our $\mathrm{OEiBC}^{\bullet+}$ radicals did not exhibit resolvable hyperfine splitting.

Figure 3 shows that the overall reaction eq 2 can be broken down into three separate equilibria (MAC = POR, CHL, or iBC):

$$\mathrm{Fe^{III}(MAC)X + CO \rightleftharpoons Fe^{II}(MAC^{\bullet+})(CO)X} \tag{2}$$

(a) oxidation of the $\mathrm{Fe^{III}(MAC)X}$ macrocycle by one electron, (b) reduction of the $\mathrm{Fe^{III}(MAC^{\bullet+})X}$ to $\mathrm{Fe^{II}(MAC^{\bullet+})X}$ by one electron, and (c) binding of CO to $\mathrm{Fe^{II}(MAC)^{\bullet+})X}$. We estimate the difference of $\Delta E_{1/2}$ ($E_{1/2}$(iBC) − $E_{1/2}$(POR)) for equilibrium a to be −0.60 V, based on the literature values of $E_{1/2}$ for the reversible oxidations of Zn(OEiBC) and Zn(OEP);[4c] $\Delta E_{1/2}$ for equilibrium b is estimated to be 0.04 V, based on the literature values of $E_{1/2}$ for the reversible reductions of $\mathrm{Fe(OEiBC)(py)_2^+}$ and $\mathrm{Fe(OEP)(py)_2^+}$;[2b] the ratio $K_{eq}(\mathrm{iBC})/K_{eq}(\mathrm{POR})$ for equilibrium c is estimated to be 13, based on the literature value of this ratio for the related equilibrium 3.[9] Equilibrium a obviously

$$\mathrm{Fe^{II}(MAC)CO + CO \rightleftharpoons Fe^{II}(MAC)(CO)_2} \tag{3}$$

has the most profound effect on the overall reaction (eq 2). When the estimated free energy changes are summed for equilibria a–c, we conclude that $\Delta G_{\mathrm{iBC}} - \Delta G_{\mathrm{POR}}$ is probably equal to approximately −60 kJ mol^{-1}. Therefore, while it is not possible to compare directly the OEiBC and OEP equilibrium constants for eq 2, we conclude that the CO affinity for a five-coordinate iron(III) iBC complex is probably larger by several orders of magnitude than the CO affinity for the corresponding iron(III) porphyrin complex.[15]

Recent studies have demonstrated that iron(III) iBC π cation radicals are viable species for at least two reaction states of the hemoprotein subunit of *Escherichia coli* sulfite reductase.[6d] Together with the results for iron(II) iBC π cation radicals and for nickel(II) and nickel(III) iBC π cation radicals,[13] the emerging picture is that iBC π-oxidation may be as important, or more important, in siroheme enzymology than porphyrin π-oxidation is in heme biochemistry.

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(15) K_{eq} for eq 1, measured by a visible spectrophotometric titration, is approximately 10^2 M^{-1} for X$^-$ = NCS$^-$ and L = *t*-BuNC in dichloromethane at −78 °C. Details for this and related experiments will be reported in the full paper.

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Synthesis and Structure of $\mathrm{Ti(OAr\text{-}2,6Pr^i{}_2)_2(py\text{-}4Ph)_3}$ ($\mathrm{OAr\text{-}2,6Pr^i{}_2}$ = 2,6-Diisopropylphenoxide; py-4Ph = 4-Phenylpyridine): A Compound Containing both Reduced and Nonreduced 4-Phenylpyridine Ligands Bound to Titanium

The last few years have seen some dramatic developments in the field of low-valent early d-block element chemistry.[1] In particular, the use of sterically demanding oxygen donor ligands, e.g. alkoxides, siloxides and aryloxides, attached to group 4–6 metal centers containing d^n (n = 1–4) electron configurations results in metal-based systems capable of carrying out a variety of interesting reduction chemistry.[2–5] During our studies of the chemistry associated with the lower oxidation states of titanium supported by sterically demanding aryloxide ligands, we have demonstrated a ligand-induced reductive-elimination method for the generation of highly reducing titanium(II) compounds.[5] In this communication, we wish to report on an extension of this work that results in the formation of an interesting compound that structural studies clearly demonstrate as containing both reduced and nonreduced 4-phenylpyridine ligands bound to the same metal center.[6]

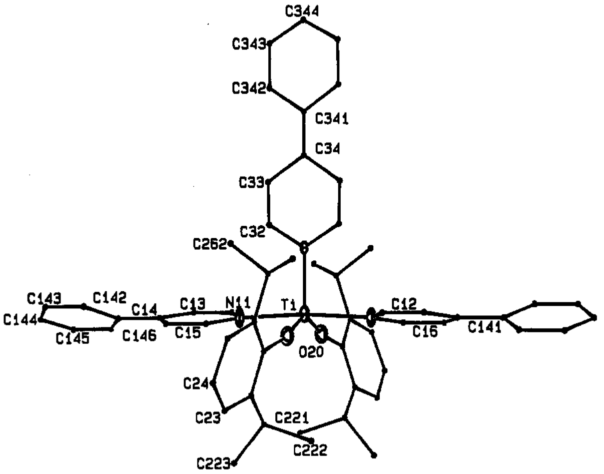
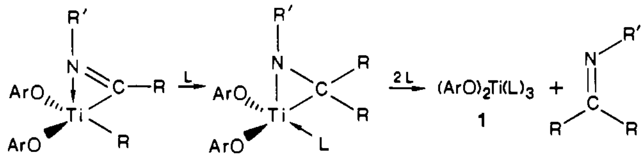


Figure 1. ORTEP view of **1** emphasizing the central coordination sphere. Selected bond distances (Å) and angles (deg) area as follows: Ti–O(20) = 1.864 (4), Ti–N(11) = 2.236 (4), Ti–N(31) = 2.090 (7); O(20)–Ti–O(20)′ = 138.2 (3), O(20)–Ti–N(11) = 90.3 (2), O(20)–Ti–N(11)′ = 87.6 (2), O(20)–Ti–N(31) = 110.9 (1), N(11)–Ti–N(11)′ = 174.2 (3), N(11)–Ti–N(31) = 92.9 (2), Ti–O(20)–C(21) = 165.6 (4).

Scheme I[a]



[a] L = py-4Ph; R = CH$_2$Ph; R′ = *tert*-butyl; ArO = 2,6-diisopropylphenoxide.

The η^2-imine compound $\mathrm{Ti(OAr\text{-}2,6Pr^i{}_2)_2[\eta^2\text{-}Bu^tNC(CH_2Ph)_2](py\text{-}4Ph)}$[5] is formed readily by treatment of the η^2-iminoacyl precursor $\mathrm{Ti(OAr\text{-}2,6Pr^i{}_2)_2(\eta^2\text{-}Bu^tNCCH_2Ph)(CH_2Ph)}$[7] with 4-phenylpyridine (py-4Ph; 1 equiv) in benzene. Further treatment of the red-orange η^2-imine with excess 4-phenylpyridine in benzene/hexane (1:1) causes the development of a deep purple color, and after 12 h, long purple needles of a new paramagnetic product of stoichiometry $\mathrm{Ti(OAr\text{-}2,6Pr^i{}_2)_2(py\text{-}4Ph)_3}$ (**1**) are produced (Scheme I).[8] Examination of the supernatant of the

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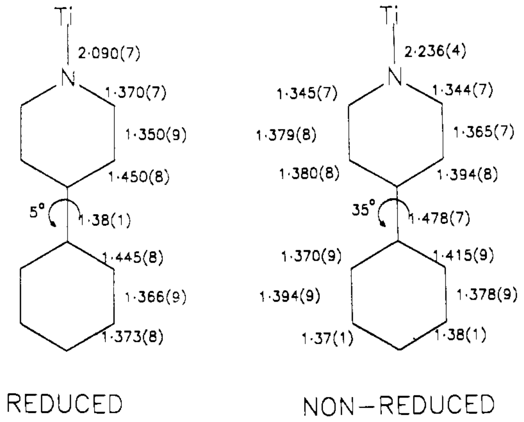

Figure 2. Comparison of bond distances (Å) and twist angles (deg) within the two types of 4-phenylpyridine ligands in compound **1**.

reaction showed the presence of the displaced organic imine $Bu^tN{=}C(CH_2Ph)_2$ as well as its enamine tautomers.[5] Compound **1** exhibits greater solubility in hydrocarbon solvents than its simple pyridine counterpart of stoichiometry "$Ti(OAr\text{-}2,6Pr^i_2)_2(py)_3$". This latter compound was shown to actually be dimeric due to the intermolecular reductive coupling of two pyridine ligands through their 4-position.[5] A single-crystal X-ray diffraction analysis of (**1**) (Figure 1)[9] clearly shows that no dimerization has occurred via carbon–carbon bond-forming processes. The geometry about the titanium atom is best described as trigonal bipyramidal, while the presence of a crystallographic 2-fold axis makes the two aryloxide ligands and two axial 4-phenylpyridine groups equivalent. The unique, equatorial 4-phenylpyridine ligand lies on this 2-fold axis.

Careful scrutiny of the structural parameters for **1** shows that it is incorrect to consider the molecule as a simple titanium(II) aryloxide compound. Particularly informative are the distances to the two types of 4-phenylpyridine ligand within the coordination sphere (Figure 2). It can be seen that the equatorial ligand is much more strongly bound to the metal than the axial ones, Ti–N = 2.090 (7) versus 2.236 (4) Å. The latter value falls within the range one would expect for a simple σ-donor pyridine group bound to titanium,[6,7,10] while the much shorter distance to the equatorial nitrogen atom is much more consistent with a titanium–dialkylamido bond.[11,12] A comparison of bond lengths within the framework of the pyridine ligands is equally informative. Particularly dramatic is the shortening of the distance between the 4-phenyl substituent and the pyridine ring in the equatorial ligand and the almost coplanarity of these two rings compared to values found for the normal 4-phenylpyridine ligands in **1** (Figure 2).[13] These structural data lead us to the belief that the equatorial ligand in **1** has undergone a one-electron reduction., (i.e. becoming py-4Ph$^-$), leading to the formulation of the compound as containing a titanium(III) (d^1) metal center. Hence compound **1** appears to be a rare example where the same simple heterocyclic ligand in both its reduced and nonreduced forms is present in the same coordination sphere for direct structural comparison.[14] A detailed examination of the spectroscopic properties of **1** as well as of other related molecules is presently under way.

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Supplementary Material Available: Listings of crystallographic data, fractional coordinates, anisotropic thermal parameters, and full bond distances and angles for compound **1** (13 pages); a listing of observed and calculated structure factors for compound **1** (13 pages). Ordering information is given on any current masthead page.

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(8) Magnetic moment (Evans' method) = 2.3 μ_B for **1**. This can be compared with a value of 1.47 μ_B obtained for the titanium(III) aryloxide $Ti(OAr\text{-}2,6Pr^i_2)_3(py)_2$.[2d]

(9) Crystal data for $TiO_2N_3C_{67}H_{73}$, **1**·C_6H_6, at −140 °C: a = 22.903 (5) Å, b = 17.047 (6) Å, c = 14.829 (4) Å, β = 94.56 (2)°, Z = 4, d_{calcd} = 1.51 g cm^{-3} in space group $C2/c$ (no. 15). Of the 3907 unique data collected with Mo Kα radiation, $4° \leq 2\theta \leq 45°$, the 1816 with $I > 3\sigma(I)$ were used in the final refinements to yield R = 0.062 and R_w = 0.075. Hydrogen atoms were placed in ideal positions and were not refined.

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(12) A twist angle of 33° is observed between the pyridine and phenyl rings of the py-4Ph ligand in $Ti(OAr\text{-}2,6Pr^i_2)_2[Bu^tNC(CH_2Ph)_2](py\text{-}4Ph)$; see ref 5.

(13) It is noteworthy that the d^2-metal fragment $Ta(OSiBu^t_3)_3$ binds pyridine in an η^2-C,N fashion; see ref 3a.

(14) The electronic absorption spectrum of **1** in cyclohexane shows extremely strong bands below 400 nm. In the visible region a band at 547 nm has a very broad shoulder at 625 nm that tails off toward 875 nm.