

# Isolation and characterization of monomeric mono(iodosylbenzene) manganese(IV) tetraphenylporphyrin complexes from the (tetraphenylporphinato) manganese(III) derivatives-iodosylbenzene systems and their oxidation properties

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## Abstract

The monomeric mono(iodosylbenzene) (tetraphenylporphinato)manganese(IV) derivatives, LMn(IV)TPP(OIPh) (**2a** and **2b**) (L = 4-MeOC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> and 4-*t*-BuC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>) have been synthesized from the reaction of the corresponding (tetraphenylporphinato)manganese(III) derivatives **1a** and **1b**, LMn(III)TPP with iodosylbenzene, respectively. The complexes **2a** and **2b** have been characterized by elemental analyses, visible, infrared and ESR spectroscopy. These complexes are capable of oxidizing cyclohexane and styrene to give oxidation products in high yields at room temperature.

*Keywords:* Manganese; Tetraphenylporphyrin; Iodosylbenzene; Oxidation

## 1. Introduction

Recently chemists have been very interested in synthesizing high-valent manganese porphyrin complexes because these species are possible intermediates in cytochrome P-450 model systems that utilize manganese porphyrin complexes as catalysts for oxidation of hydrocarbons [1]. Hill et al. have isolated two types of monomeric manganese(IV) tetraphenylporphyrin complexes, L<sub>2</sub>Mn(IV)TPP (L = OCH<sub>3</sub>, N<sub>3</sub><sup>-</sup> and OCN<sup>-</sup>) [2,3] and

[PhI(OAc)O]<sub>2</sub>Mn(IV)TPP [4] and two types of dimeric manganese(IV) porphyrin complexes, [LMn(IV)TPP]<sub>2</sub>O (L = N<sub>3</sub><sup>-</sup> and OCN<sup>-</sup>) [5] and [LMn(IV)TPP(OIPh)]<sub>2</sub>O (L = Cl<sup>-</sup> and Br<sup>-</sup>) [6]. The monomeric mono(iodosylbenzene)manganese(IV) porphyrin complexes which may be the possible intermediates in P-450 model systems had not appeared until we reported the preparation, purification and characterization of two monomeric complexes, LMn(IV)TPP(OIPh) (L = 4-MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> [7] and 3-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup> [8]). Recently we have studied the affect of the axial ligand of (tetraphenylporphinato)manganese(III) derivatives, LMn(III)TPP (where L are the derivatives of phenol and benzoic acid) on the formation of monomeric mono(iodosyl-

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benzene)manganese(IV) tetraphenylporphyrin complexes. We report here the isolation and characterization of another two monomeric mono(iodosylbenzene) (tetraphenylporphinato)-manganese(IV) derivatives **2a** and **2b**, LMn(IV)TPP(OIPh) ( $L = 4\text{-MeOC}_6\text{H}_4\text{O}^-$  and  $4\text{-}t\text{-BuC}_6\text{H}_4\text{O}^-$ ) and the oxidation activity of these complexes for cyclohexane and styrene.

## 2. Experimental

### 2.1. General

Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by known methods before use. Chloro(tetraphenylporphinato)manganese(III) was prepared by the known method [9]. Visible spectra were determined on a UV-3000 spectrophotometer. Infrared spectra were obtained by a FTS-20 infrared spectrophotometer. X-band ESR spectra were determined as a solid at room temperature using a JES-FE3AS ESR spectrometer.

### 2.2. Synthesis of LMn(IV)TPP(OIPh) ( $L = 4\text{-MeOC}_6\text{H}_4\text{O}^-$ or $4\text{-}t\text{-BuC}_6\text{H}_4\text{O}^-$ )

To a solution of 1.0 g (1.4 mmol) of ClMn(III)TPP in 100 ml of ethyl alcohol was added a solution of 6.0 g (51.7 mmol) of sodium 4-methoxyphenolate in water. The reaction system was degassed with nitrogen for 1 h and then 6.0 g (158.7 mmol) of sodium borohydride was added to the mixture. The mixture was stirred for 2 h under nitrogen atmosphere. The resulting solution was distilled to remove the alcohol, filtered, rinsed with 500 ml of hot water and dried in vacuo. Crude (4-MeOC<sub>6</sub>H<sub>4</sub>O)Mn(III)-TPP (**1a**) was purified by recrystallization from dichloromethane/petroleum ether. To a solution of 100 mg (0.099 mmol) of the complex **1a** in 25 ml of dichloromethane was added 500 mg (2.30 mmol) of iodosylbenzene and the mixture

was vigorously stirred for 50 s. The resulting red-brown solution was quickly cooled to  $-30^\circ\text{C}$  and filtered. After the filtrate was poured into hexane cooled to  $-30^\circ\text{C}$ , the precipitate was filtered. The red-brown oxidation product was recrystallized three times from CH<sub>2</sub>Cl<sub>2</sub>/hexane cooled to  $-30^\circ\text{C}$  giving 0.045 g (35% yield) of pure product **2a**. It was found that: C, 67.31; H, 3.63; N, 5.03; Mn, 5.48; I, 12.57%. Values calculated for C<sub>57</sub>H<sub>40</sub>N<sub>4</sub>MnIO<sub>3</sub> were: C, 67.73; H, 3.99; N, 5.54; Mn, 5.44; I, 12.55%.

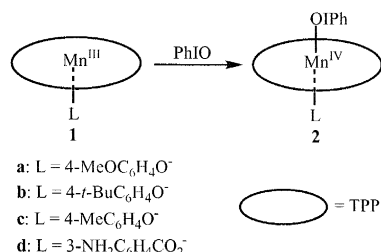
The complex **2b** was similarly isolated. To a solution of 100 mg (0.096 mmol) of the complex **1b**, which was prepared from the ClMn(III)TPP and sodium 4-*t*-butylphenolate by a similar method as was prepared **1a**. To 25 ml of dichloromethane was added 500 mg (2.30 mmol) of iodosylbenzene. The mixture was vigorously stirred for 45 s. The subsequent procedure was similar to the method for preparation of complex **2a**. The pure product **2b** was obtained in 50% yield. It was found that: C, 68.28; H, 3.91; N, 5.06; Mn, 5.62; I, 12.17%. Values calculated for C<sub>60</sub>H<sub>46</sub>N<sub>4</sub>MnIO were: C, 68.45; H, 4.40; N, 5.32; Mn, 5.22; I, 12.05%.

### 2.3. Oxidation of cyclohexane or styrene by **2**

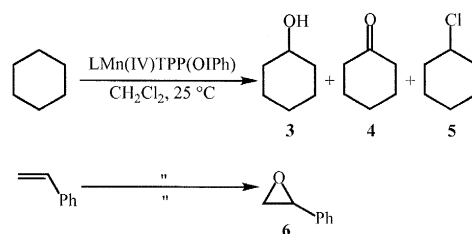
To the mixture of 6 ml of dichloromethane and 2 ml of cyclohexane or 0.5 ml of styrene degassed by N<sub>2</sub> was added about 0.02 mmol of high-valent manganese complexes **2**. The mixture was stirred for 1 h under N<sub>2</sub> at room temperature. After the reaction mixture was passed through a short silica gel column to remove the reduced complex, the product was analysed by GLC.

## 3. Results and discussion

The formation of the monomeric mono(iodosylbenzene)manganese(IV) tetraphenylporphyrin complexes was affected by the axial ligand of (tetraphenylporphinato)manganese(III) derivatives, LMn(III)TPP. It was reported that



Scheme 1.



Scheme 2.

the reaction of LMn(III)TPP (L = N<sub>3</sub><sup>-</sup>, OCN<sup>-</sup>, Cl<sup>-</sup>, and Br<sup>-</sup>) with iodosylbenzene produced dimeric manganese(IV) porphyrin complexes [5,6]. However, we found that when a derivative of phenol or benzoic acid was introduced as the axial ligand of LMn(III)TPP (L = 4-MeC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> and 3-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>), dimerization was prevented and monomeric mono(iodosylbenzene)manganese(IV) tetraphenylporphyrin complexes (**2c** and **2d**) could be obtained from reaction with iodosylbenzene [7,8]. Thus, we tried various phenol or benzoic acid derivatives as the axial ligand of LMn(III)TPP to determine the scope and limitation on the formation of the monomeric mono(iodosylbenzene)manganese(IV) tetraphenylporphyrin com-

plexes with iodosylbenzene. Among the axial ligands examined, 4-MeOC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> and 4-*t*-BuC<sub>6</sub>H<sub>4</sub>O<sup>-</sup> afforded monomeric mono(iodosylbenzene)manganese(IV) tetraphenylporphyrin complexes, LMn(IV)TPP(OIPh) (**2a** and **2b**) (Scheme 1), however with longer reaction times (5–10 min) these axial ligands afforded monomeric bis(iodosylbenzene)manganese(IV) tetraphenylporphyrin complexes. In the case of axial ligands such as C<sub>6</sub>H<sub>5</sub>O<sup>-</sup>, 4-HOC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, 3-HOC<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, 4-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, 3-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>, 4-MeC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>, 3-HOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>, and 3-MeOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub><sup>-</sup>, only monomeric bis(iodosylbenzene)manganese(IV) tetraphenylporphyrin complex, Mn(IV)TPP-(OIPh)<sub>2</sub> was isolated.

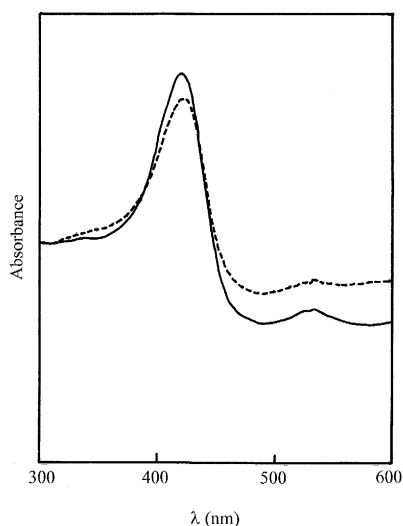
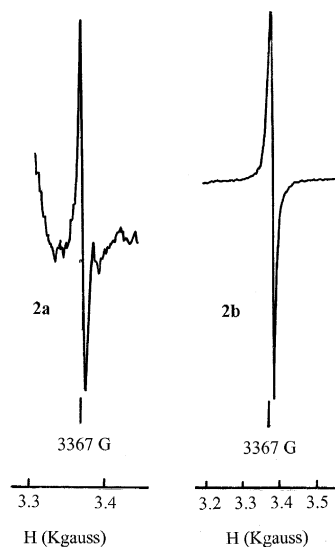
Fig. 1. Electronic spectra of **2a** (—) and **2b** (---).Fig. 2. ESR spectra of **2a** and **2b** (microwave frequency = 9.435 GHz).

Table 1  
Oxidation of cyclohexane <sup>a</sup>

LMn(IV)TPP(OIPh)	Products and yield (%) <sup>b</sup>		
	3	4	5
<b>2a</b>	32	34	26
<b>2b</b>	25	18	46
<b>2c</b>	– <sup>c</sup>	11	36
<b>2d</b>	67	– <sup>c</sup>	33
[PhI(Cl)OMnTPP] <sub>2</sub> O <sup>d</sup>	16	5	24

<sup>a</sup> All reactions were run under nitrogen at room temperature with cyclohexane present in excess.

<sup>b</sup> Determined by GLC. Based on one oxidizing equivalents for **2**.

<sup>c</sup> Below detective limit.

<sup>d</sup> Ref. [10].

The composition, visible, infrared and ESR spectra of the complexes **2a** and **2b** have been studied. The visible absorption spectra of **2a** and **2b** in chloroform shows an intense Soret band at 422 nm and a broad shoulder band near 520 nm (Fig. 1). This demonstrates that the complexes **2a** and **2b** are tetravalent manganese porphyrin complexes. The infrared spectra of the complexes **2a** and **2b** as KBr pellets display an intense absorption band near 580 cm<sup>-1</sup> which is assigned to a Mn–O–I stretch [6], and two weak peaks at 2860 and 2920 cm<sup>-1</sup> which are characteristic of methoxy and *t*-butyl groups. The intense absorption band at 810 cm<sup>-1</sup> is characteristic of dimeric  $\mu$ -oxo manganese porphyrin complexes and is not present in these complexes **2a** and **2b**. Thus, it is clear that the complexes **2a** and **2b** are not dimeric  $\mu$ -oxo

Table 2  
Oxidation of styrene <sup>a</sup>

LMn(IV)TPP(OIPh)	Yield (%) <sup>b</sup> of <b>6</b>
<b>2a</b>	84
<b>2b</b>	93
<b>2c</b>	43
<b>2d</b>	89
[PhI(Cl)OMnTPP] <sub>2</sub> O <sup>c</sup>	87

<sup>a</sup> All reactions were run under nitrogen at room temperature with styrene present in excess.

<sup>b</sup> Determined by GLC. Based on one oxidizing equivalents for **2**.

<sup>c</sup> Ref. [10].

manganese porphyrin complexes. The X-band ESR spectra of both **2a** and **2b** as solid powder at room temperature show an intense absorption band in the *g* region ( $\sim 2$ ) which shows that **2a** and **2b** are monomeric manganese porphyrin complexes [10] (Fig. 2).

The monomeric mono(iodosylbenzene)-manganese(IV) tetraphenylporphyrin complexes (**2a–2d**) react with cyclohexane and styrene in dichloromethane at room temperature for 1 h to give high yields of oxidized products (Scheme 2). The oxidation of cyclohexane by the complex **2c** selectively produced cyclohexanone (**4**), and that by the complex **2d** selectively produced cyclohexanol (**3**). Both **2c** and **2d** produced cyclohexyl chloride (**5**). Cyclohexane activation of the complexes (**2a**, **2b** and **2d**) is higher than that of dimeric  $\mu$ -oxo(tetraphenylporphinato)-manganese(IV), [PhI(Cl)OMnTPP]<sub>2</sub>O. Styrene activation of the complexes (**2a**, **2b** and **2d**), however, is similar to that of the complex, [PhI(Cl)OMnTPP]<sub>2</sub>O. Typical results for cyclohexane and styrene are summarized in Tables 1 and 2, respectively.

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