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Aerobic oxidation of tetrahydrofuran by a series of iron (III) containing POSS compounds

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ABSTRACT

A series of iron (III) containing POSS compounds, $[Bu_4N][(R)_7Si_7O_{12}FeCl]$ (R = isobutyl- (1), ethyl- (2), phenyl- (3), and cyclopentyl- (4)) were investigated as potential catalysts for aerobic oxidation of tetrahydrofuran (THF). The oxidation products for this reaction were characterized by IR, GC and GC–MS. The major oxidation product was γ -butyrolactone (C₄H₆O₂, GBL); while the two minor products were 2-hydroxy-THF and its tautomer, 4-hydroxybutanal. A third minor oxidative product is believed to be an isomer of dihydroxy-THF. THF free syntheses of 2–4 have been developed and all three compounds were characterized by elemental analysis, IR, and X-ray diffraction studies. The crystallographic data for 1–4 demonstrate a similar iron coordination sphere between the four compounds, but the different substitutents on the various POSS. The corresponding turnover numbers for the aerobic oxidation of THF suggest that smaller substitutents on the POSS ligands improve the stability of the catalytic species. When compared to other published catalytic iron systems, these turnover numbers appear to be the largest for the aerobic conversion of THF to GBL.

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1. Introduction

Metal containing polyhedral oligomeric silsesquioxanes (POSS) have been used to model a variety of industrial catalysts consisting of silica (SiO₂) supported metals [1,2]. As a result, our laboratory has been investigating the use of POSS ligands as potential models for the Fe-ZSM-5 catalyst [3]. During this process, we synthesized and fully characterized four different iron (III)-containing POSS compounds, [Bu₄N][(R)₇Si₇O₁₂FeCl] (R = isobutyl- (1), ethyl- (2), phenyl- (3), and cyclopentyl- (4)) (Fig. 1).

In the crystal structure of the isobutyl derivative (**1**) an equivalent of γ -butyrolactone (C₄H₆O₂, GBL) had crystallized with the complex [4]. Since GBL had not been added to the reaction mixture, we hypothesized that it was formed from the aerobic oxidation of the solvent, tetrahydrofuran (C₄H₈O, THF), during the synthesis of **1** (Reaction 1).

The aerobic oxidation of ethers, such as THF, has been facilitated by a variety of transition metal complexes [5–12]. However, oxidation of ethers using an iron containing complex is especially significant because of iron's importance in biological reactions [13,14]. We offer here our results of the controlled aerobic oxidation of THF in the presence of four different iron (III) chloro-POSS compounds (1-4) and a control of iron (III) chloro complex that does not contain the POSS, $[Bu_4N][FeCl_4]$ (**5**). In addition, we present the synthesis and structural characterization of the ethyl- (**2**) and phenyl- (**3**) derivatives, and an improved synthesis and structural characterization for the cyclopentyl- derivative (**4**) [15].

2. Experimental

2.1. Materials and instrumentation

All procedures were performed under aerobic conditions. Hexane and toluene were dried over Na and stored over 4 Å molecular sieves. Acetonitrile was dried over CaH2 and stored over 4 Å molecular sieves. IR spectra were recorded on a Nicolet Impact 410 FTIR Spectrometer using a KBr pellet or NaCl plates. Elemental analysis was performed by Galbraith Laboratories Inc. (Knoxville, TN) using a Perkin-Elmer 240 CHN Analyzer. Gas chromatography (GC) was recorded on a GOW-MAC Series 400 Thermal Conductivity GC using a carbowax column. Gas chromatography-mass spectrometry (GC-MS) analysis was performed on an Agilent 6890 gas chromatograph coupled to a Waters GCT time-of-flight mass spectrometer using a Varian VF5-MS column (20 m, 0.18 mm i.d., 0.15 μ m) programmed from 40 (1 min hold) to 300 °C at 15 °C/ min) operating in 20 to 1 split injection mode (Injector T = 250 °C). The compounds were ionized via electron ionization. The X-ray diffraction data were collected under a cooled N₂ stream





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Fig. 1. Iron (III) chloro-POSS compounds, R = isobutyl- (1), ethyl- (2), phenyl- (3), and cyclopentyl- (4)



Reaction 1. Oxidation of tetrahydrofuran to γ -butyrolactone.

at 150 K on a Bruker Apex CCD diffractometer (sealed-tube Mo radiation) which is controlled via Bruker Smart software. Trisilanolethyl-POSS, $(CH_3CH_2)_7Si_7O_{12}H_3$, the trisilanolphenyl-POSS, $(C_6H_5)_7Si_7O_{12}H_3$, and the trisilanolcyclopentyl-POSS, $(cyclo-C_5H_9)_7-Si_7O_{12}H_3$ were all obtained from Hybrid Plastics or as a gift from Dr. Andre Lee from Michigan State University and used as received. Triethylamine, anhydrous tetrahydrofuran (THF), γ -butyrolactone (GBL), and dodecane were all obtained from Sigma–Aldrich chemical and used as received. Compound **1** was synthesized as described in the literature [16]. Compound **5** was prepared according to the literature procedure [17].

2.2. Synthesis of compound 2

A colorless solution of the trisilanol-POSS, $(CH_3CH_2)_7Si_7O_{12}H_3$, (0.200 g, 0.336 mmol) in toluene (4.0 mL) was treated with 3 equiv. of triethylamine (141 µL, 1.01 mmol). The mixture was stirred for 5 min at room temperature before 1 equiv. of solid **5** (0.148 g, 0.336 mmol) was added. The yellow solid did not immediately dissolve. After stirring for 10 min, the solution had turned yellow and a precipitate had formed. A white precipitate was collected by filtration. The yellow filtrate was concentrated in vacuo giving a yellow oil, which was then extracted with acetonitrile. A majority of the yellow oil dissolved except for a small amount of insoluble white precipitate. These were removed by filtration, and the filtrate was concentrated in vacuo to give yellow crystalline material, which was then extracted with toluene and then concentrated in vacuo.

2.2.1. Compound 2

Yield: 83.9%. Anal. Calc. for $C_{30}H_{71}$ FeClNO₁₂Si₇ (925.81): C, 38.92; H, 7.73; N, 1.51. Found: C, 38.89; H, 7.63; N, 1.54%. IR (KBr, ν (cm⁻¹)): 2967s, 2877s, 1481m, 1461m, 1415w, 1383w, 1252s, 1086vs, 940s, 881m, 753s, 696vs, 492s, 458s.

2.3. Synthesis of compounds 3 and 4

Compounds **3** and **4** were prepared following a procedure analogous to the synthesis of **2**. Similar molar quantities of the appropriate trisilanol-POSS were used, but due to their lower solubility in toluene, twice the volume of solvent was used as well as longer reaction times were necessary.

2.3.1. Compound **3**

Yield: 82.2%. Anal. Calc. for C₅₈H₇₁FeClNO₁₂Si₇ (1262.09): C, 55.19; H, 5.67; N, 1.11. Found: C, 55.12; H, 5.49; N, 1.12%. IR

(KBr, v (cm⁻¹)): 3137w, 3071s, 3049s, 2965s, 2931s, 2874s, 2719w, 1961m, 1891m, 1824m, 1776m, 1593s, 1480s, 1431s, 1381s, 1068vs, 879s, 744vs, 694vs, 645s, 594m, 551s.

2.3.2. Compound 4

Yield: 73.8%. Anal. Calc. for $C_{51}H_{99}FeCINO_{12}Si_7$ (1206.24): C, 50.78; H, 8.27; N, 1.16. Found: C, 50.61; H, 8.72; N, 1.26%. IR (KBr, ν (cm⁻¹)): 2948vs, 2864s, 1481m, 1471m, 1454m, 1383m, 1243s, 1099vs, 1040vs, 943s, 906w, 736m, 496vs.

2.4. X-ray analysis of iron (III) chloro-POSS compounds

Crystallization of **2** from a minimum amount of toluene afforded yellow crystals of **2**. $C_{30}H_{71}$ ClFeNO₁₂Si₇, M = 925.81, monoclinic space group, $P2_1/c$, a = 9.8962(5), b = 29.5660(15), c = 16.1237(8) Å, $\beta = 90.7710(10)^{\circ}$, V = 4717.2(4) Å³, Z = 4, $D_{calc} = 1.302$ Mg/m³; $F(0 \ 0 \ 0) = 1976$, $\mu_{Mo} = 0.422$ mm⁻¹; crystal dimensions: $0.32 \times 0.28 \times 0.25$ mm. The structure was solved via direct methods. Least-squares refinement on F^2 using all reflections converged to $R_{F^2} = 15.29\%$. One of the ethyl methylene carbons was disordered 50:50 over two sites.

Crystallization of 3 from a minimum amount of toluene afforded yellow crystals of **3**. C₅₈H₇₁ClFeNO₁₂Si₇-2(C₆H₅CH₃), M = 1446.36, monoclinic space group, $P2_1/n$, a = 15.079(3), $b = 20.224(4), c = 25.423(4) \text{ Å}, \beta = 100.642(4)^{\circ}, V = 7619(2) \text{ Å}^3,$ Z = 4, $D_{\text{calc}} = 1.261 \text{ Mg/m}^3$; $F(0 \ 0 \ 0) = 3052$, $\mu_{\text{Mo}} = 0.401 \text{ mm}^{-1}$; crystal dimensions: 0 $0.22 \times 0.34 \times 0.35$ mm. The structure was solved via direct methods. Least-squares refinement on F^2 using all reflections converged to $R_{F^2} = 27.52\%$. There are two toluene solvate molecules per asymmetric unit which were constrained to fit approximately rigid hexagons. The crystal was very weakly diffracting which caused problems in the refinement including poorly shaped ADP's, unexpected variations in U_{eq} values, and some atypical bond lengths. These problems are noted in the checkcif report. Crystallization of 4 from a minimum amount of toluene afforded yellow crystals of **4**. $C_{51}H_{99}CIFeNO_{12}Si_7$, M = 1206.24, monoclinic space group, $P2_1/c$, a = 15.4303(16), $b = 22.127(2), c = 40.539(4) \text{ Å}, \beta = 93.408(2)^\circ, V = 13817(2) \text{ Å}^3,$ Z = 8, $D_{\text{calc}} = 1.159 \text{ Mg/m}^3$; $F(0\ 0\ 0) = 5192$, $\mu_{\text{Mo}} = 0.428 \text{ mm}^{-1}$; crystal dimensions: $0.21 \times \ 0.28 \times 0.34 \ mm.$ The structure was solved via direct

methods. Least-squares refinement on F^2 using all reflections converged to $R_{F^2} = 23.54\%$. Crystals diffracted very weakly which caused problems in the refinement including poorly shaped ADP's, unexpected variations in U_{eq} values, and some atypical bond lengths. These problems are noted in the checkcif report. One of the cyclopentyl groups was disordered over two 50% occupancy orientations.

2.5. Aerobic oxidation of the tetrahydrofuran

In a 10-mL micro-scale round bottom flask, 0.0500 mol% of the iron complex was dissolved in 2.00 mL of THF. The resulting solution was golden yellow. Three stacked micro-scale water condensers were added to the round bottom flask to prevent evaporation of the solvent. The mixture was stirred for 5 days at room temperature. Afterwards, the reaction mixture was analysed by infrared spectroscopy (IR) and gas chromatography (GC). Dodecane was used as an internal standard during the GC analysis, and the turnover number from four separate trials were averaged to give the reported values. On separate occasions, similar reaction mixtures were analysed by gas chromatography-



Reaction 2. THF free synthesis of 1-4.

mass spectrometry (GC–MS) to determine the identities of the THF oxidation products.

3. Results and discussion

3.1. Synthesis of iron (III) chloro-POSS compounds

The conversion of THF to GBL was originally detected when 1 was synthesized and crystallized in a solution of THF under aerobic conditions [4]. A general THF free synthesis was therefore developed in order to prepare 1-4 (Reaction 2). The corresponding POSS trisilanol was treated with 3 equiv. of triethylamine in toluene. Although 5 was insoluble in toluene, the reaction between 5 and the POSS ligand still occurred albeit slower and with a considerable amount of stirring. After reaction times ranging from 5 to 60 min, depending on the POSS, triethyl ammonium chloride salt and a small amount of unreacted 5 were removed by filtration. The resulting yellow toluene solution was concentrated under reduced pressure to give a yellow oil, which was then extracted with acetonitrile. The trisilanol POSS ligands are insoluble in acetonitrile, while 1-4 are soluble, therefore unreacted trisilanol POSS ligand can be easily removed from the reaction mixture increasing the purity of the product. A final extraction with either hexane or toluene, depending on the product, resulted in the formation of 1–4 in relatively high yields.



Fig. 2. Infrared spectral data of pure THF (top) and a typical reaction mixture (bottom).

3.2. X-ray analysis of iron (III) chloro-POSS compounds

The iron (III) center in **2–4** all have the same coordination geometry previously observed in **1** [15,16], a distorted tetrahedral geometry composed of a single chlorine atom and three trisilanate oxygen atoms. The Fe–Cl bond distances in **1–4** are very similar [Fe–Cl: **1**, 2.2536(10) Å; **2**, 2.2534(5) Å, **3**, 2.227(2) Å, and **4**, 2.256(1) Å], while the average Fe–O_{trisilanate} bond length of **1–4** are also very close [Fe–O_{trisilanate}: **1**, 1.842 (±0.008) Å; **2**, 1.84 (±0.01) Å, **3**, 1.835(±.009) Å, and **4**, 1.825(±.009) Å]. Clearly, the four complexes are structurally comparable within the coordination environment of the iron and differ only in the type and thus the size of the hydrocarbon substitutents on the POSS ligand.

3.3. Aerobic oxidation of the tetrahydrofuran

A yellow solution of 0.0500 mol% **1–5** in anhydrous THF was stirred open to the atmosphere for five days. The IR spectrum of the reaction mixtures of each sample was compared to the IR spectrum of pure THF (Fig. 2). New bands were detected that are indicative of oxidation products: a shoulder at 3416 cm⁻¹, a broad band at 3293 cm⁻¹, and two sharper bands at 1778 cm⁻¹ and 1726 cm⁻¹. The peaks in the 3000 cm⁻¹ range are characteristic of hydroxyl (–OH) functionality, while the peaks in the 1700 cm⁻¹ range support the presence of carbonyl (C=O) groups [18]. The 1778 cm⁻¹ peak is consistent with the IR of pure GBL obtained in our laboratory as well as the literature value [19].

According to the GC-MS results, GBL was confirmed as the major oxidation product for the aerobic oxidation of THF. In addition, two minor products were also detected. The more abundant of the two minor species was 2-hydroxy-THF. The shoulder at 3416 cm⁻¹ in the IR also supports its presence [20]. It can undergo a ring-chain tautomerism to form 4-hydroxybutanal [21], however, the GC-MS did not detect the ring opened species (Reaction 3). In the liquid phase, however, the 1726 cm⁻¹ peak in the IR is consistent with 4-hydroxybutanal [22]. Therefore, it is possible that either the gas phase equilibrium favoured the cyclic tautomer in the MS or the ring-opened form did not elute from the GC column. The third most abundant species detected by the GC-MS is believed to be a dihydroxy-THF molecule. An M⁺ peak of 104 in the mass spec is consistent with a molecular formula of C₄H₈O₃, and the broad band at 3293 cm⁻¹ in the IR would also support the presence of a second hydroxyl containing species. We were unable to definitively confirm which dihydroxy-THF isomer was present in the reaction mixture.



Reaction 3. Ring-chain tautomerism of 2-hydroxy-THF and 4-hydroxybutanal.

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Table 1

Turnover numbers for THF oxidation products.

Iron (III) chloro complex	THF to GBL turnover number	Total oxidation turnover number
Isobutyl POSS (1) Ethyl POSS (2) Phenyl POSS (3) Cyclopentyl POSS (4) No POSS (5)	74 (±7) 114 (±9) 89 (±7) 82 (±7) 6 (±2)	100 (±8) 170 (±10) 130 (±10) 120 (±9) 14 (±3)

As of this study, it is not clear that the iron (III) chloro-POSS complexes (1–4) remain intact during the oxidation of THF, and are thus responsible for the catalytic conversion of THF to GBL. In our previous report [4], we showed that an equivalent of GBL cocrystallized with 1, suggesting that 1 remains intact during the oxidation of THF. In this work, though, we were unable to isolate 1–4 from any of the THF reaction mixtures, possibly due to its low concentration. Also, the iron (III) center is paramagnetic [4], making simple spectroscopic methods for characterizing the catalytic iron species difficult. It is possible that the iron (III) chloro-POSS complexes could function as a pre-catalyst by potentially loosing the chloride ligand or reacting with water or oxygen to generate the catalytic species. As a result, we calculated turnover numbers for the THF oxidation reaction based on the initial number of moles of iron (III) in 1–5.

Since the reaction mixture contained multiple oxidation products of THF, we calculated both the THF to GBL turnover numbers as well as the turnover numbers for the total oxidation of THF (Table 1). The iron (III) chloro-POSS complexes (**1–4**) generated between 74 and 114 equiv. of GBL per mole of iron (III), while the total number of oxidation equivalents per iron (III) ranged from 100 to 170. As a control, **5** was dissolved in THF under the same conditions and only 6 turnovers of GBL and 14 total oxidation turnovers were measured. Apparently, the POSS ligand enhances the stability of the catalytic species resulting in the higher turnover numbers. This may be a result of the POSS ligand's electron withdrawing ability, which would result in a more Lewis acidic iron center [23].

To place the iron (III) chloro-POSS system's turnover numbers in context, a review of the literature was conducted revealing only two previously published examples of the catalytic oxidation of THF to GBL by dioxygen in the presence of an iron complex. The first system used FeCl₂·(1.5 THF) under a pressure of dioxygen and carbon dioxide [14]. The second system used a carboxylate-bridged diiron complex in the presence of a triarylphosphine in air-saturated THF [13]. Both systems produce multiple THF oxidation products, including GBL. Approximately 2.5 turnovers of GBL were obtained after a reaction time of about 8 days from the FeCl₂·(1.5 THF) system, while the carboxylate-bridged diiron system did not report turnover numbers. Therefore, the iron (III) chloro-POSS system appears to provide the highest published THF to GBL turnovers for an iron system to date.

4. Conclusion

Clearly, the GBL observed in the crystal structure of **1** is formed by the aerobic oxidation of THF [4]. By first synthesizing the four iron (III)-containing POSS compounds (**1–4**) in toluene and then dissolving them in THF, we have demonstrated that all four complexes are capable of either catalysing this oxidation reaction or acting as pre-catalysts. The low turnover numbers observed with **5** supports that the presence of the POSS ligand significantly stabilizes the catalysts allowing for dramatically higher yields of GBL. A comparison of the turnover numbers for **1–4** also shows that by varying the substitutent on the POSS, the stability of the catalyst can be improved: the POSS with the smallest substitutent, **2**, provides the most stable catalyst.

Supplementary data

CCDC 706342, 706344 and 706343 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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