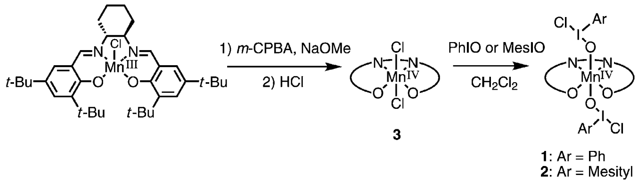
DOI: 10.1002/anie.201202835

Oxygen Transfer

Structure and Reactivity of an Iodosylarene Adduct of a Manganese(IV)–Salen Complex[**]

*Chunlan Wang, Takuya Kurahashi, and Hiroshi Fujii**

Enantioselective transition-metal-catalyzed oxygenation reactions have received much attention because of their demand in organic synthesis strategies and their biological relevance with respect to metalloenzymes.[1] Terminal oxidants, such as peroxides, iodosylarenes, and peracids, have been utilized as oxygen source for these oxygenation reactions. Because the terminal oxidants must be stable for easy handling, the primary role of the transition-metal catalyst is to activate the stable oxidant and to generate a transient species that remains active enough to transfer an oxygen atom to a substrate. The activation of a terminal oxidant is initiated by binding to the metal complex to form a terminal-oxidant adduct of the metal complex. Recently, evidence has been mounting in support of the proposal that the terminal-oxidant adduct of a metal complex is not only a precursor to a reactive high-valent metal–oxo species, but that the adduct itself may also serve as a reactive species in an oxygenation reaction.[2] Although terminal-oxidant adducts of metal complexes are unstable and reactive compounds in most cases, metal-complex adducts with hydrogen peroxide, alkylperoxides, and *m*-CPBA have been isolated and structurally characterized.[3] In contrast to these successful reports, and much to our surprise, there have been no examples of structural characterization of any iodosylarene adducts of metal complexes, although they have emerged as useful oxidants for various organic reactions.[4] The most intensive spectroscopic study was performed by Hill and co-workers, who thoroughly investigated an iodosylbenzene adduct of a manganese–porphyrin complex with ^{1}H NMR, IR, and ^{127}I Mössbauer spectroscopy.[5] However, the nature of the bonding interaction between iodosylbenzene and the metal ion remains unclear. Here, we report the preparation and X-ray crystal structure of an iodosylarene adduct of a manganese(IV)–salen complex that bears a *trans*-cyclohexane-1,2-diamine linkage as chiral unit.[6]



Scheme 1. Synthesis of manganese(IV)–iodosylarene adducts.

We used iodosylbenzene (PhIO) and iodosylmesitylene (MesIO) as iodosylarene compounds. PhIO and MesIO adducts (**1** and **2**, respectively) of a manganese(IV)–salen complex were prepared by reaction of a dichloromanganese(IV)–salen complex, [Mn^{IV}(salen)(Cl)$_2$] (**3**), with an excess of solid PhIO and MesIO, respectively, in dichloromethane at room temperature (Scheme 1). Adducts **1** and **2** were characterized by absorption, ^{1}H NMR, electron paramagnetic resonance (EPR), circular dichroism (CD), and infrared (IR) spectroscopy, and electrospray ionization mass (ESI-MS) spectrometry (Figure S1–S7). The ligand-to-metal charge transfer (LMCT) band at 700 nm for **3** is shifted to a shorter wavelength upon reaction with iodosylarene, thus indicating binding of a strong electron donor ligand to the manganese center. ^{1}H NMR spectra of **1** and **2** are similar to that of **3**, thus suggesting the formation of bis-iodosylarene adduct. EPR spectra clearly indicate high-spin manganese(IV) oxidation states ($S = 3/2$) for **1** and **2**. Adducts **1** and **2** show IR bands at 598 and 608 cm^{-1}, which are shifted to 558 and 567 cm^{-1}, respectively, with ^{18}O isotope labeling of iodosylarene. This result is consistent with the assignment of this mode as the I–O–Mn stretching band.[5a] ESI-MS spectra of **1** and **2** show major signals at m/z 1074.11 and 1158.43, and their isotope patterns were fully consistent with [Mn^{IV}(salen)(PhIO)$_2$Cl]$^+$ and [Mn^{IV}(salen)(MesIO)$_2$Cl]$^+$, respectively. The CD spectra of **1** and **2** show strong bands at 280 nm, while that of **3** does not show a strong CD band, thus indicating that the structures of **1** and **2** are chirally distorted in solution. All of these spectroscopic data are consistent with bis-iodosylarene adducts of manganese(IV)–salen complex having stepped conformations.

Brown crystals of **2** suitable for X-ray crystal-structure determination were obtained by slow diffusion of pentane into a solution of **2** in dichloromethane at −20 °C.[7] The X-ray crystal structure of **2** shows a monomeric bis-MesIO adduct of the manganese(IV)–salen complex (Figure 1). Structure **2** shows a chirally distorted stepped conformation with one of two salicylidene rings pointing upward and the other pointing downward as a result of the steric bias from the *trans*-cyclohexane-1,2-diamine moiety. Because **3** shows an almost flat structure,[8] the stepped conformation must be induced by axial iodosylmesitylene ligands. In a previous study, the stepped conformation was observed for manganese(IV)–salen complexes with tightly bound axial ligands.[8] In fact, the

---

[*] C. Wang, Dr. T. Kurahashi, Prof. Dr. H. Fujii
Institute for Molecular Science and Okazaki Institute for Integrative Bioscience, National Institutes of Natural Sciences and Department of Functional Molecular Science, The Graduate University for Advanced Studies (SOKENDAI)
Myodaiji, Okazaki 444-8787 (Japan)
E-mail: hiro@ims.ac.jp

[**] This work was supported by grants from the Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research, Grant No. 22350030 and 23550086).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201202835.

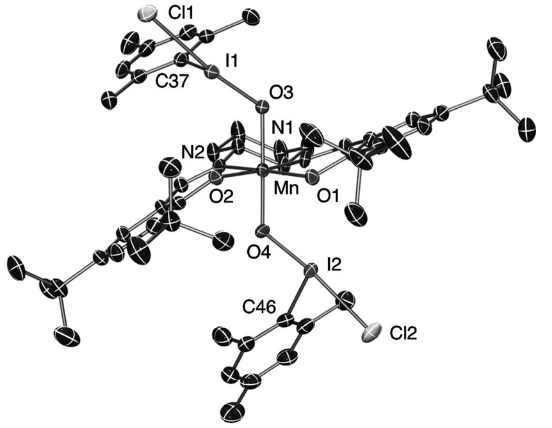


Figure 1. X-ray crystal structure of **2** (50% probability ellipsoids). Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Selected bond distances [Å] and bond angles [°]: Mn–N1 1.982(4), Mn–N2 1.963(4), Mn–O1 1.885(4), Mn–O2 1.867(3); N1-Mn-N2 82.75(14), N1-Mn-O1 90.18(14), N2-Mn-O2 91.06(14), N1-Mn-O3 85.42(14), N1-Mn-O4 89.78(15), O3-Mn-O4 173.04(14).

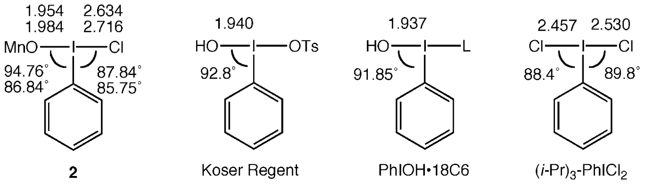


Figure 2. Comparison of structural parameters of **2** with monomeric hypervalent iodine(III) compounds. Substituents of the benzene rings are omitted for clarity. L = 18C6 = [18]crown-6, OTs = tosylate.

lengths of the Mn–O bonds are short (1.853 and 1.888 Å) and comparable to those of the manganese(IV)–salen complex that bears tightly bound alkoxide ligands (1.866 and 1.880 Å).[8] The binding of the counteranion (Cl^-) to the I atom of the manganese-bound MesIO converts the neutral MesIO to the anionic $MesIClO^-$ ligand and increases the binding strength. As a result of the formation of the stepped conformation, the salen ligand and the O–I–Cl moieties of two MesIO molecules are located in a nearly C_2-symmetric position along the axis, which is perpendicular to the O3–Mn–O4 axis. The position of the mesityl moiety significantly deviates from the C_2-symmetry, thus indicating a relatively weak steric influence on the mesityl moiety upon the formation of the stepped conformation.

The structural parameters of the manganese-bound iodosylmesitylene of **2** and relevant monomeric hypervalent iodine(III) compounds are summarized in Figure 2.[9] The geometry around the I^{III} center of **2** is T-shaped with O–I–Cl and O–I–C bond angles of 172.63/172.57° and 94.76/86.84°, respectively. These angles are typical of hypervalent I^{III} compounds and provide a clear indication that Cl is not just a counterion but contributes to the formation of a three-center, four-electron hypervalent bonding arrangement with the I^{III} center.[4] The I^{III}–OMn bond lengths of 1.954 and 1.984 Å are slightly longer than the I^{III}–OH bond lengths of 1.937 Å in a monomeric iodosylarene compound and 1.940 Å in the Koser reagent.[9a,b] This result indicates that the I^{III}–O bond is activated upon coordination to the Mn^{IV} center. In addition, the I^{III}–Cl bond lengths of 2.634 and 2.716 Å are significantly lengthened relative to the I^{III}–Cl bond of (iPr)$_3$-$PhICl_2$ (2.457 and 2.530 Å).[9c] These structural parameters clearly indicate that the coordination of MesIO to the Mn^{IV} center enhances the electrophilic nature of the I–O center.

The reactivities of **1** and **2** with substrates were studied. Upon dissolving in dichloromethane that contains ^{18}O-labeled water, the main ESI-MS signals at m/z 1074.11 and 1158.43 for **1** and **2** are shifted by 4 Da at 1078.37 and 1162.62 within four hours, respectively (Figure S7). This result clearly indicates that the oxygen atoms in the iodosylarene adducts are readily exchanged with oxygen atoms of water in CH_2Cl_2.[10] This exchange is possibly a result of the enhancement of electrophilicity of the I^{III} center with the coordination of the Mn^{IV} center.

Single-turnover reactions of **1** and **2** with an excess of thioanisole afford methyl phenyl sulfoxide as a major product (with **1**: 38%, with **2**: 49%; Table 1). The yields were not high because of thermal decomposition of **1** and **2** in the reaction. Under the conditions using an excess of thioanisole, only a trace amount of methyl phenyl sulfone is formed (with PhIO: <2%; with MesIO: <1%). The reaction of the ^{18}O-labelled iodosylbenzene adduct (70% ^{18}O) affords ^{18}O-labelled methyl phenyl sulfoxide (50% ^{18}O) and methyl phenyl sulfone (30% ^{18}O; see Figure S8 and S9 in the Supporting Information). The loss of ^{18}O is a result of the exchange of $PhI^{18}O$ in the adduct with residual $H_2{}^{16}O$ in CH_2Cl_2 during the reaction, as shown above. Absorption and ^1H NMR spectra indicate that **3** is formed after the reaction of **1** and **2** with excess thioanisole (Figure S10 and S11). This result demonstrates that the iodosylarene adducts transfer the oxygen atoms to the sulfide without a change in the oxidation state of the Mn^{IV} center. It also suggests that the two manganese-bound iodosylarenes in **1** and **2** have similar reactivity with thioanisole. The reaction of **2** with 4-methoxythioanisole was faster than that with 4-methylthioanisole (Figure S12), thus indicating the electrophilic character of the manganese-bound iodosylarene. Enantioselectivity of the single-turnover reactions of the iodosylarene adducts with thioanisole is very low, but a slight excess of

Table 1: Stoichiometric oxidation of thioanisole and styrenes with **1** and **2**.[a]

Substrate	Product	*ee* [%]; Yield [%][b] with **1**	 with **2**	Config.
thioanisole	methyl phenyl sulfoxide	(6±1); 38	(3±1); 49	*S*
styrene	styrene oxide	(21±5); 26	(52±1); 20	*R*
4-fluorostyrene	4-fluorostyrene oxide	(31±4); 40	(56±1); 27	*R*
cis-β-methylstyrene	*cis*-β-methylstyrene oxide	(44±1); 10	(63±1); 25	1*R*, 2*S*
	trans-β-methylstyrene oxide	(27±1); 12	(27±4); 8	1*S*, 2*S*
trans-β-methylstyrene	*trans*-β-methylstyrene oxide	(22±3); 23	(41±1); 47	1*R*, 2*R*

[a] Reaction conditions: iodosylarene adduct (45 μmol), substrate (99 μmol), dichloromethane (1 mL), 25 °C, 5 h. Details regarding the reaction and analytical conditions are provided in the Supporting Information. [b] Yields are based on manganese-bound PhIO or MesIO.

the (*S*)-sulfoxide (PhIO, 6 %ee; MesIO, 3 %ee) is obtained from the (*R*,*R*)-adducts (Table 1). This observation is consistent with previous catalytic studies.[11]

Single-turnover reactions of **1** and **2** with 2.2 equivalents of olefins afford epoxides as major products (Table 1). The reactions of the iodosylarene adducts with *cis*-β-methylstyrene afford a mixture of *cis* and *trans* epoxide, thus indicating that the oxygen-atom insertion into the olefin is not concerted. The oxygen atom in styrene oxide originates from the iodosylbenzene molecule, as confirmed in an ^{18}O isotope experiment, in which the ^{18}O-labelled iodosylbenzene adduct (70 % ^{18}O) affords the styrene oxide with 60 % ^{18}O enrichment (Figure S13). The enantioselectivities observed for the present single-turnover reactions with **1** and **2** are similar to the enantioselectivities of catalytic epoxidation by manganese(III)–salen complex with PhIO and MesIO as the terminal oxidant, respectively.[12] This observation indicates that the iodosylarene adduct of the manganese(IV)–salen complex may be involved as a reactive species in the catalytic reaction with PhIO and MesIO. Enantioselectivity of the single-turnover reactions with olefins is much higher than that for thioanisole (Table 1). This result suggests that the oxygen-atom transfer from the iodosylarene adducts to olefins might be mechanistically different. Adduct **2** gives better enantioselectivity than **1** for all of the olefins tested, thus indicating that the manganese-bound iodosylarene can directly transfer the oxygen atom to a substrate. The electronic and stereochemical variation of the substrates also affects the enantioselectivity (Table 1). The reactions of **1** and **2** with styrenes did not produce **3** as the final compound because **3** decomposes within a similar timescale by chlorinating olefins, as reported for a dichloromanganese(IV) Schiff base complex.[13]

In summary, we have reported the preparation and X-ray crystal structure of the iodosylarene adduct of the manganese(IV)–salen complex. The structural analysis provided herein shows how iodosylarene is activated to enable the transfer of an oxygen atom to a substrate by the manganese(IV)–salen complex.

Experimental Section

Instruments and materials are mentioned in the Supporting Information.

Synthesis of ArIO adducts (**1** and **2**): 5 equiv of MesIO (59 mg, 0.225 mmol) were added to a solution of $[\mathrm{Mn^{IV}(salen)(Cl)_2}]$ (**3;** 30 mg, 0.045 mmol) in anhydrous CH_2Cl_2 (1 mL) at room temperature. The mixture was stirred for about 20 min, and the resulting solution was passed through a membrane filter (Millex-FG, poresize 0.20 μm, diameter 25 mm, Millipore). Adding anhydrous pentane and leaving the biphasic solution standing at −20 °C overnight gave the analytically pure MesIO adduct (**2**). Anal. Calcd for $C_{54}H_{74}Cl_2I_2MnN_2O_4$-$(H_2O)_{2.2}(C_5H_{12})_{0.3}$: C, 53.07; H, 6.58; N, 2.23. Found: C, 53.00; H, 6.37; N, 1.93.

The PhIO adduct (**1**) was synthesized in exactly the same manner. Anal. Calcd for $C_{48}H_{62}Cl_2I_2MnN_2O_4$: C, 51.91; H, 5.63; N, 2.52. Found: C, 51.82; H, 5.63; N, 2.60.

The details of the other reactions are given in the Supporting Information.

Received: April 13, 2012

Keywords: bioinorganic chemistry · high-valent complexes · iodosylarenes · manganese · oxygenation

[1] *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*, Imperial College Press, London, **2000**.

[2] a) W. Nam, S. W. Jin, M. H. Lim, J. Y. Ryu, C. Kim, *Inorg. Chem.* **2002**, *41*, 3647–3652; b) W. Nam, S. K. Choi, M. H. Lim, J. U. Rohde, I. Kim, J. Kim, C. Kim, L. Que, Jr., *Angew. Chem.* **2003**, *115*, 113–115; *Angew. Chem. Int. Ed.* **2003**, *42*, 109–111; c) K. P. Bryliakov, E. P. Talsi, *Angew. Chem.* **2004**, *116*, 5340–5342; *Angew. Chem. Int. Ed.* **2004**, *43*, 5228–5230; d) S. H. Wang, B. S. Mandimutsira, R. Todd, B. Ramdhanie, J. P. Fox, D. P. Goldberg, *J. Am. Chem. Soc.* **2004**, *126*, 18–19; e) G. Yin, M. Buchalova, A. M. Danby, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper, D. H. Busch, *J. Am. Chem. Soc.* **2005**, *127*, 17170–17171; f) M. J. Zdilla, M. M. Abu-Omar, *J. Am. Chem. Soc.* **2006**, *128*, 16971–16979, g) W. J. Song, Y. J. Sun, S. K. Choi, W. Nam, *Chem. Eur. J.* **2006**, *12*, 130–137.

[3] a) P. Ghosh, Z. Tyeklar, K. D. Karlin, R. R. Jacobson, J. Zubieta, *J. Am. Chem. Soc.* **1987**, *109*, 6889–6891; b) N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata, Y. Morooka, *J. Am. Chem. Soc.* **1993**, *115*, 7872–7873; c) A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa, H. Einaga, *Angew. Chem.* **1998**, *110*, 874–875; *Angew. Chem. Int. Ed.* **1998**, *37*, 798–799; d) K. Hashimoto, S. Nagatomo, S. Fujinami, H. Furutachi, S. Ogo, M. Suzuki, A. Uehara, Y. Maeda, Y. Watanabe, T. Kitagawa, *Angew. Chem.* **2002**, *114*, 1250–1253; *Angew. Chem. Int. Ed.* **2002**, *41*, 1202–1205; e) J. Cho, H. Furutachi, S. Fujinami, M. Suzuki, *Angew. Chem.* **2006**, *118*, 7065–7068; *Angew. Chem. Int. Ed.* **2006**, *45*, 6911–6914; f) J. Cho, S. Jeon, S. A. Wilson, L. V. Lei, E. A. Kang, J. J. Braymer, M. H. Lim, B. Hedman, K. O. Hodgson, J. S. Valentine, E. I. Solomon, W. Nam, *Nature* **2011**, *478*, 502–505.

[4] a) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299–5358; b) I. M. Geraskin, O. Pavlova, H. M. Neu, M. S. Yusubov, V. N. Nemykin, V. V. Zhdankin, *Adv. Synth. Catal.* **2009**, *351*, 733–737.

[5] a) J. A. Smegal, B. C. Schardt, C. L. Hill, *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515; b) T. Birchall, J. A. Smegal, C. L. Hill, *Inorg. Chem.* **1984**, *23*, 1910–1913.

[6] a) E. N. Jacobsen, W. Zhang, A. R. Muci, J. R. Ecker, L. Deng, *J. Am. Chem. Soc.* **1991**, *113*, 7063–7064; b) E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563–1602.

[7] CCDC 875831 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] a) T. Kurahashi, H. Fujii, *Inorg. Chem.* **2008**, *47*, 7556–7567; b) T. Kurahashi, M. Hada, H. Fujii, *J. Am. Chem. Soc.* **2009**, *131*, 12394–12405.

[9] a) G. F. Koser, R. H. Wettach, *J. Org. Chem.* **1976**, *41*, 3609–3611; b) M. Ochiai, K. Miyamoto, M. Shiro, T. Ozawa, K. Yamaguchi, *J. Am. Chem. Soc.* **2003**, *125*, 13006–13007; c) A. K. Mishra, M. M. Olmstead, J. J. Ellison, P. P. Power, *Inorg. Chem.* **1995**, *34*, 3210–3214.

[10] W. W. Nam, J. S. Valentine, *J. Am. Chem. Soc.* **1993**, *115*, 1772–1778.

[11] E. Wojaczyńska, J. Wojaczyński, *Chem. Rev.* **2010**, *110*, 4303–4356.

[12] J. P. Collman, L. Zeng, J. I. Brauman, *Inorg. Chem.* **2004**, *43*, 2672–2679.

[13] N. A. Law, T. E. Machonkin, J. P. Mcgorman, E. J. Larson, J. W. Kampf, V. L. Pecoraro, *J. Chem. Soc. Chem. Commun.* **1995**, 2015–2016.