

## References and Notes

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### Reversible Binding of Dioxygen by Tris(3,5-di-*tert*-butylcatecholato)manganese(III) in Dimethyl Sulfoxide

Sir:

For several years the redox chemistry of manganese complexes has been of interest to our group,<sup>1,2</sup> especially systems that involve polyhydroxy ligands.<sup>3</sup> We report here that an oxidation product of the tris(3,5-di-*tert*-butylcatecholato)manganese(III) complex (**1**) reversibly binds molecular oxygen in dimethyl sulfoxide solutions. Figure 1 illustrates spectra for **1** in the absence and presence of O<sub>2</sub>. When the latter solutions are deaerated with argon the dominant peak at 450 nm is eliminated; this change is reversible upon addition of O<sub>2</sub>.

The results for a series of spectrophotometric experiments that further illustrate the formation of a reversible O<sub>2</sub> adduct with the oxidation product of **1** are summarized in Table I. The variability in the data is characteristic of the system and undoubtedly is due to the chemical oxidation of the catechol ligands of **1**. The extent of such reactions is affected by concentration, solution acidity, O<sub>2</sub> partial pressure, moisture, and possibly light. In addition, the reaction products probably undergo exchange reactions, disproportionation, and further redox reactions. However, under dilute conditions the major process is the reversible formation of the O<sub>2</sub> adduct. Additional studies are in progress to find the optimum conditions for the stable formation of the adduct.

The redox chemistry of **1** is illustrated by the cyclic voltammogram of Figure 2a. Curve b is for O<sub>2</sub> at 1 atm in the absence of **1** and curve c is for **1** plus O<sub>2</sub> at 1 atm. The anodic

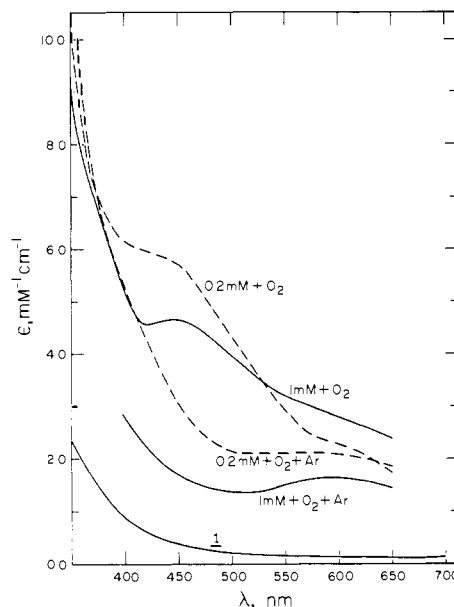


Figure 1. Absorption spectra for the tris(3,5-di-*tert*-butylcatecholato)manganese(III) complex (**1**) in dimethyl sulfoxide in the absence and presence of molecular oxygen. The complex was formed in situ by combining Mn<sup>III</sup>(OAc)<sub>3</sub>, 3,5-di-*tert*-butylcatechol, and tetraethylammonium hydroxide in a mole ratio of 1:3:6. Oxygen was added to the complex solution by bubbling with O<sub>2</sub> at 1 atm for 5 min, and removed by bubbling with argon for 20 min. Molar absorptivity values,  $\epsilon$ , are based on the formal concentrations of **1** in the solutions.

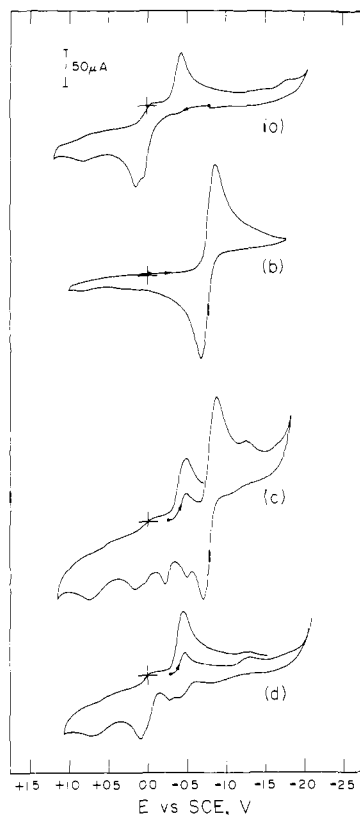
peak at  $-0.5$  V vs. SCE represents the reduction product of the reversible O<sub>2</sub> adduct. Deaeration of the latter solution with argon results in the cyclic voltammogram of curve d; addition of O<sub>2</sub> reverses the change and results in a voltammogram identical with curve c.

Analysis of the spectrophotometric and electrochemical data indicates that for low metal-to-oxygen ratios a 1:1 O<sub>2</sub> adduct is formed. When the ratio is increased and with higher concentrations of **1**, the extent of the irreversible chemical oxidation of the coordinated catechol ligands by O<sub>2</sub> increases (indicated by the absorption band at 580 nm for the spectra in Figure 1 and by the initial reduction peak at  $-0.5$  V, curve c, Figure 2). The reduction peak at  $-0.5$  V is due to the re-

Table I. Visible Spectrophotometric Data for **1**, the O<sub>2</sub> Adduct (450-nm Band), and the Oxidation Products of **1** (580-nm band) in Dimethyl Sulfoxide<sup>a</sup>

Expt	Solution conditions	450 nm. $\epsilon$ (mM <sup>-1</sup> cm <sup>-1</sup> )	580 nm. $\epsilon$ (mM <sup>-1</sup> cm <sup>-1</sup> )
a	<b>1</b> (0.1 mM $\rightarrow$ 20 mM)	0.35	0.15
b	1.0 mM <b>1</b> + O <sub>2</sub> , 1 atm (5 min)	4.65	2.95
c	b + Ar (20 min)	1.70	1.65
d	1.0 mM <b>1</b> + O <sub>2</sub> , 1 atm (3 min)	3.60	1.90
e	d + Ar (20 min)	1.90	2.80
f	e + O <sub>2</sub> , 1 atm (3 min)	3.60	1.90
g	f + Ar (20 min)	1.65	2.75
h	g + Ar (10 h)	1.53	2.30
i	h + O <sub>2</sub> , 1 atm (25 min)	3.25	1.55
j	0.1 mM <b>1</b> + O <sub>2</sub> , 1 atm (3 min)	3.25	0.93
k	j + Ar (20 min)	1.55	1.00
l	0.2 mM <b>1</b> + O <sub>2</sub> , 1 atm (3 min)	3.45	1.10
m	l + Ar (20 min)	1.65	1.45
n	5 mM <b>1</b> + O <sub>2</sub> , 1 atm (3 min)	4.30	3.65
o	n + Ar (20 min)	2.76	5.04
p	1.0 mM <b>1</b> + O <sub>2</sub> , 1 atm (5 min)	4.65	2.95
q	1.0 mM <b>1</b> + air (5 min)	3.65	3.50
r	10 mM <b>1</b> + O <sub>2</sub> , 1 atm (5 min)	6.20	5.30
s	10 mM <b>1</b> + air (5 min)	5.15	6.55

<sup>a</sup> Solutions of **1** were prepared in situ by combining Mn<sup>III</sup>(OAc)<sub>3</sub>, 3,5-di-*tert*-butylcatechol, and tetramethylammonium hydroxide in a mole ratio of 1:3:6. The apparent molar absorptivities,  $\epsilon$ , are based on the formal concentrations of **1** in the solutions.



**Figure 2.** Cyclic voltammograms for solutions of the tris(3,5-di-*tert*-butylcatecholato)manganese(III) complex (**1**) in the absence and presence of  $O_2$  in dimethyl sulfoxide that contained 0.1 M tetraethylammonium perchlorate. The complex was formed *in situ* by combining  $Mn^{III}(OAc)_3$ , 3,5-di-*tert*-butylcatechol, and tetraethylammonium hydroxide in a mole ratio of 1:3:6. (a) 1.0 mM complex **1**; (b)  $O_2$  at 1 atm ( $\sim 2.1$  mM); (c) 1.0 mM complex plus  $O_2$  at 1 atm (bubbled for 5 min); (d) preceding solution after deaeration by bubbling argon through it for 20 min. Measurements were made at a platinum electrode (area,  $0.23$  cm $^2$ ) at a scan rate of  $0.1$  V s $^{-1}$ ; temperature,  $25$  °C.

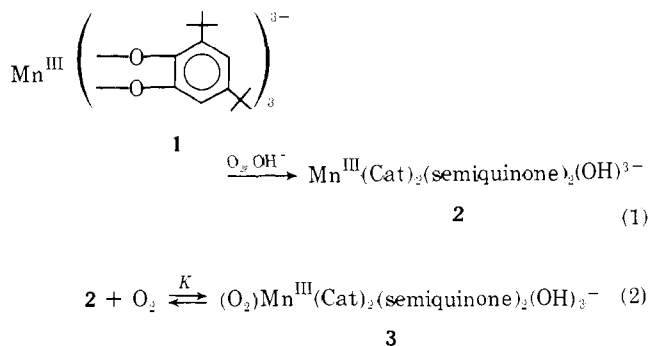
sulting semiquinone of catechol. Also, the absence of an initial oxidation peak for free catechol anion (at  $-0.25$  V) in curve 2c confirms that the adduct contains three catechol or semiquinone ligands per manganese(III).

Combination of  $Mn^{III}(OAc)_3$ , di-*tert*-butylcatechol, tetraethylammonium hydroxide, and di-*tert*-butyl-*o*-quinone in a mole ratio of 1:2:5:1 results in the formation of a mixed semiquinone-catechol complex with an absorption spectrum almost identical with that which results from argon deaeration of the manganese(III)-catechol-oxygen adduct (Figure 1). Addition of  $O_2$  to this solution results in the reversible formation of the reddish brown adduct. When di-*tert*-butyl-*o*-quinone is added to a solution of the tris(di-*tert*-butylcatecholato)manganese(III) complex (**1**), formation of the blue semiquinone complex also occurs, but it does not yield any of the reddish brown complex that is characteristic of the oxygen adduct.

ESR studies of complex **1** do not yield an observable spectrum. However, addition of  $O_2$  (1 atm) to a 1 mM solution of the complex results in the reddish brown  $O_2$  adduct which has an ESR spectrum with a broad doublet ( $g$ , 2.01). The latter is consistent with the expected spectrum for the semiquinone of di-*tert*-butyl catechol. When the latter solution is deaerated with argon, the blue solution that is characteristic of the manganese(III) semiquinone complex results. This has an ESR spectrum with each line of the semiquinone doublet split by at least 11 hyperfine lines from coupling with coordinated manganese(III) ions (nuclear spin,  $5/2$ ); average  $g$ , 2.00. Addition of  $O_2$  causes the spectrum to be reversed to the doublet of the

semiquinone complex. Just as in the case of the absorption spectra (Figure 1), the ESR spectra confirm that formation of the oxygen adduct is a reversible process and that a semiquinone-catechol complex of manganese(III) is the active oxygen-binding system.

These results indicate that the primary step in the oxygenation of **1** is the irreversible formation of a manganese(III) mixed catechol-semiquinone complex (which may be binuclear on the basis of its ESR spectrum) (eq 1). The latter species in turn reversibly binds molecular oxygen (eq 2). The absorption



band at 580 nm in Figure 1 appears to be due to **2**. Such an assignment is consistent with previous data for semiquinone complexes of manganese(III) in aqueous media ( $\lambda_{\text{max}}$  610 nm ( $\epsilon$   $1.7$  mM $^{-1}$  cm $^{-1}$ )).<sup>4</sup> At higher concentrations of **1** and  $O_2$  the remaining catechol ligand of **2** is oxidized to semiquinone to give an enhanced absorbance at 580 nm.

Because the adduct **3** has a distinct absorption band ( $\lambda$  450 nm ( $\Delta\epsilon_{O_2, 1 \text{ atm}}$   $2.7$  mM $^{-1}$  cm $^{-1}$ )) from that for **1** ( $\lambda$  700 nm ( $\epsilon$   $120$  M $^{-1}$  cm $^{-1}$ )) and **2** as well as the unique reverse oxidation peak at  $-0.50$  V, the data of Figures 1 and 2 (along with supplementary measurements) can be used to obtain an approximate value for  $K$ ; the average value is  $0.8$  atm $^{-1}$ . Quantitative measurements are complicated by the apparent tendency of the higher and lower oxidation states of **2** to bind  $O_2$  reversibly also.

Although numerous synthetic oxygen carriers have been reported,<sup>5</sup> we believe this is the first example of a manganese system that involves solely oxygen donor groups from the ligand rather than porphyrin or nitrogen groups. A recent report<sup>6</sup> describes a dioxygen adduct of a manganese(II) porphyrin.

Because of the similarity in the solution chemistry of manganese(III) and iron(III), the present system may provide insight into the chemistry of natural oxygen binding systems such as hemerythrins. The ability of **1** to enhance the total concentration of dissolved oxygen may make it an effective activator for oxygenation reactions. In particular, complexes similar to **1** may prove especially useful for the enhancement of delignification of wood pulp.<sup>7</sup>

Our primary interest in **2** is as a model for the terminal step of photosystem II, the manganese-catalyzed oxygen evolution reaction of green plant photosynthesis. The plastiquinones in the grana of the biomembranes<sup>8</sup> may bind the manganese ions in a manner similar to **2** and result in the reversible release of the dioxygen that is produced by photosystem II.

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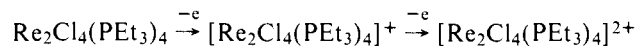
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### Novel Electrochemical Reactions of Compounds Containing Strong Metal-Metal Bonds. Oxidation of Rhenium(II) Dimers, $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , by Both EECC and ECEC Pathways

Sir:

The use of electrochemistry to probe the chemical properties of metal systems is well established.<sup>1</sup> However, while much interest has centered on the structural and chemical properties of rhenium dimers,<sup>2,3</sup> little use has been made, with the exception of studies involving the octachlorodirhenate(III) anion,<sup>4-6</sup> of electrochemical techniques for the study of these and other metal halides containing strong metal-metal bonds.

As previously reported,<sup>2,7</sup> the reduction of the octahalodirhenate(III) anions by monodentate tertiary phosphines affords complexes of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , where X = Cl or Br. Subsequently, Cotton and Pedersen<sup>8</sup> investigated the properties of  $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$  and  $[\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4]^+$  using electrochemical and electron paramagnetic resonance experiments. While they found that the rhenium(II) dimer can be oxidized to the 1+ and 2+ ions



and that the 1+ ion was reasonably stable, electrochemical studies on this system were not pursued further. As a consequence of our interest in the chemical and redox properties of metal phosphine complexes which contain metal-metal bonds of multiple bond orders,<sup>7,9</sup> we have investigated the electrochemical properties of the complete series of rhenium(II) dimers of the type  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ , where X = Cl, Br, or I and R = Et, Pr<sup>n</sup> or Bu<sup>n</sup>,<sup>10</sup> in order to explore the consequences of oxidizing species which possess two electrons over and above those of a fully occupied  $\sigma^2\pi^4\delta^2$  configuration.<sup>2</sup> This study has led to the discovery of a novel form of electrochemical behavior for this series of transition metal complexes.

The electrochemical properties of this series of complexes are summarized in Table I. In Figure 1A is shown a cyclic voltammogram<sup>12</sup> of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  (this compound will be used as a representative example of all the  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$  compounds studied) which demonstrates that the dimer has two electrochemical reversible,<sup>13</sup> one-electron (by coulometry) oxidations.

However, upon electrolysis at 0.0 V ( $n = 0.98$ ),<sup>14</sup> in addition to the major product,  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^+$ , two new waves ( $E_{1/2} = +0.31$  and  $-0.88$  V) appear in the resultant cyclic voltammogram (Figure 1B). The origin of these new waves was found to be  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$ , since a cyclic voltammogram of an analytically pure sample of  $\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3$  shows two waves at  $E_{1/2} = +0.31$  and  $-0.88$  V. Further oxidation at +1.0 V (i.e., past the second wave of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  ( $n = 0.95$ )) produces  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^{2+}$ ,  $[\text{Re}_2\text{Cl}_5(\text{PPr}_3)_3]^+$ , and another wave at

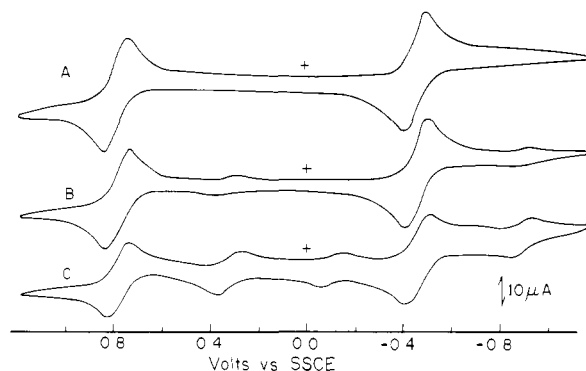


Figure 1. Cyclic voltammograms in 0.2 M TBAH-dichloromethane of A,  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$ ; B, solution A following oxidation at 0.0 V; C, solution A following oxidation at +1.0 V (scan rate 200 mV/s at a Pt-bead electrode vs. the saturated sodium chloride calomel electrode at  $22 \pm 2$  °C).

Table I.  $E_{1/2}$  Values for Rhenium Dimers,  $\text{Re}_2\text{X}_4(\text{PR}_3)_4$ ,<sup>a</sup> in Dichloromethane<sup>b</sup>

Complex	$E_{1/2}(\text{ox})(1)^c$	$E_{1/2}(\text{ox})(2)^c$
$\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$	-0.42	0.80
$\text{Re}_2\text{Br}_4(\text{PEt}_3)_4$	-0.31	0.825
$\text{Re}_2\text{I}_4(\text{PEt}_3)_4$	-0.27	0.77
$\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$	-0.44	0.79
$\text{Re}_2\text{Br}_4(\text{PPr}_3)_4$	-0.38	0.84
$\text{Re}_2\text{I}_4(\text{PPr}_3)_4$	-0.22	0.85
$\text{Re}_2\text{Cl}_4(\text{PBu}_3)_4$	-0.44	0.82
$\text{Re}_2\text{Br}_4(\text{PBu}_3)_4$	-0.40	0.82
$\text{Re}_2\text{I}_4(\text{PBu}_3)_4$	-0.25	0.825

<sup>a</sup> X = Cl, Br, I; R = C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub>. <sup>b</sup> With 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. <sup>c</sup> Volts vs. the saturated sodium chloride calomel electrode (SSCE) with a Pt-bead working electrode.

$E_{1/2} = -0.11$  V in the resultant cyclic voltammogram (Figure 1C). This new wave at  $E_{1/2} = -0.11$  V was found to be associated with  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$ ; a pure sample of  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  was found to have a wave at  $-0.11$  V in its cyclic voltammogram.  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  can also be electrochemically generated by oxidation of  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  at +0.5 V. These two pathways for the electrochemical production of  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$  from  $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$  are summarized in Schemes I and II and are representative of EECC and ECEC processes,<sup>15</sup> respectively. The difference between these two schemes is the potential used for the oxidation. If the oxidation is carried out at 1.0 V, then the initial product will be  $[\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4]^{2+}$  which will then, by a series of chemical reactions ( $C_1'$  and  $C_2$ ), produce  $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_2$ . If the oxidation potential is 0.5 V, then the first product will be  $[\text{Re}_2\text{Cl}_4(\text{Pr}_3)_4]^+$  which will, by a chemical step ( $C_1$ ), be converted to  $\text{Re}_2\text{Cl}_5(\text{Pr}_3)_3$ . Since 0.5 V is anodic of the  $E_{1/2}$  for  $\text{Re}_2\text{Cl}_5(\text{Pr}_3)_3$ , then this complex will in turn be oxidized and the resultant  $[\text{Re}_2\text{Cl}_5(\text{Pr}_3)_3]^+$  will, by a chemical step ( $C_2$ ), form  $\text{Re}_2\text{Cl}_6(\text{Pr}_3)_2$ . Therefore, the choice of pathway which produces  $\text{Re}_2\text{Cl}_6(\text{Pr}_3)_2$  from  $\text{Re}_2\text{Cl}_4(\text{Pr}_3)_4$  is governed by the electrochemical potential used for the oxidation.

#### Scheme I. EECC Process

