

at 22.0, 40.0, and 50.0 (± 0.1) °C. A typical kinetics run is shown in Figure 1.

The kinetic data were found to agree with an integrated rate law derived by King⁷ for second-order reversible reactions. Similar rate constants, for a given temperature, were obtained from King's rate law regardless of the initial concentrations used. This indicates that the rate behavior of eq 1 is first order in each reactant. This is analogous to the second-order rate law found for the double ligand exchange between (OEP)Mn≡N and (TPP)Cr—Cl reported by Bottomley.⁸ Rate constants for eq 1 are listed in Table I. The activation parameters for eq 1 derived from the rate data are $\Delta H^\ddagger = 17.4 \pm 1.4$ kcal/mol and $\Delta S^\ddagger = -8.7 \pm 1.0$ eu. These values are typical of those found for a variety of electron-transfer reactions.⁹

It is clear that eq 1 involves a formal two-electron redox process. Mechanistically, it is not likely that this reaction proceeds via an outer-sphere pathway. Evidence supporting this is provided by chemical reduction of nitrido manganese porphyrins. Buchler has shown that sodium anthracenide, an outer-sphere reagent, is capable of adding two electrons to the porphyrin ligand of (OEP)Mn≡N but does not reduce the metal.¹⁰ Furthermore, Bottomley has demonstrated that the first and second electrochemical reductions of (OEP)Mn≡N and (TTP)Mn≡N are ligand-based.¹¹ Since eq 1 involves changes in the Mn oxidation states, it most likely proceeds through an inner-sphere mechanism.

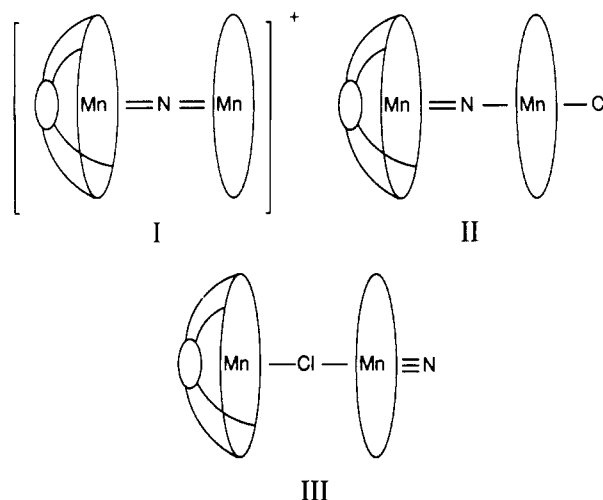
Since chloro and nitrido ligands are both good bridging species, it is of fundamental interest to establish which is the preferred bridging ligand in this inner-sphere process. A series of mechanistic studies are all consistent with a pathway that involves initial chloride dissociation followed by nitrogen atom transfer through a μ -nitrido binuclear intermediate. For example, addition of 1 equiv of tetra-*n*-butylammonium chloride inhibits the rate by more than a factor of 1400. It is not likely that the excess chloride inhibits this reaction by taking up the sixth coordination site on the Mn(III) complex. In nonpolar solvents, only five-coordinate manganese(III) complexes have been observed.¹² Furthermore, replacement of the Mn(III) axial ligand with the more easily dissociated iodide ligand enhances the rate 500-fold, whereas use of the less easily dissociated acetate as the axial ligand decreases the reaction rate by a factor of 23 with respect to the chloride case.

Other evidence that supports the proposed mechanism is established by replacing the TTP ligand with Baldwin's C₂-capped porphyrin,¹³ CAP, which has an aryl ring blocking one face of the macrocycle. Thus, when (CAP)Mn—Cl is treated with (OEP)Mn≡N, formation of (CAP)Mn≡N and (OEP)Mn—Cl is observed by ¹H NMR and UV-vis spectroscopy. In order for this reaction to proceed, it is likely that chloride must dissociate from the CAP complex before a μ -nitrido intermediate can form. Moreover, the reverse reaction, (CAP)Mn≡N plus (OEP)Mn—Cl, also proceeds to produce (CAP)Mn—Cl and (OEP)Mn≡N. Since the capped porphyrin prevents formation of a chloride bridge trans to the axial ligand of the starting nitride complex, this reaction most likely proceeds through a μ -nitrido-bridged intermediate. The most compelling argument for the existence of a μ -nitrido-bridged intermediate is evidenced by the reversibility of eq 2. The equilibrium constant for this process



is 4.8 ± 1.8 at 50 °C. Of the three possible intermediates, species I is the most chemically feasible for both the forward and reverse

pathways for eq 2. Intermediate II is ruled out by the forward process while III is inconsistent with the reverse direction. Thus,



it appears that for nitrido/chloro ligand-exchange reactions of metalloporphyrins, a distinct preference for a bridging nitrido ligand over a bridging chloro ligand exists. This is consistent with a mechanism proposed by Bottomley⁸ for an analogous process involving the reduction of (OEP)Mn≡N by (TPP)Cr—Cl. However, in this case, chloride dissociation from the chromium(II) complex is proposed not to precede formation of the μ -nitrido intermediate. Further work to elucidate the mechanisms of these atom-transfer processes is in progress.

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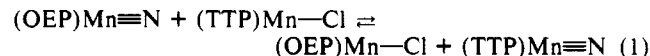
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Oxo-Transfer Reactions of Chromium and Titanium Porphyrins

Examples of intermetal oxygen atom transfer are rare. In general, inner-sphere electron transfer mediated through an oxo ligand typically leads to formation of μ -oxo-bridged products.¹ For example, when (TPP)Cr^{IV}=O is treated with Cr^{II}(TPP) in toluene, formation of (TPP)Cr^{III}—O—Cr^{III}(TPP) is observed.^{2,3} Intermetal oxo transfer thus far has been limited to molybdenum and tungsten complexes.⁴ Oxo transfer between two ruthenium centers has been implicated in the aerobic epoxidation of olefins by ruthenium porphyrins.⁵ As an extension of our studies on inner-sphere redox reactions and nitrogen atom transfer,⁶ we have initiated an investigation of oxygen atom transfer. Our approach to oxo transfer developed as a result of our recent finding that nitrogen atom transfer occurs reversibly between (OEP)Mn≡N and (TTP)Mn—Cl as shown in eq 1.⁷ Bottomley has shown that



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- (2) Abbreviations: TTP = 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion.
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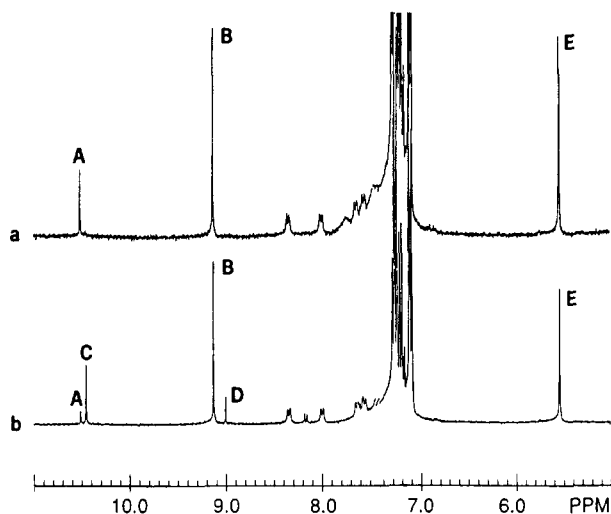
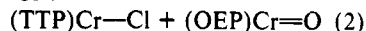


Figure 1. (a) 300-MHz ^1H NMR spectrum for eq 3. (b) 300-MHz ^1H NMR spectrum for eq 4. A is the *meso*-H signal for (OEP)Ti=O, B is the β -pyrrole signal for (TTP)Ti=O, C is the *meso*-H signal for (OEP)TiCl₂, D is the β -pyrrole signal for (TTP)TiCl₂, and E is the methine signal of Ph₃CH.

a similar, but irreversible transfer occurs between (OEP)Mn≡N and (TTP)Cr—Cl.⁸ We report herein that analogous reactions occur for oxometalloporphyrins.

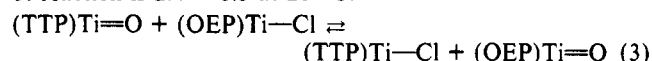
In the case of oxo chemistry, it is possible to disfavor μ -oxo formation by steric factors. Holm⁹ and Spence¹⁰ have very elegantly demonstrated this in molybdenum oxo complexes bound to ligands bearing bulky substituents. In an effort to examine what factors determine whether oxo transfer occurs versus μ -oxo formation, we have investigated the chemistry of a number of metalloporphyrin oxo complexes. Of interest was the possibility of inducing oxo transfer on electronic grounds. Thus, we monitored the reaction of oxochromium porphyrins and chlorochromium porphyrins by using TTP and OEP as spectroscopic labels.² When benzene solutions of (TTP)Cr=O and (OEP)Cr—Cl are combined, the UV-vis spectrum of the mixture shows new Soret bands at 450 and 416 nm. This is consistent with the formation of (OEP)Cr=O (416 nm) and (TTP)Cr—Cl (450 nm). The complementary experiment starting with (OEP)Cr=O and (TTP)Cr—Cl generates a final UV-vis spectrum with identical peak positions, indicating the reversibility of this process. The overall reaction is represented by eq 2. Independent verification



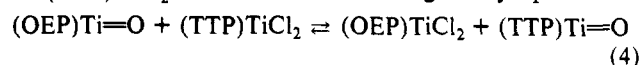
was obtained by ^1H NMR studies. In a typical example, an NMR tube containing a C₆D₆ solution of 1.28 mM (OEP)Cr=O, 0.65 mM (TTP)Cr—Cl, and 1.33 mM Ph₃CH as an internal standard was prepared and monitored over a period of days. The chromium(IV) oxo complexes are diamagnetic and easily detected by NMR. Thus, the (OEP)Cr=O resonances at δ 10.59 (s, *meso*-H), 3.98 (m, CH₂), and 1.85 (t, CH₃), gradually diminish and new peaks grow in at δ 9.24 (s, β -H), 8.02 (m, aryl H), 7.92 (m, aryl H), and 2.40 (s, CH₃), indicating the formation of (TTP)Cr=O. No precipitates are observed and integration against the internal standard shows that, within experimental error ($\pm 10\%$), the total oxo concentration ($[(\text{OEP})\text{Cr}=\text{O}] + [(\text{TTP})\text{Cr}=\text{O}]$) remains equal to the initial concentration of (OEP)Cr=O used. Thus, mass balance is maintained, and no competing side reactions

consume the starting materials. Reaction 2 has an equilibrium constant of 4.0 ± 0.5 at 20 °C and involves a net one-electron redox.

We have found that a similar reaction occurs for the analogous titanium complexes. These reactions were carried out under scrupulously dry and anaerobic conditions by using vacuum-line and glovebox techniques. In a representative experiment, an NMR tube containing 1.45 mM (TTP)Ti—Cl, 1.46 mM (OEP)Ti=O, and 4.35 mM Ph₃CH in CDCl₃ was flame-sealed. As in the above example, the ^1H NMR resonances of (OEP)Ti=O decrease and new peaks corresponding to (TTP)Ti=O appear. Figure 1a shows a partial NMR spectrum for this sample. No precipitates appear, and the total oxo concentration as measured against the internal standard Ph₃CH remains constant within experimental error. The net reaction is shown in eq 3. The equilibrium constant for the Ti reaction is 2.4 ± 0.5 at 20 °C.



Surprisingly, we have also discovered that oxotitanium(IV) porphyrins undergo oxo transfer with dichlorotitanium(IV) porphyrins. In a typical reaction, 1.49 mM (TTP)TiCl₂, 1.53 mM (OEP)Ti=O and 5.67 Ph₃CH in CDCl₃ are flame-sealed in an NMR tube under high vacuum. In this case, all species involved are diamagnetic and can be observed by ^1H NMR as shown in Figure 1b. The final spectrum is the superposition of the individual spectra of the starting materials plus the products, (TTP)Ti=O and (OEP)TiCl₂. The overall reaction is given by eq 4. Mass



balance is maintained in this reaction and indicates that formation of the new oxo product cannot be due to adventitious water. This example is an unusual case in which oxo transfer occurs, but no net redox takes place. The equilibrium constant for eq 4 is 47 ± 13 at 20 °C. We have also monitored the approach to equilibrium from the reverse direction for both eqs 3 and 4.

The reduction of oxochromium porphyrins produces products that are highly dependent on the nature of the reductant. In the O=Cr^{IV}/Cr^{II} redox process, the reaction stops at μ -oxo formation. This is in contrast to the O=Cr^{IV}/Cl—Cr^{III} reaction, which undergoes reversible oxygen atom transfer. Note that for the IV/III reaction, oxygen atom transfer still occurs if Cl[−] is replaced with ClO₄[−] as the axial ligand. Furthermore, since tetra-*p*-tolylporphyrins or tetraphenylporphyrins are used in both the IV/III and the IV/II processes, the difference in reactivity cannot be based on steric effects. A significant factor involves the reduction potentials of the two reducing agents. (TTP)Cr—Cl has a 4+/3+ reduction potential of +0.80 V vs SCE¹¹ whereas (TTP)Cr^{II} has a 3+/2+ reduction potential of −1.06 V vs SCE.¹² Since Cr(TPP) is a much stronger one-electron-reducing agent, formation of the μ -oxo Cr^{III} dimer on reaction with (TTP)Cr=O is thermodynamically downhill.

These are the first examples of intermetal oxo transfer for Cr and Ti. With metalloporphyrin nitrido complexes, we now have a family of compounds in which atom transfer reactions involving zero-, one-, two-, and three-electron changes can be systematically investigated. We are currently undertaking mechanistic and thermodynamic studies with this series of atom transfer reactions and examining the extension of this chemistry to other types of metal complexes.

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