Table I. Characterization of the Bimetallic Particles

precursor complexes	metal content/wt %	atomic ratio Fe/M cluster	atomic ratio Fe/M particle[a]	particle size/Å	comments
$H_2FeOs_3(CO)_{13}$	1,0	0.33	0.27 (0.05)	10–15	bimetallic particles only
$Fe_3(CO)_{12} + Os_3(CO)_{12}$	0,8	0.33	0	10–15	no Fe detected in all the particles
$H_2FeRu_3(CO)_{13}$	0,8	0.33	0.30 (0.15)	10–15	bimetallic particles only
$Fe_3(CO)_{12} + Ru_3(CO)_{12}$	1,1	0.33	0	10–50	no Fe detected in all the particles
$HFeCo_3(CO)_{12}$	0,9	0.33	0.33 (0.03)	20–40	bimetallic particles only

[a] Average ratios. The errors given in parentheses encompass all the values measured on at least 20 particles.

shown that, in the initial stage of the chemisorption, these clusters underwent proton abstraction by OH groups of the surface to give respectively $[HFeOs_3(CO)_{13}]^-$, $[HFeRu_3(CO)_{13}]^-$, and $[FeCo_3(CO)_{12}]^-$ (the cation being Mg^{2+} from the surface).[16] After removal of the solvent under vacuum, these supported anionic clusters were then treated under H_2 (400 torr) at 400 °C for 16 h. The final metal content was usually close to 1% (wt).

Coadsorption of two separate clusters ($Fe_3(CO)_{12} + M_3(CO)_{12}$ (M = Ru, Os); Fe/M = 1/3) was carried out under identical conditions. The two clusters were first adsorbed simultaneously on the magnesia support from a CH_2Cl_2 solution. $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$ were first strongly chemisorbed as $[HFe_3(CO)_{11}]^-$,[17] $[HRu_3(CO)_{11}]^-$,[18] and $[HOs_3(CO)_{11}]^-$.[19] Then, after removal of the solvent under vacuum, they were treated under H_2 (400 torr) at 400 °C for 16 h.

All these systems have been characterized by high-resolution analytical electron microscopy. Images were taken with a JEOL 100 C TEM and with a VGHB 501 field emission gun STEM. The latter, equipped with a Si-Li X-ray detector and TRACOR 5500 analyzer, was used to perform quantitative energy dispersive analysis (EDX) with a spatial resolution as small as 1 nm^2. Analysis has been carried out on large area of magnesia as well as on individual particles ranging from 1 to 5 nm. The atomic ratios between two elements were determined with an accuracy of 15%. Figure 1 gives a TEM view of a 2-nm FeCo bimetallic particle supported on magnesia.

The results of Table I indicate that for all the mixed-metal clusters studied, the particles are small and have a bimetallic composition. Besides, in two cases, the bulk composition of these particles is the same, within experimental error, as that of the starting clusters. Interestingly, the coimpregnation of $Fe_3(CO)_{12} + Os_3(CO)_{12}$ or $Fe_3(CO)_{12} + Ru_3(CO)_{12}$ does not result, after H_2 treatment, in the formation of bimetallic particles. In contrast, $H_2FeRu_3(CO)_{13}$ osmium or ruthenium particles are observed. Although iron was detected by EDX on large ensembles of MgO crystallites, the images did not show any contrast that could be attributed to Fe particles. This might indicate that iron is scattered all over the magnesia, probably in an oxidized form. With the $H_2FeRu_3(CO)_{13}$ precursor, the particles were found to be bimetallic but a reliable quantitative analysis of the Fe/Ru ratio could not be achieved. Although both Fe Kα and Ru Kα peaks were detected when the electron beam was scanned over the metal particles, the number of counts that could be accumulated under each peak was low, which leads to large statistical errors. Low counting rate was due to the instability of the Fe–Ru particles moving under the intense electron beam. In contrast Fe–Os particles were stable because of the low mobility of osmium (high melting point) and Fe–Co particles did not move because of their large size.

These results indicate that heteropolynuclear clusters supported on magnesia can be used to obtain small supported bimetallic particles of the same composition. Besides, coimpregnation of magnesia by two different monometallic clusters does not lead to the same results. The reasons why bimetallic molecular clusters exhibit such behavior is not clear. Indeed, the temperatures at which two different monometallic clusters start to decompose into metal particles are different,[18] and this may lead to separate metallic phases. In contrast, upon destruction of the heteropolynuclear clusters, the preexistence of metal–metal bonds might favor the formation of new metal–metal bonds between the two elements in the metal particles.

Acknowledgment. Support from NATO to S.G.S. and J.M.B. and support to S.G.S. from the National Science Foundation through Grant No. CHE 84-11630 is gratefully acknowledged.

Registry No. MgO, 1309-48-4; $H_2FeOs_3(CO)_{13}$, 12563-74-5; $H_2FeRu_3(CO)_{13}$, 12375-24-5; $HFeCo_3(CO)_{12}$, 21750-96-9; Fe, 7439-89-6; Os, 7440-04-2; Ru, 7440-18-8; Co, 7440-48-4.

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An Efficient Electrocatalytic Model Cytochrome P-450 Epoxidation Cycle

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We describe here an electrocatalytic cycle (Scheme I) in which molecular oxygen is activated toward olefin epoxidation by electrolytic reduction. This cycle is of special interest since it contains the essential elements of the cytochrome P-450 catalytic cycle:[1] dioxygen, reducing equivalents, metalloporphyrin catalyst, substrate, and activator.

The cycle has three major segments, each independently having literature precedent: (1) Initial reduction to Mn(II) with loss of chloride[2] followed by strong dioxygen binding[3] promotes a second reduction step to a Mn(II) superoxo complex.[4] (2) The latter, $(Mn^{II}Por)O_2^-$, complex has been shown to react with benzoyl chloride[5a] and with anhydrides[5b] to give metallo-acylperoxy complexes that undergo O–O bond heterolysis at room temperature to yield a high-valent manganese porphyrin complex capable of transferring one oxygen atom to a suitable substrate. (3) The reactivity of high-valent manganese with olefins has been extensively studied.[5a,6] Typically, the high-valent form is generated

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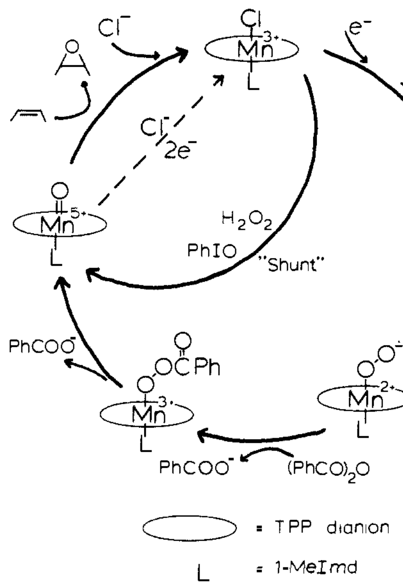
Table I. Olefin Epoxidation Systems[a]

entry	system	substrate (rel ratios)[b]	product (rel ratios)[c]	faradaic efficiency	turn-overs
1	Mn(TPP)Cl, O_2, electrons[d,e]	C			0[i]
2	Mn(TPP)Cl, O_2, electrons, anhydride[d–f]	C	CO	56%	11
3	Mn(TPP)Cl, O_2, electrons, anhydride[d–f]	C:T (1:1)	CO:TO (15:1)	44%	5
4	Mn(TPP)Cl, PhIO[d,g]	C:T (1:1)	CO:TO (15:1)		20
5	3-chloroperoxybenzoic acid[g]	C:T (1:1)	CO:TO (4:1)		
6	Mn(TPP)Cl, H_2O_2, anhydride[d,f,h]	C	CO	95[j]	20
7	H_2O_2, anhydride[f,h]	C	CO	3[j]	

[a] All experiments done in stirred dichloromethane containing 1-methylimidazole (20 mM). [b] Substrates: C = cyclooctene, T = *trans*-2-octene, all olefins 100 mM. [c] Products: CO = cyclooctene oxide, TO = *trans*-2-octene oxide, as identified using retention times and standards. [d] Mn(TPP)Cl = 0.5 mM. [e] Electrolysis potential = –0.4 V vs. NaSCE. [f] Anhydride = benzoic anhydride, 0.44 M. [g] Added oxidant = 12.5 mM. [h] H_2O_2 gradually added as 30% solution to give a final concentration 10 mM (20 equiv/Mn). [i] Partial catalyst destruction. [j] Efficiency based upon H_2O_2 added.

Scheme I



from manganese porphyrin and an oxygen-atom transfer agent, such as iodosobenzene,[6c,g–i] hypochlorite,[6a,b] or peroxides[6d,n] (Scheme I, "shunt" pathway). Recent reports[6e,j–m] have used chemical reducing agents with dioxygen to effect epoxidation; these schemes tend to suffer from low efficiencies with respect to reducing agent, poor catalyst stability, and conditions under which product is unstable.

We have electrolyzed CH_2Cl_2 solutions of manganese(III) tetraphenylporphyrin chloride [Mn(TPP)Cl, 0.5 mM] containing an axial base (1-methyl imidazole, 20 mM), olefin (cyclooctene, 100 mM), benzoic anhydride (0.44 M), and supporting electrolyte (Bu_4NClO_4, 0.2 M). In a typical experiment (Table I; entry 2), a 6-h reductive electrolysis at –0.4 V vs. NaSCE at a glassy carbon plate electrode, with continuous O_2 purging, led to 5.7 mM of the epoxide, cyclooctene oxide, as the only detectable (GLC) product in the resulting solution. This corresponds to a minimum of 11 turnovers of the porphyrin catalyst and, from the amount of epoxide produced and reductive charge passed during the electrolysis, a faradaic efficiency of 56% based on two electrons per turnover. This is a high efficiency compared to analogous systems[6e,j–m] in the literature where the reducing equivalents were supplied by a chemical reductant. Furthermore, the current and the faradaic efficiency remain constant during the electrolysis, consistent with an electrocatalytic process that is fast on the electrolysis time scale. Visible spectra detect no loss (±2%) of porphyrin catalyst during electrolysis.

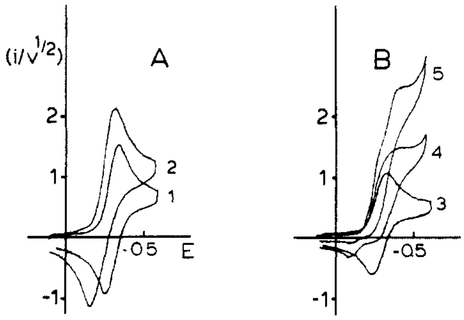


Figure 1. Cyclic voltammetry of Mn(TPP)Cl in 0.2 M Bu_4NClO_4/dichloromethane at glassy carbon, vs. NaSCE reference: (A) Mn(TPP)Cl only in (1) deareated, 50 mV/s, and (2) dioxygen-saturated solution, 50 mV/s; (B) Mn(TPP)Cl plus 5 mM 1-methylimidazole and 0.44 M benzoic anhydride in (3) deaerated, 50 mV/s, and in dioxygen-saturated solution at (4) 50 and (5) 10 mV/s. All current normalized to (sweep rate)$^{1/2}$, with dimensions μa s$^{1/2}$ mV$^{-1/2}$.

Both Mn(TPP)Cl and anhydride are needed to realize epoxidation. Without porphyrin, only background current is observed, amounting to <3% of the charge passed with porphyrin present and producing no detectable epoxide. Electrolysis without anhydride (compare entries 1, 2; Table I) leads to currents that die away, partial spectroscopic decay of catalyst, and again no epoxide production.

Metalloporphyrin-based epoxidations typically favor cis olefins, whereas more conventional oxidants such as *m*-chloroperoxybenzoic acid (MCPBA) favor trans olefins.[8] In a competition electrolysis (Table I; entries 3–5) using a 1:1 mixture of a cis olefin (cyclooctene) and a trans olefin (*trans*-2-octene), the cis/trans selectivity of the scheme (entry 3) matches that of the Mn(TTP)Cl/iodosobenzene/1-MeIm system (entry 4), not that of MCPBA (entry 5), confirming that the reactivity is metalloporphyrin based.

Hydrogen peroxide has been a nemesis[6d] of previous epoxidation schemes since directly added peroxide leads to epoxide production (Table I; entries 6, 7) and, in excess, to partial destruction of catalyst. It is accordingly significant that our experiment employs a combination of electrode material (glassy carbon) and electrolysis potential where direct electrolytic reduction of O_2 to H_2O_2 is kinetically inhibited. This ensures that our chemistry is based on reduction of Mn(III) and maintains the formal similarity to cytochrome P-450 (Scheme I), albiet with Mn not Fe.

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Cyclic voltammetry (Figure 1) was used to further probe the electrocatalytic system. Without dioxygen, all solutions have voltammograms typical of a one-electron reversible Mn(III/II) couple (Figure 1, curve 1, $E° = -0.27$ V). With dioxygen, the Mn(TPP)Cl reduction and oxidation peak currents[9] are increased (Figure 1, curve 2), consistent with partial oxygen binding and a net two-electron reversible reduction to a Mn(III) superoxo complex.[4] Voltammetry of a similar solution containing porphyrin and benzoic anhydride (Figure 1, curve 3) gives, upon dioxygen addition, greatly enhanced reduction currents (Figure 1, curves 4 and 5)[10] that, after normalization with respect to (scan rate)$^{1/2}$, have characteristic catalytic wave shapes and scan-rate dependencies. In Scheme I, the postulated high-valent manganese oxo-porphyrin should[11] be easily reduced (Scheme I, dashed arrow) at the potentials of the catalytic waves. In an electrolysis with olefin present, such a reduction occurs in competition with epoxidation, perhaps accounting for the less than 100% faradaic efficiencies. This kinetic competition should be amenable to further study by electrochemical methods.

This paper shows that electrochemistry provides a powerful new format within which to study model cytochrome P-450 systems. Judicious choice of electrode material and applied potential allows one to discriminate against undesired reaction pathways and background processes. We anticipate that the available electrochemical methodology will permit detailed study of the kinetics and mechanism of this and similar systems.

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Registry No. Mn(TPP)Cl, 32195-55-4; cyclooctene, 931-88-4; *trans*-2-octene, 13389-42-9; cytochrome P-450, 9035-51-2.

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(9) We have observed that the increases in current are less when larger quantities of chloride or axial base are used, owing to competition with O_2 binding (unpublished results, see also ref 6n).

(10) The transient oxidation wave at $E_p = -0.11$ V in Figure 1, curves 4 and 5, is associated with benzoate produced from the anhydride cleavage as will be detailed later. Benzoate may act as an axial base (L in Scheme I), displacing 1-MeImd at different stages of the cycle.

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Mechanistic Insight into the Photoinduced Rearrangement of the Tricyclo[4.1.0.0^{2,7}]heptyl Skeleton

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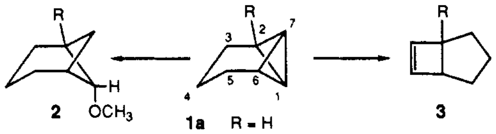
Electrochemically[1] and photochemically[2] induced single electron transfers from the HOMOs of highly strained polycyclic molecules have recently attracted considerable attention.[1-3] Although extensive effort has been focused on the photoinduced generation of one-electron carbon–carbon bonds within the framework of these polycyclic molecules, relatively little is understood concerning those factors which determine whether the intermediate cation radicals undergo valence isomerization,[3] nucleophilic solvent addition,[2a,b] or molecular rearrangement.[2c,d,4] This problem is illustrated by the conversion of **1a** [R = H, $E_{1/2}$ = 1.50 V][5] into **2a** and of **1b** [R = $CH_2Si(CH_3)_3$, $E_{1/2}$ = 1.37 V] into **3b** under identical photochemical conditions.[6] We now wish to report studies of a series of 2-substituted tricyclo[4.1.0.0^{2,7}]heptanes which provide additional mechanistic insights into the behavior of the intermediate cation radicals.



2 **3**

1a R = H
1b R = $CH_2Si(CH_3)_3$
1c R = $C(CH_3)_3$
1d R = $Si(CH_3)_3$
1e R = 1-Methylcyclopropyl

The first question to be answered was whether the rearrangement of the cation radical generated from **1b** was the result of the steric effect or of the electronic effect of the trimethylsilylmethyl substituent at C2. This was evaluated initially by placing a *tert*-butyl moiety at C2 of **1** [**1c**, R = $C(CH_3)_3$, $E_{1/2}$ = 1.38 V].[7,8] Under our standard photosensitized reaction conditions,[6] **1c** gave **2c** as the only isolable product (78% yield). In order to demonstrate that there was no major unique factor associated with the presence of a silicon moiety in the molecule, a trimethylsilyl group was placed at C2 of **1** [**1d**, R = $Si(CH_3)_3$, $E_{1/2}$ = 1.38 V]. Again, under our standard photosensitized reaction conditions, only **2d** was formed (86% yield). In addition, neither **1c** or **1d** gave rearrangement products related to **3** on prolonged photosensitized irradiation in tetrahydrofuran. These two studies suggest that it was neither the steric bulk nor the presence of the silyl group which promoted the rearrangement of **1b** to **3b** but rather the propensity of the trimethylsilylmethyl group to stabilize an adjacent incipient carbocationic center.[9] If the effect was primarily electronic, a group intermediate between the *tert*-butyl group and the trimethylsilylmethyl group in carbocation stabilizing power should give a mixture of **2** and **3**.

In order to test this theory, we prepared **1e**[7] (R = 1-methylcyclopropyl, $E_{1/2}$ = 1.26 V) and subjected it to our reaction conditions. Irradiation of a tetrahydrofuran solution of **1e** and 1-CN in Pyrex gave a 79% yield of **3e** as the only volatile product.[10] In contrast, irradiation of a methanolic solution containing 2 ×

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(5) The nonreversible oxidation potentials listed were determined by single-sweep cyclic voltammetry at a platinum electrode and referenced to a saturated calomel electrode.[1] The solvent used for these measurements was acetonitrile and the electrolyte was tetra-*n*-butylammonium perchlorate (0.1 M).

(6) The photochemical reactions were carried out in methanol containing 1-cyanonaphthalene (1-CN) as photosensitizer.[2] In general, a Rayonet reactor containing 16 300-nm lamps was used as the light source and the reactions were carried out in a Pyrex reaction vessel. Normally, 0.1% potassium hydroxide was added to the reaction mixture in order to prevent the acid-catalyzed rearrangement of **1**.

(7) The synthesis of **1** involved the addition of dibromo- or dichlorocarbene to the appropriate 3-substituted cyclohexene to yield the intermediate 2-substituted 7,7-dihalobicyclo[4.1.0]heptane. Treatment of this intermediate with methyllithium or *n*-butyllithium produced **1** via insertion of the initially generated cyclopropylidine. Experimental details will be provided in a full paper on this subject.

(8) Satisfactory elemental analyses and/or exact mass molecular weights have been obtained on all new compounds. In all cases, IR, ^{1}H NMR, and ^{13}C NMR data were consistent with the assigned structures.

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(10) Compound **3e** showed the following properties: bp 45–70 °C (10 mm); IR (neat) 3120, 3060, 2940, 1380, 730 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.90 (2 H, br s), 2.08 (1 H, br d), 2.0–1.2 (7 H, m), 1.15 (3 H, s), 0.50 (4 H, m); ^{13}C NMR (C_6D_6) δ 138.76 (d), 135.73 (d), 62.84 (s), 49.03 (d), 29.88 (t), 27.01 (t), 24.49 (t), 21.62 (q), 19.36 (s), 11.50 (t); mass spectrum, *m/e* 148.1250 (calcd for $C_{11}H_{16}$ 148.1252). Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.14; H, 11.06.

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