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 Me$_2$SO, 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 Me$_2$SO 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$_4$S$_4$ 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$_4$S$_4$ 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$_4$S$_4$(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.

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(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.

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(34) Unexpectedly different binding constants for iron–isobacteriochlorin complexes relative to those for iron–porphyrin complexes could eliminate the problem of reaction 1.

(35) The reduction potentials of [Fe$_4$S$_4$(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.

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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$\equiv$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$\equiv$N > M$\equiv$O > M$\equiv$NR have been suggested.[1] Isotopic labeling studies for Cp*$_2$VNPh (Cp* = η-C$_5$(CH$_3$)$_5$ and Ph = C$_6$H$_5$) 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*$_2$VNPh, the structure of which has been established[5] by X-ray crystallography.

$$\mathrm{Cp^*_2V + N_3Ph \rightarrow N_2 + Cp^*_2VNPh} \qquad (1)$$

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*$_2$V^{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

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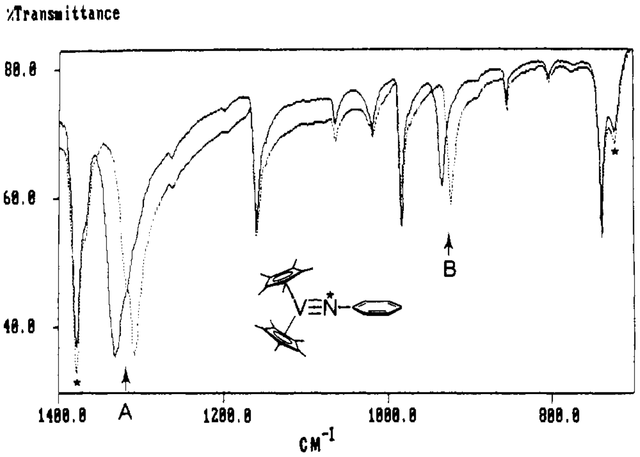

Figure 1. Nujol mull FTIR (IBM IR32) spectra (50 scans, 2-cm^{-1} resolution) of $Cp^*_2V^{14}NPh$ (solid line) and $Cp^*_2V^{15}NPh$ (dashed line). Peaks marked with an asterisk result from Nujol. Peak A is attributed to the C–N stretch and peak B to the V–N stretch.

Table I. Stretching Frequencies (cm^{-1}) in Decamethylvanadocene Nitrenes[a]

compd	ν_{C-N}	ν_{V-N}	compd	ν_{C-N}	ν_{V-N}
Cp^*_2VNPh	1330	934	Cp^*_2VN(2-biphenyl)	1314	937
$Cp^*_2V^{15}NPh$	1307	923	$Cp^*_2VN(C_6F_5)$	1303	968
$Cp^*_2VN(2,6\text{-}Me_2C_6H_3)$	1293	940			

[a] Spectra taken in Nujol mulls.

as the V–N stretch. Only IR peaks at 1330 and 934 cm^{-1}, labeled A and B in Figure 1, shift by more than 0.5 cm^{-1} on isotopic substitution. The 1330-cm^{-1} band shifts to 1307 cm^{-1} in the spectrum of the ^{15}N derivative and is assigned to the N–C stretching vibration. For comparison the N–C stretches appear as doublets at 1295, 1284 cm^{-1} and 1271, 1256 cm^{-1} in the IR spectra of N_3Ph and $N_2{}^{15}NPh$, respectively. For Cp^*_2VNPh the 934-cm^{-1} band shifts to 923 cm^{-1} in the spectrum of the ^{15}N derivative. We assign this absorption, B, to the V–N stretching vibration, a value outside the proposed range[1] of 1100–1300 cm^{-1}. Other nitrene derivatives (Table I) exhibit peaks attributable to V–N and N–C stretches in the same spectral region. The shifts of the N–C and V–N stretches between the NPh and $N(2,6\text{-}Me_2C_6H_3)$ derivatives (Table I) parallel changes in the C–N bond lengths (1.345 (9) Å in NPh[5] and 1.387 (9) Å in $NMe_2C_6H_3$[4]) and V–N bond lengths (1.730 (5) Å in NPh[5] and 1.706 (6) Å in $NMe_2C_6H_3$[4]).

By use of the harmonic oscillator approximation[8] the C–N stretch in the ^{15}N derivative is predicted at 1309 cm^{-1}, which is close to that observed (1307 cm^{-1}). The calculated value for the V–^{15}N stretch of 909 cm^{-1} is 14 cm^{-1} lower than the experimental number and suggests that motion of the N atom in the V–N stretch may be decreased by coupling to other vibrations. Attempts to apply force field calculations derived for linear triatomics[9–11] led either to nonphysical solutions or to unreasonably large interaction constants. Therefore, the V–N–C oscillator appears to be coupled to the remainder of the molecule. This may result in a wide range of M–N stretching frequencies depending on the N substituent and the other vibrations within the molecule. It is interesting to note that Cl_3VNCl, where the N–Cl stretch (510 cm^{-1}) lies just below the M–N stretch, exhibits[12] a high ν_{V-N} = 1107 cm^{-1}. Assignment of the M–N stretch in this complex is not complicated by the presence of nearby ligand vibrations. Earlier attempts[13] to determine M–N stretches in arylimido complexes by isotopic labeling revealed the high frequency N–C stretch, but the M–N stretch was obscured by ligand vibrations.

Given the low intensity of the V–N stretch and the strong vibrational coupling between M–N and N–substituent stretches, the identification of metal–nitrene stretches should be made with caution. We suspect that a reasonable range for stretching frequencies in these compounds is 850–1150 cm^{-1}, but other well-characterized examples are needed.

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