other hydrocarbons of Table IX can then be approximated from their percentage yields (Table XII). Included in Table XII for comparison are rate constants for epoxidation of the various alkenes by *m*-chloroperoxybenzoic acid (**MCPBA**). Inspection of Table XII shows that the $[(TPP)(Cl)Fe^{IV}=O]^{+\cdot}$ species is more reactive and less selective as an epoxidizing agent then is **MCPBA**. Though there are few rate constants available for comparison, the data that are available provide the linear free energy relationship of eq 23. The reactivity of the $[(TPP)(Cl)Fe^{IV}=O]^{+\cdot}$

$$\log k_{[(TPP)(Cl)Fe^{IV}=O]^{+\cdot}} = 0.3 \log k_{MCPBA} + 1.4 \quad (23)$$

is obviously much less sensitive to the nucleophilicity of the alkene then is *m*-chloroperoxybenzoic acid.

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Note Added in Proof. The results of this study establish without doubt that the *N*-oxide of *p*-cyano-*N*,*N*-dimethylaniline transfers an oxygen atom to *meso*-(tetraphenylporphinato)iron(III) chloride quantitatively. The arguments by Burka et al.[47] that this is not so must now be considered as erroneous.

Registry No. NO, 62820-00-2; **DA**, 1197-19-9; **MA**, 4714-62-9; **MA** ethyl carbamate derivative, 97860-70-3; **MA**-*methyl*-d_3 ethyl carbamate derivative, 97860-71-4; **MA**-methyl-d_3, 97860-72-5; **A**, 873-74-5; **A** ethyl carbamate derivative, 21703-06-0; H, 79121-26-9; **FA**, 97860-68-9; **MD**, 97860-69-0; **PNO**, 51279-53-9; Cl_2CH_2, 75-09-2; $(TPP)Fe^{III}Cl$, 16456-81-8; HCHO, 50-00-0; ClC(O)OEt, 541-41-3; $PhN(Me)CD_3$, 88889-00-3; *p*-$CNC_6H_4N(CD_3)_2$, 88889-02-5; $(CH_3)_2C{=}C(CH_3)$, 563-79-1; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHPh, 103-30-0; D_2, 7782-39-0; $[(TPP)(Cl)Fe^{IV}=O]^{+\cdot}$, 97877-23-1; cyclohexane, 110-82-7; cyclohexene, 110-83-8; cyclohexanol, 108-93-0; 2-cyclohexen-1-ol, 822-67-3; bicyclo[2.2.1]hept-2-ene, 498-66-8; tetramethyloxirane, 5076-20-0; 7-oxabicyclo[4.1.0]heptane, 286-20-4; 3-oxatricyclo[3.2.1.$0^{2,4}$]octane, 278-74-0; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2; 2,4,6-tri-*tert*-butylphenol, 732-26-3.

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Communications to the Editor

Trichloro(1-methylcytosinato)gold(III). Model for Gold–DNA Interactions

Marko S. Holowczak, Mark D. Stancl, and Geoffrey B. Wong*

Department of Chemistry
University of Southern California
Los Angeles, California 90089-1062

Received January 7, 1985

Attention to gold coordination chemistry has been growing in recent years because of its relevance to the gold antiarthritic drugs and the possible antitumor properties of certain gold compounds.[1-3] One specific area of interest has been the interaction between DNA and gold(I) or gold(III). Studies using viscometry and UV spectroscopy suggest that $AuCl_4^-$ binds to DNA.[4] Model gold(III) complexes with various adenine derivatives have been studied chromatographically.[5] Complexes with guanosine and related compounds also have been isolated and characterized by NMR, infrared, and Mössbauer spectroscopies.[6,7] Triethylphosphinogold(I) has recently been found to bind to DNA in a nondenaturing fashion.[8] Complexes between gold(I) and guanosine (and the related inosine) have been partially characterized.[6] However, structural data have not been reported on any gold–DNA model compounds. We present here the first such complex to be characterized crystallographically, trichloro(1-methylcytosine)-gold(III).

The title compound was prepared by mixing 300 mg (0.83 mmol, 1 ml H_2O) of $NaAuCl_4$ with 104 mg (0.83 mmol, 3 mL of H_2O) of 1-methylcytosine (MeCyt) (Vega Biochemicals). Soon afterward, the product precipitated as a fine yellow powder. It was collected, washed with water, dried, and recrystallized from acetonitrile/isopropyl alcohol by slow evaporation: mp ~183 °C dec. Anal.[9] Calcd for $C_5H_7AuCl_3N_3O$: C, 14.02; H, 1.65. Found: 14.27; 1.68. Proton NMR (CH_3CN-d_3) δ 7.25 (br, NH_2, 7.55 d, H(6), 5.98 (d, H(5)), 3.40 (s, CH_3).

Crystal data: space group $P2_1/c$; a = 6.944 Å, b = 22.930 c = 13.061 Å, β = 94.54; Z = 8. Intensity data were collected on a Syntex $P2_1$ automated four-circle diffractometer with Mo Kα radiation. Full-matrix least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms, converged to a final R factor of 0.048. Two crystallographically independent molecules were located.

A view of one of the molecules is shown in Figure 1. Three chlorine atoms and the N3 define a nearly square-planar coordination geometry, which is typical for Au(III). The Au–N distance of 2.031 Å (2.039 (15) and 2.023 (16) Å) compares with other reported Au–N distances: 2.09 and 2.58 (axial) in [Au(2,9-dimethylphenanthroline)Cl_3];[10] 2.08 and 2.61 (axial) in [Au(2,9-dimethylphenanthroline)Br_3];[10] 1.93 (shorter for steric reasons), 2.029, and 2.018 in $[Au(terpy)Cl]^{2+}$;[11] 1.98–2.04 in [Au(tetraphenylporphyrin)Cl];[12] 2.031 in [Au(1,4-benzodiazepin-2-one)Cl_3],[13] and 2.01 in $[Au(NH_3)Cl_3]$.[14] In Au(MeCyt)Cl_3 the cytosine ring lies almost perpendicular to the $AuCl_3$ plane, with a dihedral angle of 85° between the two least-squares planes. Such a large angle would be expected to minimize steric repulsion. Within the ligand, bond distances and angles appear to be relatively little affected by gold binding, although the C2–N3–C4 angle of 123° is slightly larger than the usual range for cytosines. Typically, the C2–N3–C4 and C6–N1–C2 angles are 119–121° and 119–123°, respectively, in a

* Present address: Raychem Corporation, 300 Constitution Dr., Menlo Park, CA 94025.

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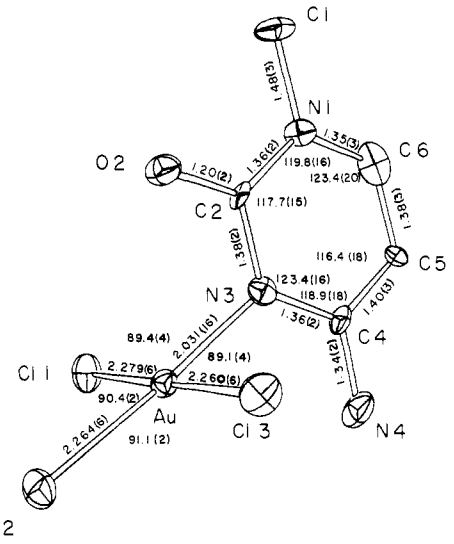

Figure 1. ORTEP drawing of trichloro (1-methylcytosine) gold. Non-Hydrogen atoms shown as 20% ellipsoids. Values averaged from two independent molecules. Additional angles: C1-AuCl3, 178.2 (2)°; Cl2-Au-N3, 177.8 (4)°.

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 $Au(III)Cl_4^-$, 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.

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Registry No. $NaAuCl_4$, 15189-51-2; (1-methylcytosine)trichlorogold, 97752-09-5.

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

John T. Groves* and Robert Quinn

Department of Chemistry, The University of Michigan Ann Arbor, Michigan 48109

Received April 29, 1985

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 O_2 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-

*Current address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

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