and the results (Table 4) show that TiITQ-6 is an active and selective olefin epoxidation catalyst with H_2O_2 as an oxidizing agent. Moreover, its activity is much higher than that of TiFER, owing to the higher accessibility of titanium sites, and very similar to the activity of Ti-Beta.

Table 4. Catalytic activity[a] of titanium-containing zeolites for the epoxidation of 1-hexene with hydrogen peroxide.

Sample	X_{hexene}[b] [%]	Selectivity [%][c] to epoxide	of the H_2O_2	TON
TiFER	3.2	85.2	23	6
TiITQ-6	19.7	95.5	73	23
Ti-Beta	18.0	97.2	77	20

[a] Reaction conditions are: 16.5 mmol of olefin, 11.8 g acetonitrile, 4.5 mmol H_2O_2, 300 mg catalyst, 323 K, 5 hours. [b] Consumption of 1-hexene relative to the maximum possible. [c] Selectivity values scaled against the maximum possible.

In conclusion, a new zeolitic material, ITQ-6, has been prepared by delamination of a layered precursor of ferrierite. This zeolitic material is stable upon calcination and zeolitic acid sites can be generated. It presents a very high external surface area for reactant accessibility. A novel introduction of titanium into the framework of the ferrierite precursor gives titanium ferrierite and, by direct synthesis, the active and selective epoxidation catalyst TiITQ-6.

Experimental Section

ITQ-6: Silica (10 g, Aerosil 200, Degussa), alumina (2.3 g, as boehmite, Catapal B), NH_4F (9.2 g, Aldrich, 98 %), HF (3.1 g, Aldrich, 49.8 %), (*R*)-4-amino-2,2,6,6-tetramethylpiperidine (26 g, Fluka, 98 % purity), and Milli-Q water (27.9 g) were mixed in an autoclave and left at 448 K for five days. The resulting product (PreFER,[9] Si:Al = 30:1) was filtered, washed with water, and dried at 333 K (XRD in Figure 1 a). The PreFER was expanded to PreITQ-6 through a 16 hours reflux at 368 K as a suspension in an aqueous cetyltrimethylammonium bromide/tetrapropylammonium hydroxide ($CTMA^+Br^-/TPA^+OH^-$) solution (XRD in Figure 1 b). Delamination was performed by placing the PreITQ-6 slurry in an ultrasound bath (50 W, 40 kHz) for one hour, maintaining a pH of 12.5 and a temperature of 323 K. The solid phase was washed thoroughly with water, dried at 373 K (Si:Al = 30:1), and calcined at 853 K for 7 hours yielding ITQ-6 (Si:Al > 40:1; XRD in Figure 1 c). A portion of PreFER was calcined at 853 K without previous treatment to yield FER (XRD in Figure 1 d).

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Ligand-Directed Structural Modification of Imidotin(II) Cubanes: The Mixed Oxidation State Double-Cubanes $[Sn_7\{2\text{-}NR\}_8]\cdot n\,THF$ (R = Pyrimidinyl, 5-Methylpyridinyl)**

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In memory of Ron Snaith

Imidotin(II) cubanes of general formula $[\{SnNR\}_4]$ are the prototypical imidotin(II) compounds. Previous studies have shown that these species are accessible using a variety of synthetic strategies. In certain cases nucleophilic substitution of $SnCl_2$[1] or $SnCp_2$[2] ($Cp = \eta^5\text{-}C_5H_5$) with RN^{2-} or RNH^- can be employed. However, acid–base reactions of the Sn^{II} reagents $[\{Me_2Si(NMe)_2\}Sn]$,[3] $[Sn\{N(SiMe_3)_2\}_2]$,[4] and $[Sn(NMe_2)_2]$[5] with primary amines (RNH_2), hydrazines (H_2NNR), and borylamines (R_2BNH_2) provide more general approaches to these species. Of particular interest to us has been reactions involving $[Sn(NMe_2)_2]$ which have the advantages that they give clean formation of the cubanes for a broad range of amines at low temperatures.[5] The isolation of intermediates of the type $[\{Sn(NR)_2\}(SnNMe_2)_2]$ from the

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reactions of [$Sn(NMe_2)_2$] with sterically demanding amines, such as $DippNH_2$ (Dipp = 2,6-$iPr_2C_6H_3$),[6] suggests that cubane formation involving acid–base reactions occurs by a common stepwise process, rather than through the aggregation of discrete [SnNR] monomers.

On the basis of the extensive synthetic investigations previously undertaken and the overwhelming propensity for imidotin(II) complexes of this type to aggregate into cubanes,[1–5] we anticipated no structural or chemical variations would result from the reactions of 2-aminopyrimidine [2-H_2N(pm)] and 2-amino-5-methylpyridine [2-H_2N(5-MePy)] with [$Sn(NMe_2)_2$]. However, surprisingly these reactions (in THF as the solvent) do not lead to the anticipated cubanes of the type [$Sn(NR)]_4$ but to unique mixed oxidation state Sn^{II}/Sn^{IV} complexes of the formula [$Sn_7(NR)_8$] (**1**: R = pyrimidinyl; **2**: R = 5-methylpyridinyl),[7] together with finely divided Sn metal (see Experimental Section). Although the precise mechanism of formation of the complexes is uncertain, clearly the presence of the heterocyclic substituent directly bonded to the imidonitrogen center is key to this process. This is highlighted by the fact that discrete cubane structures are sustained for both Ph[1] and CH_2(2-pyridine)[5] substituents. Evidence that substituents can have a direct effect on the electrochemistry of imido cubanes is provided by cyclic voltammetry of [$\{Sn(NtBu)\}_4$] and [$\{Sn(NPh)\}_4$] (in MeCN). Although complicated by unidentified reduction processes, the cyclic voltammogram of [$\{Sn(NtBu)\}_4$] exhibits one irreversible oxidation wave at about 1.00 V (vs. Fe/Fe^{2+}), which we attribute to a Sn^{II}/Sn^{IV} oxidation. However, this irreversible oxidation process is significantly more favorable in [$\{Sn(NPh)\}_4$], now occurring at 0.63 V (vs. Fe/Fe^{2+}).

The low-temperature X-ray crystal structures of **1** (Figure 1) and **2** (see Supporting Information)[8] show that both consist of similar, centrosymmetric molecules, composed of two interlocked Sn_4N_4 imido cubane fragments which share a common Sn^{IV} apex (located at the crystallographic centers of symmetry). In addition, there are two THF and 0.33 THF molecules per formula unit in the lattices of **1** and **2**, respectively. The N-Sn-N angles and Sn–N bond lengths associated with the Sn^{II} centers (Sn(2), Sn(3), and Sn(4)), and the Sn-N-Sn angles within the cubane units of **1** and **2** are similar to those observed in the structurally characterized cubanes [$\{SnNR\}_4$] (mean Sn-N-Sn 98.4, N-Sn-N 81.9°; Sn–N range 2.15(1)–2.34(2) Å[1–5]). It therefore appears that there is comparatively little strain resulting from the incorporation of the Sn^{IV} center (Sn(1)) into the cubane frameworks, despite the presence of significantly shorter Sn–N bonds at the Sn^{IV} centers of **1** and **2** (range 2.157(3)–2.177(5) Å). The compression in the internal N-Sn-N angles at the Sn^{IV} centers in both complexes (cf. ca. 99° for those between the cubane units) gives pseudo-octahedral metal geometries which are similar to that observed in the [$Sn(NHCy)_6$]$^{2-}$ amido dianion of [THF · Li(μ-NHCy)$_3$Sn(μ-NHCy)$_3$Li · THF] (Cy = cyclohexyl).[8] A further interesting feature present in the structures of **1** and **2** are the relatively short Sn ··· N interactions which span the two cubane halves of the molecules (2.807(3)–2.935(3) in **1**, 2.761–2.784(5) Å in **2**). In addition to the electrochemical influence of the substituents, these interactions (which are similar to those found in [$\{SnN[CH_2$(2-pyridine)]$\}_4$] (2.86–2.92 Å)[9]) may play a role in promoting the stability of the double-cubane cage arrangements of the complexes.[10]

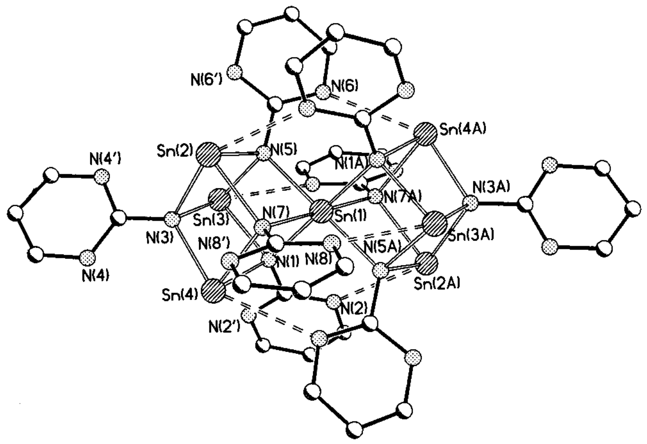

Figure 1. Molecular structure of **1** (hydrogen atoms and the disordered THF molecule in the lattice are omitted for clarity). The core structure of **2** is identical (see Supporting Information). Key bond lengths [Å] and angles [°]: for **1;** Sn(1)-N(1) 2.157(3), Sn(1)-N(5) 2.161(3), Sn(1)-N(7) 2.157(3), Sn(2)-N(3) 2.295(3), Sn(2)-N(5) 2.200(3), Sn(2)-N(7) 2.333(3), Sn(3)-N(1) 2.236(4), Sn(3)-N(3) 2.236(4), Sn(3)-N(5) 2.225(3), Sn(4)-N(1) 2.273(3), Sn(4)-N(3) 2.190(3), Sn(4)-N(7) 2.237(3), range N(2,6,8) ··· Sn(2A,3A,4A) 2.807(3)–2.935(3), range N-Sn(2,3,4)-N 76.6(1)–80.7(1) (mean 78.8), range Sn-N(1,3,5,7)-Sn 96.9(1)–101.6(1) (mean 99.7), N-Sn(1)-N range 80.8(1)–99.3(1); for **2;** Sn(1)-N(1) 2.166(5), Sn(1)-N(5) 2.169(5), Sn(1)-N(7) 2.177(5), Sn(2)-N(1) 2.247(5), Sn(2)-N(3) 2.261(5), Sn(2)-N(7) 2.212(5), Sn(3)-N(1) 2.222(5), Sn(3)-N(3) 2.240(6), Sn(3)-N(5) 2.212(5), Sn(4)-N(3) 2.266(5), Sn(4)-N(5) 2.225(5), Sn(4)-N(7) 2.191(5), N(2,6,8) ··· Sn(2A,3A,4A) 2.761–2.784(5), range N-Sn(2,3,4)-N 78.1(2)–80.9(2) (mean 79.5), range Sn-N(1,2,3,4)-Sn 96.3(2)–101.9(2) (mean 99.1), N-Sn(1)-N range 81.0(2)–99.0(2).

A survey of the literature reveals that, although rare compared to discrete cubanes, molecular double-cubane structures related to **1** and **2** have been identified for a range of transition metal and main group metal complexes.[11] However, this arrangement has only been observed for species containing alkoxide, sulfide, or halide bridges. The closest relative to **1** and **2** is the Sn^{IV} complex [$\{[nBuSnS(O_2PPh_2)]_3\}_2Sn$],[11c] composed of two interlocked Sn_4OS_3 cubane units which share a Sn center. Complexes **1** and **2** are the first imido complexes having this design and the only mixed oxidation state Sn^{II}/Sn^{IV} imido complexes to be structurally characterized. Their structures can be viewed alternatively as composed of two tripodal [$Sn_3(NR)_4$]$^{2-}$ ligands which coordinate the central Sn^{4+} ions. Such a tripodal ligand has been observed in the anion [$tBuNSn_3(Nnaph)_3Li$]$^-$ (naph = 1-naphthalene).[12]

This study has revealed that organic substituents have an unforeseen and dramatic effect on the structures of simple imidotin(II) cubanes. Similar structural effects and underlying electrochemistry may well be worthy of study in related main group metal compounds.

Experimental Section

1, 2: $Sn(NMe_2)_2$ (0.52 g, 2.5 mmol) in THF (25 mL) was added dropwise to a solution of 2-aminopyrimidine (0.24 g, 2.5 mmol, for **1**) or 2-amino-5-methylpyridine (0.27 g, 2.5 mmol, for **2**) in THF (30 mL) at −78°C. The reaction mixture was allowed to warm to about 0°C and then stored immediately in the dark at room temperature (12 h). Crystals form as small lemon-yellow cubes in the case of **1** and as colorless cubes in the case of **2**. Elemental analysis and spectroscopic investigations were complicated by the presence of finely dispersed Sn metal in samples of the complexes and by their sparing solubility in organic solvents. For **1**: Yield 0.10 g, 19 % (on the basis of 2-aminopyrimidine). Decomposition occurred at about 250°C to give a brown solid. IR (Nujol, NaCl): no N–H str; ^{119}Sn MAS-NMR (relative to $SnCl_2/D_2O$, 148.99 MHz, 8 KHz spin speed); $\delta = 353.7$ (Sn^{VI}, Sn(1)), -180.4 (Sn^{II}, Sn(2,3,4)); elemental analysis: calcd: C 27.9, H 2.3, N 19.6; found: C 25.5, H 2.2, N 17.3. For **2**: Yield 0.10 g, 19 % (on the basis of 2-amino-5-methylpyridine). Decomposition occurred at about 150°C to give a brown solid. IR (Nujol, NaCl): no N–H str; elemental analysis: calcd: C 34.3, H 2.8, N 13.3; found: C 33.7, H 3.1, N 12.3.

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[8] a) X-ray crystal structure data for **1**: $C_{40}H_{40}N_{24}O_2Sn_7$, $M_r = 1719.79$, monoclinic, space group $P2_1/c$, $Z = 2$, $a = 13.9577(5)$, $b = 12.7540(5)$, $c = 14.8385(5)$ Å, $\beta = 107.182(2)°$, $V = 2523.6(2)$ Å^3, $\mu(Mo_{K\alpha}) = 3.470$ mm^{-1}, $T = 180(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 5231 reflections collected, 3156 were independent ($R_{int} = 0.044$). All of the O and C atoms of the THF molecule in the lattice are disordered over two 50:50 sites. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Final $R1 = 0.032$ $[I > 2\sigma(I)]$ and $wR2 = 0.073$ (all data).[8c13] b) X-ray crystal structure data for **2**: $C_{49.33}H_{50.67}N_{16}O_{0.33}Sn_7$, $M_r = 1703.89$, trigonal, space group $R\bar{3}$, $Z = 9$, $a = b = 20.8640(8)$, $c = 34.147(2)$ Å, $V = 12872.9(11)$ Å^3, $\mu(Mo_{K\alpha}) = 3.055$ mm^{-1}, $T = 180(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 7095 reflections collected, 4527 were independent ($R_{int} = 0.033$). The lattice-bound THF molecule (one for every three molecules of **2**) is disordered about a threefold axis. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Final $R1 = 0.038$ $[I > 2\sigma(I)]$ and $wR2 = 0.086$ (all data).[8c13]c) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137024 (**1**) and 137025 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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How Important is the Inert Matrix of Supported Enantiomeric Catalysts? Reversal of Topicity with Two Polystyrene Backbones[**]

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The development of efficient polymer-supported chiral reagents and catalysts has become an important research topic.[1, 2] This is a result of the advantages of heterogeneous systems for large-scale reactions and of the availability of new materials and methods provided by the advances in combinatorial chemistry.[3]

The preparation of these kinds of functionalized resins involves the immobilization of a modified chiral auxiliary in a polymeric matrix by grafting or copolymerization.[1–4] The role of the polymeric backbone is sometimes underestimated, but it is known that the chemical and textural properties of the polymer affect the efficiency of the supported species.[2] Therefore, important changes in the catalytic activity of a compound can be expected upon its immobilization. Although much less is known about the role played by the

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