**Figure 1.** ORTEP drawing of trichloro (1-methylcytosine) gold. Non-Hydrogen atoms shown as 20% ellipsoids. Values averaged from two independent molecules. Additional angles: Cl–AuCl3, 178.2 (2)°; Cl2–Au–N3, 177.8 (4)°.

variety of cytosines and metal-coordinated cytosines.[15] Examples include 119.3° and 120.3° in MeCyt,[16] 119.4° and 120.9° in cytidine,[19] ca. 119° and ca. 122° in cytosine,[15] usually 120–121° and 119–122° in platinum–MeCyt complexes,[17] and 121.5° and 121.2° in a dimeric mercury(II)–MeCyt complex.[20] A notable exception occurs when the ligand is protonated at the N3 position. The C2–N3–C4 bond angle in MeCyt·HBr expands to 127°, and the C6–N1–C2 angle shrinks to 114°.[18]

Due to the strong oxidizing ability of Au(III)Cl4⁻, this particular Au(III) species probably would not be stable in biological fluids. However, the Au(III) oxidation state could be stabilized by coordination to appropriate ligands. In the hard–soft–acid–base context of Pearson,[21] nitrogen ligands should favor the harder Au(III) oxidation state, in contrast to the soft sulfur and phosphorus ligands that form very stable complexes with the softer Au(I) ion. Thus, Au(III) could be biologically relevant if coordinated to DNA bases or other suitable ligands. Redox potentials for complexes of this type would provide information on the relative stability of the Au(III) oxidation state.

**Supplementary Material Available:** Tables of final atomic positional parameters, final anisotropic thermal parameters, selected interatomic distances, and bond angles for trichloro(1-methylcytosine)gold (4 pages). Ordering information is given on any current masthead page.

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## Aerobic Epoxidation of Olefins with Ruthenium Porphyrin Catalysts

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Interest in hydrocarbon oxidation has stimulated a major effort to model the oxygen activation and transfer reactions characteristic of cytochrome P-450.[1,2] Model and enzymic studies have implicated the intermediacy of an oxoiron intermediate in the probable catalytic cycle.[3,4] The stoichiometry of the reaction requires two electrons from an exogenous source. Thus, most of the model systems have employed peroxidic oxidants such as iodosylbenzene or hypochlorite. The reductive activation of dioxygen has been reported in several cases[2g,i] but each requires the consumption of at least stoichiometric amounts of a reducing agent. Clearly, the development of a practical catalyst for the oxidation of hydrocarbons must achieve access to the reactive oxometal species without the need for a coreductant. We describe here the first such system.

We have discovered that dioxo(tetramesitylporphyrinato)ruthenium(VI) [Ru(TMP)(O)₂, **1**][5] catalyzes the aerobic epoxidation of olefins at ambient temperature and pressure. In a typical experiment, 8–12 mM **1** in benzene was stirred with a 50-fold excess of the olefin under an O₂ atmosphere for 24 h at 25 °C. After isolation of volatile components by vacuum distillation, quantitative analysis and identification of the products were performed by GLPC and GC–MS. As shown in Table I, 16–45 equiv of epoxide, based on the amount of catalyst, was produced over 24 h for a number of olefins.

While the mechanism of this oxygen activation and transfer is not yet certain, the following observations severely limit the possibilities. Manometric measurements of oxygen uptake during the oxidation of cyclooctene indicated that 2 mol of epoxide were produced for each mole of dioxygen consumed. The yield of cyclooctene oxide was found to be independent of oxygen pressure over the range of 15–60 psi and olefin concentrations of 0.5–1.5 M. The epoxide yield varied linearly with the amount of catalyst used. After 24 h, traces of **1** and Ru(TMP)CO and a large amount of an unstable paramagnetic ruthenium porphyrin complex were isolated from the reaction mixture.

The epoxidation of *cis-* and *trans-β*-methylstyrene proceeded with nearly complete retention of configuration, similar to the results we have reported for iron[2c] and chromium[2b] based metalloporphyrin systems. Also similar to the iron tetramesityl-

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**Table I.** Olefin Epoxidation by Ru(TMP) (O)$_2$ (1)$^a$

| substrate | M | cis-oxide | equivalents of epoxide | |
| --- | --- | --- | --- | --- |
| | | | trans-oxide | norbornene oxide |
| cyclooctene | 0.5 | 26$^b$ | | |
| cis-β-methylstyrene | 0.5 | 32.7 | 1.5 | |
| trans-β-methylstyrene | 0.5 | 0.1 | 16.2 | |
| norbornene | 0.5 | | | 43$^c$ |
| cis-β-methylstyrene | 0.4 ⎫ | 28.6 | 2.0 | |
| trans-β-methylstyrene | 0.4 ⎬ | | | |
| cis-β-methylstyrene | 0.5 ⎫ | 7.3 | 0.4 | 22.6 |
| norbornene | 0.5 ⎬ | | | |
| trans-β-methylstyrene | 0.44 ⎫ | | 0.6 | 45.6$^c$ |
| norbornene | 0.44 ⎬ | | | |

$^a$ All reactions in benzene at 25 °C with 10 mM **1**. β-Methyl-styrenes did not isomerize under the reaction conditions. $^b$ Cyclooctene oxide. $^c$ Simultaneous runs with a separate batch of **1**.
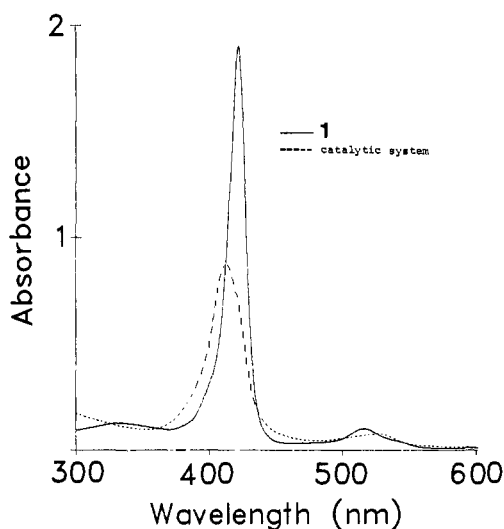


**Figure 1.** [1] 6.4 × 10$^{-6}$ M in benzene (—), λ$_{max}$ = 422 nm (1.904); [1] 6.4 × 10$^{-6}$ M with cyclooctene, 0.6 M in benzene after 130 min (---), λ$_{max}$ = 412 nm (0.876).

porphyrin–iodosylbenzene system was the observation that the cis olefin was 14.5 times more reactive than the trans in a competitive oxidation, suggesting a mechanistic similarity between the iron and ruthenium systems. This rate difference could be used advantageously to remove cis olefin from a stereoisomeric mixture. Thus, the catalytic oxygenation of a mixture that was initially 0.12 M in cis- and trans-β-methylstyrene (20 equiv each with respect to catalyst) with Ru(TMP)(O)$_2$ afforded >18 equiv of recovered olefin which was *99% trans*. In competitive oxidations of these olefins with added norbornene, a relatively constant amount of total epoxide was produced. Further, the rate of oxidation (of cyclooctene) was invarient with time and the total yield of epoxide was independent of olefin concentration above 50 equiv. The results show that norbornene was significantly more reactive than either cis- or trans-β-methylstyrene but that a step other then oxygen transfer must be rate limiting.

Under anaerobic conditions, Ru(TMP)(O)$_2$ was found to be a competent *stoichiometric* oxidant. The reaction of **1** with excess norbornene in benzene/pyridine under helium afforded 1.6 equiv of norbornene oxide and Ru(TMP)(pyr)$_2$. Further, the aerobic oxidation of Ru$^{II}$TMP(THF)$_2$ under these reaction conditions was observed to produce **1**. Thus, stirring a benzene solution of Ru$^{II}$TMP(THF)$_2$ under 1 atm of dioxygen afforded a 50% isolated yield of Ru$^{VI}$(TMP)(O)$_2$. A catalytic system of Ru$^{II}$TMP(THF)$_2$, dioxygen, and cyclooctene in benzene afforded 4 equiv of cyclooctene oxide after 24 h. Similarly, with Ru$^{II}$TMP(CH$_3$CN)$_2$ as the catalyst, 7.5 equiv of epoxide were produced but Ru(TMP)CO and Ru(TMP)[P(OMe)$_3$]$_2$ were completely inactive under these

**Scheme I**
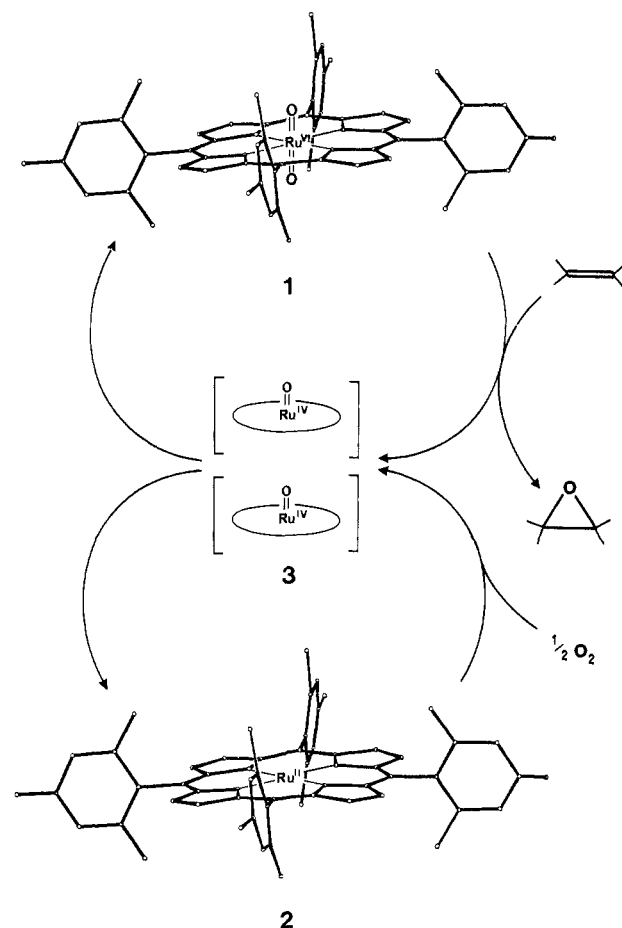


conditions. The ortho buttressing of the TMP ligand was found to be essential for catalytic activity. Thus, the tetra-p-tolyl-porphyrin Ru(TTP)(THF)$_2$, which is known to form a μ-oxo dimer upon oxygenation,[6] was also inactive as an oxygenation catalyst.

Taken together these results are consistent with Ru(TMP)(O)$_2$ (**1**) as the active oxidant and a transient ruthenium(II) complex **2** as the species reactive toward dioxygen. As we have reported elsewhere,[5] the oxidation of Ru$^{II}$TMP(CO) with iodosylbenzene or peroxyacids was observed to afford **1** *without observable intermediates*. A reasonable interpretation is that an initially formed oxoruthenium(IV) complex, **3**, disproportionates rapidly to **1** and Ru$^{II}$TMP. Inspection of the visible spectrum of an active catalytic system showed that the catalyst inventory contained no Ru(II) and very little **1** (Figure 1). On this basis, we suggest the mechanism in Scheme I for this catalytic oxygenation. The details of the mechanism and the nature of the catalytic intermediate are under further study.[7,8]

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## Tetrakis(1,3-dithiol-2-ylidene)cyclobutane: A Novel and Promising Electron Donor for Organic Metals

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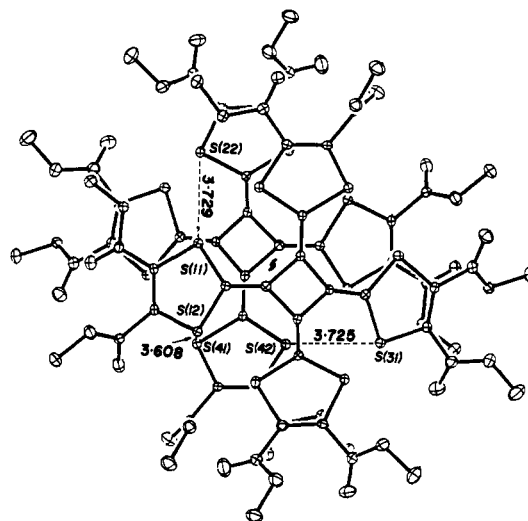Kyoto University, Yoshida, Kyoto 606, Japan*

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In the past decade much interest has been directed toward development of organic metals.[1] Some organic radical cation salts derived from tetrathiafulvalene (TTF) and tetraselenaful-valene derivatives have been found to show superconductivity albeit at very low temperatures.[2] In order to stabilize the metallic state of organic metals at higher temperatures and eventually to attain superconductivity at a technologically useful temperature, molecular design and synthesis of new electron donors having a different skeletal structure from that of TTF are needed, in addition to further modification of TTF involving replacement of sulfur with the other chalcogenides and introduction of new substituents. In this paper we wish to report the synthesis, molecular structure, and electrochemical property of a novel and promising electron donor for organic metals, tetrakis(1,3-di-thiol-2-ylidene)cyclobutane (1a, "1,3-dithiol[4]radialene")[3] whose half unit, ethanediylidene-2,2'-bis(1,3-dithiole) (2) has already been shown in our laboratory to give an organic metal composed of 1:1 charge-transfer salt with tetracyanoquinodimethane (TCNQ).[4]

The new [4]radialene was synthesized as shown in Scheme I. Thus, ethanediylidene-2,2'-bis(4,5-dicarbomethoxy-1,3-dithiole) (3)[5] was converted quantitatively to the 1,2-dibromo-substituted derivative 4 by the reaction with 2 equiv of bromine in CCl₄ (25 °C, 1 h). Treatment of a THF solution of 4 with ¹/₂ equiv of Ni(PPh₃)₄ in the presence of an excess of Zn–Cu couple (25 °C, 12 h),[6] followed by column chromatography of the reaction mixture on silica gel with CH₂Cl₂–CH₃CO₂C₂H₅ (8:1) afforded the octacarbomethoxy-substituted derivative of 1a, 1b (purple brown needles; mp 235–238 °C (benzene–hexane)) in 30% yield. The target molecule 1a[7] (reddish orange needles; mp 170 °C dec

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(4) The electrical conductivities in the single-crystal state are 12 and 23 Ω⁻¹ cm⁻¹ at 300 and 200 K, respectively. This result will be reported elsewhere.

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**Figure 1.** Stacking structure of **1b** molecules projected along the crystallographic 2₁ axis parallel with the *c* axis of the unit cell.

**Scheme I**



1a : R = H
1b : R = CO₂Me
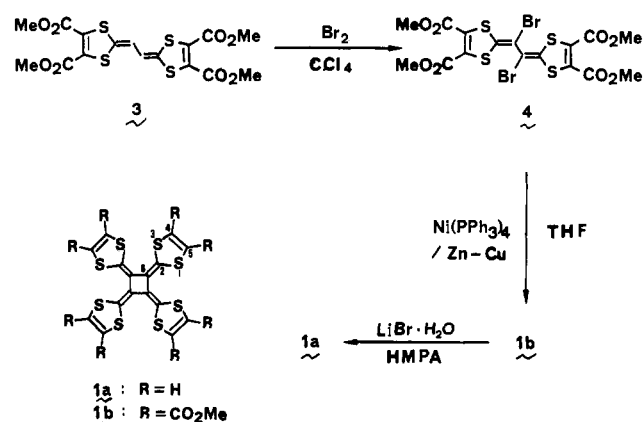
(benzene)) was obtained in 88% yield by treating **1b** with an excess of LiBr·H₂O in HMPA (95–155 °C, 2 h).

Cyclic voltammetry was performed on the [4]radialenes in CH₂Cl₂ containing (*n*-Bu)₄NClO₄ as supporting electrolyte by use of platinum working and standard silver/silver chloride reference electrodes. The three-step oxidation was found to occur at each potential of +0.19, +0.98, and +1.30 V for **1a**, and of +0.70, +1.29, and +1.79 V for **1b**, respectively. Only the first step showed complete reversibility. From the change of peak current at the first step with respect to sample concentration this step was determined to involve a two-electron transfer,[8] and according to the Myers–Shain method[9] the two-electron step was divided into two one-electron steps with oxidation potentials, $E_1$ and $E_2$, that are +0.20 and +0.24 V for **1a** and +0.65 and +0.70 V for **1b**, respectively. In compairing the $E_1$, $E_2$, and ($E_2 - E_1$) values of **1a** with those of **2** (+0.20 and +0.36 V)[5] and TTF (+0.27 and +0.63 V), we note that the $E_1$ values of **1a** and **2** are almost equal[10] and relatively smaller than that of TTF, indicating that the former two compounds have higher electron-donating ability. The $E_2$ values follow in the order TTF > 2 > 1a and follow the

(7) Satisfactory elemental analyses and spectral data were obtained for **1a** and **1b**. As compared with **1b**, **1a** is less stable and especially sensitive to light.

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(10) The unexpectedly large $E_1$ value of **1a** is due to the nonplanarity of four 1,3-dithiole rings, as seen in the X-ray structure of **1b**. However, such a nonplanar restriction should parly be released in the radical cation state (1a⁺·), providing the very smaller $E_2$ value. A similar interpretetation was made in the redox behavior of 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-[10-(1,1-dicyanomethylidene)anthryliden-9-ylidene]cyclopropane (Wellman, D. E.; West, R. *J. Am. Chem. Soc.* **1984**, *106*, 355).