Oxygen Atom Transfer Processes. Reaction of *trans*-Dinitrobis(triethylphosphine)nickel(II), $Ni(NO_2)_2(PEt_3)_2$, with Carbon Monoxide

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Abstract: The reaction of *trans*-$Ni(NO_2)_2(PEt_3)_2$ with CO under mild conditions (11 °C, 1 atm, benzene solution) has been shown to afford CO_2 in addition to the previously reported[1] $Ni(NO_2)(NO)(PEt_3)_2$. An ^{18}O-labeling study using *trans*-$Ni(N^{18}O_2)_2(PEt_3)_2$ and CO unambiguously establishes NO_2^- as the source of oxygen in the conversion of CO to CO_2. Moreover, the extent of ^{18}O enrichment in the CO_2 product indicates that the intermediate(s) involved must be sufficiently long lived to undergo appreciable—but not statistical—oxygen scrambling between carbon and nitrogen atoms prior to the irreversible loss of CO_2.

Introduction

The facile conversion of *trans*-$Ni(NO_2)_2(PEt_3)_2$ into $Ni(NO_2)(NO)(PEt_3)_2$ by CO was reported over 15 years ago by Booth and Chatt.[1] Although the fate of the CO was not mentioned, simple atom balance requires CO_2 as the additional product of the reaction:

trans-$Ni(NO_2)_2(PEt_3)_2$
$$+ \; CO \rightarrow Ni(NO_2)(NO)(PEt_3)_2 + CO_2 \quad (1)$$
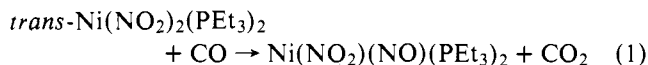
This reaction is apparently one of the earliest examples of the now well-documented[2-7] ability of CO to reduce coordinated NO_2^- to coordinated NO. One attractive mechanism for such a process is an oxygen atom transfer from coordinated NO_2^- to coordinated CO (Scheme I). An analogous oxygen atom transfer between coordinated NO_2^- and NO groups in *cis*-$Fe(NO_2)(NO)(S_2CNMe_2)_2$ has recently been demonstrated by ^{15}N-labeling studies.[8] However, the mechanism depicted in Scheme I—although frequently invoked in the literature[4,6]—has not been experimentally substantiated to date. Further impetus for the elucidation of mechanistic information is provided by the realization[6,7,9-13] that identical or closely related oxygen atom transfer processes may play a role in homogeneous catalytic systems which involve the conversion of NO and CO into N_2O and CO_2. Accordingly, we have carried out a detailed ^{18}O-labeling investigation of reaction 1.
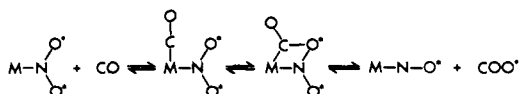
Experimental Section

Material. All solvents (reagent grade) were dried by appropriate methods, distilled, and saturated with nitrogen prior to use. The following compounds were purchased from commercial sources and were used without further purification: $NiCl_2 \cdot 6H_2O$, PEt_3, KNO_2, and AgCN. Water enriched in ^{18}O at the nominal level of 1.5% was purchased from YEDA (Rehovoth, Israel). Research grade CO (99.99%) was used as purchased from Matheson.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer calibrated with carbon monoxide, polystyrene, and indene. Solution spectra were run in NaCl cells using dichloromethane as solvent. Mull spectra were recorded in Nujol and hexachlorobutadiene between NaCl plates.

The $^{31}P\{^1H\}$ NMR spectra were recorded at 36.43 MHz on a Bruker WH-90DS spectrometer operating in the FT mode. A C_6H_6 solution of the complex was placed in a nitrogen-filled 8-mm NMR tube held coaxially in a 10-mm NMR tube. The outer tube contained D_2O which served as an external lock. ^{31}P chemical shifts are referenced to an external sample of 85% H_3PO_4; positive chemical shifts are *downfield* from H_3PO_4.

Routine mass spectrometry measurements were carried out on a Hitachi Perkin-Elmer RMU-6 mass spectrometer. Mass spectrometric analyses of ^{18}O-enriched CO_2 samples were carried out on a Nuclide Analysis Associates RMS-11 isotope ratio mass spectrometer. The isotopic composition of the purified CO_2 sample was determined by measuring the ratio of the mass 46 to the (mass 44 + mass 45) peaks using the double collector procedure.[14,15]

Data Treatment. The following symbols are used in this paper.

E_X is the ^{18}O enrichment in the species X relative to a normal sample of species X. E_X is determined experimentally from the mass 46/(mass 44 + mass 45) ratio for an enriched CO_2 sample compared to that in a sample of natural isotopic abundance. Thus, for a substance of natural isotopic abundance $E_X = 1.000$.

n_t represents the number of oxygen atoms per CO_2 molecule which derive from *trans*-$Ni(N^{18}O_2)_2(PEt_3)_2$. Values of n_t can be calculated from the relationship

$$n_t = \left[\frac{E_{CO_2} - E_{CO}}{E_{complex} - E_{CO}}\right] [2.000]$$

Preparation of Complexes. A method similar to that of Venanzi[16] was used to prepare *trans*-$NiCl_2(PEt_3)_2$. Addition of PEt_3 (6.3 mL, 42.6 mmol) to a methanol solution of $NiCl_2 \cdot 6H_2O$ (5.06 g, 21.3 mmol) gave immediate precipitation of red, crystalline *trans*-$NiCl_2(PEt_3)_2$. The precipitate was filtered, washed with cold methanol, and dried in vacuo (yield 7.51 g, 96%). The compound was used without further purification in subsequent reactions.

The complex *trans*-$Ni(NO_2)_2(PEt_3)_2$ was prepared from *trans*-$NiCl_2(PEt_3)_2$ and KNO_2 according to the method of Booth and Chatt.[1] The infrared spectrum of the complex exhibited three strong absorptions at 1374, 1319, and 813 cm^{-1}, indicating[17] the presence of N-bound NO_2^-. These frequencies are in good agreement with the literature[1] values. The $^{31}P\{^1H\}$ NMR spectrum of the complex showed a singlet at +12.6 ppm.

The ^{18}O-enriched *trans*-$Ni(NO_2)_2(PEt_3)_2$ was synthesized similarly from $KN^{18}O_2$ which was prepared by exchange with $H_2^{18}O$ as described by Samuel and Wasserman.[18]

Determination of ^{18}O Enrichment in *trans*-$Ni(N^{18}O_2)_2(PEt_3)_2$. The ^{18}O enrichment of the nickel complex was determined by mass spectrometry after conversion of the oxygen in the complex to CO_2 with AgCN according to the method of Shakhashiri and Gordon.[19] The mean value of the ^{18}O enrichment in the complex, $E_{complex}$, was 5.17₄ ± 0.12₇ for four determinations. The precision lies within the expected experimental uncertainty associated with the AgCN method.[19]

Reaction of *trans*-$Ni(NO_2)_2(PEt_3)_2$ with CO. Approximately 1 mmol of *trans*-$Ni(NO_2)_2(PEt_3)_2$ was placed in the reaction vessel illustrated in Figure 1. The reaction vessel was evacuated on a high-vacuum line and benzene (~15 mL), previously degassed by several freeze-pump-thaw cycles, was introduced by vacuum distillation. The working manifold of the vacuum line was isolated from the pumps and brought to ambient pressure with CO. The benzene solution was cooled in a dioxane slush bath at 11 °C and CO was admitted to the
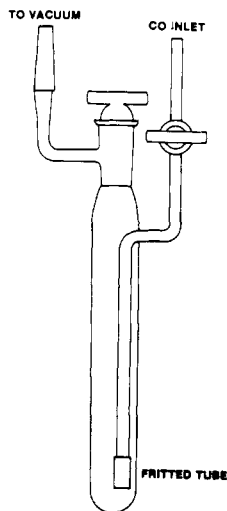
Scheme I

Figure 1. Reaction vessel used for study of reaction 1.

Figure 2. Reaction vessel used for reversibility study.

reaction vessel via the fritted tube. The yellow solution turned deep purple within a few seconds. Flow of CO was maintained for 15 min while the volatile product was trapped in a methylcyclohexane slush bath at -130 °C. The volatile material in the -130 °C trap was purified by a series of trap to trap distillations and was transferred to an evacuated tube for mass spectrometric analysis. A ^{31}P NMR spectrum of the reaction mixture at this stage showed resonances due only to $Ni(NO_2)(NO)(PEt_3)_2$ ($+29.3$ ppm) and starting material ($+12.6$ ppm) with relative intensities $\sim6:1$, respectively.

Preliminary studies were carried out on unenriched *trans*-$Ni(NO_2)_2(PEt_3)_2$. Mass spectrometric analysis established CO_2 as the only volatile product of the reaction. Studies involving ^{18}O-labeled nickel complex were carried out similarly except that mass spectrometric measurements were performed only on the RMS-11 instrument.

Reversibility Study. A sample of $Ni(N^{18}O_2)(N^{18}O)(PEt_3)_2$ was prepared by the above method in the reaction vessel shown in Figure 2. Following thorough degassing of the solution by several freeze-pump-thaw cycles, the reaction vessel was isolated from the vacuum line at A and B. The benzene solution was cooled in a dioxane slush bath at 11 °C and the tube (C) containing a measured sample of unenriched CO_2 (~1 mmol) was slowly opened, allowing the gas to enter the solution via the fritted tube. After 20 min the reaction vessel was cooled in liquid nitrogen and rethawed to ensure that the solution was saturated with CO_2. After an additional 30 min, the solution was degassed and the CO_2 was trapped and purified as described previously. Analysis of the purified CO_2 sample on the RMS-11 mass spectrometer showed no incorporation of ^{18}O ($E_{CO_2} = 1.005$).

Investigation of Exchange between *trans*-$Ni(N^{18}O_2)_2(PEt_3)_2$ and CO_2. A benzene solution of *trans*-$Ni(N^{18}O_2)_2(PEt_3)_2$ (~1 mmol) was prepared as described previously in the reaction vessel shown in Figure 2. Treatment of this solution with a measured sample of unenriched CO_2 and subsequent operations followed the procedure outlined in the previous experiment. Mass spectrometric analysis of the recovered purified CO_2 on the RMS-11 instrument showed no incorporation of ^{18}O ($E_{CO_2} = 0.997$).

Results and Discussion

Reaction of *trans*-$Ni(NO_2)_2(PEt_3)_2$ with CO. Initial studies were carried out in order to completely establish the course of the reaction of *trans*-$Ni(NO_2)_2(PEt_3)_2$ with CO. Introduction of CO to a benzene solution of the nickel complex at 11 °C was accompanied by an immediate color change from yellow to the characteristic[1] intense purple color of $Ni(NO_2)(NO)(PEt_3)_2$. Mass spectrometric analysis of the purified volatile material produced in the reaction showed CO_2 as the only detectable product. A ^{31}P{^{1}H} NMR spectrum of the reaction mixture exhibited singlets at $+12.6$ and $+29.3$ ppm assigned to *trans*-$Ni(NO_2)_2(PEt_3)_2$ and $Ni(NO_2)(NO)(PEt_3)_2$, respectively, by comparison with authentic samples. The peak at-

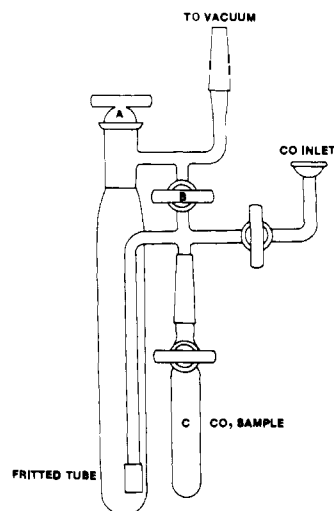tributable to starting material gradually disappeared over a period of ~1 h, during which time a CO flow of ~15 cm^3/min was maintained. The reaction thus proceeds quite rapidly under relatively mild conditions (11 °C, 1 atm CO), undoubtedly at a rate which is primarily limited by the amount of CO dissolved in the solvent benzene.[20]

No other phosphorus-containing products, in particular the logical degradation products PEt_3 (-20.4 ppm[23]) and $POEt_3$ ($+48.3$ ppm[23]), were observed by ^{31}P NMR spectroscopy throughout the course of the reaction. The absence of $POEt_3$ in the reaction mixture indicates that oxygen transfer from NO_2^- to PEt_3 is not competitive with oxygen transfer to CO, in contrast to related[4,24,25] transition-metal systems involving PPh_3 ligands. The infrared spectrum of the purple solid isolated from the reaction exhibited a strong $\nu(NO)$ band at 1715 cm^{-1} in excellent agreement with the literature[1] value for $Ni(NO_2)(NO)(PEt_3)_2$. In summary, the reaction appears to be correctly described by eq 1.

It is interesting to note that the closely related *cis*-$M(NO_2)_2L_2$ ($L = PPh_3$, $PMePh_2$) complexes of palladium and platinum undergo a much more complicated reaction with CO which leads ultimately to the trinuclear clusters $M_3(CO)_3L_4$.[6] In contrast to the nickel system, $M(NO_2)(NO)L_2$ complexes were not detected, although they are thought to be intermediates in the overall reaction sequence.[6] This difference in reactivity has been attributed[6] to the inability of $Ni(NO_2)(NO)(PEt_3)_2$ to undergo a facile linear $Ni-NO \rightarrow$ bent $Ni-NO$ interconversion which is presumably necessary to create a coordinately unsaturated metal center prior to CO association.[26] However, there is good reason to expect that the $Ni-N-O$ bond angle in $Ni(NO_2)(NO)(PEt_3)_2$ is already significantly bent in the ground state. A distinctly nonlinear $Ni-N-O$ bond angle of 152.7° has been reported[27] for the closely related $Ni(N_3)(NO)(PPh_3)_2$. It is more likely that the different behavior of the *cis*-$M(NO_2)_2L_2$ ($M = Pd$, Pt) complexes is due in large part to the different steric and/or electronic properties[28] of the phosphine ligands involved. The recent observation[29] that $Pt(NO_2)_2(PMe_2Ph)_2$ reacts with CO to afford only $Pt(NO_2)(NO)(PMe_2Ph)_2$ would support this contention.

^{18}O-Labeling Studies. An ^{18}O-labeling study was carried out in an effort to determine the nature of the oxygen atom transfer process which accompanies eq 1. A sample of ^{18}O-enriched *trans*-$Ni(NO_2)_2(PEt_3)_2$ was allowed to react with CO of normal isotopic abundance. Pertinent ^{18}O enrichment data for the CO_2 product from three separate experiments are given in Table I.

Table I. ^{18}O Enrichment of CO$_2$ Derived from the Reaction of *trans*-Ni(N^{18}O$_2$)$_2$(PEt$_3$)$_2$ with CO^a

| trial	E	n_t
1	3.698	1.29$_2$
2	3.702	1.29$_5$
3	3.697	1.29$_2$
mean	3.699	1.29$_3$

^{a} See Experimental Section for explanation of terms; $E_{complex}$ = 5.17$_4$ ± 0.12$_7$.

The presence of a substantial amount of ^{18}O in the CO$_2$ product (n_t = 1.29) unambiguously establishes NO$_2^-$ as the source of oxygen. Moreover, the degree of enrichment is significantly *larger* than that expected for the oxygen-transfer process depicted in Scheme I (n_t = 1.000), although it is apparent that statistical distribution of the ^{18}O label (n_t = 1.600) has not been achieved. Two control experiments established that the observed ^{18}O enrichment of CO$_2$ was not merely due to exchange between free CO$_2$ and either Ni(N^{18}O$_2$)-(N^{18}O)(PEt$_3$)$_2$ or *trans*-Ni(N^{18}O$_2$)$_2$(PEt$_3$)$_2$. First, CO$_2$ of normal isotopic abundance was admitted to an equimolar amount of Ni(N^{18}O$_2$)(N^{18}O)(PEt$_3$)$_2$ in benzene solution. Conditions were similar to the previous experiment except that a closed system was used rather than a flow system. Particular care was taken to ensure that CO$_2$ was adequately dissolved in the solution. In fact, CO$_2$ was allowed to remain in contact with the solution of the nickel complex for a longer period of time than that employed in the flow experiment. Mass spectrometric analysis of the recovered CO$_2$ showed no ^{18}O enrichment within experimental error (E_{CO_2} = 1.005). A similar experiment was carried out with normal CO$_2$ and *trans*-Ni(N^{18}O$_2$)$_2$(PEt$_3$)$_2$. No ^{18}O enrichment was detected in the recovered CO$_2$ sample (E_{CO_2} = 0.997).

The results of our ^{18}O-labeling studies cannot be interpreted in terms of the simple oxygen transfer process depicted in Scheme I. In order to account for the observed ^{18}O enrichment in CO$_2$ (Table I), any correct mechanism must clearly incorporate an intermediate (or intermediates) in which the two carbon-bound oxygen atoms lose their integrity. A simple modification of Scheme I is sufficient to provide a mechanism consistent with the experimental observations (Scheme II). The initial two steps of the modified mechanism are identical with the first two steps of Scheme I. Coordination of CO to the coordinately unsaturated 16-electron complex *trans*-Ni(NO$_2$)$_2$(PEt$_3$)$_2$ is followed by reversible intramolecular oxygen transfer from NO$_2^-$ to CO. The second step has precedent in the closely related interconversion of coordinated NO$_2^-$ and NO groups in *cis*-Fe(NO$_2$)(NO)(S$_2$CNMe$_2$)$_2$ via intramolecular oxygen atom transfer.[8]

The crucial feature of Scheme II is the formation of an intermediate nickel–CO$_2$ complex (**3**) which is sufficiently long lived to undergo partial scrambling of oxygen atoms between nitrogen and carbon prior to the *irreversible* loss of CO$_2$. Dissociation of CO$_2$ is required to be irreversible by the experimental observation that CO$_2$ does not undergo ^{18}O exchange with Ni(N^{18}O$_2$)(N^{18}O)(PEt$_3$)$_2$. Simple repetition of the sequence **1** ⇌ **2** ⇌ **3** at a rate much faster than that of CO$_2$ dissociation would, of course, lead to a statistical distribution of the ^{18}O label over the carbon and nitrogen atoms. From the observed ^{18}O enrichment in the CO$_2$ product (n_t = 1.29) one can conclude that the rate of oxygen-atom scrambling (**1** ⇌ **2** ⇌ **3**) is comparable to the rate of CO$_2$ dissociation.[30]

Of relevance to the proposed intermediacy of a Ni–CO$_2$ complex in Scheme II is the recent report[31] of the synthesis and X-ray structure of the 16-electron complex Ni(η^2-CO$_2$)-(PCy$_3$)$_2$. The failure[31] to obtain the corresponding PEt$_3$

Scheme II

L$_n$Ni = Ni(NO$_2$)(PEt$_3$)$_2$
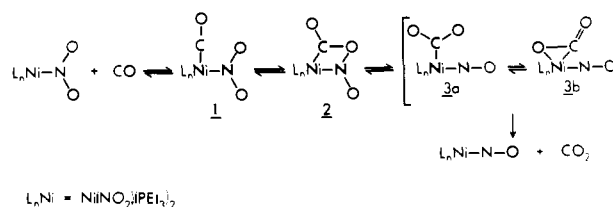
complex by similar routes is consistent with the recognized[28] ability of bulky phosphine ligands like PCy$_3$ to stabilize unusual low-valent complexes. In view of these observations and the paucity[31,32] of well-characterized metal–CO$_2$ complexes in general, it is not surprising that our attempts to isolate or obtain spectroscopic evidence for the proposed Ni–CO$_2$ intermediate (Scheme II) were unsuccessful. It seems likely that the presence of bulky phosphine ligands will be required if such an intermediate is to be successfully identified at all. In this context we have prepared Ni(NO$_2$)$_2$(PCy$_3$)$_2$ and are currently investigating its reaction with CO.

It should be noted that the present results do not rule out the possibility of an intermolecular mechanism for the oxygen-transfer process in reaction 1. Unfortunately, the reactivity of **1** precludes the isolation of appropriately labeled derivatives—e.g., Ni(NO$_2$)$_2$(C^{18}O)(PEt$_3$)$_2$ and Ni(N^{18}O$_2$)$_2$-(CO)(PEt$_3$)$_2$—necessary for carrying out a double-tagged tracer experiment. We are presently investigating related group 8 metal systems which hopefully will be more amenable to study by the double-tagged tracer technique.

Conclusions

Although several questions concerning reaction 1 remain unanswered, the results of our investigation clearly establish that the mechanism depicted in Scheme I is an oversimplification of the oxygen atom transfer process. Regardless of whether an intramolecular or intermolecular mechanism is operative, the intermediate(s) involved must necessarily have a sufficient lifetime to undergo substantial oxygen scrambling between nitrogen and carbon atoms prior to the irreversible loss of CO$_2$. The implications of these results with respect to similar oxygen atom transfer processes involved in homogeneous catalysis[6,7,9-13] are obvious and our work in this area is continuing.

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Porphyrin Core Expansion and Doming in Heme Proteins. New Evidence from Resonance Raman Spectra of Six-Coordinate High-Spin Iron(III) Hemes

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Abstract: Resonance Raman spectra are reported for high-spin bis(dimethyl sulfoxide) $(Me_2SO)_2Fe^{III}$ complexes of protoporphyrin IX dimethyl ester (PP), octaethylporphyrin (OEP), and tetraphenylporphyrin (TPP), and for aquo- and fluoromethemoglobin (Hb) and myoglobin (Mb), with emphasis on the three bands (II, IV, and V) which have previously been shown to be sensitive to iron spin state. These frequencies are essentially the same for $[(Me_2SO)_2Fe^{III}PP]^+$ as for aquo-metHb and Mb, which had previously been thought to be anomalously low. Since recent crystal structure determinations have shown the high-spin bisaquo and bis(tetramethylene sulfoxide) complexes of $Fe^{III}TPP$ to be planar porphyrins, with expanded cores, this experiment strongly supports core expansion as the determinant of the metHb and Mb spin-marker frequencies, and renders the hypothesis of protein-induced doming unlikely. Since protein crystallography has placed the iron atom 0.40 Å from the mean heme plane in metMb and 0.23 and 0.07 Å from the mean heme plane in the β and α chains of metHb, the lack of any associated variation in the spin-marker frequencies indicates that the core size is not determined by the disposition of the iron atom, but probably by steric interactions of the axial ligands with the pyrrole nitrogen atoms. Binding of fluoride to metHb and Mb leaves bands II and V unshifted, but lowers band IV by 5 cm^{-1}. The similarity in spin-marker frequencies between native horseradish peroxidase (HRP) or cytochrome c' and the previously studied five-coordinate Fe^{III} hemes indicates that these proteins contain five- rather than six-coordinate Fe^{III} hemes; in the case of HRP six coordination is accessible with exogenous ligands. It is suggested that the intermediate-spin state observed for these proteins results from weakening of the bond between Fe^{III} and the single axial ligand. The correlation with core size of the spin-marker frequencies is reexamined. Nonplanar hemes are found to have frequencies that are significantly depressed, presumably due to loss of π conjugation at the methine bridge. The relation between pyrrole tilt and the methine dihedral angles is derived for both ruffled and domed hemes, and is used to develop a simple relation that satisfactorily reproduces the spin-marker frequencies for both planar and nonplanar hemes. This model gives reasonable estimates of the σ and π contributions to the methine bond-stretching force constant. It is concluded that both core expansion and pyrrole tilting contribute to frequency lowerings, with core expansion dominant for moderate tilt angles. There is no evidence in any of the heme proteins so far studied of extra doming induced by the protein.

Introduction

Resonance Raman spectra of heme proteins contain a rich assortment of porphyrin vibrational modes, whose frequencies have been well catalogued.[1-7] Some of the modes are sensitive to chemical alterations at the central iron atom, and are therefore of great interest as potential structure monitors. In an early study[2] it was observed that one set of bands was sensitive to changes in oxidation state of the iron atom while another set was sensitive to changes in its spin state. The oxidation state marker bands were suggested[2,7a] to be responding to changes in porphyrin π^* orbital occupancy via back-donation from the iron d_π orbitals. This interpretation was subsequently confirmed[8] with a graded series of π-acceptor axial ligands, which compete with the porphyrin ring for the iron d_π electrons. An interesting consequence of this mechanism is that π-donor ligands can shift the oxidation state marker frequencies to values below the typical ones associated with nonacceptor ligands, as has recently been observed by Champion and Gunsalus[6] and by Kitagawa et al.[7b] for cytochrome P_{450}, which is believed to have cysteine mercaptide, a π donor, as an axial ligand.

With respect to the spin-state marker bands our interpretation[2] was that the frequency decreases observed for high-spin hemes resulted from a doming of the porphyrin ring accompanying the well-known out-of-plane displacement of the iron atom toward the proximal ligand.[9] The pyrrole rings are expected to tilt, in order to maintain overlap with the iron orbitals, but this would be at the expense of π conjugation at the porphyrin methine bridges, resulting in the observed frequency lowerings. A subsequent normal-coordinate calculation[10a] indicated that this mechanism could account for the experimental data. A discrepancy between the spin marker