First *in situ* ^{1}H NMR spectroscopic monitoring of manganese species in the Mn^{III}(salen) + PhIO catalytic system

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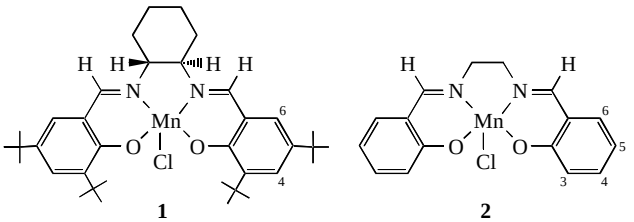
High-valence manganese species formed in the Mn^{III}(salen) + PhIO catalytic system were characterised using ^{1}H NMR spectroscopy.

The Jacobsen catalyst (*R*,*R*)-(–)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diaminomanganese(III) chloride, [Mn^{III}(salen)] **1** and related manganese complexes are practically attractive catalysts for enantioselective epoxidation of unfunctionalised alkenes.[1–5] The observed enantioselectivities were explained by models based on a reactive oxomanganese(V) species. However, in none of these cases the reactive species was isolated or characterised. Only recently, direct evidence for its existence was obtained by electrospray tandem mass spectrometry.[6] Nevertheless, it is still unclear whether the detected [(salen)Mn^{V}=O]$^+$ intermediate really exist in a detectable amount in the catalytic system (**1** + PhIO) or it is formed in the course of a MS experiment *via* fragmentation of the μ-oxo dimeric complex [(salen)Mn^{IV}–O–Mn^{IV}(salen)]$^{2+}$. Thus, the *in situ* spectroscopic characterization of the [(salen)Mn^{V}=O]$^+$ species remains an intriguing problem. Jin and Groves[7] observed an unstable diamagnetic (porphyrin)Mn^{V}=O species by ^{1}H NMR spectroscopy.[7] Here we describe the first ^{1}H NMR spectroscopic monitoring of manganese species formed in the Mn^{III}(salen) + PhIO catalytic system. Based on the ^{1}H NMR spectrum and the reactivity pattern some of these species can be identified as the oxomanganese(V) intermediate [(salen)Mn^{V}=O]$^+$.

To assign ^{1}H NMR resonances of complex **1**, the signals were compared with those of *N*,*N*′-bis(salicylidene)ethylenediaminomanganese(III) chloride **2** and *N*,*N*′-bis(3,4,5,6-tetradeuterosalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride **3**.†



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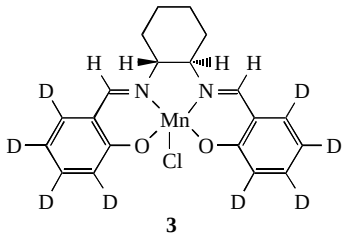

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The ^{1}H NMR spectrum of complex **2** in [$^2H_6$]DMSO at 20 °C is shown in Figure 1(*a*). The resonances at –22.2 ppm ($\Delta\omega_{1/2}$ = = 450 Hz) and –26.0 ppm ($\Delta\omega_{1/2}$ = 500 Hz) were previously unambiguously assigned to protons at the 5- and 4-positions of aromatic rings of complex **2**, respectively.[10] We have additionally observed the resonance at –125 ppm ($\Delta\omega_{1/2}$ = 4 kHz) assigned to two protons of the ethylene bridge of complex **2** and a very broad resonance at –405 ppm ($\Delta\omega_{1/2}$ = 10 kHz) assigned to the imine protons. The latter signal can be detected in complexes **1**, **2** and **3** at approximately the same field position. The resonances of protons at the 3- and 6-positions of aromatic rings of complex **2** are masked by those of residual undeuterated water and DMSO [Figure 1(*a*)]. The ^{2}D NMR spectrum of complex **3** [Figure 1(*b*)] shows that the deuterons at the 3- and 6-positions (and thus protons) of complex **3** display resonances at –1.9 and 2.0 ppm, respectively. Thus, the protons at the 3- and 6-positions of complex **2** and protons at the 6-position of complex **1** would exhibit signals in the same region.

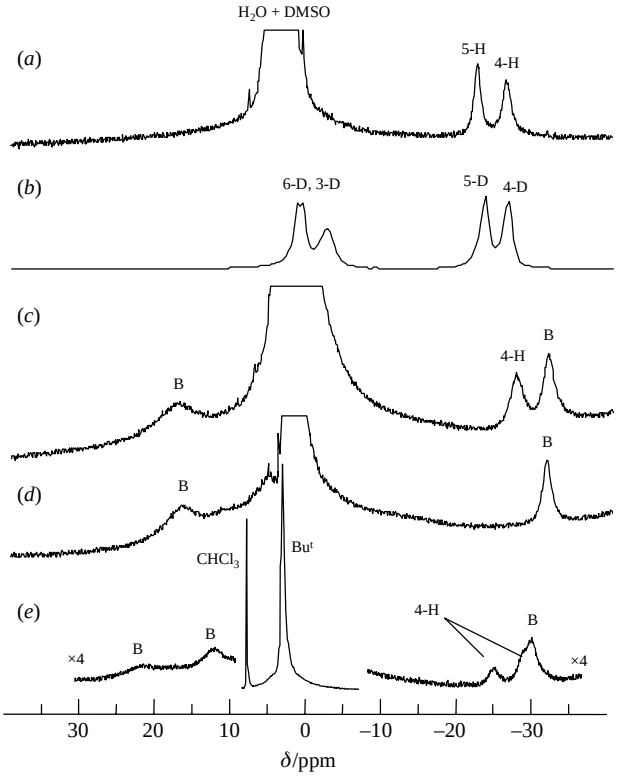

Figure 1 ^{1}H NMR spectra ([$^2H_6$]DMSO, 20 °C) of (*a*) **2**, (*c*) **1** and (*d*) **3**; (*b*) ^{2}D NMR spectrum (DMSO, 20 °C) of **3**; (*e*) ^{1}H NMR spectrum ($CDCl_3$, –20 °C) of **1** (0.025 M solutions).

Figure 1(*c*) demonstrates the ^{1}H NMR spectrum of complex **1** in [$^2H_6$]DMSO at 20 °C. A comparison of the ^{1}H NMR spectra of **1**, **3** and **2** [Figure 1(*a*), (*c*) and (*d*)] allowed us to assign the signals denoted in Figure 1(*c*) by B to the diaminocyclohexane bridge of **1**. We cannot assign these signals to particular protons of the bridge. Their total intensity corresponds to four protons. The signals of the remaining six protons of the bridge may be too broad or can be masked by the intense signals of residual H_2O and DMSO. The resonance at –27 ppm ($\Delta\omega_{1/2}$ = 700 Hz) belongs to protons at the 4-position of aromatic rings in **1**.

The ^{1}H and ^{2}D NMR spectra of **2**, **3** and **1** [Figure 1(*a*)–(*d*)] were recorded in [$^2H_6$]DMSO and DMSO, respectively. These solvents are unsuitable for the epoxidation of alkenes by the **1** + PhIO catalytic system; thus, the reaction of **1** with PhIO

† Complex **1** was purchased from Aldrich. Complexes **2** and **3** were prepared as described in ref. 8. Deuterated salicylic aldehyde for the synthesis of **3** was prepared according to ref. 9. The ^{1}H NMR spectra were recorded on a Bruker MSL 400 MHz spectrometer. The EPR spectra were recorded in 5 mm quartz tubes on a Bruker ER 200 D spectrometer.

was studied in $CDCl_3$ as a solvent. The ^{1}H NMR spectrum of **1** in $CDCl_3$ at –20 °C [Figure 1(*e*)] displays an intense resonance of four Bu^t groups at 2.6 ppm ($\Delta\omega_{1/2}$ = 200 Hz), two resonances at –29.0 ppm ($\Delta\omega_{1/2}$ = 800 Hz) and –32.7 ppm ($\Delta\omega_{1/2}$ = 800 Hz) from nonequivalent protons at the 4-positions of **1** and signals, denoted by B, from the protons of the diaminocyclohexane bridge in **1**. The signals of protons at the 6-positions of **1** are masked by that of the Bu^t groups. The nonequivalence of two aromatic rings in **1** is consistent with the X-ray diffraction data.[11] The paramagnetic line broadening prevents the detection of this nonequivalence by ^{1}H NMR. Thus, four nonequivalent Bu^t groups of **1** display a peak at 2.6 ppm. The nonequivalence of protons at the 4-positions of **1** is revealed only at low temperature. We cannot say what particular effect masks this nonequivalence at room temperature.

Stable oxomanganese(V) complexes are few in number; tetradentate ligands are used to stabilise the high-valence manganese centre.[12,13] By analogy to isoelectronic nitridomanganese(V) salen complexes[14] and known stable oxo Mn^V complexes, the reactive [(salen)Mn^V=O]$^+$ species is expected to be a low-spin d^2 complex. The ^{1}H NMR spectrum of (salen)Mn$^V\equiv$N prepared according to the known procedure[14] is as follows ($CDCl_3$, 400 MHz, –20 °C) δ: 1.28 (s, 18H, CMe_3), 1.45 (s, 9H, CMe_3), 1.49 (s, 9H, CMe_3), 2.03–3.46 (m, 10H, cyclohexane H), 6.97 (s, 1H, aromatic H), 7.02 (s, 1H, aromatic H), 7.44 (s, 1H, aromatic H), 7.46 (s, 1H, aromatic H), 7.95 (s, 1H, CH=N), 8.00 (s, 1H, CH=N). Note that Bu^t groups of (salen)Mn$^V\equiv$N display three peaks at 1.28, 1.45 and 1.49 ppm in the ^{1}H NMR spectrum, while those of uncoordinated H_2salen exhibit two peaks at 1.24 and 1.42 ppm.

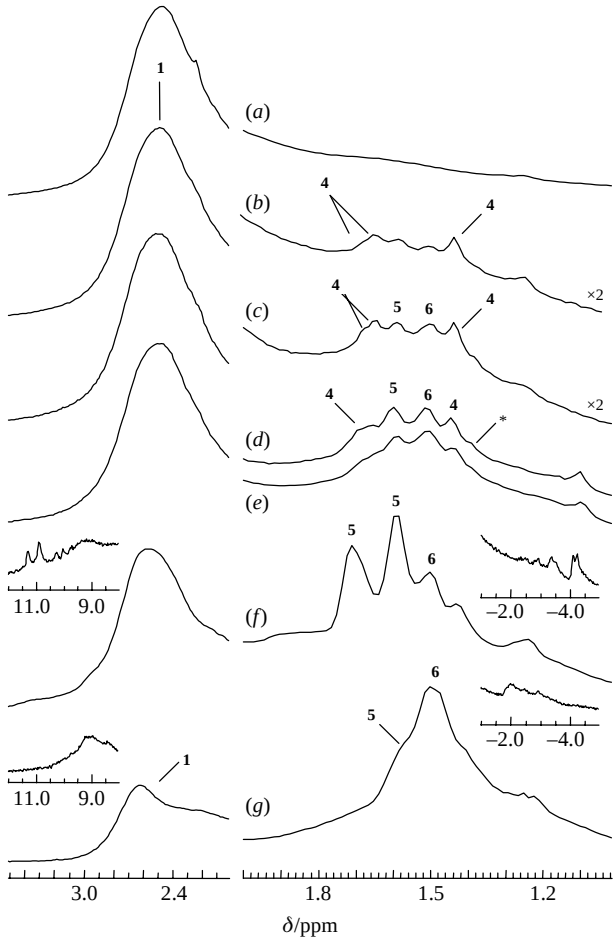

Figure 2 ^{1}H NMR spectra of a 0.02 M solution of **1** in $CDCl_3$ (0.6 ml) before and after shaking with a suspension of PhIO (2 mg) at –40 °C: (*a*) before shaking; (*b*) shaking for 30 s; (*c*) shaking for 1.5 min; (*d*) shaking for 2.5 min; (*e*) 1 min after the addition of styrene to a concentration of 0.1 mol dm^{-3} to the sample shown in Figure 1(*d*); (*f*) sample (*d*) after 2 min warming at room temperature; (*g*) sample (*f*) after shaking with an additional portion of PhIO (4 mg) at 0 °C. The ^{1}H NMR spectra were recorded at (*a*)–(*f*) –20 °C and (*g*) 0 °C.

In order to detect the oxomanganese(V) species in the catalytic system, a standard NMR tube (*d* = 5 mm) containing 0.6 ml of a cooled (–40 °C) 0.02 M solution of **1** in $CDCl_3$ was placed in an NMR spectrometer immediately after shaking the solution with PhIO powder (2 mg) at –40 °C for 30 s. Only a small portion of PhIO was dissolved as a result of this procedure. The ^{1}H NMR spectrum was recorded at –20 °C 5 min after the onset of the reaction. Several new signals are observed in the region 1.3–1.8 ppm [*cf.* Figure 2(*a*) and (*b*)]. They can be assigned to Bu^t groups of three manganese complexes **4**–**6**. Note that H_2salen is not liberated at the initial stage of the reaction. Complex **4** is very unstable. Its concentration diminished with a characteristic time of about 20 min at –20 °C and shorter than 3 min at 0 °C, while concentrations of complexes **5** and **6** increased. The attempt to increase the concentration of complex **4** by additional shaking of the sample [Figure 2(*b*)] with an initially added portion of PhIO at –40 °C gave rise to a predominant increase in the concentration of complexes **5** and **6** [Figure 2(*c*) and (*d*)]. The achieved concentration of complex **4** was no higher than 3% of the initial concentration of **1** and those of complexes **5** and **6** can be higher than 50% of the initial concentration of **1** [Figure 2(*e*) and (*f*)]. The increase in the concentrations of complexes **5** and **6** was accompanied by dissolution of PhIO.

Complexes **5** and **6** are stable at –20 °C and very slowly react with styrene at this temperature (the characteristic time was longer than 2 h, [styrene] = 0.1 mol dm^{-3}). In contrast, the addition of styrene (to a concentration of 0.1 mol dm^{-3}) to the sample presented in Figure 2(*d*) at –20 °C leads to an immediate drop (by a factor of about two) of the concentration of complex **4** [Figure 2(*e*)]. This drop was accompanied by the appearance of styrene oxide resonances in the ^{1}H NMR spectrum. In the absence of styrene, the concentrations of complexes **4**–**6** remained almost unchanged in 5 min at –20 °C. These data indicate that complex **4** can be reactive towards styrene. When styrene was added to the sample containing **1** prior to the shaking with PhIO at –20 °C, the immediate growth of the styrene oxide concentration was observed by ^{1}H NMR, while formation of complexes **4**–**6** was almost entirely suppressed.

Complex **4** displays three resonances of Bu^t groups at 1.68, 1,64 and 1.42 ppm. These peaks were assigned to one complex because of a strictly parallel change in their intensities. The overall intensity of the signals at 1.68 and 1.64 ppm equals to that of the signal at 1.42 ppm. The observed pattern for Bu^t groups of complex **4** resembles that for the nitridomanganese complex (salen)Mn$^V\equiv$N (at 1.49, 1.45 and 1.28 ppm), when one compares differences in the chemical shifts between the signals and their relative intensities. Unfortunately, we have not detected signals of the aromatic and imine protons of complex **4** using $CDCl_3$ and CD_2Cl_2 as solvents. Most probably, they are obscured by the intense resonances of PhI formed in the reaction of **1** with PhIO. It is important that the widths of the resonances of Bu^t groups in complex **4** (20 Hz) are close to those of the signals of diamagnetic species (*e.g.*, $CHCl_3$ or PhI) in our particular sample (the line broadening is caused by the presence of paramagnetic Mn^{III} species). This fact evidences in favour of complex **4** to be also diamagnetic. Corresponding signals of complexes **5** and **6** are broader than those of complex **4** (Figure 2) and can belong to paramagnetic species.

Complex **4** displays a characteristic pattern of Bu^t groups closely resembling that for diamagnetic nitridomanganese(V) salen species. It is very unstable and predominates only at the early stage of the reaction of **1** with PhIO at low temperature. The effect of styrene on the concentration of **4** evidences in favour of its reactivity towards this substrate. Based on these data, complex **4** can be identified as the oxomanganese intermediate [(salen)Mn^V=O]$^+$.

Let us discuss the structure of complexes **5** and **6**. The concentration of complex **5** grows after warming the sample [Figure 2(*d*)] for 2 min at room temperature [Figure 2(*f*)]. The sample displays two resonances of Bu^t groups at 1.72 and 1.60 ppm, two resonances at 10.9 and 11.3 ppm, several signals in the range 4–5 ppm (not shown) and two signals at –4.1 and –4.2 ppm. The field positions and widths (30–80 Hz) of the ob-

served resonances of complex **5** are typical of antiferromagnetically coupled μ-oxo dinuclear manganese(IV) species.[15,16] For these species, the ^{1}H NMR signals are placed much closer to the positions in diamagnetic complexes than for corresponding mononuclear Mn^{IV} and Mn^{III} complexes. Thus, the resonances at 10.9 and 11.3 ppm probably belong to aromatic protons of complex **5**. The concentration of complex **5** decreased and that of complex **6** increased as the sample [Figure 2(*f*)] was treated with an additional portion of PhIO (4 mg) at 0 °C [Figure 2(*g*)]. The field positions and widths of the signals of complex **6** are also typical of Mn^{IV}–O–Mn^{IV} dimers. Probably, complexes **5** and **6** are binuclear complexes $[L(salen)Mn^{IV}–O–Mn^{IV}(salen)L']^{2+}$ with different axial ligands L, L′ (iodosylbenzene and chloride anion). The dimeric cation $[(salen)Mn^{IV}–O–Mn^{IV}(salen)]^{2+}$ with PhIO molecules at axial sites was detected in the **1** + PhIO catalytic system by electrospray tandem mass spectrometry.[6]

Thus, at least three types of manganese species (**4**–**6**) are formed upon the interaction of complex **1** with PhIO at low temperature. Complexes **5**–**6** are relatively inert dimers $[L(salen)Mn^{IV}–O–Mn^{IV}(salen)L']^{2+}$ with different axial ligands. Complex **4** can be identified as the oxomanganese(V) intermediate $[(salen)Mn^{V}=O]^{+}$ based on its ^{1}H NMR spectrum and the reactivity pattern.

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