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Cr^{III}(salen)Cl Catalyzed Asymmetric Epoxidations: Insight into the Catalytic Cycle

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Intermediates of chromium–salen catalyzed alkene epoxidations were studied in situ by EPR, ^{1}H and ^{2}H NMR, and UV–vis/NIR spectroscopy (where chromium–salens were (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino chromium(III) chloride (**1**) and racemic *N*,*N*′-bis(3,4,5,6-tetra-deuterosalicylidene)-1,2-cyclohexanediamino chromium(III) chloride (**2**)). High-valence chromium complexes, intermediates of epoxidation reactions, were detected and characterized by EPR and NMR. They are the reactive mononuclear oxochromium(V) intermediate (**A**) $Cr^{V}O$(salen)L (where L = Cl^- or a solvent molecule) and an inactive chromium–salen binuclear complex (**B**) which acts as a reservoir of the active species. The latter complex demonstrates an EPR signal characteristic of oxochromium(V)–salen species and ^{1}H NMR spectra typical for chromium(III)–salen complexes, and it is identified as mixed-valence binuclear L_1(salen)$Cr^{III}OCr^{V}$(salen)L_2 (L_1, L_2 = Cl^- or solvent molecules). The intermediates $Cr^{V}O$(salen)L and L_1(salen)$Cr^{III}OCr^{V}$(salen)L_2 exist in equilibrium, and their ratio can be affected by addition of donor ligands (DMSO, DMF, H_2O, pyridine). Addition of donor additives increases the fraction of **A** over that of **B**. The same two complexes can be obtained with m-CPBA as oxidant. Reactivities of the $Cr^{V}O$(salen)L complexes toward *E*-β-methylstyrene were measured in DMF. The L_1(salen)$Cr^{III}OCr^{V}$(salen)L_2 intermediate has been proposed to be a reservoir of the true reactive chromium(V) species. The chromium–salen catalysts demonstrate low turnover numbers (ca. 5), probably due to ligand degradation processes.

Introduction

Chromium−salen complexes are well-known catalysts of stereoselective alkene epoxidations,[1−5] kinetic resolution of epoxides,[6−8] alcohol oxidations,[9] asymmetric addition of organometallic reagents to aldehydes,[10−12] and asymmetric hetero Diels−Alder reactions.[13] Although it was alkene epoxidation that pioneered the wide use of chromium−salens as catalysts, except the works of Kochi,[1,2] there have not been mechanistic studies of its catalytic action. As distinct from the manganese−salen alkene epoxidations (for recent findings on mechanisms see refs 14−18), chromium−salens give good enantioselectivities for *E*-alkenes,[4] and the established oxygen transferring Cr^{V}=O species[1] is relatively stable and EPR active. At the same time, the fact that some questions (e.g., how the donor ligands affect the intermedi-

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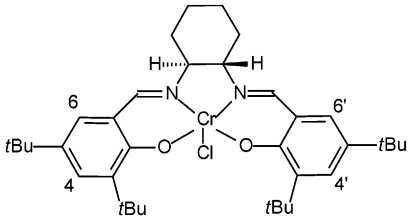
ates[19,20] and why the ee's observed in the stoichiometric reaction are not maintained in the catalytic one[19]) have not been answered so far, and the considerable interest in chromium−salen epoxidations, stimulates mechanistic investigations.

Recently, we have reported an EPR and NMR spectroscopic study of Cr^{III}(salen)Cl type catalysts.[21] The Cr^{III} complexes have been found to be $S = {}^3/_2$ species, demonstrating characteristic EPR and $^1H(^2H)$ NMR spectra. The reactive oxochromium(V) species (electronic configuration d^1) should display rather sharp and informative EPR spectra.[4] In this paper, we report EPR and NMR detection and characterization of the chromium(III)− and chromium(V)−salen complexes that appear to be involved into the epoxidation catalytic cycle. Cr^{III}(salen)Cl complexes **1** and **2** were selected as representative model catalysts, due to their sharply differing reactivities.[19] To assign the NMR signals of chromium(III) catalysts, a fruitful methodology reported for Mn^{III}(salen) complexes[22] was used: namely, a deuterated salicylaldehyde derivative was used in the case of complex **2** with a view of ^2H NMR studies.



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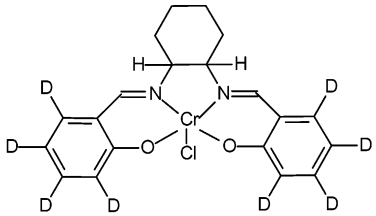

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Experimental Section

General and Spectroscopic Measurements. Diacetoxyiodo-(benzene), meta-chloroperoxybenzoic acid (m-CPBA), *E*-β-methylstyrene, CD_2Cl_2, and phenol-d_6 were purchased from Aldrich and used as received. (*S*,*S*)-(+)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-chromium(III) chloride (**1**) was synthesized as described in Supporting Information for ref 23. Iodosylbenzene was prepared as described in ref 24. Acetonitrile, CH_2Cl_2, CD_2Cl_2, and CD_3CN were dried over molecular sieves (4 Å) prior to use. All other chemicals were reagent grade and used without further purification.

^1H NMR spectra were recorded on a Bruker MSL-400 spectrometer at 400.13 MHz, using 5 mm cylindrical tubes. Chemical shifts were referenced to the solvent residual protons (CD_2Cl_2, $\delta = 5.35$ ppm; CD_3CN, $\delta = 1.96$ ppm; DMF-d_7, $\delta = 2.79$, 2.94, 7.90 ppm). Typical operation conditions for ^1H measurements were as follows: a spectral width 125000 Hz, spectrum accumulation frequency 10 Hz, number of scans 1K−10K, 5 μs radio frequency pulse, 16K data points. ^2H NMR spectra were recorded on a Bruker MSL-400 spectrometer at 61.425 MHz, using 10 mm cylindrical tubes. Chemical shifts were referenced to solvent residual deuterons (CH_2Cl_2, $\delta = 5.35$ ppm; CH_3CN, $\delta = 1.96$ ppm; DMF, $\delta = 2.79$, 2.94, 7.90 ppm). Typical operation conditions for ^2H measurements were as follows: a spectral width 15000 Hz, spectrum accumulation frequency 10 Hz, number of scans 1K−4K, 5 μs radio frequency pulse, 4K data points (on processing, data were zero filled to 16K). Experimental uncertainty for ^1H chemical shifts were ±0.5 ppm and for ^2H chemical shifts ±0.1 kHz.

EPR spectra were recorded on a Bruker ER-200D spectrometer at 9.4 GHz. Measurements at room temperature were performed in a flat quartz ampule of 0.2 mL volume. Periclase crystal (MgO) with impurities of Mn^{2+} and Cr^{3+}, which served as a side reference, was placed into the second compartment of the dual cavity. For kinetic measurements, concentrations of chromium(V) species were obtained by double integration of the corresponding EPR signals.

Preparation of Cr^{III}(salen)Cl Complex 2. *rac*-*N*,*N*′-Bis(3,4,5,6-tetra-deuterosalicylidene)-1,2-cyclohexanediamine ligand was prepared from d_6-phenol according to procedures described in refs 25 and 26. To prepare the complex, all operations were performed in argon atmosphere: 170 mg (0.52 mmol) of the ligand followed by 70 mg (0.57 mmol) of $CrCl_2$ was dissolved in 15 mL of dry THF and magnetically stirred for 2 h under argon. Then, the mixture was exposed to air, and stirring was continued for 2 h. The green-yellow solid was filtered off and dried in vacuo. Yield 0.175 g (80%).

Preparation of Cr^V(salen) Samples for EPR and NMR Measurements. For EPR measurements, Cr^V(salen) samples were prepared by stirring appropriate amounts of Cr^{III}(salen) complexes **1** or **2** with PhIO (0.5−2.5 equiv) in different solvents (CH_3CN, toluene, CH_2Cl_2, DMF, etc., 1−3 mL total volume). Concentrations of Cr^{III}(salen)Cl complexes used were 5×10^{-3} to 1.5×10^{-2} M. Aliquots (0.2 mL) were transferred in a flat quartz ampule, and EPR spectra were measured. Samples for NMR probe were prepared in an analogous manner, using nondeuterated (in case of **2**) or deuterated (in case of **1**) solvents (CD_2Cl_2, CD_3CN, DMF-d_7). Taking into account the low stability of Cr^VO complexes derived from **2**, sample preparation was performed at 0 °C. For ^1H (for **1**) and ^2H (for **2**) NMR measurements, concentrations of the starting complexes **1** and **2** were on the order of 1×10^{-2} and 3×10^{-3} M, respectively. For variable temperature measurements, the samples were thermostated at the desired temperature in the NMR probehead.

Stability/Reactivity Measurements. Complex A (in DMF, 290 K). Complex **A** was generated by stirring 1 mg of the Cr^{III}(salen) complex (**1** or **2**) and 1.5−2.5 equiv of PhIO in 0.25 mL of DMF for 1−2 min. Then, if necessary, a desired amount of the substrate (*E*-β-methylstyrene) was added, and the concentration of complex **A** in different moments of time was measured by EPR.

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Complex B (in CH_3CN, 298 K). A mixture of complexes **A** and **B** was generated by stirring 1 mg of complex **1** and 0.2 mg of PhIO (0.6 equiv) for 2 min. Then, if necessary, a desired amount of *E*-*β*-methylstyrene was added and the sample stored in the EPR resonator until the disappearance of complex **A** was detected by EPR. After this, the concentration of complex **B** in different moments of time was measured by EPR. For representative EPR spectra, see Supporting Information.

Catalytic Epoxidation of *E*-*β*-Methylstyrene. Complex **1** (3.0 mg, 4.8 μmol) was dissolved in 1.2 mL of dried CH_3CN, and 20 μL (150 μmol) of *E*-*β*-methylstyrene followed by 8.8 mg (40 μmol) of PhIO was added. The mixture was stirred at room temperature (290 K) until the complete disappearance of solid PhIO (ca. 2 days). Solvent was removed in vacuo, and the residue extracted with Et_2O. Ether washings were flushed through a short silica gel column with Et_2O, then solvent removed in vacuo and 0.7 mL of C_6D_6 added. The latter solution was dried over 4 Å molecular sieves and ee determined by ^{1}H NMR with a chiral shift reagent (tris(3-heptafluoropropyl-hydroxymethylene-(+)-camphorato) europium(III) derivative).

Results and Discussion

Formation of Intermediates A and B. It was found that upon stirring of complex **1** with PhIO in dry acetonitrile two EPR active high-valence chromium species are formed (Figure 1a−e). The first one denoted as $\mathbf{A_1}$ (green solution, $g = 1.970$, $a_{Cr} = 19.3$ G, natural abundance of ^{53}Cr 9.55%, $I = {}^3/_2$) is unstable and almost completely decays within 3 h at room temperature. The other complex denoted as $\mathbf{B_1}$ (brown solution) is more stable, and after disappearance of $\mathbf{A_1}$, it adopts a concentration nearly constant for several hours (hereinafter subscript "**1**" is to highlight that species **A** and **B** originate from the starting complex **1**). The spectroscopic parameters obtained for $\mathbf{B_1}$ ($g = 1.976$, $a_N = 2.1$ G, $a_{Cr} = 19.3$ G, natural abundance of ^{53}Cr 9.55%, $I = {}^3/_2$) are close to those for Cr^VO(salen) complexes reported by Kochi[1] and to isoelectronic Cr^VN(salen) complexes.[27] When complex **2** was taken as the chromium precursor, formation of complex $\mathbf{A_2}$ (decays with $\tau_{1/2}$ of ca. 5 min, CH_3CN, 290 K) and complex $\mathbf{B_2}$ ($\tau_{1/2} = 25$ min, CH_3CN, 290 K) was observed. According to NMR data, self-decay of the Cr^V species was accompanied by partial destruction of the salen ligand.

It was revealed that the initial concentration of $\mathbf{A_1}$ depended strongly on the amount of PhIO added (Figure 1f−i). Namely, when 4.5 μmol of PhIO was added to 7.5 μmol of complex **1**, only vanishing concentration of complex $\mathbf{A_1}$ was detected (Figure 1f), complex $\mathbf{B_1}$ being the predominant Cr^V species in solution. When additional portions of PhIO were added, detectable quantities of complex $\mathbf{A_1}$ appeared (Figure 1g,h). Cr^V species $\mathbf{A_1}$ and $\mathbf{B_1}$ are unstable and with time reduce to Cr(III) species. Indeed, after disappearance of the less stable complex $\mathbf{A_1}$, its concentration can be partially restored by interaction with additional PhIO (Figure 1b−e). At the same time, species $\mathbf{A_1}$ can convert into $\mathbf{B_1}$ (Figure 1h,i). Note that the total Cr^V content in Figure 1i amounts only ca. 90% of that in Figure 1h, indicating that

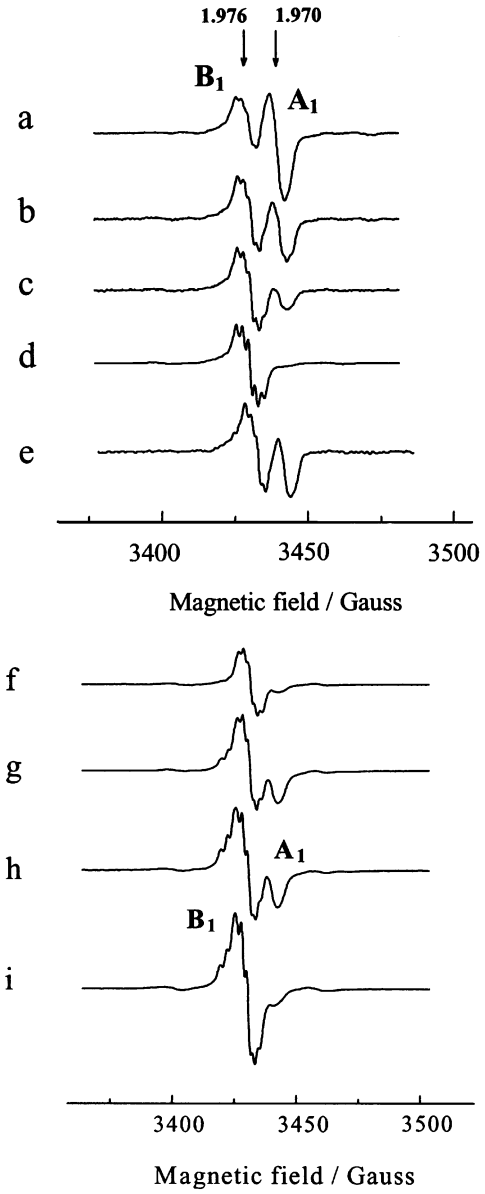

Figure 1. EPR spectra (290 K) of chromium(V) complexes formed upon stirring 16 μmol of complex **1** and 35 μmol of PhIO in 3 mL of CH_3CN: 10 min stirring (a); 30 min stirring (b); 50 min stirring (c); 150 min stirring (d); 4.5 mg addition followed by mixture stirring for 10 min (e). EPR spectra (290 K) of chromium(V) complexes formed upon stirring 7.5 μmol of complex **1** and various amounts of PhIO in 1 mL of CH_3CN: 4.5 μmol PhIO, 5 min stirring (f); the same + 4.5 μmol PhIO + 5 min stirring (g); the same + 2.2 μmol PhIO + 5 min stirring (h); the same after 45 min stirring (i).

concentrational redistributions between **A** and **B** and reduction to Cr^{III} occur with comparable rates.

EPR parameters of complexes **A** and **B** in different solvents are presented in Table 1. It is seen that EPR parameters of complexes **A** noticeably differ from those of **B** (*g*-factors and a_N in the regions of 1.970−1.974 and 1.6−2.0 G for **A** and 1.976−1.980 and 2.0−2.3 G for **B**). Spectra recorded in noncoordinating solvents (toluene, CH_2Cl_2) demonstrate resolved hyperfine structure from two nitrogens with equal hyperfine constants. However, the EPR spectra of species of type **A** in acetonitrile display poorly resolved (in case of complex **2**) or virtually unresolved (in case of complex **1**) hyperfine structures (hfs). This evidences that

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Table 1. EPR Parameters of the Oxochromium(V)−Salen Intermediates[a]

no.	species	solvent additive	$g_{iso} \pm 0.001$	$A(^{14}N)_{iso} \pm 0.2$ G	$a(^{53}Cr)_{iso} \pm 0.3$ G	additional notes
1	$\mathbf{A_1}$	toluene	1.970	1.8	19.3	$g_1 = 1.985$, $g_2 = 1.974$, $g_3 = 1.958$ (77 K)
2	$\mathbf{As_1}$	CH_3CN	1.970	*b*	19.3	
3	$\mathbf{A_1}$	CH_2Cl_2	1.971	1.6	19.3	
4	$\mathbf{A_1}$	CH_3CN, DMSO	1.972	1.9	19.3	$C_{DMSO}/C_{Cr} = 140$, $C_{Cr} = 5 \times 10^{-3}$ M
5	$\mathbf{A_1}$	DMF	1.973	1.9	19.1	
6	$\mathbf{A_1}$	CH_3CN, Py	1.974	2.0	*c*	
7	$\mathbf{A_1}$	toluene	1.971	1.9		m-CPBA as oxidant
8	$\mathbf{B_1}$	toluene	1.978	2.2	19.5	$g_1 = 1.986$, $g_2 = 1.977$, $g_3 = 1.961$ (77 K)
9	$\mathbf{B_1}$	CH_3CN	1.976	2.1	19.3	
10	$\mathbf{B_1}$	CH_2Cl_2	1.977	2.2	19.8	
11	$\mathbf{B_1}$	CH_3CN, DMSO	1.978	2.0	*d*	$C_{DMSO}/C_{Cr} = 140$, $C_{Cr} = 5 \times 10^{-3}$ M
12	$\mathbf{B_1}$	DMF	1.979	2.2	*d*	
13	$\mathbf{B_1}$	CH_3CN, Py	1.978	2.0	*c*	
14	$\mathbf{B_1}$	toluene	1.979	2.2		m-CPBA as oxidant
15	$\mathbf{A_2}$	CH_3CN	1.973	1.9[e]	19.8	
16	$\mathbf{A_2}$	DMF	1.974	2.0	19.3	
17	$\mathbf{B_2}$	CH_3CN	1.977	2.0[e]	19.6	
18	$\mathbf{B_2}$	DMF	1.980	2.3	*d*	

[a] Concentrations of Cr^{III}(salen)Cl complexes used were 5×10^{-3} to 1.5×10^{-2} M, PhIO/Cr^{III}(salen)Cl ratio was 0.5−2.5, when appropriate. [b] Structure unresolved due to axial ligand (CH_3CN) exchange. [c] Poorly resolved satellites; complexes **A** and **B** present in comparable concentrations. [d] Not measured because of low intensity of the EPR signal of **B**. [e] Structures poorly resolved, $a(^{14}N)$ values estimated by computer simulations of the spectrum.

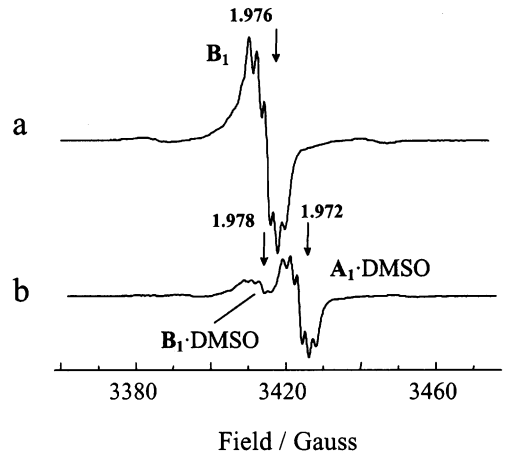

Figure 2. EPR spectra (290 K) of chromium(V) complexes formed upon stirring 16 μmol of complex **1** and 35 μmol of PhIO in 3 mL of CH_3CN: 150 min stirring (a); addition of 140-fold excess of DMSO (b).

CH_3CN coordinates to Cr^V species **A** and coordinated CH_3CN in **A**·CH_3CN is readily exchanged by another solvent molecule (eq 1).[28]

$$\mathbf{A}\cdot CH_3CN + CH_3CN' \rightleftarrows \mathbf{A}\cdot CH_3CN' + CH_3CN \quad (1)$$

If tightly coordinating donor ligands were added (DMSO, DMF, H_2O, pyridine), well-resolved hyperfine structures of Cr^V spectra were observed due to slower ligand exchange (Table 1). Also, it was shown that addition of donor molecules to complexes of type **B** results in a decrease of the concentration of **B** and an increase of that of **A** (Figure 2). This effect is the case for DMSO, DMF, pyridine, and H_2O, indicating equilibria like that shown below (D stands for a donor ligand molecule).

$$\underset{\mathbf{B}}{O{=}Cr^V(salen)L'} + D \rightleftarrows \underset{A}{O{=}Cr^V(salen)D} + L' \quad (2)$$

(The nature of L′ is to be discussed later.)

Reactivities of Complexes A and B toward *E*-β-Methyl Styrene. To evaluate the reactivity of the intermediate **A**, DMF was used as a solvent: in this case, complex **A** is the predominant species, and contribution of **B** into the reaction pathways is insignificant. The results of the kinetic measurements are presented in Figure 3. Concentrations of the substrate (*E*-β-methyl styrene) always satisfied the condition [substrate] ≫ [Cr(salen)], so one could neglect the changes of substrate concentration in the course of the reaction. Kinetic curves obtained for complexes **A** decay at differing *E*-β-methyl styrene concentrations demonstrated good accordance with a pseudo-first-order kinetic law with a rate constant k_1 (Figure 3), so that

$$k_1 = k_0 + k_2[\text{substrate}] \quad (3)$$

For complex $\mathbf{A_2}$, k_0 was obtained as $6 \pm 2 \times 10^{-4}$ s^{-1} and $k_2 = 3.2 \pm 0.3 \times 10^{-3}$ $L\cdot mol^{-1}\cdot s^{-1}$, whereas for complex $\mathbf{A_1}$, k_0 and k_2 were estimated as $3 \pm 3 \times 10^{-5}$ s^{-1} and $1.3 \pm 0.3 \times 10^{-4}$ $L\cdot mol^{-1}\cdot s^{-1}$, respectively (experiments carried out at 290 K; k_0 reflects the existence of self-decay pathways). According to these measurements, catalyst **1** would demonstrate a reactivity much lower than **2** in practical epoxidations. This is in accordance with earlier observations by Gilheany et al.:[19] in their stoichiometric procedures carried out at 0 °C, reaction times were on the order of hours for unsubstituted chromium(III)−salen complexes (like **2**) and up to weeks for *tert*-butyl substituted complexes (like **1**).

Kinetic measurements with complex **B** have also been undertaken. A mixture of complexes $\mathbf{A_1}$ and $\mathbf{B_1}$ was generated in CH_3CN by stirring **1** with PhIO. Then, a desired amount of *E*-β-methylstyrene was added, and the sample was stored in the EPR resonator until the disappearance of complex $\mathbf{A_1}$ was detected by EPR. After this, the kinetics of complex $\mathbf{B_1}$

(28) The exchange rate constant could be estimated from $\pi\Delta\nu_{1/2} = 1/T_2 + 1/\tau$ (see, e.g., ref 29), where $\Delta\nu_{1/2}$ is the observed line width, T_2 the spin−lattice relaxation time without exchange, and τ is the characteristic time of the chemical exchange, so that $\tau^{-1} = k\cdot[CH_3CN]$. In our case, $1/T_2$ can be assigned to the line width in noncoordinating solvent (in toluene, line width is 1.8 G). Computer simulations demonstrate that HFS practically disappears at $\Delta\nu_{1/2} = 2.8$ G. Thus, an estimate gives $k \approx 10^{-6}$ $L\cdot mol^{-1}\cdot s^{-1}$.

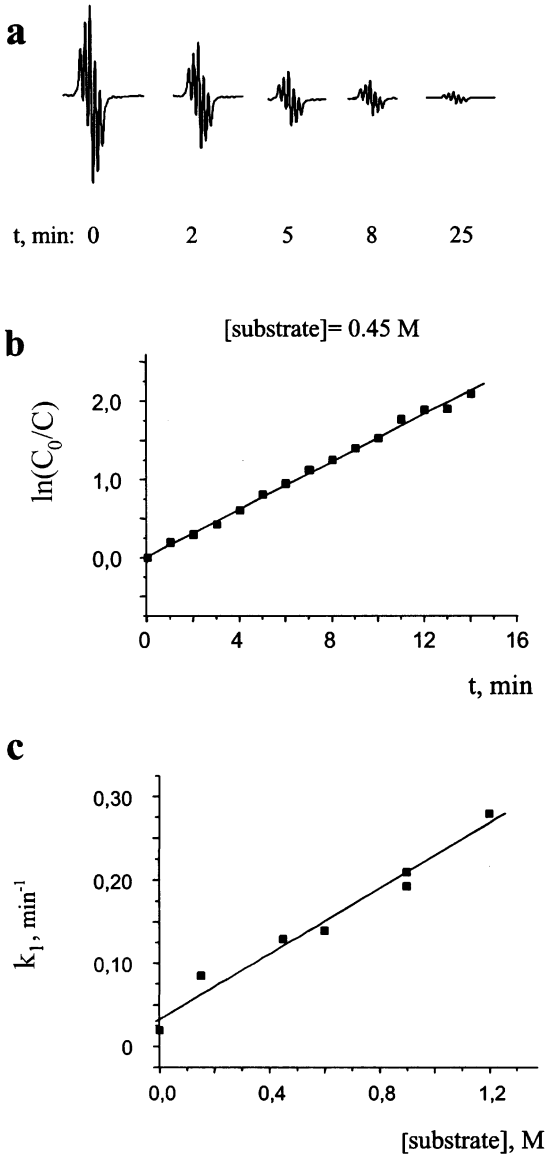

Figure 3. EPR spectra (290 K) of chromium(V) complex $\mathbf{A_2}$ in different moments of time after addition of excess of *E*-*β*-methyl styrene (a). Kinetic plot of Cr^V (complex $\mathbf{A_2}$) concentration in the above sample (b). Dependence of the pseudo-first-order rate constant k_1 on the concentration of *E*-*β*-methyl styrene (c).

decay was registered by EPR. It was found that the half-life time of $\mathbf{B_1}$ (18 min without substrate, 298 K) was affected by the substrate ($\tau_{1/2}$ = 11 min at [substrate] = 0.6 M and $\tau_{1/2}$ = 9 min at [substrate] = 0.9 M). In practical epoxidations, of course, only one species is likely to conduct the catalytic reaction, namely, the most reactive one. This leads to a conclusion that complex **A** could act as the active species, complex **B** being a reservoir of the active oxo chromium(V) functionality.

It was found that coordination of DMF reduced the reactivity of complex **A** significantly: this could be seen from $\tau_{1/2}$ values of complexes **A** in DMF ($\tau_{1/2}(\mathbf{A_1}$, DMF) > 1 day; $\tau_{1/2}(\mathbf{A_2}$, DMF) = 6 h). The increased enantioselectivity (+11% ee upon addition of DMF;[19] stoichiometric procedure; catalyst, nonracemic nondeuterated analogue of **2**) could result from reduced reactivity, thus representing the effect of axial ligation.

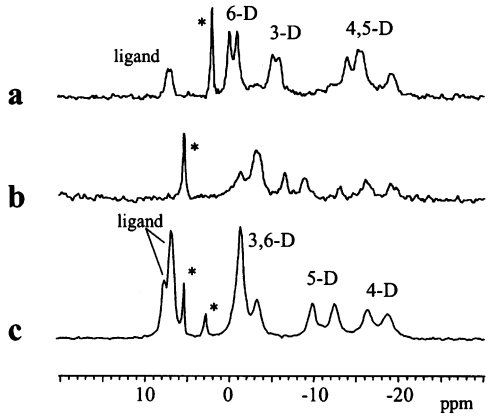

Figure 4. ^2H NMR spectra (293 K) of chromium(III)−salen complex **2** in different solvents: in CH_3CN (a); in CH_2Cl_2 (b); in CH_2Cl_2−DMF (2:1) mixed solvent (c). Asterisks mark ^2H peaks of residual deuterons of the solvents.

Structures of Complexes A and B. In Figure 4, the ^2H NMR spectra of **2** at 293 K in different solvents are presented. First, we have to note that signals at 6.8 and 7.5 ppm (previously assigned to the sixth deuterons of complex **2**[21]) belong to an admixture (ca. 20%) of uncoordinated ligand. Both in CH_3CN and in DMF, two sets of the signals for each deuteron were observed, demonstrating stereochemical nonequivalence of 3,3′, 4,4′, 5,5′, and 6,6′ deuterons. In the spectrum recorded in CH_2Cl_2, a greater number of peaks were observed. This may be due to the existence of two forms differing in axial ligand or due to an aggregation between salen units of (*R*,*R*)-**2** and (*S*,*S*)-**2** (Figure 4b).

Figure 5a represents NMR and EPR spectra of chromium species formed upon interaction of **2** with PhIO in CH_2Cl_2−DMF combined solvent. Stirrings with PhIO were carried out at 0 °C, and spectra were run at −10 °C to prevent reduction of Cr^V species. The combined solvent allowed us to obtain relatively narrow NMR lines due to the low viscosity of CH_2Cl_2 and suppressed transformation of complex $\mathbf{A_2}$ into $\mathbf{B_2}$ due to coordination of DMF. We point out that Cr^V species with d^1 configuration of the metal ion could not be detected by NMR because of long spin relaxation time on the order 10^{-9} s or longer.[30,31] Comparison of the NMR spectrum of Figure 5a with that of the initial complex **2** (Figure 5b) reveals that the concentration of Cr^{III} decreased after stirring with PhIO. At the same time, free ligand or/and products of its degradation are observed (Figure 5a) at 6.5−7.5 ppm. Moreover, deuterons of heavy water (HDO or D_2O) are observed at 3.5 ppm (addition of D_2O into the same sample resulted in the enhancement of this line), indicating that ligand degradation may proceed, probably, via oxidation of the deuterated ligand by high-valence Cr species. As soon as DMF prevents formation of complex $\mathbf{B_2}$, chromium(V) complex $\mathbf{A_2}$ (see insert in Figure 5a) is

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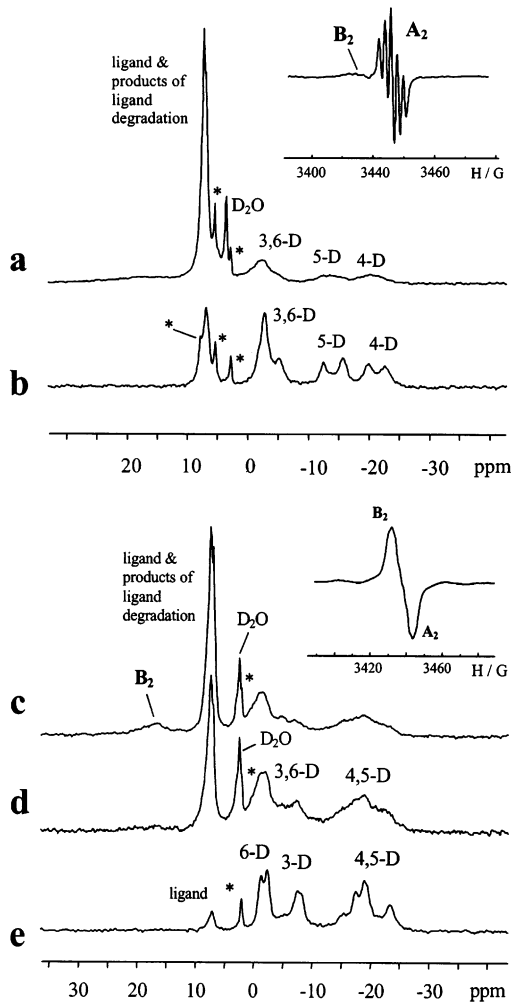

Figure 5. ^{2}H NMR spectrum (263 K) of chromium(III)−salen species generated by stirring complex **2** (15 μmol) and PhIO (25 μmol) in 3 mL of CH_2Cl_2−DMF (2:1) solvent (a). In the insert, EPR spectrum of the same sample is presented. ^{2}H NMR spectrum of complex **2** at the same conditions (b). ^{2}H NMR spectra (263 K) of chromium(III)−salen species generated by stirring complex **2** (15 μmol) and PhIO (25 μmol) in 3 mL of CH_3CN (c); insert demonstrates EPR spectrum of the same sample ($\mathbf{A_2}$:$\mathbf{B_2}$ ratio ca. 1:1). The same sample warmed to RT for 5 min and NMR spectrum recorded at 263 K (d). ^{2}H NMR spectrum of complex **2** at the same conditions (e). Asterisks mark ^{2}H peaks of residual deuterons of the solvents.

the major species and unreacted **2** (Figure 5a) is the minor species in solution.

The picture was different in CH_3CN (Figure 5c−e). After stirring **2** with PhIO, both $\mathbf{A_2}$ and $\mathbf{B_2}$ formed in comparable concentrations (insert in Figure 5c). This resulted in appearance of a new ^{2}H signal at 16.8 ppm, indicating the presence (along with unreacted **2**) of chromium(III) species $\mathbf{B_2}$. When the sample was warmed to RT, the concentration of **2** increased (Figure 5d). At the same time, EPR detected almost quantitative disappearance of Cr^V compounds $\mathbf{A_2}$ and $\mathbf{B_2}$. It is also seen that the peak of $\mathbf{B_2}$ (at 16.8 ppm) has disappeared after warming. Our hypothesis is that complex **B** at the same time contains Cr^{III} and Cr^V moieties, thus displaying NMR spectra characteristic of Cr^{III} and EPR spectra typical for Cr^V. Earlier, on the basis of indirect data, formation of binuclear structures was proposed by Gilheany[32] to give a $Cr^{IV}OCr^{IV}$ dimer. However, oxidation state +4 is particularly atypical in chromium coordination chemistry, and the formation of

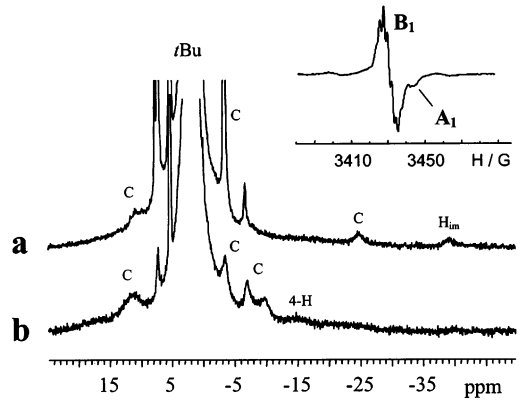

Figure 6. ^{1}H NMR spectrum (290 K) of chromium(III)−salen species $\mathbf{B_1}$ generated by stirring complex **1** (8 μmol) and PhIO (4 μmol) in 0.6 mL of CD_2Cl_2 (a). In the insert, EPR spectrum of the same sample is presented. ^{1}H NMR spectrum of **1** at the same conditions (b). "C" denotes cyclohexanediamine protons, and "H_{im}" stands for imine protons.

the $[(salen)Cr^VOCr^{III}(salen)]^{2+}$ binuclear species rather than the $Cr^{IV}OCr^{IV}$ one could be expected.

Similar experiments with complex **1** have also been undertaken. For chromium catalyst **1** in DMF-d_7, EPR indicated creation of complex $\mathbf{A_1}$ upon stirring with PhIO, and at the same time almost complete disappearance of ^{1}H NMR resonances of **1**. Representative ^{1}H NMR spectra for complex $\mathbf{B_1}$ were obtained in CD_2Cl_2 at 290 K (Figure 6). When 0.7 equiv of PhIO was added to a solution of **1** in CD_2Cl_2 and the mixture was mechanically stirred for 15 min, the EPR spectrum indicated the presence of mainly complex $\mathbf{B_1}$ (Figure 6a, insert). Figure 6a represents the corresponding ^{1}H NMR spectrum, which is quite different from that of the source complex **1** (cf. Figure 6b), displaying significant distinctions in the ligand surrounding of Cr^{3+} ion in **1** and $\mathbf{B_1}$. Some NMR data for chromium(III) complexes are collected in Table 2.

UV−Vis/NIR Spectroscopic Study of Cr^V(salen) Complexes. To support our assignment of complex **B** to a mixed-valence dinuclear complex, UV−vis and near-IR spectra of complexes **1**, $\mathbf{A_1}$, and $\mathbf{B_1}$ in acetonitrile were recorded. The starting complex **1** (orange solution) does not demonstrate significant absorption in the region 600−200 nm (Figure 7a). Exposure of **1** to a suspension of 1.2 equiv of PhIO results in formation of green-black species $\mathbf{A_1}$. The latter corresponds to an intense absorption band centered at ca. 675 nm with a long tail extending beyond 1000 nm (Figure 7b). However, when 0.5 equiv of PhIO was taken, the picture was different (this experiment is similar to that in Figure 1f). In this case, only traces of complex $\mathbf{A_1}$ could be detected on the basis of its absorption at 675 nm, the brown complex $\mathbf{B_1}$ being the predominant high-valence chromium species in solution. Complex $\mathbf{B_1}$ was found to display a well-defined peak in the near-IR region (λ_{max} = 1075 nm), attributable to an intervalence charge transfer transition (Figure 7c). As soon as the portion of **1** converted into $\mathbf{B_1}$ is not exactly known, ϵ can be estimated as 350 to ca. 500 M^{-1} cm^{-1}. By applying

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Table 2. ^{1}H and ^{2}H NMR Shifts, ppm (Line Widths, kHz), of the Chromium−Salen Complexes[a]

species	nucleus	solvent	aromatic protons (deuterons)	cyclohexane diamine protons (C)	tBu protons	imine protons "H_{im}"
$\mathbf{A_1}$	^{1}H	CD_2Cl_2	−15.2 (1.0) 4-H	−9.7 (0.7)	2.0 (0.2)	−40 (1.0)
				−6.9 (0.3)		
				−3.4 (0.4)		
				11.4 (1.1)		
				19.0 (1.5)		
$\mathbf{A_1}$	^{1}H	DMF-d_7	−18.3 (0.7) 4-H	−20.7 (1.5)	1.8 (0.05)	
				−9.5 (0.8)		
				−7.0 (0.5)		
				11.4 (0.7)		
				19.6 (1.7)		
$\mathbf{B_1}$	^{1}H	CD_2Cl_2		−24.8 (0.7)	1.8	−39.2 (0.7)
				−6.7 (0.12)		
				−3.3 (0.1)		
				10.9 (0.6)		
$\mathbf{A_2}$	^{2}H	CH_3CN	−23.5 (0.12)		19.3	
			−19.2 (0.12)			
			−17.5 (0.06)			
			−15.4 (0.1)			
			−8.4 (0.06) 3-D			
			−7.5 (0.11) 3-D			
			−2.4 (0.07) 6-D			
			−1.3 (0.06) 6-D			
$\mathbf{A_2}$	^{2}H	CH_2Cl_2−DMF[b]	−22.7 (0.13) 4-D			
			−20.0 (0.10) 4-D			
			−15.7 (0.10) 5-D			
			−12.6 (0.08) 5-D			
			−5.2 (0.11)			
			−2.9 (0.08)			
$\mathbf{B_2}$	^{2}H	CH_3CN	16.8 (0.35)			

[a] $T = 290$ K for all experiments with **1** and $T = 263$ K for **2**. Only reliably detected resonances included. [b] CH_2Cl_2−DMF ratio 2:1

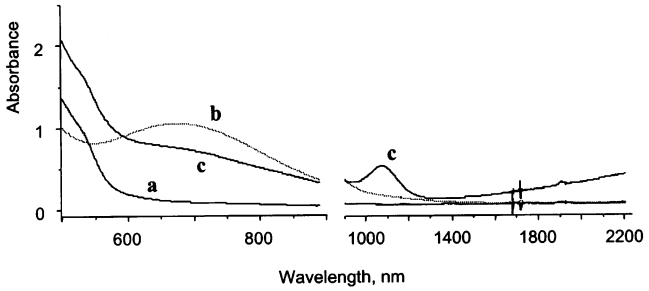
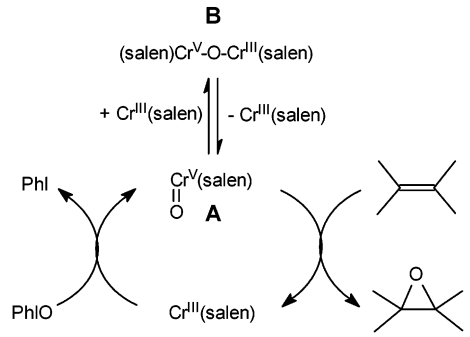


Figure 7. UV−vis (left)/NIR (right) absorption spectra in acetonitrile: complex **1** (4.5×10^{-3} M) (a); complex $\mathbf{A_1}$ obtained by exposure of 1×10^{-3} M solution of **1** to 1.2 equiv of PhIO (b); complex $\mathbf{B_1}$ obtained by exposure of $4.5 \cdot 10^{-3}$ M solution of to 0.5 equiv of PhIO (c).

the Hush theory,[33] moderate V coupling energy value was obtained 360 cm^{-1} ($V = 360$ cm^{-1} assuming that R_{MM} is ca. twice as large as the Cr−O bond length in Kochi's crystallographically characterized $Cr^{V}O$(salen) complex,[1] i.e., 2×1.56 Å, $\nu_{max} = 9300$ cm^{-1}, $\Delta\nu_{1/2} = 930$ cm^{-1}, and ϵ 350 M^{-1} cm^{-1}). In turn, the ground-state free energy difference $\Delta G°$ for the process $Cr^{III}/Cr^{V} \rightarrow Cr^{IV}/Cr^{IV}$ can be estimated from $\Delta\nu_{1/2} = [2310 \cdot (\nu_{max} - \Delta G°)]^{1/2}$ as 8900 cm^{-1}, or 100 kJ mol^{-1} (the case of nonsymmetric systems).[34] This provides a quantitative equivalent of our assertion that $Cr^{IV}OCr^{IV}$ binuclear complexes could not be formed in this system.

We note that EPR parameters of crystallographically characterized "$Cr^{V}O$(salen)" complexes by Kochi et al.[1] ($g = 1.978$, $a_N = 2.05-2.17$ G) are close to those obtained for our complexes of the type **B** ($g = 1.976-1.980$ and $a_N = 2.0-2.3$ G). This implies that although the authors[1] succeeded in separation of mononuclear $Cr^{V}O$(salen) complexes of the type **A**, in solution they observed binuclear species of the type **B**. Also, incorrect interpretation of UV−vis spectra seems to take place in ref 1: the absorption curve marked as "$O{=}Cr^{V}L^{+}$" must be ascribed to complex **B**.

The data obtained imply that Cr(salen) catalyzed epoxidation of alkenes proceeds in accordance with a catalytic scheme which is a modified Groves' "oxygen rebound cycle" [35] (L′ in eq 2 stands for "Cr^{III}(salen)"):



We have performed epoxidation of *E*-β-methylstyrene, catalyzed by **1** in CH_3CN, and obtained the corresponding epoxide in a 37% yield (based on PhIO) and 41% ee, with the green color of complex $\mathbf{A_1}$ being detected until the complete disappearance of solid PhIO. Low chemical yield was assigned to significant ligand degradation. Interestingly, we have shown that chromium(V) intermediates **A** and **B**

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can be obtained upon reaction of Cr^{III}(salen)Cl precursors **1** and **2** with *meta*-chloroperoxybenzoic acid (m-CPBA) (Table 1, entries 7 and 14). This leads to a conclusion that PhIO is not the unique oxidant to give an active $Cr^{V}O$ species, and heavy atom catalyzed spin conversion supposed by Norrby et al. in ref 36 may not be the crucial factor of epoxidation. However, attempts to conduct a catalytic reaction with m-CPBA as the terminal oxidant would be unsuccessful, as soon as concerted noncatalytic oxidation of *E*-*β*-methylstyrene by m-CPBA would compete with the chromium−salen catalyzed pathway.

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Supporting Information Available: Figure showing EPR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034578W

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