

by ca. 0.035 Å relative to that in **4** and **5**.<sup>10</sup>

A fundamental difference is found to exist between the  $\pi$  components of metal-alkene and metal-( $\eta^2$ -P<sub>4</sub>) bonding, in that the former involves a 2e-2 MO system while for the latter a 4e-3 MO framework is produced (b<sub>1</sub> symmetry in Figure 2) involving both filled and unfilled ligand orbitals<sup>18</sup>.

The perpendicular conformation on the  $\eta^2$ -bonded P<sub>4</sub> ligand is favored with respect to the parallel conformation by increased  $\pi$  bonding. EHMO calculations on perpendicular and parallel models of [Rh(P<sub>4</sub>)(PH<sub>3</sub>)<sub>2</sub>Cl] show that both types of Rh-P bond are weakened in the latter,<sup>19</sup> and yield a barrier to rigid rotation of the P<sub>4</sub> ligand, about the z axis, of ca. 5 eV.

Computed overlap populations for the  $\eta^2$ - $\perp$  model successfully reproduce the weakening of the P(3)-P(4) connectivity that is inferred from its crystallographically observed lengthening. It is noteworthy that the opposite tetrahedral edge is not substantially altered upon formation of complex **1**, possibly suggesting that complexes with bridging di-( $\eta^2$ )-P<sub>4</sub> ligands might be feasible. Furthermore, given the overall strength of the Rh-P<sub>4</sub> bonding, we can see no prima facie reason why other examples of  $\eta^2$ -coordinated P<sub>4</sub> should not be amenable to synthesis. Experiments designed to explore these possibilities are currently in hand.

Registry No. 1·2CH<sub>2</sub>Cl<sub>2</sub>, 85939-99-7.

**Supplementary Material Available:** Atom coordinates (Table 1), thermal parameters (Table 2), internuclear distances (Table 3), and interbond angles (Table 4) (4 pages). Ordering information is given on any current masthead page.

(18) The iridium analogue of **1**, with higher lying metal valence orbitals, presumably has a weaker M-P<sub>4</sub>  $\sigma$  bond and a  $\pi$  interaction more closely similar to that of an alkene complex.

(19) Overlap populations:  $\perp$ , Rh-P<sub>4</sub>, 0.355; Rh-PH<sub>3</sub>, 0.530; P-P, 0.689 (metal-bonded edge), 0.782 (opposite edge), 0.788 (other edges);  $\parallel$ , Rh-P<sub>4</sub>, 0.129; Rh-PH<sub>3</sub>, 0.350.

### Oxygen Activation by Metalloporphyrins. Formation and Decomposition of an Acylperoxymanganese(III) Complex

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The catalytic cycle of the monooxygenase cytochrome P-450 is considered to involve the binding and reduction of molecular oxygen at the heme center and ultimate formation of a reactive iron oxo complex that is responsible for the oxidation of the substrate.<sup>1</sup> While synthetic porphyrin complexes have been shown to bind oxygen<sup>2</sup> and to be oxidized to oxometalloporphyrin complexes capable of oxidizing even saturated hydrocarbons,<sup>3</sup> the

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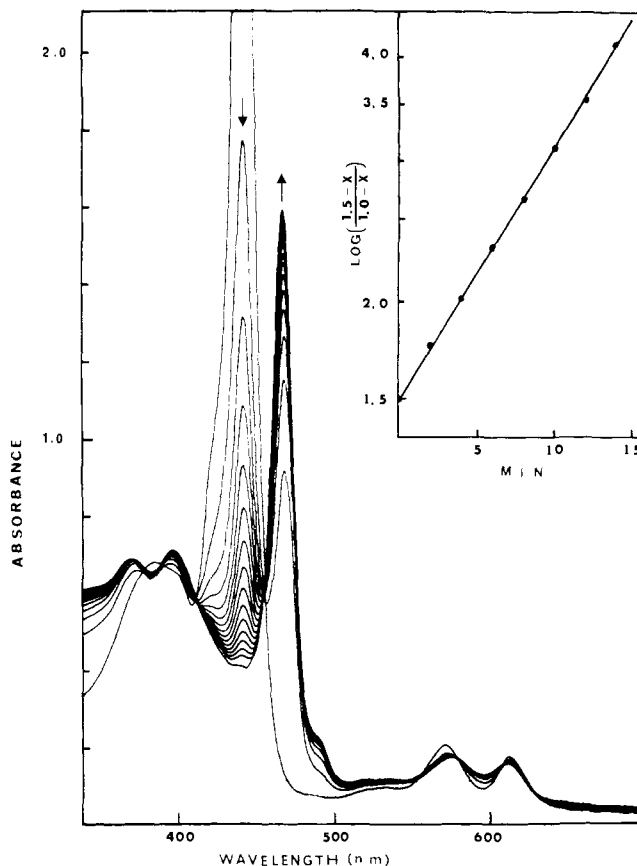
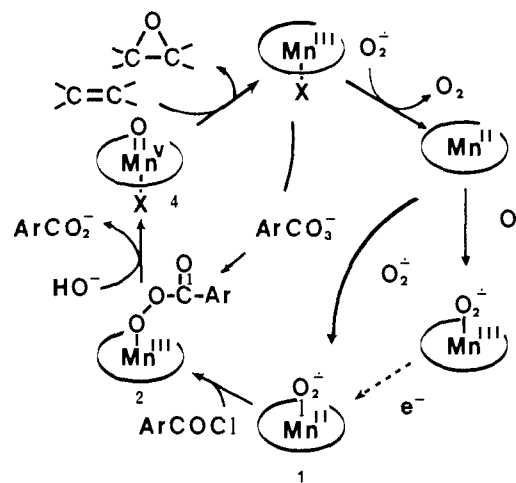


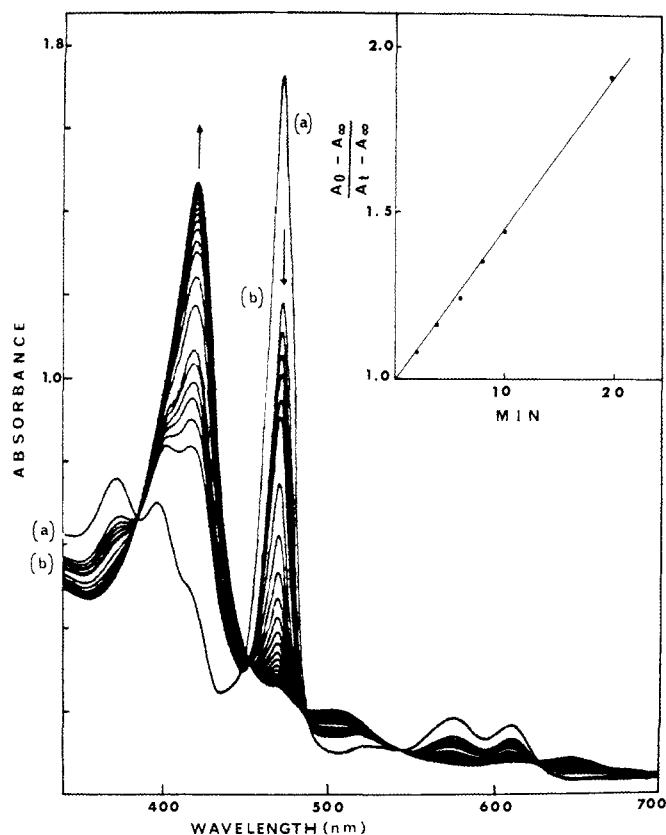
Figure 1. Visible spectral changes for the reaction of 1.5 equiv of *m*-chlorobenzoyl chloride with TMPMn<sup>II</sup>-O<sub>2</sub><sup>-</sup> (**1**) in acetonitrile at -20 °C. Inset: second-order plot of the time course of the decrease of **1**, X = (A<sub>0</sub> - A<sub>t</sub>)/(A<sub>0</sub> - A<sub>∞</sub>) at 445 nm, 1.3 × 10<sup>-5</sup> M.

Scheme I



conversion of a metalloporphyrin-dioxygen complex to a reactive oxo species is still without precedent in model systems.<sup>4</sup> In this paper we demonstrate (i) the acylation of an oxygenated manganese-porphyrin complex to form an acylperoxymanganese(III) complex, (ii) the independent preparation of this acylperoxy complex by the direct addition of peroxyacid salts, (iii) the decomposition of the acylperoxymanganese(III) complex to an oxomanganese(V) species, and (iv) oxygen atom transfer from this manganese oxo complex to olefins to regenerate the starting manganese(III) porphyrin.

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**Figure 2.** (a) Visible spectrum of TMPMn<sup>III</sup> hydroxide in methylene chloride [ $1.3 \times 10^{-5}$  M] at  $-30$  °C; (b) visible spectral changes for the conversion of **2** [ $1.3 \times 10^{-5}$  M] to **4** in methylene chloride at  $-30$  °C in the presence of 1 equiv of excess hydroxide ion. Inset: Reciprocal plot of the time course of the decomposition of **2**, 473 nm.

The reaction of chloro(5,10,15,20-tetramesitylporphyrinato)-manganese(III) (TMPMn<sup>III</sup>Cl) with potassium superoxide in acetonitrile containing 2 equiv of 18-crown-6 at 25 °C produced, initially, TMPMn<sup>II</sup> and then TMPMn-O<sub>2</sub><sup>-</sup> (**1**).<sup>5</sup> The visible spectrum (445 nm) and the <sup>1</sup>H NMR spectrum (25 °C;  $\delta$  32.8 ( $\beta$ -pyrrole), 8.99, 8.44 (*m*-H), 2.86 (*p*-methyl)) of this dioxygen adduct were consistent with a manganese(II) superoxide structure for **1**.<sup>6</sup> Particularly, the low-field position of the  $\beta$ -pyrrole hydrogens has been shown to be indicative of a half-filled  $d_{x^2-y^2}$  metal orbital.<sup>7</sup> After removal of unreacted KO<sub>2</sub>, the resulting light green solution of **1** was cooled to  $-40$  °C, and 1.5 equiv of *m*-chlorobenzoyl chloride was introduced. Rapid changes in the visible spectrum of the solution at  $-20$  °C (Figure 1) indicated the smooth, second-order conversion of **1** (Scheme I) to a new complex, **2**, with the visible spectrum of a typical manganese(III) complex.<sup>8,9</sup> The identification of **2** as an acylperoxymanganese(III) species is based on the following observations. Treatment of **2** with cyclooctene afforded cyclooctene oxide in 30–40% yield. Less than 3% epoxide was produced under these conditions in the absence of the manganese porphyrin. Treatment of TMPMn<sup>III</sup>Cl with 1 equiv of tetramethylammonium *m*-chloroperoxybenzoate in acetonitrile at  $-40$  °C also produced **2**. The visible spectrum of

**2** and those of TMPMn<sup>III</sup> *m*-chlorobenzoate and TMPMn<sup>III</sup> hydroxide (**3**, Figure 2) were very similar except for the lower extinction coefficient for **2** at 469.5 nm.

The acylation of **1** to give **2** finds precedent in the reaction of benzoyl chloride with platinum(II) peroxy complexes.<sup>10</sup> Acylation of an iron–oxygen complex in the cytochrome P-450<sub>cam</sub> cycle has been suggested on the basis of <sup>18</sup>O<sub>2</sub> incorporation into lipoic acid.<sup>11</sup>

Solutions of **2** prepared in methylene chloride at  $-78$  °C by the addition of 1.2 equiv of *m*-chloroperoxybenzoic acid to TMPMn<sup>III</sup>Cl containing 2 equiv of tetramethylammonium hydroxide were much less stable than those in acetonitrile. Warming these solutions to  $-30$  °C caused the smooth decomposition of **2** to a new species, **4**, in a process which was first order in **2** and first order in hydroxide (Figure 2). The blue-shifted Soret maximum of **4** (422 nm) was the same as that observed for the product of manganese(III) oxidation by iodosylbenzene<sup>3</sup> or hypochlorite.<sup>12</sup> That **4** does have the formal oxidation equivalents of a manganese(V) complex is supported by the reduction of **4** by cyclooctene to give TMPMn<sup>III</sup> *m*-chlorobenzoate (**3a**) and an 80% yield of cyclooctene oxide. Further, 2 equiv of iodide was required to reduce **4** to **3a**. Observation of the visible spectrum of **4** during an iodide titration revealed modest changes during the addition of the first equivalent of iodide. Only during the addition of the second equivalent did manganese(III) appear. These observations are consistent with the initial reduction of **4** to manganese(IV) and then to manganese(III). The similarity of the visible spectra of TPPMn<sup>IV</sup> and TPPMn<sup>V</sup> complexes has been noted by Porter.<sup>12</sup> The <sup>1</sup>H NMR spectrum of **4**, though broad, showed a resonance at  $\delta$  10.5 (*m*-H) at  $-31$  °C, which shifted to  $\delta$  12 upon cooling to  $-68$  °C. The direction of this shift argues against an antiferromagnetically coupled dimeric structure for **4**.<sup>13</sup>

Further indications that **4** was a manganese(V) complex derived from its reaction with TMPMn<sup>III</sup>Cl. The addition of 1 equiv of TMPMn<sup>III</sup>Cl to a basic solution of **4** in methylene chloride at  $-20$  °C led initially to a solution with the visible spectrum expected for a superimposition of TMPMn<sup>III</sup>Cl and **4**. The absorption of Mn(III) at 472 nm then decayed in a second-order process with a half-life of 50 min and with a concomitant increase in the absorption at 422 nm. This observation is consistent with the comproportionation of **4** and TMPMn<sup>III</sup>Cl to give 2 equiv of Mn(IV). By contrast, the oxidation of TMPMn<sup>III</sup>Cl by the more sterically hindered tetra-*o*-phenyl derivative<sup>14</sup> of **4** proceeded very slowly under these conditions.

Taken together, these results now provide evidence for each individual step in the oxygen binding, acylation, and oxygen rebound<sup>15</sup> outlined in Scheme I with this manganese–porphyrin model system.

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**Registry No.** **1**, 85956-38-3; **2**, 85956-39-4; TMPMn<sup>III</sup>Cl, 85939-49-7; TMPMn<sup>II</sup>, 85939-50-0; potassium superoxide, 12030-88-5; *m*-chlorobenzoyl chloride, 618-46-2; cyclooctene, 931-88-4; cyclooctene oxide, 286-62-4; tetramethylammonium *m*-chloroperoxybenzoate, 85939-51-1.

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