



Original article

Chiral electron deficient ruthenium helical coordination polymer as a catalyst for the epoxidation of substituted styrenes



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ABSTRACT

An air and moisture stable ruthenium(III) formate complex $[\text{Ru}(\text{HCO}_2)_2\text{Cl}_2]_n$ has been synthesized and examined in the epoxidation of substituted styrenes. X-ray crystallographic data of this complex were determined and showed that the formate ligand coordinates to the ruthenium centers in a $\mu^2-\eta^2$ fashion (syn, syn). Its asymmetric unit contains one Ru(III) ion together with the half of a formate ligand and one chloride anion, which are bridged between the metal centers, forming a 1-D chain coordination polymer. This electron deficient helical coordination polymer was employed in the epoxidation of *para*-fluorostyrene, affording the epoxide product in 92% yield. Natural chirality of this coordination polymer is applicable in asymmetric epoxidation reactions.

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1. Introduction

The intense interest in the synthesis of coordinately unsaturated transition metal complexes arises from the essential role that such compounds play as key intermediates in significant catalytic processes [1–3]. In the context of catalytic epoxidation, C–H bond activation and functionalization, d^6 and d^8 electron deficient metal complexes (14 and 16-electron) are of great significance. In recent years a number of electron deficient transition metal complexes with 14 [4–8] and even 12 valence electrons [9–11] have been prepared and characterized. A survey of relevant literature shows that a key strategy in successful preparation of the electron deficient species is the application of bulky ligands to sterically inhibit the addition of electron donating groups. Several studies have been performed on the synthesis and properties of disilene electron deficient complexes [10,12,13]. Berry *et al.* reported disilene complexes of $\text{Cp}_2\text{W}(\text{Si}_2\text{Me}_4)$. Kira and co-workers reported several 12, 14 and 16-electron disilene Pt(II) and Pd(II) complexes [9,10]. Nolan's research group discovered a 14-electron Rh(III) complex that was active in C–H bond activation [5]. Van der Schaar and co-workers synthesized a 14-electron Ru(II) benzylidene complex (the Grubbs' catalyst) [6,7]. Nevertheless, electron deficient complexes of transition metals have been ignored so far. To the best of our knowledge, no electron deficient coordination polymer has

been reported. Since such unsaturated compounds can be key intermediates in catalytic olefin epoxidation reactions [14–16], their isolation and characterization remain a necessary goal. Electron deficient species have been proposed as the key intermediates in the catalytic olefin epoxidation and the asymmetric epoxidation of olefins [15] is a very important organic transformation since the resulting enantiomerically pure epoxides are highly useful intermediates and building blocks. Several chiral catalysts that can carry out an asymmetric epoxidation reaction effectively have been developed. The most successful examples are the chiral Ru(II) and Ru(III) complexes. Beller *et al.* reported a high yielding and moderately enantioselective epoxidation reaction of styrenes using a chiral Ru(II) complex as catalysts to produce styrene oxides [17]. Kureshy's research group has revealed that chiral ruthenium Schiff base complexes could improve the enantiomeric excess of the epoxidation products [18,19]. Subsequently, Katsuki and co-workers described ruthenium(III) complexes in combination with 2,6-dichloropyridine *N*-oxide (DCPNO) or tetramethylpyrazine *N,N'*-dioxide as oxidant act as an efficient epoxidation catalyst [20]. Ideally, more efforts should be devoted to these catalytic systems. As a part of current interest in our research group on the oxidation reactions, we describe here the synthesis, crystal structure and catalytic activity of an unprecedented polymeric electron deficient ruthenium(III) complex for the epoxidation of styrene and its derivatives with *tert*-butyl hydrogen peroxide, TBHP, as an oxidant. The selective epoxidation of styrenes was performed with excellent yields.

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2. Experimental

All chemicals and reagents were purchased from Aldrich Strem chemical companies. Single-crystal X-ray diffraction data were collected on a STOE IPDS-II diffractometer with graphite monochromated Mo K α radiation at room temperature using the Stoe X-AREA software [21]. The structure was solved using STR-92 [22] and refined using the full-matrix least-squares methods on F^2 , within SHELXTL V6.1 [23]. For monitoring of reaction products and their identity, a gas chromatograph, Agilent Technologies 7890A Instrument equipped with a HP-1 capillary column, a FID detector, and a mass spectroscope model 5975C with a triple-axis detector was used. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. The determination of ruthenium was performed on a Varian model VISTA-PRO inductively plasma optical emission spectrometer (ICP-OES).

Preparation of Ru complex (**1**): A solution of RuCl₂(PPh₃)₃ (100 mg, 0.104 mmol) in CHCl₃ (10 mL) was stirred in the presence of air at ambient temperature, then a solution of triazine (16 mg, 0.208 mmol) in acetone (10 mL) was added. The color of the reaction changed from dark brown to deep blue immediately. After filtration of reaction mixture over celite, diethyl ether (15 mL) was added. Partial evaporation of the solvents yielded a brown precipitate. Recrystallization from 10 mL of the 2:1 MeCN/MeOH mixture gave yellow microcrystals after 2 days (yield 63%). Elemental analysis: Calcd. for [Ru(HCO₂)Cl₂]: C, 5.53; H, 0.46; Cl, 32.72; Ru, 46.54. Found: C, 5.48; H, 0.49; Cl, 32.62; Ru, 46.33.

Catalytic epoxidation: In a 25 mL Schlenk tube, the catalyst (0.01 mmol) was stirred at room temperature in MeCN (10 mL) for 15 min. Substrate (1 mmol) and *n*-decane (GC internal standard, 50 mL) were added. A solution of 70% TBHP (1.5 mmol) in MeCN (10 mL) was added over a period of 24 h by a syringe pump to the reaction mixture. The reaction products were monitored by gas chromatography.

3. Results and discussion

The result of single crystal X-ray diffraction of the prepared crystals is shown in Table 1. The structure crystallizes in a chiral hexagonal space group *P*6₁22 with six molecules in the unit cell. The asymmetric unit contains one Ru(III) ion, the half of a formate ligand and one chloride anion. Each ruthenium atom is six-coordinated, comprising four bridging chloride anions and two oxygen atoms of two formate groups bridged between ruthenium centers (Fig. 1).

The coordination environment of ruthenium is best described as distorted octahedral, in which the axial positions are occupied by one oxygen atom from the formate ligand and one bridging chloride ligand. The equatorial plane involves another oxygen atom of chelating formate together with three bridging chlorides. Packing diagram of the structure is shown in Fig. 2. Expansion of the structure leads to the formation of an infinite 1-D chain coordination polymer that could be formulated as [Ru(HCO₂)Cl₂]_n (Fig. 3).

The chelation of the carboxylate O atoms in the formate groups in [Ru(HCO₂)Cl₂]_n shows the *syn, syn* coordination fashion [Ru–O bond distances = 2.304(5) Å]. As reported previously [24], carboxylate anions bridged between two identical metal cores *via* both oxygen atoms in a μ_2 - η^2 fashion can adopt *anti, anti*; *syn, anti* and *syn, syn* manner for the formate ion unless the metal atoms are bound together or connected by other bridging ligands. In the latter cases, only the *syn, syn* mode is possible. Extension of the structure through the formate ligands and the crystallographic symmetry generates 6-fold homochiral right-handed (Δ) [Ru(HCO₂)Cl₂]_n helix that is oriented along the *c* direction (Fig. 4).

Table 1

Crystal data and structure refinement for [Ru(HCO₂)Cl₂]_n.

Empirical formula	CH ₃ Cl ₂ O ₃ Ru
Formula weight	235.00
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	<i>P</i> 6 ₁ 2 2
Unit cell dimensions	<i>a</i> = 7.2833(10) Å <i>b</i> = 7.2833(10) Å <i>c</i> = 19.591(4) Å
Volume	900.0(3) Å ³
<i>Z</i>	6
Density (calculated)	2.602 mg/m ³
Absorption coefficient	3.405 mm ⁻¹
<i>F</i> (0 0 0)	666
Crystal size	0.16 × 0.14 × 0.14 mm ³
Theta range of data collection	3.23°–27.46°
Index ranges	–6 ≤ <i>h</i> ≤ 9, –9 ≤ <i>k</i> ≤ 8, –24 ≤ <i>l</i> ≤ 25
Reflections collected	4976
Independent reflections	698 [<i>R</i> (int) = 0.0350]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.968 and 0.889
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	698/0/36
Goodness-of-fit on F^2	1.128
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0356, <i>wR</i> 2 = 0.0887
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0378, <i>wR</i> 2 = 0.0904
Absolute structure parameter	–0.20(19)
Extinction coefficient	0.0115(15)
Largest diff. peak and hole	0.931 and –0.770 e Å ⁻³

Crystallographic data, selected bond lengths (Å) and angles [°] of [Ru(HCO₂)Cl₂]_n are depicted in Tables 1 and 2.

The Ru···Ru distances are approximately 3.604 Å, significantly longer than the bond length expected for the corresponding metal–metal bonds [25]. Bridging the formate groups between the two metal centers makes a torsion angle of around 7.90°. There are also

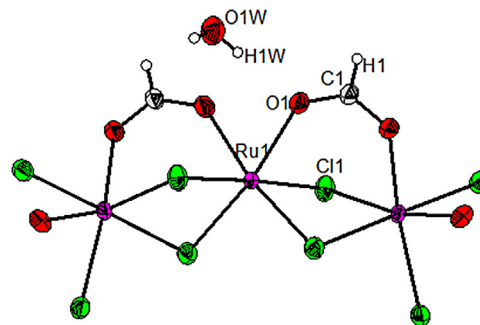


Fig. 1. Molecular structure of **1** with 50% probability of thermal ellipsoids. Symmetry independent part is labeled.

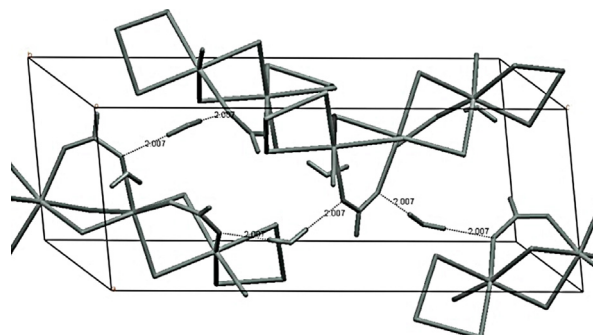


Fig. 2. Packing diagram of [Ru(HCO₂)Cl₂]_n.

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