Table I. Heterobimetallic Compounds with Phosphido Bridges Containing a Phosphorus–Hydrogen Bond[a]

compd[b]	yield, %	IR ν(CO) freq,[c] cm^{-1}	^{31}P NMR[d] δ(P)	$\lvert^{1}J(PH)\rvert$, Hz	^{1}H NMR[d] δ(P–H)	δ(C$_5$H$_5$)	δ(CH$_3$)
		(A) Compounds without a Metal–Metal Bond					
CpFe(CO)$_2$P(H)(N-i-Pr$_2$)Cr(CO)$_5$	73[e]	2040 w, 2005 m, 1970 s, 1955 w, 1935 s, 1920 s	62.6	295	7.31	5.04	1.23
CpFe(CO)$_2$P(H)(N-i-Pr$_2$)Mo(CO)$_5$	66[e]	2056 w, 2006 m, 1973 s, 1939 s, 1931 s	36.7	302	7.20	4.90	1.25
CpFe(CO)$_2$P(H)(N-i-Pr$_2$)W(CO)$_5$	69[e]	2060 w, 2010 m, 1970 s, 1945 s, 1935 m, 1920 s	6.7	310	7.57	4.98	1.22
CpFe(CO)$_2$P(H)(N-i-Pr$_2$)Mn(CO)$_2$Cp	63[e]	2001 s, 1956 s, 1928 s, 1874 s	98.7	306	7.7	4.9, 4.5	1.2
CpFe(CO)$_2$PHClW(CO)$_5$	57[f]	2069 w, 2038 m, 2003 m, 1954 s, 1948 s, 1933 s	89.9	290	7.72	5.17	none
CpFe(CO)$_2$PHBrW(CO)$_5$	43[f]	2069 w, 2037 m, 1995 m, 1940 s, 1935 s, 1925 s	63.7	286	6.82	5.18	none
		(B) Compounds with a Metal–Metal Bond					
CpFeCr(CO)$_6$P(H)(N-i-Pr$_2$)	53[g]	2031 m, 1963 s, 1959 s, 1926 s, 1811 m[h]	206.3	360	9.2	4.6	1.3
CpFeW(CO)$_6$P(H)(N-i-Pr$_2$)	52[g]	2047 m, 1968 s, 1952 s, 1931 s, 1810 vw[h]	159.8	363	9.9	4.6	1.3
Cp$_2$FeMn(CO)$_3$P(H)(N-i-Pr$_2$)	21[g]	1940 s, 1876 s, 1755 s[h]	224.8	347	i	4.6, 4.5	1.3

[a] All compounds in this table gave correct analyses for carbon, hydrogen, and nitrogen or halogen. [b] Cp = η^5-cyclopentadienyl, i-Pr = isopropyl. [c] These ν(CO) frequencies were measured in hexane or cyclohexane. [d] These NMR spectra were measured in CDCl$_3$ solution. [e] Yield from the NaFe(CO)$_2$Cp + i-Pr$_2$NP(H)XM(CO)$_5$ or i-Pr$_2$NP(H)XMn(CO)$_2$Cp reaction. [f] Yield from the CpFe(CO)$_2$P(H)(N-i-Pr$_2$)W(CO)$_5$ + HX reaction. [g] Yield from the photolysis of CpFe(CO)$_2$P(H)(N-i-Pr$_2$)M(CO)$_5$ or CpFe(CO)$_2$P(H)(N-i-Pr$_2$)Mn(CO)$_2$Cp. [h] Bridging ν(CO) frequency. [i] Paramagnetic impurities in solution prevented observation of the proton P–H resonance.

(7) Å in CpFeCr(CO)$_6$P(H)(N-i-Pr$_2$) and Fe–C = 2.12 (3), W–C = 2.07 (2) Å in CpFeW(CO)$_6$P(H)(N-i-Pr$_2$)) and a i-Pr$_2$NPH phosphido group (Fe–P = 2.207 (2), Cr–P = 2.292 (2) Å in CpFeCr(CO)$_6$P(H)(N-i-Pr$_2$) and Fe–P = 2.201 (5), W–P = 2.433 (6) Å in CpFeW(CO)$_6$P(H)(N-i-Pr$_2$)). The bridging carbonyl group is symmetrical within experimental error despite the dissimilarity of the metal atoms being bridged.

Table I indicates substantial changes in various NMR parameters upon decarbonylation of I to III with heteronuclear metal–metal bond formation leading to a FePM three-membered ring. Most dramatic is the ~150 ppm downfield phosphorus-31 chemical shift upon conversion from I to III, which is undoubtedly a consequence of the ring formation. Also noticeable is a ~60 Hz increase in the $\lvert^1J$(P–H)$\rvert$ coupling constant and a ~2 ppm downfield proton chemical shift of the P–H hydrogen.

Related bimetallic compounds containing cyclopentadienylmanganese carbonyl units can also be prepared. Thus treatment of a hexane solution of (i-Pr$_2$N)$_2$PHMn(CO)$_2$Cp with hydrogen chloride gives an 89% yield of yellow i-Pr$_2$NP(H)ClMn(CO)$_2$Cp [infrared ν(CO) in cyclohexane, 1961 and 1901 cm^{-1}; phosphorus-31 NMR, δ 144.2 ($\lvert^1J$(PH)$\rvert$ = 373 Hz)]. Reaction of i-Pr$_2$NP(H)ClMn(CO)$_2$Cp with NaFe(CO)$_2$Cp in tetrahydrofuran gives deep red CpFe(CO)$_2$P(H)(N-i-Pr$_2$)Mn(CO)$_2$Cp, formulated as IV on the basis of its spectroscopic properties (Table I).

IV

V
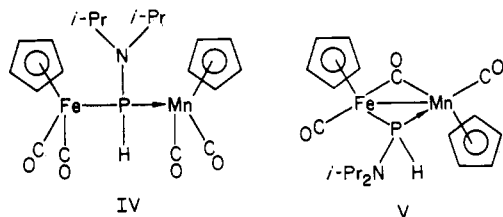
Ultraviolet irradiation of IV in cyclohexane solution gives black Cp$_2$FeMn(CO)$_3$P(H)(N-i-Pr$_2$) formulated as V because of the observation of a bridging ν(CO) frequency at 1755 cm^{-1} in its infrared spectrum.

The preliminary observations described in this communication suggest that the selective cleavage of diisopropylamino groups from metal carbonyl complexes of (i-Pr$_2$N)$_2$PH can lead ultimately to a rich variety of interesting heterobimetallic derivatives. These derivatives contain potentially reactive phosphorus–nitrogen bonds in contrast to the numerous known diarylphosphido heterobimetallic derivatives such as WIrH(μ-PPh$_2$)$_2$(CO)$_5$(PPh$_3$),[6] (OC)$_4$Mn(μ-PR$_2$)(μ-H)Mo(CO)$_2$Cp (R = p-tolyl),[7] (OC)$_5$W(μ-

PPh$_2$)Re(CO)$_4$,[8] and Cp$_2$ZrW(μ-PPh$_2$)$_2$(CO)$_4$.[9]

Supplementary Material Available: Listings of crystal data, positional parameters, anisotropic thermal parameters, bond angles, and bond distances in the two complexes CpFeM(CO)$_6$P(H)(N-i-Pr$_2$) (M = Cr and W) and an ORTEP diagram of CpFeW(CO)$_6$P(H)(N-i-Pr$_2$) (8 pages). Ordering information is given on any current masthead page.

(8) Mercer, W. C.; Whittle, R. R.; Burkhardt, E. W.; Geoffroy, G. L. *Organometallics* **1985**, *4*, 68.
(9) Targos, T. S.; Rosen, R. P.; Whittle, R. R.; Geoffroy, G. L. *Inorg. Chem.* **1985**, *24*, 1375.

Department of Chemistry   **R. B. King***
University of Georgia   **W.-K. Fu**
Athens, Georgia 30602

Department of Chemistry   **E. M. Holt**
Oklahoma State University
Stillwater, Oklahoma 74078

In Pursuit of the Active Site of Assimilatory Sulfite Reductases. Reactions of Ferric Porphyrin and [Fe$_n$S$_n$(SPh)$_4$]$^{2-}$ Complexes (n = 2, 4)

Sir:

Spectroscopic investigations of the catalytically active β subunit of *E. coli* NADPH-sulfite reductase have established that the two prosthetic groups at the active site, siroheme and an Fe$_4$S$_4$ cluster, are chemically linked.[1-7] Exchange interactions between these centers are observed in several different oxidation and ligation states of the enzyme and during substrate reduction. Similar

(1) Christner, J. A.; Munck, E.; Janick, P. A.; Siegel, L. M. *J. Biol. Chem.* **1981**, *256*, 2098–2101.
(2) Janick, P. A.; Siegel, L. M. *Biochemistry* **1982**, *21*, 3538–3547.
(3) Christner, J. A.; Munck, E.; Janick, P. A.; Siegel, L. M. *J. Biol. Chem.* **1983**, *258*, 11147–11156.
(4) Christner, J. A.; Janick, P. A.; Siegel, L. M.; Munck, E. *J. Biol. Chem.* **1983**, *258*, 11157–11164.
(5) Janick, P. A.; Rueger, D. C.; Krueger, R. J.; Barker, M. J.; Siegel, L. M. *Biochemistry* **1983**, *22*, 396–408.
(6) Janick, P. A.; Siegel, L. M. *Biochemistry* **1982**, *22*, 504–514.
(7) Christner, J. A.; Munck, E.; Kent, T. A.; Janick, P. A.; Salerno, J. C.; Siegel, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 6787–6794.

(6) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069.
(7) Casey, C. P.; Bullock, R. M. *Organometallics* **1984**, *3*, 1100.

active-site structures are thought to be present in an assimilatory sulfite reductase[8] isolated from *Desulfovibrio vulgaris* and in plant nitrite reductases.[1,9] The nature of the linkage is unknown at present. Structures with a bridging ligand linking heme iron and an Fe_4S_4 iron are strong candidates. The bridging group could be derived from an amino acid side chain, an exogenous ligand (O^{2-}, S^{2-}, etc.), or a substrate.

The investigation of models of the active sites of these enzymes is an important and challenging endeavor. Several features of the chemistry of iron–porphyrin[10] and Fe_4S_4 complexes relevant to rational syntheses of these models have not been examined extensively. These include the relative affinities of cluster iron and heme iron for various ligands, the kinetics of ligand dissociation from the two classes of complexes, and possible redox reactions between these complexes. Preparatory to efforts to model the resting-state active sites of these enzymes (ferric siroheme and $Fe_4S_4^{2+}$ core), we have examined the reactions of ferric porphyrin and $[Fe_nS_n(SPh)_4]^{2-}$ complexes (n = 2 or 4) in the absence of good potential bridging ligands. Our results establish that these complexes are mutually reactive.

Experimental Section. (1) General Information. All manipulations were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or with use of Schlenk techniques. Fe-(OEP[12])X (X = ClO_4^- or $CF_3SO_3^-$),[13,14] [Y]$_2$[Fe$_4$S$_4$(SPh)$_4$] (Y = [(C$_2$H$_5$)$_4$N] or [PPh$_4$]),[15,16] and [PPh$_4$][Fe$_2$S$_2$(SPh)$_4$][16] were prepared by literature methods. Toluene was distilled from sodium benzophenone ketyl. Acetonitrile was distilled from calcium hydride. Sulfolane (tetramethylene sulfone) was passed through a heated column of activated alumina and vacuum distilled from calcium hydride. 1,1,3,3-Tetramethylurea was dried over barium oxide and vacuum distilled. Propylene carbonate was stored over 5A sieves and vacuum distilled. Me$_2$SO was dried over calcium hydride and vacuum distilled. DMF and NMP (Burdick and Jackson distilled in glass) were stored over 4A sieves. NMP was passed through an activated alumina column immediately prior to use. Other reagents and solvents were the best available commercially and were used without further purification.

Absorption spectra were recorded on Cary Model 14 or Perkin-Elmer Model 552 spectrophotometers. Nuclear magnetic resonance spectra were determined on a Varian XL-300 spectrometer. Chemical shifts are reported relative to (CH$_3$)$_4$Si internal standard. Electrochemical measurements were performed under an argon atmosphere by using thoroughly degassed solutions containing 0.1 M [(n-C$_4$H$_9$)$_4$N]ClO$_4$ as the supporting electrolyte with a Princeton Applied Research Model 173 potentiostat-galvanostat, a Model 176 current–voltage converter, and a Model 175 universal programmer. Data were recorded on a Bascom-Turner Model 3120T digital recorder at a digitization rate sufficient to record data points at 2-mV intervals or less. Potentials reported are at a Pt-disk electrode and are reported vs. a saturated calomel electrode. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

(2) Reactions of Fe(OEP)X (X = ClO_4^- or $CF_3SO_3^-$) with [Fe$_4$S$_4$(SPh)$_4$]$^{2-}$. The course and products of the reaction are

unaffected by the identity of X or of the Fe_4S_4 counterion but are dependent upon the solvent employed. Given below are representative examples of the reaction in acetonitrile and in DMF. The latter may be taken as typical of reactions in Me$_2$SO, sulfolane, propylene carbonate, and NMP.

(a) Fe(OEP)(ClO$_4$) (**1a**) (50 mg, 7.3 × 10^{-2} mmol) and [PPh$_4$]$_2$[Fe$_4$S$_4$(SPh)$_4$] (**2a**) (107 mg, 7.3 × 10^{-2} mmol) were reacted with stirring in acetonitrile (100 mL). A precipitate began to appear after a few minutes of reaction. After 14 h, the precipitate was collected, washed with diethyl ether, and dried by pulling a stream of nitrogen gas through the solid on the fritted glass filter; 45 mg of a fine black powder identified as Fe-(OEP)(SPh) (**3**) was obtained (88% yield). Identification was based upon the identical chemical behavior, UV–vis spectrum, ^{1}H NMR spectrum, and electrochemical properties observed for the black powder and an authentic sample of Fe(OEP)(SPh).[17] The latter two characterization data are reported here for the first time. ^{1}H NMR spectrum of Fe(OEP)(SPh) in CDCl$_3$, 20 °C: 58.5 (br, aryl H), 45.5 (br, aryl H), 41.8 (br, 8 H), 39.4 (br, 8 H), 34.8 (br, aryl H), 7.3 (br, 24 H), −48.2 ppm (v br, 4 H). Aryl H resonances were too broad to obtain satisfactory integrations. Cyclic voltammetry of Fe(OEP)(SPh) in acetonitrile revealed reversible one-electron-reduction processes at $E_{1/2}$ = −0.64 V (Fe^{III}/Fe^{II}) and at $E_{1/2}$ = −1.28 V. A chemically irreversible oxidation was observed with $E_{p,anodic}$ = 0.55 V (thiolate oxidation). Processes due to Fe(OEP)(ClO$_4$) were observed following this oxidation.

Average yields for this reaction were more typically 60%, but individual runs such as that above gave yields as high as 92%. The reaction can be filtered at times as short as 10 min, but with some decrease in yield.

(b) Fe(OEP)(ClO$_4$) (205 mg, 0.3 mmol) and [PPh$_4$]$_2$[Fe$_4$S$_4$-(SPh)$_4$] (438 mg, 0.3 mmol) were reacted with stirring in DMF (100 mL). A solid was visible after 5 min of reaction. After 25 h, the precipitate was collected by filtration, washed with diethyl ether, and dried by pulling a stream of nitrogen gas through the solid on the fritted glass filter; 150 mg of a purple black microcrystalline solid was obtained. We discuss below the means by which the solid was established to be Fe(OEP) (**4**) contaminated by a variable amount of DMF and by a small amount of a sulfur-containing insoluble solid (probably an iron sulfide). Recrystallization of the solid from toluene afforded 129 mg of analytically pure **4**[11] (73% from **1a**) and 10 mg of the insoluble solid.

In one case, the above reaction was filtered after 1.5 h. The yield of the solid was approximately 10% less. The DMF filtrate was immediately reduced sixfold in volume on a rotary evaporator. Diethyl ether was slowly added to the point of incipient crystallization. The solution was stored at −30 °C overnight. Upon filtration, 25% of the starting **2a** was recovered. (This is likely a lower bound of the amount of unreacted **2a** rather than an indication of reaction stoichiometry.)

(3) Reactions of Fe(OEP)X (X = ClO_4^- or $CF_3SO_3^-$) with [Fe$_2$S$_2$(SPh)$_4$]$^{2-}$. Fe(OEP)(ClO$_4$) (105 mg, 1.53 × 10^{-1} mmol) and [PPh$_4$]$_2$[Fe$_2$S$_2$(SPh)$_4$] (**6**) (198 mg, 1.53 × 10^{-1} mmol) were reacted with stirring in DMF (50 mL). A precipitate was collected by filtration after 1 h, washed with diethyl ether, and dried in vacuum; 58 mg of a fine black powder identified as Fe(OEP)(SPh) was obtained (54% yield). The solid was contaminated by a small amount of Fe(OEP). At longer reaction times (up to 24 h) the proportion of Fe(OEP) in the mixture increased until it was the predominant species. These observations are consistent with initial formation and precipitation of Fe(OEP)(SPh) followed by slow dissolution and autoreduction to Fe(OEP).[11,17-19]

The identity of X or of the Fe$_2$S$_2$ counterion did not affect the outcome of the reaction. The time course and yield of the reaction

(8) Huynh, B. H.; Kang, L.; DerVartanian, D. V.; Peck, H. D., Jr.; LeGall, J. *J. Biol. Chem.* **1984**, *259*, 15373–15376.
(9) Lancaster, J. R.; Vega, J. M.; Kamin, H.; Orme-Johnson, N. R.; Orme-Johnson, W. H.; Krueger, R. J.; Siegel, L. M. *J. Biol. Chem.* **1979**, *254*, 1268–1272.
(10) The most accurate model of the active site would contain an iron–isobacteriochlorin complex. We have begun our investigations with iron–porphyrin complexes for ease of accessibility and study. These complexes should have qualitatively similar reactivity.[11]
(11) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763.
(12) Abbreviations: OEP, 1,2,3,4,5,6,7,8-octaethylporphyrin dianion; TPP, 5,10,15,20-tetraphenylporphyrin dianion; P, porphyrin dianion; DMF, *N,N*-dimethylformamide; Me$_2$SO, dimethyl sulfoxide; NMP, *N*-methylpyrrolidinone.
(13) Ogoshi, H.; Watanabe, E.; Yoshida, Z. *Chem. Lett.* **1973**, 989.
(14) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.
(15) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1093.
(16) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.

(17) Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414.
(18) Collman, J. P.; Sorrell, T. N.; Hoffman, B. M. *J. Am. Chem. Soc.* **1975**, *97*, 913.
(19) Ogoshi, H.; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1975**, 2289.

were affected by the solvent employed. Formation of Fe(OEP) occurred more slowly and to a lesser extent in poorly coordinating solvents (acetonitrile).

(4) Spectroscopic Monitoring of Reactions. (a) Reactions of 1 and 2 and of 1 and 6 were monitored at 0.35 and 0.02 mM concentrations by using 0.2-mm and 1-cm path length cells, respectively. The solution of the Fe_nS_n complex was placed in the appropriate cell, which was sealed with a septum cap, and its spectrum was examined. One equivalent of a more concentrated solution of the desired ferric porphyrin was then added by syringe. The resulting solution was rapidly mixed, and an initial spectrum was recorded immediately. Additional spectra were taken at appropriate intervals until no further change was noted. (b) A 0.75-mL sample of a 12.5 mM solution of $[(C_2H_5)_4N]_2[Fe_4S_4(SPh)_4]$ in Me_2SO-d_6 was placed in a NMR tube, which was sealed with a serum cap. After the ^1H NMR spectrum was examined, 1 equiv of Fe(OEP)(ClO$_4$) dissolved in a small volume of Me_2SO-d_6 was added by syringe. An initial spectrum was recorded immediately. Additional spectra were taken at appropriate intervals. The limited solubility of products 3 and 4 in CD_3CN prevented similar attempts to monitor the reaction by ^1H NMR in this solvent.

Results. Reaction of equivalent amounts of Fe(OEP)X (X = ClO$_4^-$ or CF$_3$SO$_3^-$) (1) and of $[(C_2H_5)_4N]_2[Fe_4S_4(SPh)_4]$ (2) at mM concentrations in acetonitrile solution, reaction 1, resulted

$$Fe(OEP)X + [Fe_4S_4(SPh)_4]^{2-} \xrightarrow{CH_3CN} Fe(OEP)(SPh) \qquad (1)$$
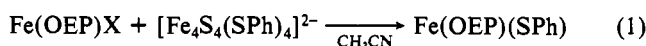
in the precipitation in high yield of Fe(OEP)(SPh) (3). The analogous reaction in DMF or Me_2SO, reaction 2, resulted in

$$Fe(OEP)X + [Fe_4S_4(SPh)_4]^{2-} \xrightarrow{DMF \text{ or } Me_2SO} Fe(OEP) \qquad (2)$$
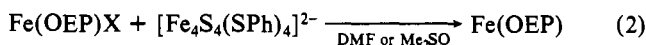
precipitation of a sulfur-containing solid.[20] Immediate workup of the DMF supernatant permitted a 25% or better recovery of 2. Solids from reaction 2 in either solvent had UV–vis spectra in benzene (<0.5 mM) identical with that of authentic Fe(OEP) (4).[21] Recrystallization of the solid in toluene afforded analytically pure 4 in 73% isolated yield from 1 and a small amount of a sulfur-containing insoluble solid (probably an iron sulfide). Solids with UV–vis spectra identical with that of 4 were also obtained from reactions in sulfolane, NMP, and propylene carbonate solution. The identity of the counterion in 2 did not affect the course of reactions 1 or 2. Fe(OEP)Cl also reacted with 2 in DMF to yield 4, but over a much longer period and with lesser yield (36% after 24 h). [Fe(OEP)]$_2$O was unreactive. Preliminary results suggest that Fe(TPP)(ClO$_4$) reacts with 2 in a manner similar to its reaction with 1.

The ^1H NMR spectra of C_6D_6 or C_7D_8 solutions of the crude solid isolated from reactions in DMF (about 2 mM) were identical with that of 4,[22] excepting the presence of DMF. At similar concentrations the spectra of the products from Me_2SO reactions were substantially different. Relatively sharp resonances due to 4 at 75.2 (4 H), 33.5 (16 H), and 12.8 (24 H) ppm (relative to Me_4Si) were replaced by three broad resonances at positions upfield. The sharpness and upfield shift of these resonances relative to those of 4 increased with the amount of Me_2SO observed in the sample. Upon addition of a large excess of Me_2SO-d_6 to the sample, the resonances shift to 10.4 (br, 4 H), 5.1 (br, 16 H), and 1.9 (t, 24 H) ppm, identical with those in the spectrum of 4 in neat Me_2SO-d_6. Hence, rapid equilibration of Fe(OEP) and [Fe(OEP)(Me$_2$SO)$_2$] (5a) is being observed in the spectrum of the Me_2SO reaction product. Qualitative titrations of 4 with Me_2SO and DMF (monitored by UV–vis spectra) established that substantial amounts of the bis(solvate) complex form at Me_2SO concentrations comparable to the concentration of adventitious

Me_2SO in the NMR samples (10 mM), but significantly higher concentrations are required for complexation by DMF.[23] Thus, the solid isolated from reaction 2 contains 4, a variable amount of the reaction solvent, and a small amount of an iron sulfide.

Reaction of equivalent amounts of 1 and $[PPh_4]_2[Fe_2S_2(SPh)_4]$ (6) at millimolar concentrations in *both* acetonitrile and DMF, reaction 3, resulted in the initial precipitation of 3 contaminated

$$Fe(OEP)X + [Fe_2S_2(SPh)_4]^{2-} \rightarrow Fe(OEP)(SPh) \qquad (3)$$
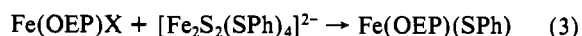
by a trace of 4. At long reaction times (solvent dependent), [Fe(OEP)(solvent)$_2$] (5) became the predominant species in the solid.

Reactions 1–3 were monitored by UV–vis spectroscopy at 0.02 and 0.35 mM concentrations. Reactions involving 2 proceeded rapidly at both concentrations to yield 3 in acetonitrile and 5 in DMF or Me_2SO.[23] A small amount of 3 (<10%) was detected in the first minutes of the reaction in DMF but disappeared as the reaction progressed. Intermediates were not detected in reactions in Me_2SO, which went to completion within 2 min. Reactions involving 6 also proceeded rapidly at both concentrations in acetonitrile and DMF to yield 3. Conversion of the initially formed 3 to 5 in the 0.35 mM DMF reaction was nearly complete after 15 min. Precipitates formed only in the reactions at the higher concentration. Similarly, no precipitate formed during the reaction of 1 and 2 in millimolar tetramethylurea solutions, but 5 was observed in solution. Thus, product formation is not controlled by precipitation equilibria.

Attempts to monitor the reaction of 1 and 2 at 5–10 mM concentration in CD_3CN or Me_2SO-d_6 by ^1H NMR spectroscopy were complicated by the precipitation of reaction products. The solubility in CD_3CN was sufficiently limited that only the disappearance of 1[24] and of 2 could be observed. (Satisfactory spectra of authentic 3 or 4 could not be obtained in this solvent.) Observations on the reaction in Me_2SO-d_6 were consistent with the results of the UV–vis experiments. In the initial spectrum (obtained within 2 min) 1 was almost totally converted to 5 and to a small amount of 3, the quantity of 2 was significantly reduced, and diphenyl disulfide was present. All lines were substantially broadened, either by ligand exchange between species or by a paramagnetic intermediate with appropriate T_1. Later, line widths and the quantities of 1, 3, and 5 decreased through reaction and/or precipitation. Some 2 remained at the conclusion of the reaction.

Discussion. On a superficial level, examination of the products of reactions 1–3 suggests that reactions 1 and 3 are ligand substitution reactions and that reaction 2 is a redox reaction. Reduction potentials of Fe(P)(ClO$_4$) complexes vary with the solvent[25] but are sufficiently positive that some oxidized 2[26,27] should be present at equilibrium. (The positive potentials are a reflection of the inability of the weak-field axial ligand and/or coordinating solvent to stabilize the ferric oxidation state.) 2 decomposes irreversibly to disulfide and other uncharacterized products upon oxidation.[27] This should displace the redox equilibrium and provide a pathway for formation of FeS. Alternatively, the mechanism of reaction 2 could consist of an initial ligand substitution to form 3 followed by rapid autoreduction in coordinating solvents, a known reaction.[11,17–19] The detection of 3 during the initial phase of reaction 2 in DMF is consistent with the latter interpretation.

Several lines of evidence support a redox mechanism for reaction 2. The initial *isolated* product of the reaction of 1 and 6 in both acetonitrile and DMF is 3. In contrast, reaction of 1 and 2 in

(20) Sulfur was detected by elemental analysis and by catalysis of the iodine–azide reaction. See: Fiegel, F.; Anger, V. "Spot Tests in Inorganic Analysis", 6th ed.; Elsevier: New York, 1972; p 437.

(21) Stolzenberg, A. M. Ph.D. Thesis, Stanford University, 1980. λ_{max}, nm (ϵ, mM): 330 (25.7), 381 (62.7), 410 (74.9), 436 sh (29.3), 528 (9.4), 562 (13.6), 770 (1.6).

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

(23) UV–vis spectra of [Fe(OEP)(solvent)$_2$] in neat solvent are as follows [λ_{max}, nm (A/A_{ref})]. DMF: 410 (18.7), 415 (18.7), 536 (1.67), 554 (1.66), 576 (1). Me$_2$SO: 340 (4.48), 390 (2.72), 412 (22.40), 514 (0.78), 545 (1).

(24) ^1H NMR spectra of Fe(OEP)(ClO$_4$), 20 °C, Me$_2$SO-d_6: 47.63 (br, 16 H), 40.45 (br, 4 H), 7.39 ppm (br, 24 H). CD$_3$CN: 35.45 (br, 16 H), 16.75 (br, 4 H), 5.64 ppm (br, 24 H).

(25) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348.

(26) DePamphilis, B. V.; Averill, B. A.; Herskovitz, T.; Que, L., Jr.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 4159.

(27) Mascharak, P. K.; Hagen, K. S.; Spence, J. T.; Holm, R. H. *Inorg. Chim. Acta* **1983**, *80*, 157.

DMF yields **5**, a ferrous porphyrin complex. The difference in products is puzzling if the second mechanism for reaction 2 is invoked but is readily explicable for a redox mechanism. Formally, **2** contains two ferric and two ferrous irons, but both irons in **6** are ferric. The inability of **6** to reduce **1** is not surprising. Further evidence against the second mechanism may be found by examining the rate of autoreduction of **3**. At comparable concentrations in DMF and Me₂SO, authentic solutions of **3** take roughly 10 times longer to undergo complete autoreduction than is required for reaction 2 to go to completion. Furthermore, addition of an equivalent amount of **3** to **2** in DMF (0.02 mM) does not result in significant formation of **5**.[28] These observations establish that **3** is relatively stable under the reaction conditions and cannot be an intermediate on the predominant pathway for formation of **5**. The detection of **3** during the initial phase of reaction 2 could result from a small amount of material following reaction 1 or from a secondary reaction of initially formed **5** with diphenyl disulfide.[11]

A curious feature of these reactions is that reduction of **1** by **2** occurs in all solvents excepting the one (acetonitrile) in which the reduction potential of the Fe^{III}/Fe^{II} couple of **1** has the most positive value.[25] This apparent paradox can be rationalized on the basis of solvent ligation equilibria and of Franck–Condon barriers to electron transfer. The negative shift of the reduction potentials of $Fe(P)(ClO_4)$ complexes in solvents such as DMF and Me₂SO reflect the formation of labile high-spin six-coordinate $[Fe(P)(solvent)_2]^+$ complexes.[29] These complexes are also present to some extent in solutions of Fe(P)Cl in these solvents.[25,30] The higher ligand field strength of the bis(solvate) complexes stabilizes the ferric oxidation state relative to that of the weak-field ClO_4^- ligand.[31] In addition, the iron atom moves from roughly 0.3 Å out of plane in the ClO_4^- complex to an in-plane position upon formation of the bis(solvate) complexes.[32] Acetonitrile interacts weakly with **1**. The rate of electron transfer to **1** in acetonitrile will be slow, owing to the substantial structural reorganization and spin-state change that occur upon reduction of **1** and to the small E_0 for the reaction with **2**. The lifetime of **1** is long enough to permit formation of **3**, either by reaction with thiolate dissociated from the labile complex **2**[33] or by attack of the heme iron on a bound thiolate ligand of **2**. The potential of the Fe^{III}/Fe^{II} couple in **3** is sufficiently negative that no redox reaction with **2** occurs. Acetonitrile is such a weak ligand that autoreduction of **3** should be slow. In contrast to the situation in acetonitrile, little structural reorganization and no ligation change occur upon reduction of the ferric bis(solvate) complexes in more strongly coordinating solvents. Reduction by **2** will be relatively rapid. At present, the evidence does not permit us to choose between an inner-sphere (with thiolate bridging between a heme and a Fe_4S_4 iron, for example) or an outer-sphere mechanism.

Our results establish that a successful synthetic approach to a model of the active site must eliminate several undesirable reactions between ferric porphyrin and Fe_4S_4 complexes. Reactions 1 and 3 imply that the affinity of heme iron for thiolate is significantly greater than that of an iron in **2** or **6**. Unless the bridging ligand utilized in the model adequately stabilizes the ferric iron in the porphyrin complex and kinetics favor model assembly, thiolate abstraction by heme will always be a problem when simple $[Fe_4S_4(SR)_4]^{2-}$ complexes are employed.[34] Reaction 2 points out that oxidative decomposition of **2** will occur when it is reacted

with ferric heme complexes containing weak and/or labile axial ligands in coordinating solvents.[35] On the basis of the above, the most promising approaches to the synthesis of models of the active site proceed from porphyrin complexes containing an inert axial ligand capable of stabilizing the ferric oxidation state. Approaches of this type are being examined in our laboratory.

---

(35) The reduction potentials of $[Fe_4S_4(SR)_4]^{2-}$ complexes with more biologically relevant alkanethiolate ligands are shifted negative to those of the R = Ph complex.[26,27] Complexes with alkanethiolate ligands should be more susceptible to oxidation in reaction 2.

Department of Chemistry   **Alan M. Stolzenberg***
Brandeis University   **Matthew T. Stershic**
Waltham, Massachusetts 02254


Assignment of Metal–Nitrogen Stretching Frequencies in Metal Nitrene Complexes

Sir:

The prevailing assignment[1] of IR stretching frequencies between 1100 and 1300 cm⁻¹ to metal nitrenes or imido complexes (M—NR) has led to anomalies. Metal nitrido complexes (M≡N), which are expected to have a higher bond order[2a] than metal nitrenes, exhibit IR stretches at *lower* frequencies (950–1200 cm⁻¹).[2b] Since metal–oxo and metal–imido fragments are isoelectronic, it is also noteworthy that the M—O stretch (between 900 and 1050 cm⁻¹)[3] lies below the range proposed for imido complexes. On the basis of bond lengths, the relative bond strengths M≡N > M≡O > M≡NR have been suggested.[1] Isotopic labeling studies for Cp^*_2VNPh (Cp^* = η-$C_5(CH_3)_5$ and Ph = C_6H_5) show that the M—N stretch occurs at 934 cm⁻¹, a value similar to that observed[3] in metal–oxo complexes.

We[4] and others[5] have synthesized (eq 1) Cp^*_2VNPh, the structure of which has been established[5] by X-ray crystallography.

$$Cp^*_2V + N_3Ph \rightarrow N_2 + Cp^*_2VNPh \qquad (1)$$
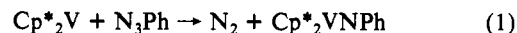
This complex exhibits a sharp peak in the IR spectrum at 1159 cm⁻¹ (Figure 1) that has been assigned[5] to the M–N stretching vibration. We prepared related derivatives (*N*-2,6-dimethylphenyl and *N*-2-biphenylyl) that did not show a similar IR absorption. Because the labeled azide precursor $N_2^{15}NPh$ is readily available,[6,7] we synthesized $Cp^*_2V^{15}NPh$ to determine the frequency of the V–N stretch.

Comparison of the IR spectra of the labeled and unlabeled derivatives (Figure 1) reveals that the peak at 1159 cm⁻¹ does not shift on isotopic substitution, thereby excluding its assignment

---

(28) Reaction of **3** and **2** at 0.5 mM in DMF does result in nearly complete conversion of **3** to **5** (without substantial loss of **2**) on a time scale slightly longer than that of reaction 2, however.
(29) Mashiko, T.; Kastner, M. E.; Spartalian, K.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354.
(30) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. N.; Budd, D. L.; LaMar, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 4345–4351.
(31) Kadish, K. M. In "Iron Porphyrins, Part 2"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; pp 161–249.
(32) Scheidt, W. R.; Gouterman, M. In "Iron Porphyrins, Part 1"; Lever, A. B. P.; Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; pp 89–139.
(33) Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427.
(34) Unexpectedly different binding constants for iron–isobacteriochlorin complexes relative to those for iron–porphyrin complexes could eliminate the problem of reaction 1.

(1) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.
(2) (a) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369–396. (b) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; p 301.
(3) Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459.
(4) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.*, in press.
(5) Gambarotta, S.; Chiesi-Villa, A.; Guastini, C. *J. Organomet. Chem.* **1984**, *270*, C49–C52.
(6) Phenyl azide, labeled with ¹⁵N in the α position, was prepared as described in ref 7. The complex was prepared according to eq 1[4,5] except the azide:Cp^*_2V ratio was 1.5:1.
(7) Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1025–1029.