INSTITUT DE FRANCE
Académie des sciences

Comptes Rendus

Chimie

Bashdar I. Meena, Dóra Lakk-Bogáth and József Kaizer

Effect of redox potential on manganese-mediated benzylalcohol and sulfide oxidation

Volume 24, issue 2 (2021), p. 281-290

Published online: 29 June 2021

https://doi.org/10.5802/crchim.88

Les Comptes Rendus. Chimie *sont membres du*
Centre Mersenne pour l'édition scientifique ouverte
www.centre-mersenne.org
e-ISSN : 1878-1543

Comptes Rendus
Chimie
2021, 24, nº 2, p. 281-290
https://doi.org/10.5802/crchim.88

Full paper / *Article*

Effect of redox potential on manganese-mediated benzylalcohol and sulfide oxidation

Bashdar I. Meena [a], Dóra Lakk-Bogáth [a] and József Kaizer*, [a]

[a] Research Group of Bioorganic and Biocoordination Chemistry, University of Pannonia, 8201 Veszprém, Hungary

E-mails: bashdarismael@gmail.com (B. I. Meena), bogidori@gmail.com (D. Lakk-Bogáth), kaizer@almos.uni-pannon.hu (J. Kaizer)

Abstract. Tridentate 1,3-bis(2′-Ar-imino)isoindolinato manganese(II) complexes were found to efficiently catalyze the mild oxidation of organic sulfides to sulfoxides and benzyl alcohols to benzaldehydes with mCPBA and PhIO, but they proved almost ineffective by the use of *t*BuOOH and H_2O_2 at room temperature. The effect of electron-withdrawing and electron-donating substituents on the substrates (thioanisole and benzylalcohol), and the redox properties of the metal center by varying the aryl groups on the bis-iminoisoindoline were investigated, and showed a significant impact on the catalytic C–H oxidation and sulfoxidation reactions. Based on these results, including the linear correlations between the oxidation reactivity of the catalysts and Mn^{III}/Mn^{II} redox potentials, the Hammett correlation with $\rho = -0.27$ for 4R-PhSMe and $\rho = -0.27$ for 4R-$PhCH_2OH$, electrophilic oxomanganese(IV) intermediate has been suggested as key oxidant. Furthermore, the small negative slope (−0.5) from the $\log k_{rel}$ versus E^o_{ox} for 4R-PhSMe gives clear evidence for the direct oxygen atom transfer (OAT) mechanism instead of electron transfer (ET) mechanism between the $Mn^{IV}O$ and PhSMe.

Keywords. Manganese complexes, Isoindolines, Oxidation, Sulfides, Benzylalcohols.

Manuscript received 19th April 2021, revised 26th May 2021, accepted 2nd June 2021.

1. Introduction

High-valent oxoiron species play important roles in both heme and non-heme monooxygenase enzymes and their biomimetic reactions. These enzymes catalyze many oxidation reactions including oxygen atom transfer (hydroxylation, epoxidation) and dealkylation, but much less activation was observed when iron was replaced by manganese. However, in biomimetic systems oxomanganese complexes mediate most of the oxidations brought by the iron oxygenases leading to a wide range of manganese catalysts for the epoxidation of alkenes, sulfoxidation of thioethers and hydroxylation of unactivated C–H bonds [1–11]. The advantage of these systems is that they are inexpensive and less toxic than other transition metal complexes. We have shown earlier that manganese 1,3-bis(2′-Ar-imino)isoindoline complexes can mediate many types of biomimetic redox reactions [12]; including the oxidation of catechols to quinones (catechol oxidase) [13], the oxidative cyclization of 2-aminophenol to phenoxazinone (phenoxazinone synthase) [13], the catalytic disproportionation of hydrogen peroxide (catalase) [14–16], and the dismutation of superoxide radicals (superoxide dismutase, SOD) [17]. Furthermore they can

* Corresponding author.

be used as hydrogen peroxide-based bleach catalysts [18]. In this ligand the introduction of various aryl groups on the *bis*-iminoisoindoline moiety provided a new method for tuning the reactivity and electronic structure of the catalyst. This work focuses on our recent efforts to tune the reactivity of our manganese system and investigate how the catalytic activity can be optimized compared to our iron system in the oxidation of organic substrates including thioanisols and benzyl alcohols. Organic sulfoxides and carbonyl compounds produced by the oxidation of alcohols are used as intermediates for the synthesis of various agrochemicals, plastic additives, pharmaceuticals and drugs [19–24]. Therefore, there has been considerable interest in the development of non-toxic, cheap and highly efficient oxidation catalysts for selective oxidation of organic sulfides and benzyl alcohols [25–53], including Mn-based systems with various oxidants such as PhIO, mCPBA and H_2O_2 [43–53].

2. Experimental section

2.1. *Materials and methods*

The ligands 1,3-bis(2′-Ar-imino)isoindolines (HL^n, n = 1–6, Ar = 4′-methyl-pyridyl, pyridyl, imidazolyl, thiazolyl, benzimidazolyl and *N*-methylbenzimidazolyl, respectively) and their complexes $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) were prepared according to published procedures (Scheme 1) [12,18]. GC analyses were performed on an Agilent 6850 gas chromatograph equipped with a flame ionization detector and 30 m SUPELCO BETA DEX225 columns. GC–MS analyses were carried out on Shimadzu QP2010SE equipped with a secondary electron multiplier detector with conversion dynode and a 30 m HP5MS column.

2.2. *Description of the catalytic oxidation reactions*

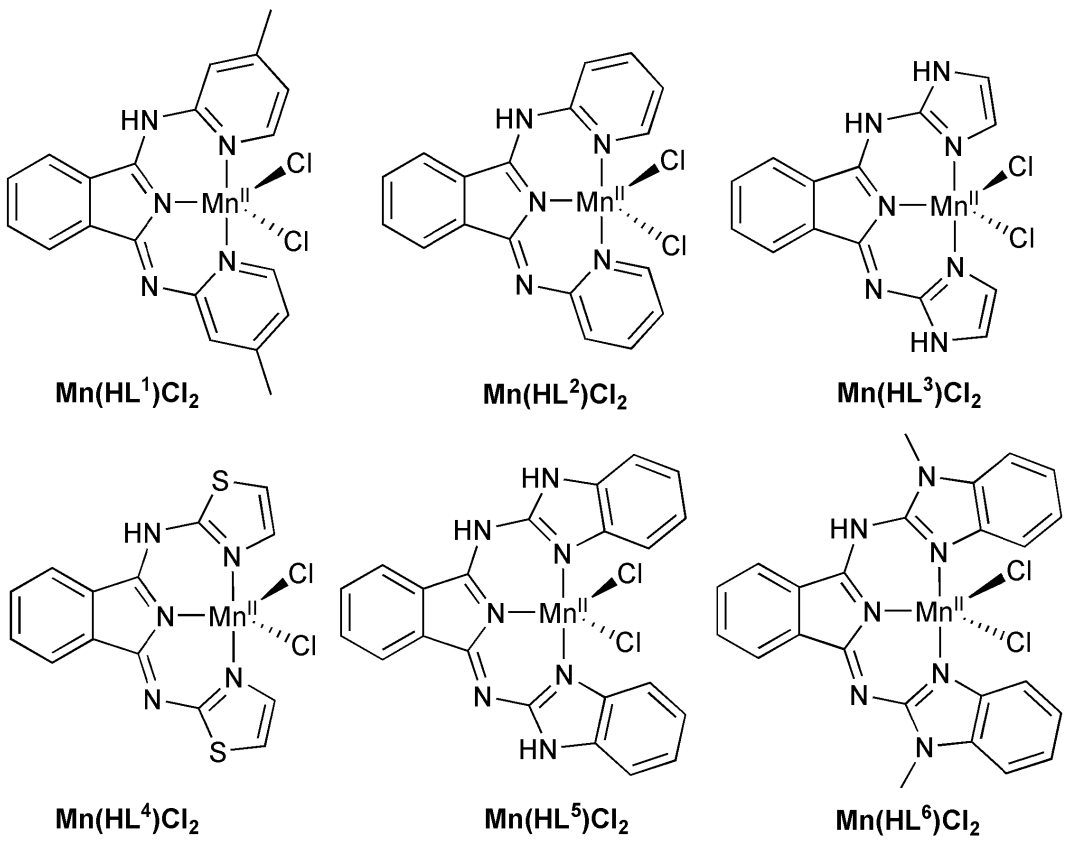
For the oxidation of thioanisoles and benzylalcohols, the reactions were carried out under argon atmosphere at room temperature (25 °C). In a typical experiment, 1 mL of H_2O_2 (diluted from 38–40% solution), mCPBA (77%), or tBuOOH (diluted from 70% solution) in acetonitrile was delivered by syringe pump to a stirred solution (2 mL) of catalyst and p-substituted thioanisole or benzylalcohol derivatives. The final concentrations were 10 mM catalyst, 250 mM co-oxidants, and 500 mM substrate. The PhIO was added as a solid into the water (100 μL) containing CH_3CN solution. The manganese complexes were removed by passing the internal standard containing reaction mixture through a silica column followed by elution with ethyl acetate. The products were identified by GC–MS based on authentic samples, and quantified by GC relative to bromobenzene as an internal standard.

PhS(O)Me: m/z (%) = 140 (100), 125 (87), 97 (78), 77 (71), 65 (34), 51 (94); 4Cl-PhS(O)Me: m/z (%) = 174 (46), 159 (100), 131 (38), 111 (25), 75 (64), 50 (51.5); 4NO_2-PhS(O)Me: m/z (%) = 185 (100), 170 (67), 139 (38.6), 76 (47.7), 63 (34), 50 (48); 4Me-PhS(O)Me: m/z (%) = 154 (67), 139 (100), 111 (21.2), 91 (44.6), 77 (55), 65 (43); 4MeO-PhS(O)Me: m/z (%) = 171 (100), 107 (80), 77 (51.2), 64 (17.6), 50 (12.4).

PhCHO: m/z (%) = 106 (95), 105 (90), 77 (100), 74 (11.2), 51 (57.6), 50 (35); 4Me-PhCHO: m/z (%) = 120 (85), 119 (90), 91 (100), 65 (51.3), 62 (17.6), 51 (25); 4Cl-PhCHO: m/z (%) = 141 (47), 140 (86), 139 (100), 713 (23), 111 (83.2), 75 (47.6), 50 (45); 4MeO-PhCHO: m/z (%) = 137 (87), 135 (100), 92 (37), 77 (84), 63 (19.2), 50 (17.7); 4NO_2-PhCHO: m/z (%) = 151 (100), 150 (95), 105 (31), 77 (81.4), 51 (77.6), 50 (34).

3. Results and discussion

Iron and manganese containing porphyrin and phthalocyanine complexes as catalysts can be used for a wide range of oxidation reactions due to their distinguishing properties such as variable oxidation states and readily tunable Lewis acidic behavior and redox properties [54–58]. Based on the advantageous properties of the above systems the solubility, electronic structure and steric properties of the ligand as well as their complexes can be further developed by the synthesis of 1,3-bis(2′-Ar-imino)isoindolines, an open-chained phthalocyanine mimic, introducing various aryl groups on the *bis*-iminoisoindoline moiety [12]. In this study we have investigated the catalytic properties of manganese 1,3-bis(2′-Ar-imino)isoindolines for the oxidation of organic sulfides and benzyl alcohols with various co-oxidants compared to the recently published iron 1,3-bis(2′-Ar-imino)isoindoline system [59,60].



Scheme 1. Structure of the 1,3-bis(2′-Ar-imino)isoindoline ligands used for the synthesis of $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) catalysts involved in this study.

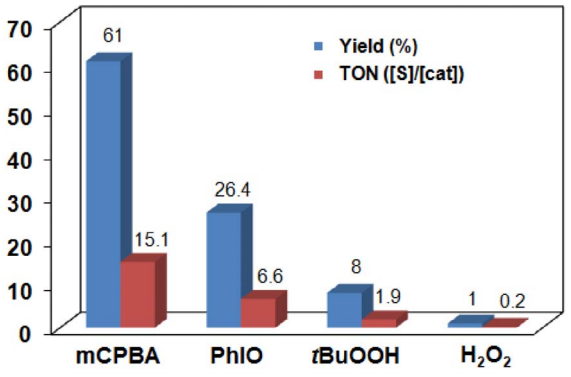


Figure 1. Comparison of the product (PhS(O)Me) formation in the manganese (**2**)-catalyzed oxidation of PhSMe with various co-oxidants in CH_3CN at 25 °C (entries 1, 6–8 in Table 1).

3.1. *Catalytic oxidation of thioanisole*

The catalytic activity of $[Mn(HL^2)Cl_2]$ (**2**) was studied in the oxidation of thioanisole and benzyl alcohol utilizing *tert*-butyl hydroperoxide (*t*BuOOH), *meta*-chloroperoxybenzoic acid (mCPBA), H_2O_2 and PhIO

Table 1. Various $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes-catalyzed thioanisole (4R-PhSMe) oxidation by H_2O_2, *t*BuOOH, PhIO and mCPBA in MeCN at 25 °C

Entry	Cat.	Time[a] (min)	Oxidant	R	E_{pc} [b] (mV)	E_{pa} [b] (mV)	$E^o_{1/2}$ [b] (mV)	Yield (%)	TON[c]
1	**1**	20	mCPBA	H	880	1016	948	66	16.4
2	**2**	10	mCPBA	H	865	987	926	34	3.4
3	**2**	15	mCPBA	H	865	987	926	48.8	4.9
4	**2**	20	mCPBA	H	865	987	926	61	15.1
5	**2**	30	mCPBA	H	865	987	926	60.4	15.1
6	**2**	20	PhIO	H	865	987	926	26.4	6.6
7	**2**	20	*t*BuOOH	H	865	987	926	8	1.9
8	**2**	20	*t*BuOOH/AcOH[d]	H	865	987	926	0.5	0.1
9	**2**	20	*t*BuOOH/AcOH[e]	H	865	987	926	1.8	0.5
10	**2**	20	H_2O_2	H	865	987	926	1	0.2
11	**2**	30	mCPBA	OMe	865	987	926	68.4	17.1
12	**2**	30	mCPBA	Me	865	987	926	65	16
13	**2**	30	mCPBA	Cl	865	987	926	52	13
14	**2**	30	mCPBA	NO_2	865	987	926	39	9.9
15	**3**	20	mCPBA	H	685	816	750	53	13.2
16	**4**	20	mCPBA	H	573	625	600	45	11.3
17	**5**	20	mCPBA	H	354	421	388	42	10.5
18	**6**	20	mCPBA	H	395	455	425	38	9.4

[a]Reaction conditions: Thioanisole (1.5 mmol), catalyst (0.03 mmol), oxidant (0.75 mmol) in MeCN (3 ml) at 25 °C. [b]mV versus SCE [18]. [c]TON = mol S/mol Cat. [d]AcOH (0.75 mmol). [e]AcOH (0.075 mmol).

as co-oxidants. Using an identical concentration of catalyst/substrate/co-oxidant (1/PhSMe/co-oxidant = 1/50/25), Table 1 and Figure 1 show that there is an increase of the yield when the co-oxidants employed are H_2O_2, *t*BuOOH, PhIO and mCPBA from 1 to 61% (entries 1, 6–8 in Table 1). The highest conversion is attained with mCPBA, where 15 turnovers were observed in the course of 20 min, after which time there was no further product formation (entries 1–5 in Table 1). Under this condition we were not able to catch the characteristic absorption band around 900 nm in case of our coordinatively unsaturated complexes, which can be assigned to the proposed metastable intermediate, $Mn^{IV}O$. It is not surprising that the best results were obtained with mCPBA compared to *t*BuOOH, because the reaction with Mn(II) complexes can be seen as following: Mn^{II} + HO–B → Mn^{II}–O–B + H^+ → $Mn^{IV}(O) + B^-$, thus the reactivity can be correlated with the pK_a of the couple BH/B^-. The pK_a values for mCPBA/$mCPBA^-$ and $tBuO^-$/tBuOH are 3.8 and 19.2, respectively. Based on previous literature, acetic acid (AcOH) as an additive may play a key role in promoting the rapid cleavage of O–O bonds [61]. In our case, unfortunately much worse or just slightly better results were obtained, depending on the amount of AcOH, which can presumably be explained by the formation of catalytically inactive complexes (Tables 1 and 2). Low yields were obtained for H_2O_2, probably because it competes with **2** for the catalase-like activity.

The reactivities of *para*-substituted thioanisols relative to that of thioanisole were also investigated (Figure 3). Hammett treatments of relative reactivities ($k_{rel} = \log(X_f/X_i)/\log(Y_f/Y_i)$, where X_i and X_f are the initial and final concentration of *para*-substituted thioanisols, and Y_i and Y_f are the initial and final concentration of thioanisole) of various substituents against σ gave ρ value of −0.26

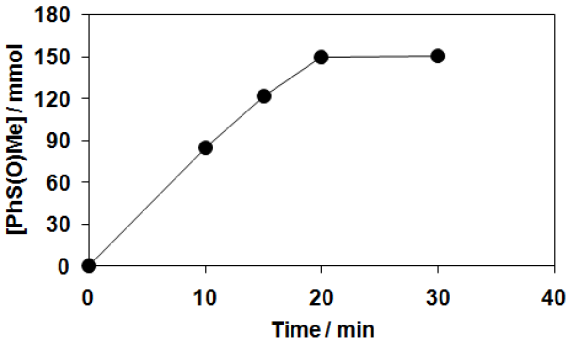


Figure 2. Catalytic oxidation of PhSMe with $[Mn^{II}(HL^2)Cl_2]$ (**2**) in CH_3CN at 25 °C (entries 1–5 in Table 1).

Table 2. Various $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes-catalyzed benzyl alcohol (4R-BzOH) oxidation by H_2O_2, *t*BuOOH, PhIO and mCPBA in MeCN at 25 °C

Entry	Cat.	Time[a] (min)	Oxidant	R	E_{pc} [b] (mV)	E_{pa} [b] (mV)	$E^o_{1/2}$ [b] (mV)	Yield (%)	TON[c]
1	**1**	20	mCPBA	H	880	1016	948	34	8.5
2	**2**	20	mCPBA	H	865	987	926	30	7.5
3	**2**	20	PhIO	H	865	987	926	8.5	2.1
4	**2**	20	*t*BuOOH	H	865	987	926	11.4	2.8
5	**2**	20	*t*BuOOH/AcOH[d]	H	865	987	926	4.5	0.5
6	**2**	20	*t*BuOOH/AcOH[e]	H	865	987	926	15.2	3.8
7	**2**	20	H_2O_2	H	865	987	926	2	0.5
8	**2**	30	mCPBA	OMe	865	987	926	40	10
9	**2**	30	mCPBA	Me	865	987	926	33	8.2
10	**2**	30	mCPBA	Cl	865	987	926	26	6.5
11	**2**	30	mCPBA	NO_2	865	987	926	21	5.2
12	**3**	20	mCPBA	H	685	816	750	26	6.5
13	**4**	20	mCPBA	H	573	625	600	22.8	5.7
14	**5**	20	mCPBA	H	354	421	388	19.2	4.8
15	**6**	20	mCPBA	H	395	455	425	16.8	4.2

[a]Reaction conditions: BzOH (1.5 mmol), catalyst (0.03 mmol), oxidant (0.75 mmol) in MeCN (3 ml) at 25 °C. [b]mV versus SCE [18]. [c]TON = mol S/mol Cat. [d]AcOH (0.75 mmol). [e]AcOH (0.075 mmol).

(Figure 4A), which suggests that the behavior of the oxidant generated from $[Mn(HL^1)Cl_2]$ with mCPBA is mildly electrophilic. Furthermore, this value is comparable to that of the closely related $[Fe(HL^2)]^{2+}/H_2O_2$ system ($\rho = -0.40$) [59]. When the $\log k_{rel}$ values were plotted against the E^0_{ox} potentials of *para*-substituted thioanisols, the plot gave a gradient of −0.50 (Figure 4B), which is a little bit smaller than that obtained for $[Fe(HL^2)]^{2+}/H_2O_2$ (−0.8). The magnitude of these values is consistent with a direct oxygen atom transfer mechanism (Scheme 2). Much higher values are typical for an electron transfer/oxygen rebound pathway [62].

3.2. *Catalytic oxidation of benzyl alcohols*

The oxidation of benzyl alcohol by $[Mn(HL^2)Cl_2]$ with mCPBA, PhIO, tBuOOH and H_2O_2 at 25 °C resulted

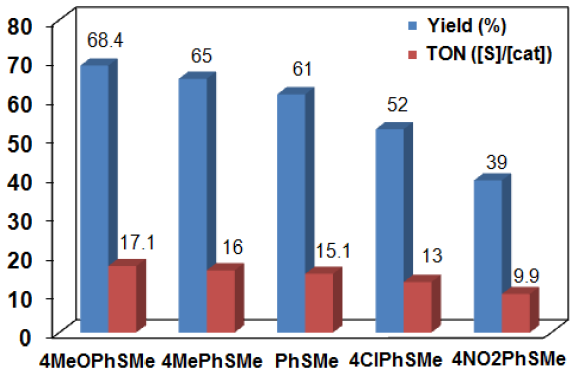


Figure 3. Comparison of the product formation in the manganese-catalyzed (**2**) oxidation of substituted thioanisols (entries 4, 9–11 in Table 1).

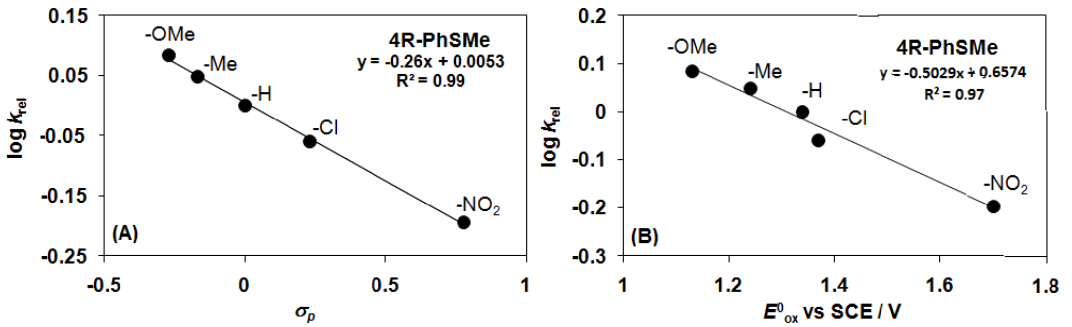
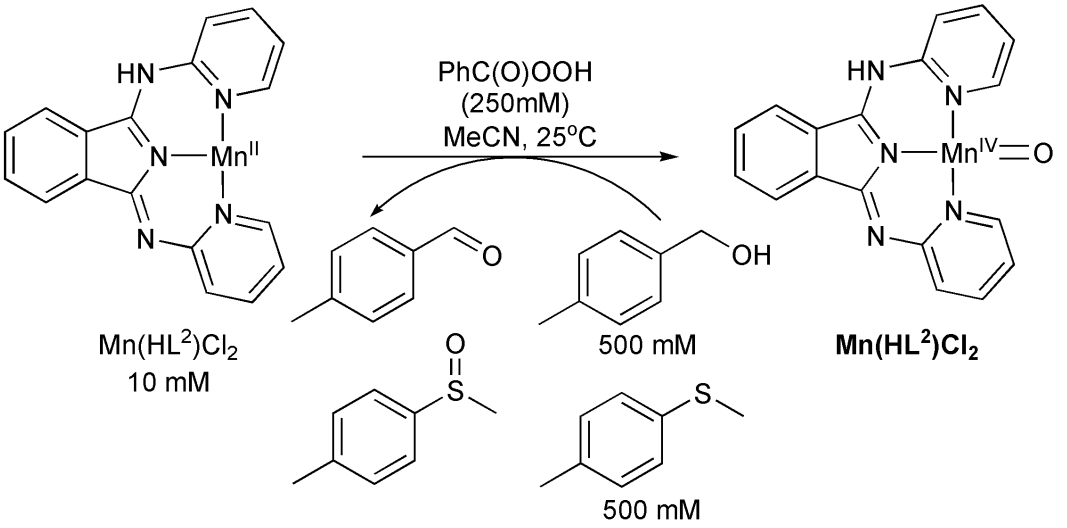


Figure 4. Catalytic oxidation of substituted thioanisols with $[Mn^{II}(HL^2)Cl_2]$ (**2**) in CH_3CN at 25 °C (Table 2). (A) Plot of $\log k_{rel}$ against the σ_p of *para*-substituted thioanisols. (B) Plot of $\log k_{rel}$ against the E_{ox} of *para*-substituted thioanisols (entries 4, 9–11 in Table 1).

in the formation of benzaldehyde in 30, 8.5, 11.4 and 2% yield, respectively (entries 2–5 in Table 2 and Figure 5). The highest reactivity with a 7.5 turnover was observed for a mCPBA co-oxidant in the course of 20 min, after which time there was no further product formation.

A Hammett plot of k_{rel} values gave a ρ value of −0.27, suggesting an electrophilic oxidant formation during the oxidation process (Figure 6, Scheme 2). This value is a little bit higher than those obtained for bona fide complexes, $[Fe^{IV}(O)(N4Py/TPA)]^{2+}$ (ρ = 0.07) [63], but three times smaller than that was observed for the closely related $[Fe(HL^2)]^{2+}/H_2O_2$ system (ρ = −0.85) [59].

Based on our previous experience we expected that varying the aryl group on the bis-iminoisoindoline moiety would directly tune electron density in the metal center and hence allow us to evaluate the influence of these electronic changes on reactivity. Cyclic voltammetry measurements on complexes **1**–**6** reveal that the Mn(III/II) redox potentials can vary by up to 560 mV between the most electron-withdrawing (948 mV for **1**) and the most electron-donating (388 mV for **5**) [18]. With a systematic series of $[Mn^{II}(HL^{1-6})Cl_2]$ (**1**–**6**) complexes, we investigated their oxidative reactivity for HAT (hydrogen atom transfer) and OAT (oxygen atom transfer) reactions with benzyl alcohol and thioanisole. Among these catalysts, we observed that the complex **5** and **6** containing the most electron-donating benzimidazole arms, show the smallest rates of oxidation for both OAT (Figure 7) and HAT (Figure 8) reactions. In other words, the electron-deficient, Lewis acidic catalyst (**1** and **2**) is much more active than the electron-rich ones (**5** and **6**). Similar trend was



Scheme 2. O-atom and H-atom transfer reactions: catalytic oxidation of sulfides and benzyl alcohols by manganese(II) complexes.

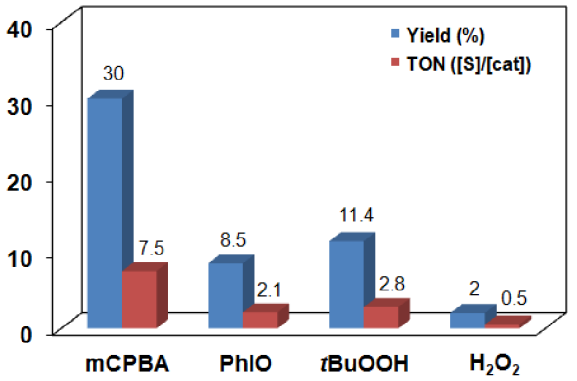


Figure 5. Comparison of the product (PhCHO) formation in the manganese (**2**)-catalyzed oxidation of BzOH with various co-oxidants in CH_3CN at 25 °C (entries 2–5 in Table 1).

observed for the disproportionation of H_2O_2 by $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes [18]. The reactivity enhancement with the appropriate aryl arm is similar to that observed for the axial ligand effect in the oxoiron(IV)-containing model complex, $Fe^{IV}(O)(PY5Me_2)$ ($PY5Me_2$ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) [64] and $Fe^{IV}(O)(TPA)$ (TPA = tris(2-pyridylmethyl)amine) [65], but it is moderate compared to the axial effect of the anionic ligand in case of $Fe^{IV}(O)(TMC)$ (TMC = tetramethylcyclam) [66,67], $Fe^{IV}(O)(TMP^{+\bullet})$ (TMP = Tetramesitylporphyrin) [68] and $Mn^{V}(O)(TBP_8Cz)$ (TBP_8Cz = octakis(*p*-tert-butylphenyl)corrolazinato^{3-}) [69–71] models. In our case the change in the ligand set varies the reactivity by less than 3-fold based on TONs.

4. Conclusion

We have investigated the effect of systematic changes on the 1,3-bis(2′-Ar-imino)isoindoline by introducing various heteroaromatic arms on the bis-iminoisoindoline moiety toward the reactivity of their manganese(II) complexes for HAT and OAT reactions. These transformations resulted in

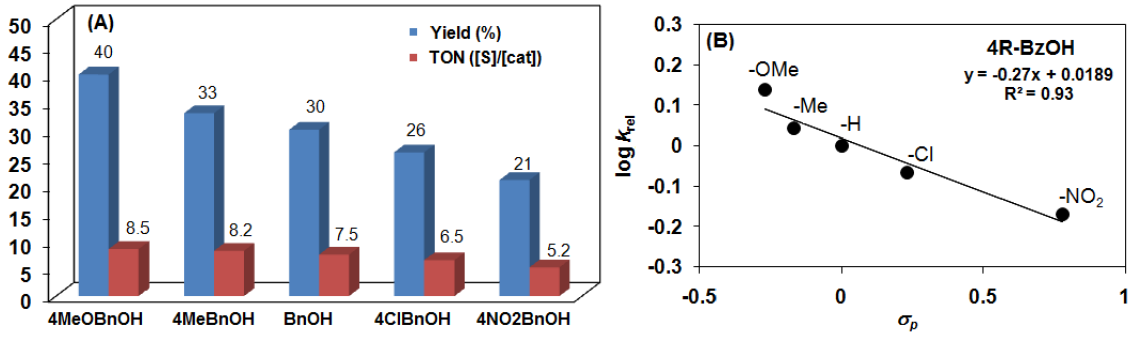


Figure 6. Catalytic oxidation of substituted benzyl alcohols with $[Mn^{II}(HL^2)Cl_2]$ (**2**) in CH_3CN at 25 °C (Table 2). (A) Comparison of the product formation in the manganese-catalyzed (**2**) oxidation of substituted benzyl alcohols. (B) Plot of log k_{rel} against the σ_p of *para*-substituted benzyl alcohols (entries 2, 6–9 in Table 2).

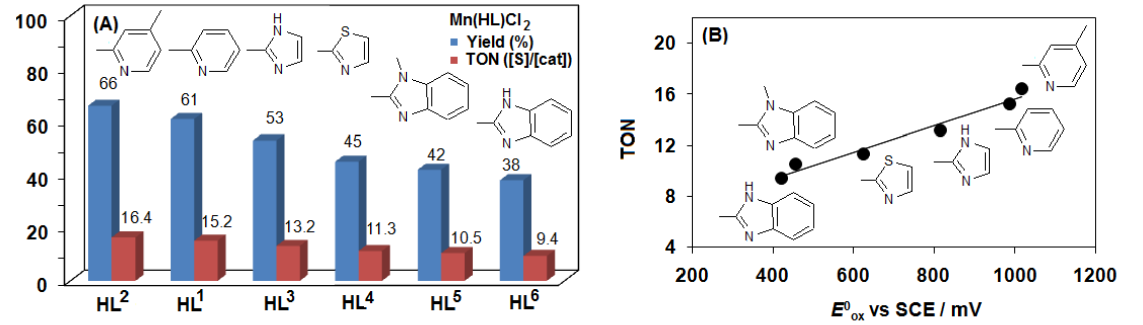


Figure 7. (A) Comparison of the oxidative reactivity of $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes for OAT reactions with thioanisole. (B) Dependence of the TON on the oxidation potential (E_{pa}) of the $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes (entries 1, 4, 13–16 in Table 1).

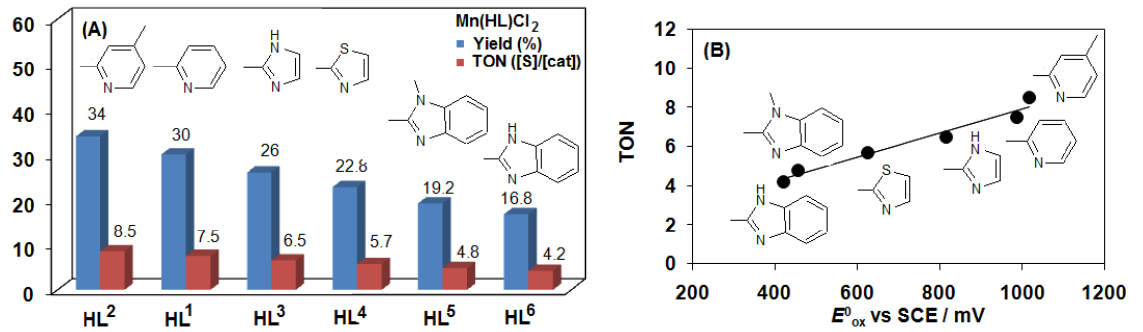


Figure 8. (A) Comparison of the oxidative reactivity of $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes for HAT reactions with benzyl alcohol. (B) Dependence of the TON on the oxidation potential (E_{pa}) of the $[Mn^{II}(HL^{1-6})Cl_2]$ (**1–6**) complexes (entries 1–2, 10–13 in Table 2).

a predictable and significant 560 mV shift in the Mn^{III}/Mn^{II} redox potentials with concomitant changes in the reactivity toward thioanisols and benzyl alcohols. The effect is small in both cases, but based on these results, including the linear correlations between the oxidation reactivity of the catalysts and Mn^{III}/Mn^{II} redox potentials and the Hammett correlations ($\rho = -0.27$ for 4R-PhSMe and $\rho = -0.27$ for 4R-$PhCH_2OH$) electrophilic oxomanganese(IV) intermediate has been suggested as key oxidant.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support of the Hungarian National Research Fund (OTKA K108489), TKP2020-IKA-07 and GINOP-2.3.2-15-2016-00049 are gratefully acknowledged.

References

[1] P. R. Ortiz de Montellano (ed.), *Cytochrome P450: Structure, Mechanism and Biochemistry*, Plenum, New York, 1986.
[2] P. R. Ortiz de Montellano, *Annu. Rev. Pharmacol. Toxicol.*, 1992, **32**, 89-107.
[3] B. Meunier, *Chem. Rev.*, 1992, **92**, 1411-1456.
[4] F. Montanari, L. Casella (eds.), *Metalloporphyrin Catalysed Oxidations*, Kluwer, Dordrecht, 1994.
[5] R. A. Sheldon (ed.), *Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker, New York, 1994.
[6] R. J. Nick, G. B. Ray, K. M. Fish, T. G. Spiro, T. J. Groves, *J. Am. Chem. Soc.*, 1991, **113**, 1838-1840.
[7] F. Montanari, S. Banfi, G. Pozzi, S. Quici, "Oxygenation Reactions under Two-Phase Conditions", in *Metalloporphyrin Catalysed Oxidations* (F. Montanari, L. Casella, eds.), Kluwer, Dordrecht, 1994, 149-169.
[8] W. Nam, *Acc. Chem. Res.*, 2007, **40**, 465.
[9] W. Nam, *Acc. Chem. Res.*, 2007, **40**, 522-531.
[10] L. Zhang, Y.-M. Lee, M. Guo, S. Fukuzumi, W. Nam, *J. Am. Chem. Soc.*, 2020, **142**, 19879-19884.
[11] A. R. McDonald, L. Que Jr., *Coord. Chem. Rev.*, 2013, **257**, 414-428.
[12] R. Csonka, G. Speier, J. Kaizer, *RSC Adv.*, 2015, **5**, 18401-18419.
[13] J. Kaizer, G. Baráth, R. Csonka, G. Speier, L. Korecz, A. Rockenbauer, L. Párkányi, *J. Inorg. Biochem.*, 2008, **102**, 773-780.
[14] J. Kaizer, B. Kripli, G. Speier, L. Párkányi, *Polyhedron*, 2009, **28**, 933-936.
[15] J. Kaizer, T. Csay, P. Kõvári, G. Speier, L. Párkányi, *J. Mol. Catal. A Chem.*, 2008, **280**, 203-209.
[16] J. Kaizer, G. Baráth, G. Speier, M. Réglier, M. Giorgi, *Inorg. Chem. Commun.*, 2007, **10**, 292-294.
[17] J. S. Pap, B. Kripli, T. Váradi, M. Giorgi, J. Kaizer, G. Speier, *J. Inorg. Biochem.*, 2011, **105**, 911-918.
[18] B. I. Meena, J. Kaizer, *Catalysts*, 2020, **10**, 404-418.
[19] M. Madesclaire, *Tetrahedron*, 1986, **42**, 5459-5495.
[20] S. Oae, *Organic Sulfur Chemistry: Structure and Mechanism*, CRC Press, Boca Raton, 1991, 67 pages.
[21] Y. Enomoto, H. Shimotori, S. Inami, K. Ishikawa, J. K. T. Kobo, "Japan Patent 60161906", 1985.
[22] M. Kutsumi, I. Shigehisa, M. Shinichiro, S. Mitsuyoshi, J. K. T. Kobo, "Japan Patent 0495077", 1992.
[23] J. Zhu, P. C. Wang, M. Lu, *Appl. Catal. A Gen.*, 2014, **477**, 125-131.
[24] J.-E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010.
[25] P. Pitchen, H. B. Kagan, *Tetrahedron Lett.*, 1984, **25**, 1049-1052.
[26] F. D. Furia, G. Modena, R. Seraglia, *Synthesis*, 1984, 325-326.
[27] I. Fernández, N. Khiar, *Chem. Rev.*, 2003, **103**, 3651-3706.
[28] E. Jacobsen, A. Pfaltz, H. Yamamoto (eds.), *Comprehensive Asymmetric Catalysis*, Springer-Verlag, Berlin, 1999.
[29] I. Ojima (ed.), *Catalytic Asymmetric Synthesis*, Wiley, VHC, New York, 2000.
[30] A. Massa, F. R. Siniscalchi, V. Bugagtti, A. Lattanzi, A. Scettri, *Tetrahedron Asymmetry*, 2002, **13**, 1227-1283.
[31] R. S. Reddy, J. S. Reddy, R. Kumar, P. Kumar, *J. Chem. Soc. Chem. Commun.*, 1992, 84-85.
[32] V. Hulea, P. Moreau, F. D. Renzo, *J. Mol. Catal. A*, 1996, **111**, 325-332.
[33] D. C. Radu, V. I. Parulescu, V. Cimpeanu, A. Jonas, P. Grange, *Appl. Catal. A*, 2003, **242**, 77-84.
[34] D. C. Radu, V. Cimpeanu, F. Bertinchamps, E. M. Gaigeaux, V. I. Paulescu, *Catal. Commun.*, 2003, **4**, 5-9.
[35] N. M. Okun, T. M. Anderson, C. L. Hill, *J. Mol. Catal. A*, 2003, **197**, 283-290.
[36] C. Drago, L. Caggiano, R. F. Jackson, *Angew. Chem. Int. Ed.*, 2005, **44**, 7221-7223.
[37] S. A. Blum, R. G. Bergman, J. A. Ellmann, *J. Org. Chem.*, 2003, **68**, 150-155.
[38] J. Legros, C. Bolm, *Angew. Chem. Int. Ed.*, 2004, **43**, 4225-4228.
[39] J. Legros, C. Bolm, *Chem. Eur. J.*, 2005, **11**, 1086-1092.
[40] M. Palucki, P. Hanson, E. N. Jacobsen, *Tetrahedron Lett.*, 1992, **33**, 7111-7114.
[41] K. Noda, N. Hosoya, R. Irie, Y. Yamashita, T. Katsuki, *Tetrahedron*, 1994, **50**, 9609-9618.
[42] K. Noda, N. Hosoya, K. Yanai, R. Irie, T. Katsuki, *Tetrahedron Lett.*, 1994, **35**, 1887-1890.
[43] C. Kokubo, T. Katsuki, *Tetrahedron*, 1997, **52**, 13895-13900.
[44] F. Xie, Z. Fu, S. Zhong, Z. Ye, X. Zhou, F. Liu, C. Rong, L. Mao, D. Yin, *J. Mol. Catal. A Chem.*, 2009, **307**, 93-97.
[45] Z. P. Ye, Z. H. Fu, S. Zhong, F. Xie, X. P. Zhou, F. L. Liu, D. L. Yin, *J. Catal.*, 2009, **261**, 110-115.
[46] M. Bagherzadeh, R. Latifi, L. Tahsini, M. Amini, *Catal. Commun.*, 2008, **10**, 196-200.
[47] M. Bagherzadeh, L. Tahsini, R. Latifi, *Catal. Commun.*, 2008, **9**, 1600-1609.
[48] I. Kani, M. Kurtca, *Turk. J. Chem.*, 2012, **36**, 827-840.

[49] M. Ghorbanloo, M. Jaworska, P. Paluch, G.-D. Li, L.-J. Zhou, *Transit. Met. Chem.*, 2013, **38**, 511-521.
[50] C. Herrero, N. Nguyen-Thi, F. Hammerer, F. Banse, D. Gagné, N. Doucet, J.-P. Mahy, R. Ricoux, *Catalysts*, 2016, **6**, 202-2013.
[51] H. M. Neu, R. A. B. Willis, B. Kash, H. Jeddi, C. Alcantar, R. Zhang, *Inorg. Chim. Acta*, 2019, **487**, 41-49.
[52] V. R. Tumula, S. Bondwai, P. Bisht, C. Pendem, J. Kumar, *React. Kinet. Mech. Catal.*, 2012, **107**, 449-466.
[53] C. Miao, X.-X. Li, Y.-M. Lee, C. Xia, Y. Wang, W. Nam, W. Sun, *Chem. Sci.*, 2017, **8**, 7476-7482.
[54] B. Meunier, A. Sorokin, *Acc. Chem. Res.*, 1997, **30**, 470-476.
[55] S. Mangematin, A. B. Sorokin, *J. Porphyr. Phthalocyanines*, 2001, **5**, 674-680.
[56] A. Sorokin, J.-L. Séris, B. Meunier, *Science*, 1995, **268**, 1163-1166.
[57] A. Sorokin, B. Meunier, *Chem. Eur. J.*, 1996, **2**, 1308-1317.
[58] B. Sorokin, *Chem. Rev.*, 2013, **113**, 152-8191.
[59] J. S. Pap, M. A. Cranswick, É. Balogh-Hergovich, G. Baráth, M. Giorgi, G. T. Rohde, J. Kaizer, G. Speier, L. Que Jr., *Eur. J. Inorg. Chem.*, 2013, 3858-3866.
[60] B. Kripli, M. Szávuly, F. V. Csendes, J. Kaizer, *Dalton Trans.*, 2020, **49**, 1742-1746.
[61] R. Mas-Balleste, L. Que Jr., *J. Am. Chem. Soc.*, 2007, **129**, 15964-15972.
[62] Y. Goto, T. Matsui, S.-I. Ozaki, Y. Watanabe, S. Fukuzumi, *J. Am. Chem. Soc.*, 1999, **121**, 4235-4239.
[63] N. Y. Oh, Y. Suh, M. J. Park, M. S. Seo, J. Kim, W. Nam, *Angew. Chem. Int. Ed.*, 2005, **44**, 4307-4311.
[64] T. Chantarojsiri, Y. Sun, J. R. Long, C. J. Chang, *Inorg. Chem.*, 2015, **54**, 5879-5887.
[65] T. K. Paine, M. Costas, J. Kaizer, L. Que Jr., *J. Biol. Inorg. Chem.*, 2006, **11**, 272-276.
[66] C. V. Sastri, J. J. Lee, K. OH, Y. J. Lee, T. A. Jackson, K. Ray, H. Hirao, W. Shin *et al.*, *Proc. Natl. Acad. Sci. USA*, 2007, **104**, 19181-19186.
[67] T. A. Jackson, J. U. Rohde, S. S. Mi, C. V. Sastri, R. DeHont, A. Stubna, T. Ohta, T. Kitagawa *et al.*, *J. Am. Chem. Soc.*, 2008, **130**, 12394-12407.
[68] A. Takahashi, D. Yamaki, K. Ikemura, T. Kurahashi, T. Ogura, M. Hada, H. Fujii, *Inorg. Chem.*, 2012, **51**, 7296-7305.
[69] K. A. Prokop, S. P. de Visser, D. P. Goldberg, *Angew. Chem., Int. Ed.*, 2010, **49**, 5091-5095.
[70] H. M. Neu, M. G. Quesne, T. Yang, K. A. Prokop-Prigge, K. M. Lancaster, J. Donohoe, S. DeBeer, S. P. de Visser, D. P. Goldberg, *Chem.-Eur. J.*, 2014, **20**, 14584-14588.
[71] H. M. Neu, T. Yang, R. A. Baglia, T. H. Yosca, M. T. Green, M. G. Quesne, S. P. de Visser, D. P. Goldberg, *J. Am. Chem. Soc.*, 2014, **136**, 13845-13852.