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Synthesis, Characterization, and Oxidation Catalysis by a Novel (μ_3-Oxo)triruthenium Carboxylate Complex

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The synthesis and characterization of the first (μ_3-oxo)triruthenium carboxylate complex containing completely fluorinated carboxylate ligands are described. This complex has been shown to catalytically oxidize a variety of olefins using molecular oxygen as the primary oxidant. Mechanistic studies indicate these oxidations involve a free radical chain pathway.

Although previous studies of the fundamental chemistry of (μ_3-oxo)triruthenium carboxylate complexes have appeared in the literature,[1] only in the past few years have these compounds been utilized as catalysts.[2] Our recent report[3] that $Ru_3O(O_2CR)_6L_3^n$ (R = CH_3, C_2H_5; L = H_2O, PPh_3; n = 0, 1+) is an efficient catalyst for the selective oxidation of primary and secondary alcohols to aldehydes and ketones[3] using molecular oxygen as the oxidant is the only instance of O_2 activation by these trimers. This result encouraged attempts to use this complex as a catalyst for other substrates; however, olefin oxidations under our conditions were unsuccessful.

A related system, the family of rhodium carboxylate dimers, showed intriguing differences in acidity[4] when carboxylate ligands were exchanged for fluorinated carboxylates. Several researchers have reported[5] the ability of the fluorinated rhodium dimer to bind olefins while the nonfluorinated dimers will not. In addition, Doyle et al. have also shown[5b] that the perfluorobutyrate dimer binds olefins 3 times better than the trifluoroacetate complex. On the basis of these reports, we attempted to prepare a completely fluorinated analogue of the trimeric alcohol oxidation catalyst containing perfluorobutyrate ligands in place of the propionate ligands, in hopes that this complex would selectively oxidize olefins. Another overwhelming reason for the choice of perfluorobutyrate rather than trifluoroacetate ligands is the reported[1b] failure of Wilkinson et al. to prepare the (μ_3-oxo)triruthenium trifluoroacetate complex.

Synthesis of this complex is modeled after a method reported from this laboratory for preparing the rhodium perfluorobutyrate dimer.[4] Crude $Ru_3O(prop)_6(H_2O)_3^+$ (where prop = $CH_3CH_2O_2^-$), prepared as previously described,[3] was refluxed in a 10:1 mixture of perfluorobutyric (pfb) acid and perfluorobutyric anhydride for 30 min. The olive green solution was evaporated to dryness, and the resulting solid was dissolved in ether and filtered. The filtrate after evaporation was dried under vacuum at 50 °C overnight.

Table I. Spectroscopic Data for $[Ru_3O(pfb)_6(Et_2O)_3](pfb)$

^{19}F NMR (ppm, Referenced to Internal $CFCl_3$ at 0 ppm)
80.8, 81.2 (t), 116.7, 117.4 (q), 126.7, 127.2 (s)

FTIR (cm^{-1}, Nujol Mull)
1704 (s), 1242 (m), 1224 (s), 1120 (s), 974 (m), 936 (m), 821 (m)

UV–Vis (Acetonitrile)

λ, nm	ε	λ, nm	ε
375 (sh)	3383	760 (sh)	1312
575 (sh)	1574	950	1444

A variety of methods were used to identify and characterize this material; the data are given in Table I. Proton NMR spectra showed the absence of all propionate resonances, supporting complete conversion to the fluorinated complex, while ^{19}F NMR indicates two different kinds of perfluorobutyrate groups (bridging and an anionic counterion). The IR spectrum of this complex is decidedly different from that of the starting material; the H_2O peak at 3400 cm^{-1} is absent, and the carboxylate stretch occurs at 1704 cm^{-1} as compared with 1567 cm^{-1}.

The UV spectrum of the perfluorobutyrate complex shows a similar shift with the absorbances at 610 and 670 nm moving to 575 and 760 nm. A new absorbance appears at 950 nm as well. As further evidence for the existence of the trinuclear species, a titration with pyridine shows distinct changes in the spectrum upon the addition of 3 equiv of base. The shoulder of the charge-transfer band at 375 nm shifts to 415 nm with a subsequent decrease in intensity (ϵ = 2500). The peak at 575 nm becomes more distinct as well.

FAB MS performed on this complex gave a parent ion peak at m/z 1675, corresponding to a protonated $Ru_3O(pfb)_6(Et_2O)_3$ species. This evidence, combined with the elemental analyses,[6] leads us to formulate this complex as $[Ru_3O(pfb)_6(Et_2O)_x](pfb)$, where x = 1, 2, or 3, depending on the length of drying time. Without a crystal structure, a precise structure assignation cannot be made; however, it seems reasonable to assume this complex has the same general structure as other basic μ_3-oxo trinuclear carboxylate complexes.

We find that the perfluorobutyrate complex catalyzes olefin oxidations using molecular oxygen as the oxidant at 65 °C. The oxidations were carried out using an apparatus previously described,[7] with initial pressures of 40 psi of dioxygen. The solutions were 10^{-4}–10^{-5} M in catalyst and contained at least a 100-fold excess of substrate in acetonitrile solvent. All reactions were periodically monitored by GC and GCMS.

Several different olefins were attempted as substrates. In the oxidation of cyclohexene, products typical of a free-radical autoxidation process were observed after an induction period of about

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1 h. The major products, cyclohexene oxide, the allylic alcohol, and the ketone, were formed in roughly a 4:16:9 molar ratio after 3 h; significant amounts of other products were also observed in the gas chromatogram. The addition of benzoquinone, a free-radical trap, completely inhibited the reaction for a finite period, after which the reaction resumed, producing products similar to those in the unadulterated oxidations. This suggests that oxidation of the alkene resumes after the oxidation of the quinone is complete.

An induction period of 24 h was observed in the oxidation of norbornene to norbornene oxide, similar to that seen in work recently reported from this laboratory[8] utilizing the high-valent oxoruthenium complex $[Ru(O)_2(dmp)_2](PF_6)_2$ or Ru(dmp) (dmp = 2,9-dimethyl-1,10-phenanthroline). The Ru(pfb) complex was slightly less active than this previously reported catalyst, producing 22 turnovers in 48 h as compared to 37 turnovers in the same period of time for the Ru(dmp) catalyst.

In order to determine the stereoselectivity of the reaction, the oxidation of *trans*-β-methylstyrene was attempted. This reaction proceeded even more slowly than the previous oxidation, producing only trace amounts of the trans epoxide after 40 h. The major products of the reaction were those due to the cleavage of the double bond—benzaldehyde and acetaldehyde.

The last substrate attempted, hexamethyl(Dewar benzene) (HMDB), was chosen in order to distinguish between a free radical chain mechanism and one involving a caged radical pair. Traylor reports[9] autoxidation processes produce hexamethylbenzene as product while a caged radical pathway produces epoxide when *m*-chloroperbenzoic acid is used as the oxidant. Under our conditions, with O_2 as the oxidant, no observable distinction in either amount or type of product formed could be made between a blank (using O_2 with no catalyst) and a typical catalytic run. Another major disadvantage of this substrate is its sensitivity to light and elevated temperatures.[10] For these reasons, HMDB has limited use as a substrate for mechanistic information in catalytic oxidation studies, especially when O_2 is used as the primary oxidant.

These reactions show a marked solvent dependency as well. With norbornene as the substrate, a series of reactions were run in a variety of solvents. In acetonitrile, 30 turnovers in a 48-h period were achieved, while no reaction was observed in benzonitrile, pyridine, or nitrobenzene. Approximately 5 turnovers in 48 h were achieved in ethanol. We attribute these results to the increased solubility of O_2 in acetonitrile compared to that in the other solvents used. The decrease in activity seen in ethanol is attributed primarily to its ability to act as a free-radical trap. These experiments, combined with the fact that addition of AIBN (azobis(isobutyronitrile), a free-radical initiator) to a norbornene reaction mixture containing catalyst decreases the induction period and increases the number of turnovers achieved (from 30 to 70 in 48 h), all indicate a free-radical mechanism is involved in these oxidations. A caveat is implicit in these results as the conversion of norbornene to the epoxide is not as inert to free-radical autoxidation processes as has been previously assumed.

The activity of the catalyst levels off after 150 h of reaction time in a typical norbornene oxidation. Analysis of the spent catalyst indicates the perfluorobutyrate complex decomposes during the reaction. Fluorine NMR spectra of aliquots taken before the reaction, at the end of the induction period (24 h), and at 48 h indicate significant changes in the catalyst are occurring. A new resonance at 119 ppm appears after 24 h of reaction time, while the resonance at 117 ppm disappears. The 117 ppm peak completely vanishes at 48 h, leaving only the 119 ppm and the original 116 ppm peak in that region. The ν_{CO} stretch in the FTIR spectrum shifts similarly toward that of the free acid, moving approximately 20 cm^{-1} higher. Several possibilities arise, including the reduction of one or more of the ruthenium centers with retention of the μ_3-oxo framework, production of a dimeric or monomeric species (which could be the active catalytic species), or complete degradation of the complex. Experiments are currently under way to examine these options.

These results lead us to believe that the mechanism for these oxidations involves generation of a hydrocarbon radical, hydrogen atom abstraction, reaction of the radical with O_2 to form a hydroperoxide, and subsequent Haber–Weiss decomposition of this hydroperoxide. Admittedly, the free-radical autoxidation of olefins is of limited interest. The mild reaction conditions and the use of molecular oxygen as the oxidant suggest potential use of this *novel* (μ_3-oxo)triruthenium carboxylate cluster as an oxidation catalyst and led us to report the characterization of this material. Further studies in the oxidation of alkanes are encouraging.

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