, or VO_2^+ would be anticipated. Our results would require effective oxidation by VO_2^+. This seems unlikely, especially in the Co^{3+} system, and further some dependence on the $[VO_2^+]$ should be seen. There is no experimental indication of this. Alternatively, oxidation of VO_3^{2+} by HSO_5^- or Co^{3+} can at least be rejected as an important process in our experiments. Finally, while we have obtained no evidence that the internal oxidation–reduction reaction of $VO_3^{2+}\cdot$ obeys first order kinetics, this is certainly the simplest assumption.

The present results thus appear to demonstrate the facile formation and clean decomposition of the intermediate $VO_3^{2+}\cdot$. The evidence is indirect in that we have relied on stoichiometric and kinetic consequences of the formation of VO^{2+}, but ESR experiments may provide more direct verification. The primary mode of oxidation of VO_3^+ is a one-electron process even with HSO_5^-. It will be interesting to see if a similar mechanism is also found with more obdurate 2-equiv oxidants. In any event, the use of peroxo complexes appears to hold promise as a means of distinguishing between one- and two-electron oxidations of the peroxide moiety.

Registry No. VO_3^+, 12179-36-1; HSO_5^-, 12188-01-1; Co, 7440-48-4; VO^{2+}, 20644-97-7.

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Carbon Monoxide Affinities of Iron(II) Octaethylporphyrin, Octaethylchlorin, and Octaethylisobacteriochlorin

S. H. STRAUSS[1] and R. H. HOLM*

Received June 30, 1981

As part of continuing research directed at the elucidation of comparative structural, electronic, and reactivity properties of iron(II,III) porphyrins and hydroporphyrins, the CO binding constants for the reactions

$$Fe(P) + CO \xrightleftharpoons{K_1} Fe(P)(CO)$$

$$Fe(P)(CO) + CO \xrightleftharpoons{K_2} Fe(P)(CO)_2$$

have been determined in toluene solutions at 20.0 ± 0.2 °C. For both reactions P = octaethylporphyrin (OEP), octaethylchlorin (OEC), and octaethylisobacteriochlorin (OEiBC) dianions. Iron complexes of the latter two macrocycles serve as synthetic representations of the heme *d* and siroheme prosthetic groups of nitrite and sulfite reductases. Constants were determined by least-squares analysis of visible absorbance/p_{CO} data based on a four-parameter model. The individual Fe(P)(CO) and $Fe(P)(CO)_2$ complexes were detected in dichloromethane solutions by infrared spectroscopy. Values of K_1 and K_2 exhibit the trend OEP < OEC < OEiBC, with those of K_2 (0.0022, 0.0073, 0.029 $torr^{-1}$) being more variant with macrocycle structure than those of K_1 (0.31, 0.43, 0.74 $torr^{-1}$). The greater relative stability of $Fe(OEiBC)(CO)_2$ among $Fe(P)(CO)_2$ complexes is the most prominent difference in species equilibrium distribution as dependent on P. However, for each reaction differences in ΔG as P is varied are $\lesssim 1.5$ kcal/mol, making it difficult to identify the factors responsible for trends in K_1 and K_2. Certain of these possible factors are briefly considered.

Introduction

The accelerating interest in the chemistry of hydroporphyrins derives in large measure from the detection of reduced heme prosthetic groups in a variety of enzymes. As prime examples, dissimilatory nitrite reductases contain heme *d*,[2] a Fe chlorin complex, and assimilatory forms of this enzyme and assimilatory and dissimilatory sulfite reductases incorporate as a common prosthetic group siroheme.[3-11] The latter

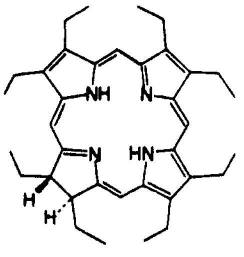
---

(1) National Institutes of Health Postdoctoral Fellow, 1979–1980.

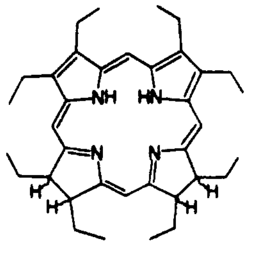
(2) Walsh, T. A.; Johnson, M. K.; Thomson, A. J.; Barber, D.; Greenwood, C. *J. Inorg. Biochem.* **1981**, *14*, 1. Horie, S.; Watanabe, T.; Nakamura, S. *J. Biochem.* **1976**, *80*, 579. Gudat, J. C.; Singh, J.; Wharton, D. C. *Biochim. Biophys. Acta* **1973**, *292*, 376. Iwasaki, H.; Matsubara, T. *J. Biochem.* **1971**, *69*, 847. Newton, N. *Biochim. Biophys. Acta* **1969**, *185*, 316. Yamanaka, T. *Nature (London)* **1964**, *204*, 253. Yamanaka, T.; Okunuki, K. *Biochim. Biophys. Acta* **1963**, *67*, 379, 394, 407.

0020-1669/82/1321-0863$01.25/0

is a Fe complex of the structurally defined[12] isobacteriochlorin sirohydrochlorin. In previous studies[13-15] we have detailed the spectroscopic and oxidation–reduction properties of certain hydroporphyrins, utilizing octaethylchlorin (**1**, H_2(OEC)) and octaethylisobacteriochlorin (**2**, H_2(OEiBC)) as synthetic representations of the difficultly accessible native macrocycles. It is reasonably well established that the reduced hemes act as substrate binding and catalytic centers in these enzymes and that the six-electron reductions $NO_2^- \rightarrow NH_3$ and $SO_3^{2-} \rightarrow S^{2-}$ are not known to occur at conventional heme prosthetic groups in other enzymes. Therefore, we have been particularly interested in uncovering any properties of macrocycle reduction level in the series porphyrin–chlorin–isobacteriochlorin that would render the derived Fe complexes, especially those of isobacteriochlorins, relatively more effective in catalyzing multielectron substrate reductions.



1



2

In a recent extensive study of comparative properties of $Fe^{II,III}$(OEP), -(OEC), and -(OEiBC) complexes,[15] only one feature of possible significance to biological substrate transformation emerged: the markedly greater ease of ring-based oxidations of Fe(OEiBC) species, raising the prospect of a functional role of the siroheme macrocycle as an electron carrier. From detailed experimental results and theoretical electronic structure calculations,[16-19] other investigators have independently raised equivalent implications for siroheme, using different model hydroporphyrins[20] as the basis for experimental work. As yet there is no direct evidence bearing on this matter.

In further pursuing intrinsic differences among members of iron porphyrin–chlorin–isobacteriochlorin series of complexes, we have turned our attention to reactivity properties (other than redox potentials, already investigated[14,15]). We had previously observed[15] that, among such properties, the rate of H_2P[21] metallation increases in the order OEP < OEC < OEiBC and that the affinities of Fe^{II}(P) complexes for carbon monoxide qualitatively differ. In this initial investigation of relative reactivity properties of Fe porphyrin and hydroporphyrin complexes, equilibrium constants for CO binding to Fe(OEP), Fe(OEC), and Fe(OEiBC) have been determined. Although CO is widely used as a reactivity and electronic structural probe with synthetic and natural hemes,[22-24] there have been only two prior reports[25,26] describing CO binding constants of four-coordinate iron(II) porphyrins. In the present work the experimental conditions used by Wayland et al.[26] in their investigation of the iron(II) tetraphenylporphyrinate (Fe(TPP))/CO system have been employed in order to afford an additional comparison with that system.

Experimental Section

Reagents and Solvents. Benzene, toluene, and hexane were distilled from sodium–potassium alloy, dichloromethane was distilled from CaH_2, and ethanethiol (Aldrich) was dried over 4-Å molecular sieves and then distilled in vacuo. These compounds were stored under argon prior to use. Carbon monoxide (Matheson Purity) and 5.1% carbon monoxide in dinitrogen (Matheson Purity, 2 ppm dioxygen by direct measurement) were used as received.

In the following preparations, physical measurements, and associated manipulations, all operations were executed with rigorous exclusion of dioxygen and water. Schlenk and high-vacuum-line techniques were employed, with purified argon used when an inert atmosphere was required.

Iron(II) Porphyrin and Hydroporphyrins. Crystalline Fe(OEP) and lyophilized powders of Fe(OEC) and Fe(OEiBC) were prepared by published procedures.[15] Crystalline Fe(OEC) was obtained by slow diffusion of an equal volume of hexane into a 10 mM solution of the compound in 9:1 v/v benzene/ethanethiol. The crystals were collected, washed three times with hexane, and dried in vacuo. Lyophilized and crystalline samples contained ~3% Fe(OEP) contaminant by ^{1}H NMR analysis; both samples were used in CO-binding studies. The ^{1}H NMR spectra of Fe(OEiBC) preparations did not give detectable signals from Fe(OEP) or Fe(OEC), whose sharp, paramagnetically shifted spectra[15,27] are quite characteristic.

Because of the extreme sensitivity of Fe(P) compounds to traces of dioxygen[28] (reaction 1), stock solutions (~1 mM) were prepared

$$2Fe(P) + {}^1/_2O_2 \rightarrow [Fe(P)]_2O \qquad (1)$$

in 95:5 v/v benzene/ethanethiol, in which oxidation is suppressed by reaction 2.[15] Even after several weeks of storage at ambient temperature, no $[Fe(P)]_2O$ formation could be detected by spectrophotometry. By series of ^{1}H NMR and spectrophotometric experiments it has been shown that ethanethiol, diethyl disulfide, and water coordinate very weakly, if at all, to Fe(P) in benzene and toluene

$$[Fe(P)]_2O + 2EtSH \rightarrow 2Fe(P) + EtSSEt + H_2O \qquad (2)$$

---

(3) Murphy, M. J.; Siegel, L. M.; Kamin, H.; Rosenthal, D.; *J. Biol. Chem.* **1973**, *248*, 2801.

(4) Murphy, M. J.; Siegel, L. M. *J. Biol. Chem.* **1973**, *248*, 6911.

(5) Murphy, M. J.; Siegel, L. M.; Tove, S. R.; Kamin, H. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 612.

(6) Vega, J. M.; Garrett, R. H.; Siegel, L. M. *J. Biol. Chem.* **1975**, *250*, 7980.

(7) Hucklesby, D. P.; James, D. M.; Banwell, M. J.; Hewitt, E. J. *Phytochemistry* **1976**, *15*, 599.

(8) Vega, J. M.; Kamin, H. *J. Biol. Chem.* **1977**, *252*, 896.

(9) Siegel, L. M.; Murphy, M. J.; Kamin, H. *Methods Enzymol.* **1978**, *52*, 436.

(10) Siegel, L. M. In "Mechanisms of Oxidizing Enzymes"; Singer, T. P., Ondarza, R. N., Eds.; Elsevier-North Holland: New York, 1978; pp 201–214.

(11) Christner, J. A.; Münck, E.; Janick, P. A.; Siegel, L. M. *J. Biol. Chem.* **1981**, *256*, 2098.

(12) Scott, A. I.; Irwin, A. J.; Siegel, L. M.; Shoolery, J. N. *J. Am. Chem. Soc.* **1978**, *100*, 316, 7987.

(13) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 364.

(14) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Chem. Soc., Chem. Commun.* **1979**, 1077.

(15) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763.

(16) Richardson, P. F.; Chang, C. K.; Hanson, L. K.; Spaulding, L. D.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3420.

(17) Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1980**, *102*, 848.

(18) Richardson, P. F.; Chang, C. K.; Spaulding, L. D.; Fajer, J. *J. Am. Chem. Soc.* **1979**, *101*, 7736.

(19) Chang, C. K.; Hanson, L. K.; Richardson, P. F.; Young, R.; Fajer, J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2652.

(20) Chang, C. K. *Biochemistry* **1980**, *19*, 1971.

(21) Here and elsewhere P represents, as appropriate, any or all of the dianions $(OEP)^{2-}$, $(OEC)^{2-}$, or $(OEiBC)^{2-}$.

(22) Alben, J. O. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 7.

(23) Collman, J. P.; Halbert, T. R.; Suslick, K. S. In "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980; Chapter 1.

(24) Traylor, T. G. *Acc. Chem. Res.* **1981**, *14*, 102.

(25) (a) Rougee, M.; Brault, D. *Biochem. Biophys. Res. Commun.* **1973**, *55*, 1364; (b) Rougee, M.; Brault, D. *Biochemistry* **1975**, *14*, 4100.

(26) Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379.

(27) Goff, H.; LaMar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641.

(28) As an example of the sensitivity of these compounds to dioxygen, dilute solutions (~0.1 mM) of Fe(P) in toluene showed extensive conversion to $[Fe(P)]_2O$ after several hours of exposure to an argon atmosphere containing <0.5 ppm O_2.

Table I. Least-Squares Parameters for Equation 8

	K_1,^{a} torr^{-1}	10^3K_2,^{a} torr^{-1}	ϵ_1, M^{-1} cm^{-1}	ϵ_2, M^{-1} cm^{-1}
Fe(OEP)^b				
$\lambda = 546.0$ nm $\epsilon_0 = 7400$ M^{-1} cm^{-1}	0.31 ± 0.05	2.2 ± 1.0	24 500 ± 600	12 200 ± 2500
Fe(OEC)				
$\lambda = 613.5$ nm $\epsilon_0 = 19\,900$ M^{-1} cm^{-1}	0.43 ± 0.17	7.3 ± 0.7	32 500 ± 1300	72 000 ± 700
Fe(OEiBC)				
$\lambda = 593.5$ nm $\epsilon_0 = 8200$ M^{-1} cm^{-1}	0.74 ± 0.14	29 ± 4	19 100 ± 900	31 600 ± 200

[a] $K_{1,2}$ (torr^{-1}) = $K_{1,2}$ (M^{-1})/(1.05 × 10^5), from Henry's constant for CO in toluene at 20 °C ($K_h = 9.87 \times 10^5$) evaluated from solubility data (Just, G. *Z. Phys. Chem.* (*Leipzig*) **1901**, *37*, 342). [b] When the data of Wayland et al.[26] for the Fe(TPP)/CO/toluene system at 20 °C are analyzed by the present procedure, the following results are obtained: $K_1 = 0.63 \pm 0.37$, $10^3K_2 = 1.9 \pm 2.1$ torr^{-1}; $\epsilon_1 = 12\,800 \pm 600$, $\epsilon_2 = 6100 \pm 3600$ M^{-1} cm^{-1}. The reported results are $K_1 = (6.6 \pm 0.3) \times 10^4$, $K_2 = 140 \pm 3$ M^{-1}; $\epsilon_1 = 12\,442$, $\epsilon_2 = 4914$ M^{-1} cm^{-1}. When expressed in pressure units for comparison with the above data, $K_1 = 0.63 \pm 0.03$ and $10^3K_2 = 1.33 \pm 0.03$ torr^{-1}.

solutions. For example, the visible spectrum of all three Fe(P) species undergo negligible changes upon addition of 100-fold molar excess of ethanethiol. Further, when all volatiles are removed under high vacuum from these solutions and the solid residues are redissolved in toluene, the visible and ^{1}H NMR spectra of the solutions are identical in every feature with those obtained from samples that have never been treated with ethanethiol.[15] The absence of resonances due to free ethanethiol in these NMR spectra places an upper limit of ~1% of the concentration of Fe(P). Consequently, the Fe(P) samples used in the experiments described below contain inconsequential amounts of axially ligated species.

Infrared Measurements. The general procedures used are described elsewhere.[15] Dichloromethane was vacuum distilled into the reservoir of a Schlenk infrared solution cell (KBr, 0.2-mm path length). The reservoir, previously charged with solid Fe(P), was maintained at −196 °C while 300 ± 10 torr of CO was added. The frozen mixture was warmed to ambient temperature, and the infrared spectrum of the solution was recorded on a Nicolet 7199 FT spectrometer.

Evaluation of Carbon Monoxide Binding Constants. The stepwise binding of CO to Fe(P) is described by the following reactions and equilibrium quotients:

$$\mathrm{Fe(P)} + \mathrm{CO} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{Fe(P)(CO)} \tag{3}$$

$$K_1 = [\mathrm{Fe(P)(CO)}]/[\mathrm{Fe(P)}]p_{\mathrm{CO}} \tag{4}$$

$$\mathrm{Fe(P)(CO)} + \mathrm{CO} \overset{K_2}{\rightleftharpoons} \mathrm{Fe(P)(CO)_2} \tag{5}$$

$$K_2 = [\mathrm{Fe(P)(CO)_2}]/[\mathrm{Fe(P)(CO)}]p_{\mathrm{CO}} \tag{6}$$

Reactions in toluene solutions were monitored spectrophotometrically in the visible region with those wavelengths, specified in Table I, at which the absorbances varied the most as the predominant solution species changed from Fe(P) to Fe(P)(CO) to Fe(P)(CO)$_2$. All measurements were made on a Cary Model 219 spectrophotometer. Aliquots of stock solutions of Fe(P) in 95:5 v/v benzene/ethanethiol were transferred to an evacuable quartz Schlenk cell (0.2-cm path length). All volatiles were removed under high vacuum (<10^{-5} torr), and toluene was vacuum distilled onto the solid residue. This procedure results in solutions of Fe(P) containing negligible amounts of [Fe(P)]$_2$O, ethanethiol, diethyl disulfide, and water. Prior to the introduction of CO, it was determined that Beer's law holds over the concentration ranges used to determine K_1 and K_2: Fe(OEP), 0.079–0.507; Fe(OEC), 0.061–0.389; Fe(OEiBC), 0.075–0.511 mM. Carbon monoxide was added to the solutions as follows. The cell, containing ~2–3 mL of solution and a volume of ~25 mL above the solution, was attached to a Hg-filled tensimeter[29] on a high-vacuum line and was thermostated to 20.0 ± 0.2 °C. Carbon monoxide was admitted to the cell-tensimeter assembly from an external storage bulb. The pressure in the assembly, $p_{\mathrm{CO}} + p_{\mathrm{toluene}}$ (22.4 torr, 20 °C), was measured with a Gaertner cathetometer. In several experiments a gas mixture of 5.1% CO in N$_2$ was used. Because the dissolved gases represent a small percentage (<0.5%) of the total gas in the system, and because the solubilities of CO and N$_2$ in aromatic hydrocarbons are similar,[30] the CO pressure is given by $p_{\mathrm{CO}} = 0.051(p_{\mathrm{total}} - 22.4)$ (torr).

Data Analysis. From the Beer–Lambert law the absorbance A at a specified wavelength is given by eq 7, which is expressible as a

$$A = \epsilon_0 l[\mathrm{Fe(P)}] + \epsilon_1 l[\mathrm{Fe(P)(CO)}] + \epsilon_2 l[\mathrm{Fe(P)(CO)_2}] \tag{7}$$

function of p_{CO} by eq 8. A_0 is the absorbance of the solution in the

$$\frac{A - A_0}{[\mathrm{Fe}]l} = \frac{(\epsilon_1 - \epsilon_0)p_{\mathrm{CO}}K_1 + (\epsilon_2 - \epsilon_0)p_{\mathrm{CO}}{}^2K_1K_2}{1 + p_{\mathrm{CO}}K_1 + p_{\mathrm{CO}}{}^2K_1K_2} \tag{8}$$

absence of CO, [Fe] is the total concentration of Fe(II) species, l is the cell path length, and ϵ_0, ϵ_1, and ϵ_2 are the molar extinction coefficients of Fe(P)(CO)$_n$, $n = 0$–2, respectively. This expression is equivalent to that employed by Wayland et al.[26] for the Fe(TPP)/CO system. Values of ϵ_0 for the three Fe(P) species have been directly measured.[15] The four unknown parameters ϵ_1, ϵ_2, K_1, and K_2 were determined by fitting the A vs. p_{CO} data to eq 8 with use of a version of the Oak Ridge Gaussian least-squares program (ORGLS).[31] Because solutions containing only Fe(P)(CO) or Fe(P)(CO)$_2$ could not be obtained, ϵ_1 and ϵ_2 were not measured directly. From the indicated number of experiments, the following number of data (A/p_{CO}) were obtained: Fe(OEP), 5, 28; Fe(OEC), 3, 22; Fe(OEiBC), 4, 22. The results of the ORGLS fits, with errors in K_1, K_2, ϵ_1, and ϵ_2 equal to ±2σ, are given in Table I. Plots of the absorbance function of eq 8 vs. p_{CO} are presented in Figure 1 together with curves generated by inserting the least-squares parameter values of Table I in eq 8. Actual experimental data are collected in Table II (supplementary material[32]).

Results and Discussion

Detection of CO Complexes. In initial experiments direct verification of formation of Fe(P)(CO) and Fe(P)(CO)$_2$ species in the series P = OEP, OEC, and OEiBC was achieved by FT infrared spectral examination of Fe(P) solutions in dichloromethane equilibrated under varying pressures of CO. Shown in Figure 2 are spectra of ~1 mM Fe(P) solutions at 2100–1900 cm^{-1} under an atmosphere of 300 ± 10 torr of CO. Each spectrum contains two bands of different relative intensity. The lower energy features (OEP, OEC, 1951 cm^{-1}; OEiBC, 1956 cm^{-1}) arise from ν_{CO} of Fe(P)(CO).[33] The higher energy bands, at 2016 ± 1 cm^{-1} in the three systems, are assigned to the asymmetric ν_{CO} of Fe(P)(CO)$_2$. These assignments are supported by the observation that A_{2016}/A_{1956}

---

(29) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; pp 58–61.

(30) Linke, W. F.; Seidell, A. "Solubilities of Inorganic and Metal-Organic Compounds"; American Chemical Society: Washington, D.C., 1958: Vol. 1, p 456; Vol. 2, p 585.

(31) Busing, W. R.; Levy, H. A. "ORGLS, A General FORTRAN Least Squares Program"; Oak Ridge National Laboratory: Oak Ridge, TN, 1962; Document ORNL-TM-271.

(32) See paragraph at the end of this article regarding supplementary material.

(33) A value of $\nu_{\mathrm{CO}} = 1975$ cm^{-1} for Fe(OEP)(CO) in benzene has been reported: Yoshida, Z.; Sugimoto, H.; Ogoshi, H. *Adv. Chem. Ser.* **1980**, *No. 191*, 307.

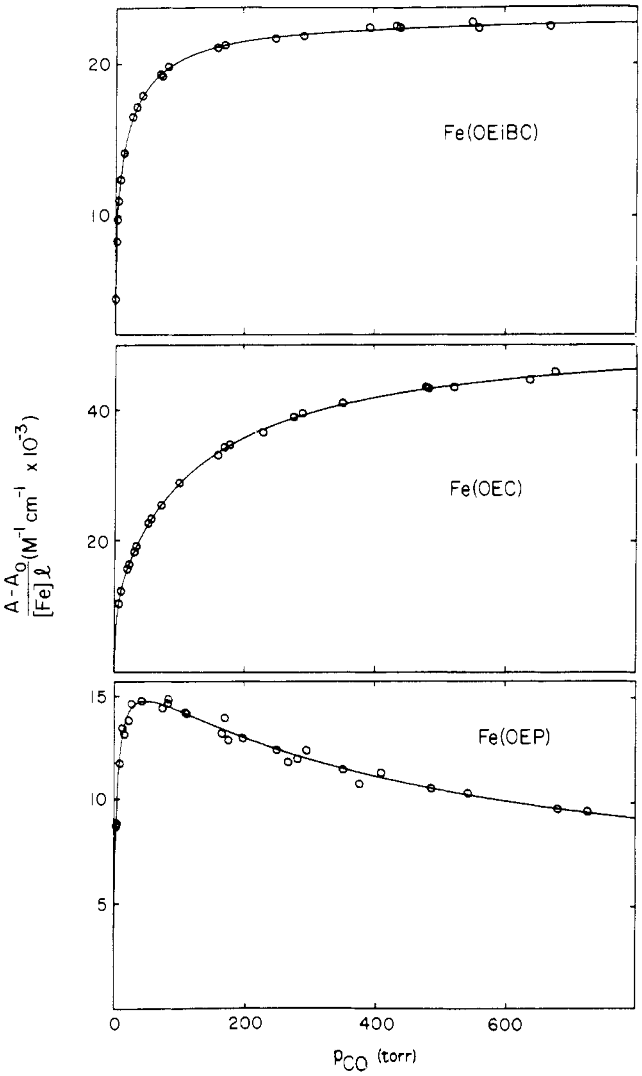


Figure 1. Plots of $(A - A_0)/[Fe]l$ (M^{-1} cm^{-1} $\times$ 10^{-3}, $l = 0.200$ cm, [Fe] = 0.066–0.552 mM) vs. p_{CO} (torr) for toluene solutions of Fe(P) at 20.0 °C. The circles represent experimental data (size is without significance) and the curves are least-squares fits to the data with the assumption of the model in eq 8.

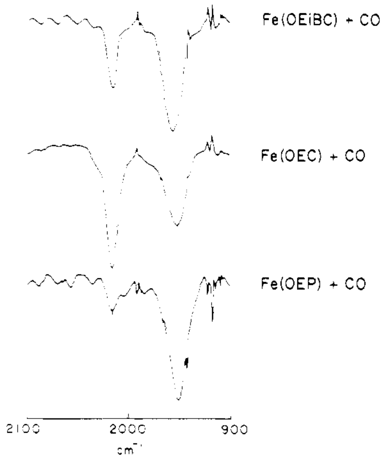


Figure 2. Infrared spectra of ca. 1 mM dichloromethane solutions of Fe(P) under 300 ± 10 torr CO. The intensity of the most intense peak (Fe(OEC) spectrum) is equivalent to ca. 2% transmittance.

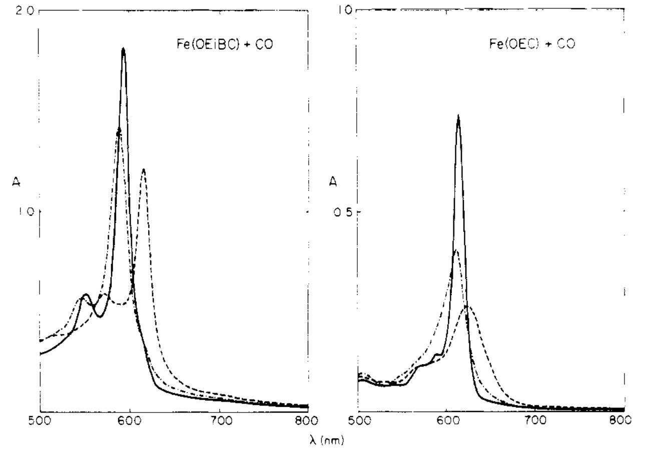


Figure 3. Visible spectra of solutions of Fe(P) in toluene at 20.0 °C under varying pressures of CO. Left: 0.255 mM Fe(OEiBC) at 0 torr (---), at 7.1 torr (-·-; 14% Fe(OEiBC), 71% Fe(OEiBC)(CO), 15% $Fe(OEiBC)(CO)_2$), and at 437 torr CO (—; <0.01% Fe(OEiBC), 7% Fe(OEiBC)(CO), 93% $Fe(OEiBC)(CO)_2$). Right: 0.100 mM Fe(OEC) at 0 torr (---), at 19.1 torr (-·-; 10% Fe(OEC), 79% Fe(OEC)(CO), 11% $Fe(OEC)(CO)_2$), and at 676 torr CO (—; <0.01% Fe(OEC), 17% Fe(OEC)(CO), 83% $Fe(OEC)(CO)_2$). The percentages of species were calculated from K_1 and K_2 in Table I.

for the Fe(OEiBC)/CO system increases as p_{CO} increases and by the expected trans effect of CO which will raise ν_{CO} in $Fe(P)(CO)_2$ vs. Fe(P)(CO). Bands in the Fe(TPP)/CO system in the solid state (1973, 2042 cm^{-1}) have been assigned similarly.[26] The different relative intensities afford the qualitative demonstration that K_2 (OEC, OEiBC) > K_2 (OEP). However, dichloromethane is not a suitable solvent for quantitative determination of CO binding constants. The relatively high vapor pressure of this solvent (~400 torr at 20 °C) precludes the use of CO pressures exceeding about 350 torr. Additionally, Fe(P) complexes slowly react with dichloromethane, producing Fe(III) species including Fe(P)Cl.

Carbon Monoxide Binding Constants. Toluene proved to be a suitable medium for quantitative determination of the binding constants of reactions 3 and 5. The solvent was rigorously dried in order to suppress aquo species, among which $Fe(DPDME)(CO)(H_2O)$ (DPDME = deuteroporphyrin IX dimethyl ester) has been detected.[25] The three Fe(P) species in toluene obeyed Beer's law over the concentration ranges (~0.06–0.5 mM) used in measurements of binding constants, consistent with the presence of monomeric Fe(P) species.[34] Visible spectral changes for toluene solutions of Fe(OEC) and Fe(OEiBC) under varying pressures of CO are presented in Figure 3. The spectral variations in the Fe(OEP)/CO system (not shown) are quite similar to those for the Fe(DPDME)/CO system in benzene.[25a] As the predominant solution species was altered from Fe(P) to Fe(P)(CO) to $Fe(P)(CO)_2$, the following color changes occurred: OEP red, pink, orange; OEC green, blue, green; OEiBC blue-green, purple, burgundy.

Values of the binding constants K_1 and K_2 in pressure units for the Fe(P)/CO systems in toluene are collected in Table I. When expressed in concentration units, $K_1 = (3.3 \pm 0.5) \times 10^4$ M^{-1} and $K_2 = 230 \pm 100$ M^{-1} for the Fe(OEP)/CO system. These values may be compared with the reported binding constants $K_1 = (6.6 \pm 0.3) \times 10^4$ M^{-1} and $K_2 = 140 \pm 3$ M^{-1} for Fe(TPP)/CO in toluene (20 °C)[26,37] and with K_1

---

(34) This observation does not require the presence of monomers only. Oligomerization of metalloporphyrins is not uncommon with species containing polar side chains in polar, usually protic, media.[35,36] Association of metalloporphyrins lacking polar groups is not well documented for systems in benzene or toluene at the concentration ranges used in this work.[35] Lacking evidence to the contrary, our CO binding model is based on monomeric Fe(P) complexes. The trans disposition of ethyl groups in **1** and in the same rings of **2** (two diastereomers)[15] should act to retard association of their Fe(II) complexes.

(35) White, W. I. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, **1978**; Vol. V, Part C, Chapter 7, and references therein.

(36) Viscio, D. B.; La Mar, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 8092, 8096.

= $(5.0 \pm 0.5) \times 10^4$ M^{-1} and $K_2 = 210 \pm 20$ M^{-1} for Fe(DPDME)/CO in benzene (25 °C).[25] Values of K_1 are intermediate of those (2×10^3–3×10^6 M^{-1}) for formation of five-coordinate diamagnetic complexes of a capped iron(II) porphyrin with phosphines and benzyl isocyanide.[38] These data together with those cited above and in Table I constitute the full set of quantitative binding constants for reactions of four-coordinate iron(II) porphyrins with strong field π-acid ligands.

Data for the Fe(P)/CO systems in Table I reveal the apparent trend OEP < OEC < OEiBC for K_1 and K_2. If the K_1 data are considered at the stated $\pm 2\sigma$ level, only the differences between OEP and OEiBC are significant whereas the three K_2 values are distinguishable. The trends may be viewed alternatively in terms of the composite equilibrium reaction 9 for which $K_3 = K_1/K_2 = 140$ (OEP), 58 (OEC), 26

$$\mathrm{Fe(P)} + \mathrm{Fe(P)(CO)_2} \overset{K_3}{\rightleftharpoons} 2\mathrm{Fe(P)(CO)} \qquad (9)$$

(OEiBC). While these values correspond to detectable differences in species concentration ratios as dependent upon macrocycle structure, the largest comparative free energy differences, $\Delta\Delta G$(OEiBC − OEP), are only −1.0 and −1.5 kcal/mol for reactions 9 and 5, respectively. These small quantities make it very difficult to identify the factors responsible for differences of significance in K_1 and K_2 values. The situation is compounded by lack of information on differential solvation effects on equilibrium positions and the absence of detailed structures of Fe hydroporphyrins. However, several observations are offered.

In the series of structurally defined pyramidal complexes Zn(P)(py), with P = *meso*-tetrakis(4-pyridyl)porphyrin,[39] *meso*-tetraphenylchlorin,[40] and *meso*-tetraphenylisobacteriochlorin,[41] the level of macrocycle reduction does not have a significant effect on parameters of the Zn coordination sphere. The size of the central core unit, the Zn–N(py) distance, and the displacement of the Zn atom from the macrocycle N_4 mean plane (Zn–Ct = 0.32–0.33 Å) are virtually constant. A similar structural uniformity of Fe(P)(CO) complexes[42] would indicate Fe–ligand interactions of accordingly similar energies (note that ν_{CO} varies by only 5 cm^{-1} in dichloromethane solutions), an effect that would tend to diminish differences in K_1 values. If this structural behavior obtains and provided solvation effects are minor, the small variation in observed K_1 values ($\Delta\Delta G \approx -0.5$ kcal/mol) implies little difference in the energies required to alter the macrocycle structure in course of changing its coordination unit from planar in Fe(P) to pyramidal in Fe(P)(CO).[42] This stereochemical change is expected from the planar structure of Fe(TPP)[43] and the pyramidal $FeN_4(CO)$ unit in Fe(DPDME)(CO)(THF).[44] In the latter complex Fe–Ct ≃ 0.10 Å and $\nu_{CO} = 1955$ cm^{-1}, close to the value of 1951 cm^{-1} for Fe(OEP)(CO). The differences of largest significance in equilibrium constants are those found with K_2, whose values may be variously interpreted to show the greater relative stability of $\mathrm{Fe(P)(CO)_2}$ when P = OEiBC. For example, in reaction 9 with equimolar reactants the mole fraction ratio of the dicarbonyls is 2.1 for OEiBC, 1.5 for OEC, and 1 for OEP. Also, in reactions 3 and 5 at constant p_{CO}, the ratio $[\mathrm{Fe(P)(CO)_2}]/[\mathrm{Fe(P)}] = 31$ for OEiBC, 4.6 for OEC, and 1 for OEP. The origin of this behavior is unclear but, judging from the constant ν_{CO} values in dichloromethane, it is unlikely to be localized in differential Fe–CO interactions. Lastly, K_1 and K_2 results in the OEiBC case are presumably composite values owing to the probable existence of two diastereomers of Fe(OEiBC) and $\mathrm{Fe(OEiBC)(CO)_2}$ and three diastereomers of Fe(OEiBC)(CO), these being generated as a consequence of the two unseparated forms (C_2, C_s) of the free macrocycle[15,45] from which Fe(OEiBC) was prepared. Space-filling models suggest little significant steric effects of ethyl groups of the different isomers in binding a molecule as small as CO. However, given the strongly puckered macrocycle conformation of one isomer of Ni(OEiBC),[45] further assessment of this matter will require structural determination of $\mathrm{Fe^{II}}$(OEiBC) complexes.

Carbon monoxide has been shown to bind to the heme prosthetic groups in reduced nitrite[6–8,46] and sulfite[47,48] reductases and to reduced heme *d*[49] and siroheme[5,9,47] extracted therefrom. These reactions differ from those studied here inasmuch as both protein-bound and free hemes contain a ligand (as yet unidentified in the native enzymes) trans to CO. Consequently, no direct comparisons with Fe(P)/CO systems can be made. In one kinetic aspect of CO binding, siroheme does not appear to be unusual compared to Fe(II) porphyrins. The rate constant k_{on} in reaction 10 (10^7 M^{-1} s^{-1} [48]) is quite

$$\text{red-siroheme} + \mathrm{CO} \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} \text{red-siroheme}\cdot\mathrm{CO} \qquad (10)$$

close to that for an imidazole-chelated protoheme (3.6×10^6 M^{-1} s^{-1} [24]). The value of k_{off} has not been reported. Its measurement for the protoheme leads to $K_{eq} = 6 \times 10^8$ M^{-1},[24] in good agreement with 4.8×10^8 M^{-1} for the Fe(DPDME)(Im)/CO system.[25b] Determination of on and off rates of CO binding involving Fe(P)(L)(CO) species with L = py and Im, previously produced in solution,[15] represents another approach to uncovering such intrinsic reactivity differences as may exist for iron porphyrins and hydroporphyrins. Values of $k_{on} \approx 10^8$ M^{-1} s^{-1} have been determined for several porphyrins.[50,51] With the exception of the greater relative stability of the OEiBC species among the $\mathrm{Fe(P)(CO)_2}$ complexes, no striking differences in equilibrium properties of CO

---

(37) As noted in Table I, analysis of the experimental data[26] for this system yields the same value of K_1 and a somewhat higher value of K_2, but with standard deviations of both values that are much greater than those reported.[26] In our least-squares analysis, the four parameters of eq 8 were varied independently until convergence, whereas in the original treatment the standard deviations on K_1 and K_2 apparently were obtained while holding the extinction coefficients constant at their least-squares values.

(38) Ellis, P. E., Jr.; Jones, R. D.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1980**, 54.

(39) Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3761. The structure of Zn(OEP)(py) is similar but with a longer Zn–N(py) bond: Cullen, D. L.; Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1976**, *B32*, 2259.

(40) Spaulding, L. D.; Andews, L. C.; Williams, G. J. B. *J. Am. Chem. Soc.* **1977**, *99*, 6918.

(41) Barkigia, K. M.; Fajer, J.; Spaulding, L. D.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 176.

(42) No diamagnetic Fe(P)L species has yet been isolated. The corresponding high-spin complexes are pyramidal with Fe–Ct ≈ 0.4 Å: Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 6769.

(43) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676.

(44) Scheidt, W. R.; Haller, K. J.; Fons, M.; Mashiko, T.; Reed, C. A. *Biochemistry* **1981**, *20*, 3653.

(45) Recently the two isomers of Ni(OEiBC) and H_2(OEiBC) have been separated by HP liquid chromatography and fractional crystallization, respectively: Johansen, J. E.; Angst, C.; Kratky, C.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 141. Kratky, C.; Angst, C.; Johansen, J. E. *Ibid.* **1981**, *20*, 211.

(46) Orii, Y.; Shimada, H.; Nozawa, T.; Hatano, M. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 983. Vickery, L. E.; Palmer, G.; Wharton, D. C. *Ibid.* **1978**, *80*, 458.

(47) Siegel, L. M.; Murphy, M. J.; Kamin, H. *J. Biol. Chem.* **1973**, *248*, 251. Siegel, L. M.; Davis, P. S.; Kamin, H. *Ibid.* **1974**, *249*, 1572.

(48) Murphy, M. J.; Siegel, L. M.; Kamin, H. *J. Biol. Chem.* **1974**, *249*, 1610.

(49) Walsh, T. A.; Johnson, M. K.; Barber, D.; Thomson, A. J.; Greenwood, C. *J. Inorg. Biochem.* **1981**, *14*, 15.

(50) White, D. K.; Cannon, J. B.; Traylor, T. G. *J. Am. Chem. Soc.* **1979**, *101*, 2443.

(51) Hoffman, B. M.; Swartz, J. C.; Stanford, M. A.; Gibson, Q. H. *Adv. Chem. Ser.* **1980**, *No. 191*, 235.

reactions have been found. In terms of differences in free energy changes for reactions 3, 5, and 9, this is certainly the case. While not necessarily anticipated by them, these results are compatible with our earlier findings from electrochemical and spectroscopic properties that variation of macrocycle structure in the series P = OEP, OEC, OEiBC results in only very slightly different cis effects.[15] As yet untested sources of possible reactivity differences of $Fe^{II,III}(P)$-type complexes are kinetic features of biologically relevant reactions such as ligand binding and electron transfer.

Acknowledgment. This research was supported by NSF Grants CHE 80-06601 and CHE 81-06017.

Registry No. Fe(OEP), 61085-06-1; Fe(OEC), 78319-96-7; Fe(OEiBC), 78319-97-8; CO, 630-08-0.

Supplementary Material Available: A listing of absorbance/p_{CO} data for the systems Fe(P)/CO (Table II) (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Organic Chemistry,
The Weizmann Institute of Science, Rehovot, Israel

Chemistry of Some (η^5-Pyrrolyl)- and (η^1-*N*-Pyrrolyl)iron Complexes[1a]

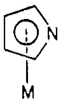
AVI EFRATY,* NUSRALLAH JUBRAN, and ALEXANDER GOLDMAN

Received December 30, 1980

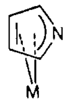
Azaferrocene undergoes a facile reaction with π-acidic ligands (L = CO, RNC, and R_2NPF_2) to afford η^1-*N*-pyrrolyl complexes of the type $(\eta^5\text{-}C_5H_5)FeL_2(\eta^1\text{-}NC_4H_4)$. A similar reaction with σ-donor ligands such as Ph_3P, Ph_2MeP, and Me_2PhP resulted in the decomposition of the starting complex. In the presence of aluminum chloride, azaferrocene reacts with aromatic solvents to afford cationic complexes of the type (η^6-arene)(η^5-cyclopentadienyl)iron(1+). The thermal degradation of azaferrocene to "bare" iron and ferrocene is thought to involve an autodisproportionation process. The ^{13}C NMR spectra of azaferrocene and some of its substituted pyrrolyl analogues, as well as of certain (η^1-*N*-pyrrolyl)iron derivatives, have been obtained and analyzed.

Introduction

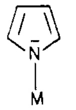
During the past 3 decades the chemistry of (cyclopentadienyl)metal complexes has received considerable attention. By contrast, the chemistry of the nearest heteroatom (π-pyrrolyl)metal system has been the subject of relatively few investigations. Azaferrocene,[1b,2] tricarbonyl(η^5-pyrrolyl)manganese,[1b,3,4] and some of their derivatives were prepared[4-7] and investigated. Limited attention has also been placed on the study of certain η^1-pyrrolyl complexes of iron,[7] manganese,[8] titanium,[9] and zirconium.[9] The bonding modes of the pyrrolyl ligand are either π (I and II) or σ (III and IV). In general, π-pyrrolyl is viewed as a symmetrically bonded ligand (I), though a certain ^{55}Mn NQR study[10] of $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$ suggested an asymmetric bonding arrangement involving the η^3-azaallylic and η^2-olefinic systems, with the Mn–C(α) distances being shorter than the Mn–C(β) distances (II). Extremes in the degree of delocalization of the π-electron density in the σ-bonded pyrrolyl ligand are exemplified by III (localized) and IV (delocalized).



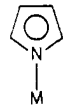
I



II



III



IV

In the context of the area of heterocyclic π complexes,[11] the current study describes the chemistry and spectroscopic properties of certain (σ- and π-pyrrolyl)iron complexes.

Experimental Section

Microanalyses were performed by the Microanalytical Laboratory at the Weizmann Institute. Infrared spectra were recorded on a Perkin-Elmer 467 grating IR spectrometer and were calibrated with the aid of a polystyrene film. NMR spectra of samples dissolved in either $CDCl_3$ or other solvents as specified were recorded on the following instruments: ^1H spectra were obtained at 60 MHz (Varian A-60) and/or 90 MHz (Bruker HFX-10). ^{13}C spectra were obtained at 20 MHz on a Varian FT-80A spectrometer. Both ^1H and ^{13}C spectra were calibrated by using Me_4Si as a reference. ^{19}F spectra were recorded at 84.66 MHz on a Bruker HFX-10 spectrometer, with Freon-11 as a reference. Mass spectra were obtained on a MAT-ATLAS CH-4 spectrometer (inlet temperature 30–50 °C; ionization chamber temperature, 270 °C).

Argon atmosphere was routinely provided for the following operations: (i) carrying out reactions, (ii) admission to evacuated vessels, (iii) handling solutions of organometallic compounds, and (iv) storage of organometallic solids. Solvents used during the course of this investigation were dried, deoxygenated, and freshly distilled before being used. Azaferrocene (V),[1b] isocyanides,[12] and (dialkylamino)difluorophosphines[13] were prepared according to known procedures.

Preparation of (Diisocyanide)(η^1-*N*-pyrrolyl)(η^5-cyclopentadienyl)iron Derivatives (VI). VI, L = $(CH_3)_3CNC$. Azaferrocene (0.5 g, 2.67 mmol) and *tert*-butyl isocyanide (0.64 g, 7.71 mmol) in benzene (50 mL) were stirred and refluxed for a period of 2 h. The reaction mixture was cooled to ambient temperature and filtered. The filtrate was stripped to dryness on a rotary evaporator [40 °C (30 torr)], and the excess of the isocyanide was removed under low pressure [40 °C (0.1 torr)]. Recrystallization of the crude product from a

---

[1] (a) Preliminary communication: Efraty, A.; Jubran, N. *Inorg. Chim. Acta.* **1980**, *44*, L191. (b) Joshi, K. K.; Pauson, P. L.; Qazi, A. R.; Stubbs, W. H. *J. Organomet. Chem.* **1964**, *1*, 471.

[2] King, R. B.; Bisnette, M. B. *Inorg. Chem.* **1964**, *3*, 796.

[3] Joshi, K. K.; Pauson, P. L. *Proc. Chem. Soc.* **1962**, 326.

[4] King, R. B.; Efraty, A. *J. Organomet. Chem.* **1969**, *20*, 264.

[5] Pauson, P. L.; Qazi, A. R. *J. Organomet. Chem.* **1967**, *7*, 321.

[6] Coleman, K. J.; Davies, C. S.; Gogan, N. J. *J. Chem. Soc. D* **1970**, 1414.

[7] Pauson, P. L.; Qazi, A. R.; Rockett, B. W. *J. Organomet. Chem.* **1967**, *7*, 325.

[8] Pyshnograeva, N. I.; Setkina, V. N.; Adrianov, V. G.; Struchkov, Yu. T.; Kursanov, D. N. *J. Organomet. Chem.* **1977**, *128*, 381.

[9] Vann Bynum, R.; Hunter, W. E.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2368.

[10] Fayer, M. D.; Harris, C. B. *Inorg. Chem.* **1969**, *8*, 2792.

[11] Pannell, K. H.; Kalsotra, B. L.; Parkanyi, C. *J. Heterocycl. Chem.* **1978**, *15*, 1057.

[12] Ugi, I. "Isonitrile Chemistry"; Academic Press: New York, 1971, and pertinent references therein.

[13] Schmutzler, R. *Inorg. Chem.* **1964**, *3*, 415.