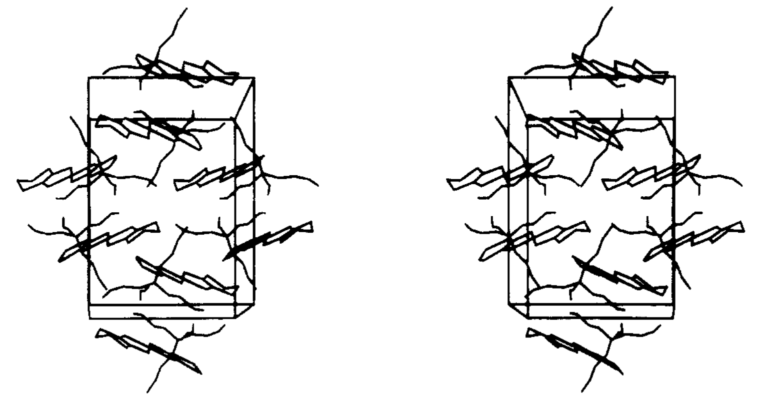

Figure 2. Stereoview of the molecular packing for $[(C_4H_9)_4N][Ni(DDDT)_2]$.

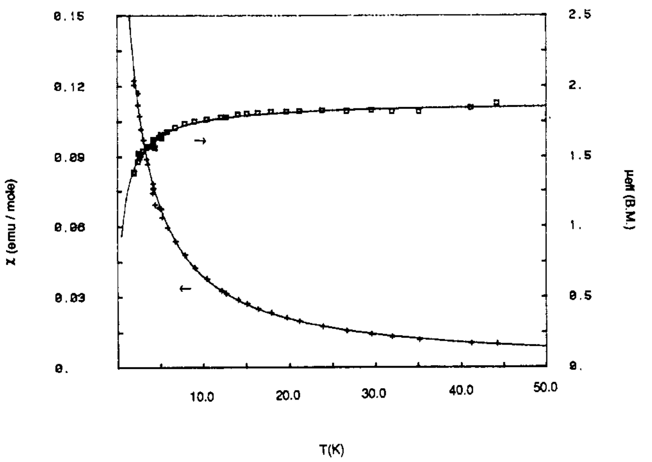

Figure 3. Magnetic susceptibility and magnetic moment of $[(C_4H_9)_4N][Ni(DDDT)_2]$. The solid lines are fit lines to the Curie–Weiss law, $\chi_m = Ng^2\beta^2S(S + 1)/3k(T - \Theta)$, with $g = 2.18$ and $\Theta = -1.54$ K.

constituent atoms were made by using Pascal's constants, and corrections for temperature-independent paramagnetism were estimated from tabulated data.[16-18]

Results and Discussion

The bond lengths and angles of the $Ni(DDDT)_2^-$ anions are essentially the same as those in the two previously published structures.[9,11] The difference in the two tetrabutylammonium structures is clearly seen by comparing the packing diagrams. The earlier published structure[11] indicates two different types of molecules, ones that form stacks aligned along the *a* axis and ones that lie almost perpendicular to these stacks. The stereoview of the unit cell packing of the monoclinic form (Figure 2) reveals association of the anions into pairs, similar to the structures of $Au(DDDT)_2$ and BEDT-TTF.[11,19]

The major difference between the pairs of $Ni(DDDT)_2^-$ anions and pairs of the two neutral complexes is the separation distance. While S···S contacts within a pair are less than 3.70 Å for $Au(DDDT)_2$ and BEDT-TTF, the shortest S···S contact in $Ni(DDDT)_2^-$ pairs is 7.32 Å. The Ni···Ni distance is 8.49 Å. This large separation can be attributed to the presence of the alkyl chains of the tetrabutylammonium cations between anions. Although distances within a pair are quite large, contacts between pairs are comparable to those of the neutral structures. Table III contains the contacts less than 5.00 Å.

Magnetic results are displayed in Figure 3. The magnetic susceptibility as a function of temperature is a smooth curve indicating simple paramagnetic behavior. However, the room-temperature magnetic moment (1.9 μ_B) decreases slowly with temperature to 10 K and drops significantly to 1.4 μ_B at 1.9 K, indicative of antiferromagnetic interactions. These interactions are weak at best and most likely correspond to interactions between anions in different pairs where the closest contacts exist between sulfur atoms. Although the S···S contacts in this tetrabutylammonium structure are comparable to those of the tetraethylammonium structure, the long-range magnetic ordering observed in the latter solid is probably the result of its layered structure.[9,20-22] The shortest S···S contacts in our structure are less than those reported for the triclinic structure, and this is reflected in the weak interactions observed in the magnetic moment data.[11]

Acknowledgment. We wish to thank Dr. E. Gabe of NRC Canada for his assistance with the cell reduction program, Dr. William E. Hatfield, Jeffery H. Helms, and Martin L. Kirk for collection of the magnetic data, and the National Science Foundation for funds toward upgrading our diffractometer (Grant CHE-8307022). This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates (3 pages); a listing of calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

---

(16) Figgis, B. N.; Lewis, J. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; Chapter 6, p 403.

(17) Konig, E. *Magnetic Properties of Transition Metal Compounds*; Springer-Verlag: West Berlin, 1966.

(18) Weller, R. R.; Hatfield, W. E. *J. Chem. Educ.* **1979**, *56*, 652.

(19) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Inokuchi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 301.

(20) Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Enoki, T.; Inokuchi, H. *J. Am. Chem. Soc.* **1983**, *105*, 297.

(21) Wudl, F. *J. Am. Chem. Soc.* **1981**, *103*, 7064.

(22) Williams, J. M.; Beno, M. A.; Appelman, E. H.; Capriotti, J. M.; Wudl, F.; Aharon-Shalom, E.; Nalewajek, D. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 319.

Contribution from the Department of Chemistry
and Laboratory for Microbial and Biochemical Sciences,
Georgia State University, Atlanta, Georgia 30303,
and Department of Chemistry, Brandeis University,
Waltham, Massachusetts 02154

Electron Self-Exchange of Low-Spin Iron Octaethylporphyrin, Chlorin, and Isobacteriochlorin Complexes

Dabney White Dixon,*[1a] Scott Woehler,[1a] Xiaole Hong,[1a]
and Alan M. Stolzenberg*[1b]

Received March 24, 1988

A perennial theme in metalloporphyrin chemistry is the effect of structure on properties and reactivity. The effects of changes in the axial ligands and porphyrin ring substituents and of such structural features as the geometry and coordination number of

---

(1) (a) Georgia State University. (b) Brandeis University.

0020-1669/88/1327-3682$01.50/0 © 1988 American Chemical Society

Figure 1. ^{1}H NMR spectra of $[Fe(OEC)(1\text{-}MeIm)_2]^+$ (A) and $[Fe(OEiBC)(1\text{-}MeIm)_2]^+$ (B) in 5:1 acetone-d_6/D_2O (v/v) at −20 °C.

the metalloporphyrin have been extensively investigated. Recently, this theme has expanded to include hydroporphyrin compounds, tetrapyrroles in which peripheral substitution of the ring has decreased the extent of the π-system.[2-13] An impetus for this is the increasingly large number of proteins that are now known to contain a hydroporphyrin prosthetic group.[14] Many of these hydroporphyrin prosthetic groups are iron complexes and are involved in substrate reduction and/or electron-transfer reactions.

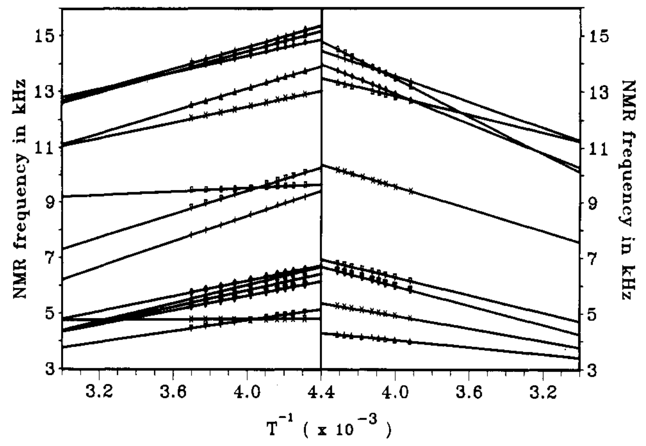

Figure 2. Plots of the chemical shifts of the paramagnetically shifted resonances of $[Fe(OEC)(1\text{-}MeIm)_2]^+$ (right panel) and $[Fe(OEiBC)(1\text{-}MeIm)_2]^+$ (left panel) in acetone-d_6 as a function of $1/T$. To facilitate comparison, the graphs have been plotted with the x axis for the right panel running from right to left and that for the left panel from left to right. Each line is a linear least-squares line from the data points over the temperature range −45 to −10 °C for $[Fe(OEC)(1\text{-}MeIm)_2]^+$ and −42 to −8 °C for $[Fe(OEiBC)(1\text{-}MeIm)_2]^+$.

Our interests in electron transfer of heme proteins[15-17] and in the reactivity of hydroporphyrin complexes[13,18] have led us to investigate the effect of macrocycle saturation on the electron self-exchange rate constant of iron porphyrin and hydroporphyrin complexes. Electron exchange of low-spin iron hydroporphyrins is of biological relevance because a class of low molecular weight proteins with sulfite reductase activity have been isolated from anaerobic bacteria. The resting state of these proteins contains low-spin siroheme, an iron isobacteriochlorin.[19,20] In this paper, we report the rate constants for electron self-exchange in the homologous series of six-coordinate, low-spin complexes $[Fe(P)(1\text{-}MeIm)_2]$, where P = OEP, OEC, and OEiBC.[21]

Results and Discussion

The ^{1}H NMR spectra of $[Fe(OEC)(1\text{-}MeIm)_2]^+$ and $[Fe(OEiBC)(1\text{-}MeIm)_2]^+$ are shown in Figure 1. The spectra are very similar; both are complex due to the low symmetry of these species. The OEiBC spectrum contains almost all resonances of the OEC spectrum. Three lines of evidence established that OEiBC was not contaminated with OEC, however. First, careful subtraction of the spectra showed that some peaks found in the OEC spectrum were not in the OEiBC spectrum. Second, a plot of the chemical shift of the resonances as a function of $1/T$ showed that lines at similar resonance frequencies in the two spectra did not have the same temperature dependence (Figure 2). Third, the rate constant for electron self-exchange was not a function of the peak used for measurement in the OEiBC samples; i.e., peaks that might have been due to the OEC macrocycle had the same rate constant as those that were clearly due to OEiBC. OEiBC is a mixture of two diastereomers. We have assumed that both have the same self-exchange rate constant.

---

(2) (a) Scheer, H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. 2, pp 1–44. (b) Scheer, H.; Inhoffen, H. H. *Ibid.*; pp 45–90.

(3) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 1970–1977.

(4) (a) Richardson, P. F.; Chang, C. K.; Hanson, L. K.; Spaulding, L. D.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3420–3424. (b) Richardson, P. F.; Chang, C. K.; Spaulding, L. D.; Fajer, J. *J. Am. Chem. Soc.* **1979**, *101*, 7736–7738.

(5) (a) Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1980**, *102*, 848–851. (b) Chang, C. K.; Hanson, L. K.; Richardson, P. F.; Young, R.; Fajer, J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2652–2656.

(6) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 364–370.

(7) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763–4778.

(8) (a) Fujita, E.; Fajer, J. *J. Am. Chem. Soc.* **1983**, *105*, 6743–6745. (b) Fujita, E.; Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1985**, *107*, 7665–7669.

(9) Chang, D.; Malinski, T.; Ulman, A.; Kadish, K. M. *Inorg. Chem.* **1984**, *23*, 817–824.

(10) (a) Feng, D.; Ting, Y.-S.; Ryan, M. D. *Inorg. Chem.* **1985**, *24*, 612–617. (b) Fernandes, J. B.; Feng, D.; Chang, A.; Keyser, A.; Ryan, M. D. *Inorg. Chem.* **1986**, *25*, 2606–2610.

(11) Strauss, S. H.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 863–868.

(12) (a) Strauss, S. H.; Silver, M. E.; Ibers, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4108–4109. (b) Strauss, S. H.; Silver, M. E.; Long, K. M.; Thompson, R. G.; Hudgens, R. A.; Spartalian, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4207–4215.

(13) (a) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 3082–3083. (b) Stolzenberg, A. M.; Stershic, M. T. *J. Am. Chem. Soc.*, in press.

(14) Leading references to the relevant biochemical literature are found in ref 3.

(15) Dixon, D. W.; Barbush, M.; Shirazi, A. *J. Am. Chem. Soc.* **1984**, *106*, 4638–4639.

(16) Dixon, D. W.; Barbush, M.; Shirazi, A. *Inorg. Chem.* **1985**, *24*, 1081–1087.

(17) Shirazi, A.; Barbush, M.; Ghosh, S. B.; Dixon, D. W. *Inorg. Chem.* **1985**, *24*, 2495–2502.

(18) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1988**, *27*, 1614–1620.

(19) Huynh, B. H.; Kang, L.; DerVartanian, D. V.; Peck, H. D., Jr.; LeGall, J. *J. Biol. Chem.* **1984**, *259*, 15373–15376.

(20) Moura, I.; Lino, A. R.; Moura, J. J. G.; Xavier, A. V.; Fauque, G.; Peck, H. D., Jr.; LeGall, J. *Biochem. Biophys. Res. Commun.* **1986**, *141*, 1032–1041.

(21) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEC, *trans*-2,3-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylchlorin); OEiBC, mixture of *tct*- and *ttt*-2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion (octaethylisobacteriochlorin); 1-MeIm, 1-methylimidazole.

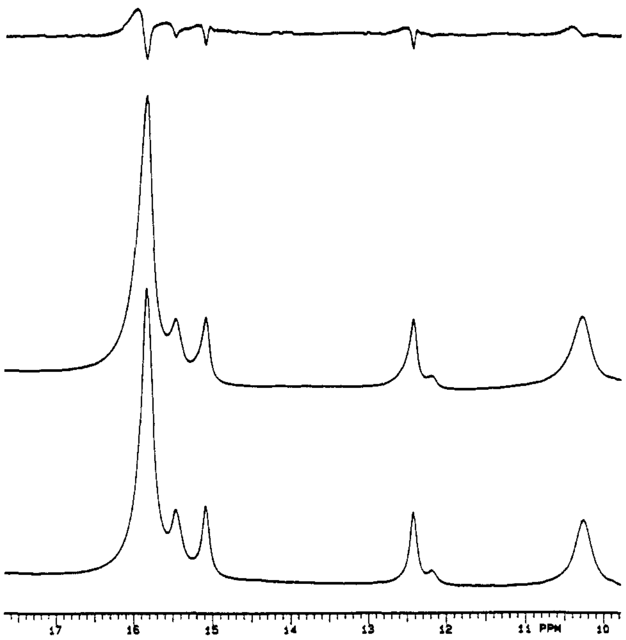

Figure 3. Subtraction of two $[Fe(OEC)(1\text{-}MeIm)_2]^+$ spectra, one taken before reduction by the addition of dithionite and one taken after reduction and reoxidation by addition of a small aliquot of O_2 ($<$10 μL). The top trace is the difference spectrum.

Rate constants were measured by standard ^1H line-broadening techniques; it was necessary to cool the solutions to assure that ligand exchange was slow on the NMR time scale.[22,23] The rate constants ($M^{-1}\ s^{-1}$) for electron self-exchange in acetone/water at −20 °C increase in the order OEC ($(2.8 \pm 1.1) \times 10^7$) $\simeq$ OEP ($(4.0 \pm 1.6) \times 10^7$) $<$ OEiBC ($(17 \pm 9) \times 10^7$). There is a factor of approximately 4 between the rate constants for OEP and OEiBC. The self-exchange of the OEP complex was also examined in CD_2Cl_2. The rate constant was within experimental error of that found in the acetone/water mixture.[24]

Because porphyrins and related compounds are prone to aggregation, we investigated the possibility of dimerization by measuring the spectrum of $[Fe(OEP)(1\text{-}MeIm)_2]^+$ as a function of concentration. Two acetone-d_6 solutions of this complex with a 3.7-fold difference in concentration (0.75 and 0.20 mM) had the same line widths and chemical shifts within experimental error, indicating no change in aggregation over this concentration range.

Both hydroporphyrin macrocycles were reasonably stable to oxidation by small amounts of O_2. Oxygen was employed to reoxidize the iron complexes following their reduction with dithionite. Addition of small aliquots of O_2 via microliter syringe usually resulted in recovery of the original spectrum of the Fe(III) complex with no evidence for oxidation of the OEC or OEiBC rings (Figure 3).

Our measurements show that the OEiBC system has a faster self-exchange rate constant than either OEP or OEC. The difference is small, however, with only about a factor of 4 between the rate constants for the OEC and OEiBC systems. In a similar fashion, only small differences in heterogenous electron-transfer rate constants have been seen in the H_2(OEP), H_2(OEC), H_2(OEiBC) series, the related TPP series, the corresponding Zn complexes,[25] and the Ni(TMP), Ni(TMC) pair.[9] There are several structural and electronic differences between porphyrins and hydroporphyrins that might affect self-exchange rates. These include steric interactions, the increased flexibility of the hydroporphyrin macrocycles, and different energies of the π MOs as well as different distributions of electron density.[3,12,13,26-28]

Steric bulk (due to the increasing number of out-of-plane ethyl groups) increases in the order OEP $<$ OEC $<$ OEiBC. This order is consistent with less outer-sphere reorganization (and larger rate constants) as the molecule becomes bulkier. Steric effects probably play a significant role in controlling electron-transfer rates in these complexes, as in other low-spin porphyrins. The increased flexibility of the hydroporphyrin macrocycles will play a role in electron transfer to the extent that the structural details of the Fe(II) and Fe(III) states and hence the inner-sphere reorganization differ. The lack of X-ray structural data on the appropriate complexes prevents speculation on this point, however. Differences in electron density distribution of hemes have been proposed to control the electron-transfer rate constant of heme proteins[29-34] and of model systems.[35-37] However, because the differences between the rate constants in this series are small and influenced by steric effects, it is difficult to correlate the rate differences with differences in orbital occupation.[38] In summary, the electron self-exchange rate constants for low-spin iron complexes with OEP, OEC, and OEiBC are similar, with the OEiBC complex the fastest. The reasons for this include differences in the outer-sphere reorganization but may include differences in inner-sphere reorganization and orbital occupation as well.

Experimental Section

Synthesis. Fe(OEP)Cl,[39] Fe(OEC)Cl,[39] and Fe(OEiBC)Cl[6] were prepared as described previously. NMR solvents were obtained from Aldrich; $Na_2S_2O_4$ was from Fisher. 1-MeIm (Aldrich) was distilled before use. NMR showed that the Fe(OEC)Cl contained about 0.5% Fe(OEP)Cl (assuming that the $[Fe(OEC)(1\text{-}MeIm)_2]^+$ singlet at approximately 24.5 ppm is a three-proton resonance). The Fe(OEiBC)Cl contained a few percent Fe(OEP)Cl (similar assumption).

Self-Exchange Measurements. Proton NMR spectra were recorded on a Varian VXR 400-MHz spectrometer operating at 400.00 MHz. The spectral width was 12.7–13.5 KHz. Typical spectra for the Fe(III) species or exchanging mixtures had approximately 30K data points and acquisition time of 1.1 s; 256 scans were taken. The temperature of the

---

(22) Because the imidazole ligands can dissociate, it was important to establish that ligand exchange was very slow on the NMR time scale and did not contribute to the line broadening of the observed resonances. Plots of the line widths of a resonance as a function of $1/T$ are linear in the absence of exchange.[23] This was true up to about −20 °C for the iron(III) bis(imidazole) complexes of both OEC and OEiBC. (Porphyrin)iron(II) and (porphyrin)iron(III) bis(imidazole) complexes have similar ligand exchange rates.[17]

(23) Satterlee, J. D.; La Mar, G. N.; Bold, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 1088–1093.

(24) (a) Four-coordinate porphyrins often react with chlorinated solvents;[24b] indeed, Fe(OEP) reacts with dichloromethane to give Fe(OEP)Cl with a half-life of approximately 3 h at 25 °C.[12b] However, hexacoordinate iron porphyrins are stable for many hours in CD_2Cl_2,[17] and no decomposition of $Fe(OEP)(1\text{-}MeIm)_2$ was observed in CD_2Cl_2 in this experiment. (b) Brault, D.; Rougee, M.; Momenteau, M. *J. Chim. Phys. Phys. Chim. Biol.* **1971**, *68*, 1621–1629.

(25) Strauss, S. H.; Thompson, R. G. *J. Inorg. Biochem.* **1986**, *27*, 173–177.

(26) Suh, M. P.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5164–5171.

(27) Kratky, C.; Waditschatka, R.; Angst, C.; Johansen, J. E.; Plaquevent, J. C.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta.* **1985**, *68*, 1312–1337.

(28) (a) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543–555. (b) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1–70.

(29) Keller, R. M.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1978**, *83*, 1132–1139.

(30) Tollin, G.; Hanson, L. K.; Caffrey, M.; Meyer, T. E.; Cusanovich, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 3693–3697.

(31) Gingrich, D. J.; Nocek, J. M.; Natan, M. J.; Hoffman, B. M. *J. Am. Chem. Soc.* **1987**, *109*, 7533–7534.

(32) Reid, L. S.; Lim, A. R.; Mauk, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 8197–8201.

(33) Bocian, D. F.; Masthay, M. B.; Birge, R. B. *Chem. Phys. Lett.* **1986**, *125*, 467–472 and references therein.

(34) (a) Beratan, D. N.; Onuchic, J. N.; Hopfield, J. J. *J. Chem. Phys.* **1987**, *86*, 4488–4498. (b) Onuchic, J. N.; Beratan, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6771–6778.

(35) Koval, C. A.; Pravata, R. L. Reidsema, C. M. *Inorg. Chem.* **1984**, *23*, 545–553.

(36) Chan, M.-S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542–2549.

(37) Nielson, R. M.; Golovin, M. N.; McManis, G. E.; Weaver, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 1745–1749.

(38) It should be noted that although these complexes may differ in their spin density distributions, the highest filled iron orbitals are of similar energy in all three systems, as evidenced by the similarities of the redox potentials of the Fe(III/II) reductions in the bis(pyridine) series: $Fe(OEP)(py)_2$, −0.15 V; $Fe(OEC)(py)_2$, −0.16 V; $Fe(OEiBC)(py)_2$, −0.19 V.[7]

(39) Whitlock, H. W.; Hanauer, R.; Oster, M. Y.; Bower, B. K. *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489.

probe was measured with a methanol thermometer.[40] Calculations of the self-exchange rate constants were performed as previously described.[15–17] Rate constants are the average of those measured from two different runs, with the values measured on at least two different peaks in each spectrum.

Sample Preparation and Data Collection. The Fe(P)Cl complex of interest was dissolved in a mixture of 1.0 mL of acetone-d_6 and 0.2 mL of D_2O. Experiments, particularly on the OEP system, were limited in part by solubility. The acetone/water mixture was used because the compound showed reasonable solubility in this mixture and the reducing agent (aqueous dithionite) could be added without precipitating. Bis(imidazole) complexes are notably more soluble than the ferric chloride complexes; therefore, it is often helpful to add the 1-MeIm initially to promote dissolution. For Fe(OEC)Cl and Fe(OEiBC)Cl, preparation of solutions was performed in a glovebox, with attempts to minimize light exposure. 1-MeIm (2.0 μL, approximately 50 equiv) was added to each solution. The solution was filtered by using an MSI cameo nylon filter (0.45 μM, Fisher) into a screw-top NMR tube with a septum in the top (Wilmad). The concentrations of the complexes were determined by optical spectroscopy by dilution of an aliquot (5–10 μL of the filtered solution) into 4.0 mL of dichloromethane. Extinction coefficients were as follows:[7] Fe(OEP)Cl, 107 000 at 376.5 nm; $[Fe(OEP)(1\text{-MeIm})_2]Cl$, 214 000 at 399.6 nm (this work, based on that for Fe(OEP)Cl); Fe(OEC)Cl, 87 000 at 374.9 nm; Fe(OEiBC)Cl, 51 000 at 377 nm. Solutions for NMR spectroscopy were purged gently with argon for 15 min before the spectra were recorded. At least 15 min was allowed for the sample to reach thermal equilibrium before data were taken. Reduction was achieved by addition of aliquots of degassed aqueous $Na_2S_2O_4$ (saturated $Na_2S_2O_4$ in D_2O diluted 1:5 with D_2O and degassed with Ar). Samples were reduced a maximum of 10%.

Error Analysis. The experimental error in these experiments is larger than usual, due primarily to the fact that individual resonances of the oxidized form could not be matched with the corresponding resonances of the reduced form because neither set of resonances has been assigned. For samples in fast exchange, the resonance frequency of a partially reduced mixture is a linear function of the mole fraction of the reduced component. Therefore, we were able to calculate reasonable resonance frequencies for the reduced species by requiring that all reduced resonances appear within the known total range of resonances in the reduced sample. Under the conditions of these experiments, the procedure gave the resonances of the reduced species within 200 Hz, leading to an uncertainty in the rate constant of 20–40%, depending on the difference in frequencies between the oxidized and reduced resonance for the given proton.

Acknowledgment. We thank the National Institutes of Health for support of this work (Grants DK 38826 to D.W.D. and GM 33882 to A.M.S.). D.W.D. thanks the National Science Foundation for a Career Advancement Award (NSF Grant CHE 8707447), and A.M.S. thanks the Camille and Henry Dreyfus Foundation for a Young Faculty Grant. The Varian VXR400 NMR spectrometer at GSU was purchased with funds from the NSF Instrumentation Program (Grant CHEM-8409599). D. W.D. thanks D. Holten and L. Hanson for helpful discussions.

Registry No. $[Fe(OEP)(1\text{-MeIm})_2]$, 65940-57-0; $[Fe(OEC)(1\text{-MeIm})_2]$, 78319-98-9; $[Fe(OEiBC)(1\text{-MeIm})_2]$, 78338-27-9.

---

(40) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227–2229.

Contribution from the Department of Chemistry and the
Materials Research Laboratory,
University of Illinois at Urbana-Champaign,
Urbana, Illinois 61801

Electrophilic Substitution of $[Re_7C(CO)_{21}]^{3-}$. Synthesis and Characterization of $[N(PPh_3)_2]_2[Re_7C(CO)_{20}(NO)]$

Chi-Mi Tai Hayward, John P. Folkers, and John R. Shapley*

Received March 31, 1988

Recently, there has been considerable attention focused on reactions of the monocapped octahedral carbide cluster $[Re_7C(CO)_{21}]^{3-}$.[1] This readily available[2] large cluster has been observed to add both post transition metal[3,4] as well as platinum metal[5,6] electrophiles to the open face opposite the capped face. It is also easily protonated to give $[HRe_7C(CO)_{21}]^{2-}$.[3,4] Beringhelli et al.[7] have recently reported the chemical oxidation of $[Re_7C(CO)_{21}]^{3-}$ with $C_7H_7^+$; the radical $[Re_7C(CO)_{21}]^{2-}$ is formed first, and then in the presence of carbon monoxide further oxidation to $[Re_7C(CO)_{22}]^-$ occurs. In this paper we report on the reaction of $[Re_7C(CO)_{21}]^{3-}$ with the electrophilic reagent NO^+, for which we observe net substitution (eq 1).

$$[Re_7C(CO)_{21}]^{3-} + NO^+ \rightarrow [Re_7C(CO)_{20}(NO)]^{2-} + CO \quad (1)$$

Experimental Section

Reactions were conducted under an atmosphere of nitrogen by using standard techniques. Dichloromethane was freshly distilled from calcium hydride. The complex $[N(PPh_3)_2]_3[Re_7C(CO)_{21}]$ was prepared as described previously.[2] Infrared spectra were obtained with a Perkin-Elmer 1750 FT-IR spectrometer. ^{13}C NMR spectra were obtained at 90 MHz with a Nicolet NT-360 NMR spectrometer. Elemental analyses and FAB mass spectra were determined respectively by the Microanalytical Laboratory and the Mass Spectrometry Laboratory of the School of Chemical Sciences. Cyclic voltammetry was performed with a Bioanalytical Systems CV-1B potentiostat and a normal three-electrode cell (Pt working, Ag/AgCl (3 M Cl^-) reference) at a typical scan rate of 100 mV/s. The dichloromethane solution was 0.1 M in electrolyte ($[NBu_4][PF_6]$) and 0.2 mM in complex. Under our conditions the $Cp_2Fe^{0/+}$ couple (0.2 mM) showed $E_{1/2} = 0.462$ V and $\Delta E_p = 74$ mV.

Reaction of $[Re_7C(CO)_{21}]^{3-}$ with $NOBF_4$. To a dry 50-mL flask containing $[N(PPh_3)_2]_3[Re_7C(CO)_{21}]$ (40 mg, 0.011 mmol) were added dichloromethane (15 mL) and $NOBF_4$ (2.2 mg, 0.019 mmol). This orange-red mixture turned brownish red after a few minutes of stirring at room temperature. After 2 h the strong IR bands of $[Re_7C(CO)_{21}]^{3-}$ at 1978 and 1968 cm^{-1} had been replaced by a new, strong band at 1997 cm^{-1}, so the reaction mixture was filtered into a second flask. The solution was concentrated to a small volume (ca. 2 mL) by evacuation; then methanol (ca. 10 mL) was carefully layered on top. This mixture was allowed to stand for 2 days at −20 °C. The brown crystals of $[N(PPh_3)_2]_2[Re_7C(CO)_{20}(NO)]$ (20 mg, 0.007 mmol, 64%) that formed were separated and dried in vacuo. Anal. Calcd for $C_{93}H_{60}N_3O_{21}P_4Re_7$: C, 37.45; H, 2.03; N, 1.41; P, 4.15. Found: C, 37.15; H, 2.17; N, 1.31; P, 4.28. IR (CH_2Cl_2): ν_{CO} 2050 (vw), 1997 (vs), 1988 (s, sh), 1914 (w) cm^{-1}; ν_{NO} 1693 (w) cm^{-1}. IR (KBr): ν_{NO} 1697 (w) cm^{-1}. Negative-ion FAB mass spectrum (^{187}Re): m/z 1911 ($Re_7C(CO)_{20}(NO)^-$).

Results and Discussion

Synthesis and Characterization of $[Re_7C(CO)_{20}(NO)]^{2-}$. Treatment of $[Re_7C(CO)_{21}]^{3-}$ with ca. 1.5 equiv of $NOBF_4$ in dichloromethane at room temperature affords $[Re_7C(CO)_{20}(NO)]^{2-}$ as the sole product observed by IR spectroscopy. Due to the 1 equiv of $[N(PPh_3)_2][BF_4]$ that is also formed, crystallization by solvent diffusion is necessary to obtain analytically pure product; the isolated yield of $[N(PPh_3)_2]_2[Re_7C(CO)_{20}(NO)]$ is then 64%. The formulation follows from elemental analyses and the FAB mass spectrum (M^-). The presence of a carbide ligand is established by ^{13}C NMR spectra of $[Re_7{}^*C({}^*CO)_{20}(NO)]^{2-}$ (vide infra), which show a resonance at δ 420.9; this position is in good agreement with other $Re_n(\mu_6\text{-}C)$ resonances.[1,2,4,5] The nitrosyl stretching frequency (1697 cm^{-1}) is consistent with that expected for a terminal, rather than a bridging, ligand. Analogous electrophilic (oxidative) reactions of NO^+ with anionic carbonyl clusters have been reported;[8] however, neutral clusters are typically substituted by nucleophilic (reductive) reactions with NO_2^-[9] or

---

(1) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339.

(2) Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.

(3) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1985**, *295*, C7.

(4) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.

(5) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441.

(6) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551.

(7) Beringhelli, T.; D'Alfonso, G.; De Angelis, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1987**, *322*, C21.

(8) Johnson, B. F. G.; Lewis, J.; Nelson, W. J. H.; Puga, J.; Braga, D.; Henrick, K.; McPartlin, M. *J. Organomet. Chem.* **1984**, *266*, 173.

0020-1669/88/1327-3685$01.50/0 © 1988 American Chemical Society