characterized[7] and has bond distances and angles similar to those in **1**. Other diferric compounds with two alkoxo,[8] phenoxo,[9] or hydroxo[10] bridges (or different combinations),[11] but lacking the bridging carboxylate ligand, have similar core geometries. From temperature-dependent magnetic susceptibility studies, compound **1** was found to be antiferromagnetically exchange coupled with a singlet ground state.[12] Such behavior is typical for complexes with a $\{Fe_2(OR)_2\}^{4+}$ or $\{Fe_2(OR)_2(O_2CR)\}^{3+}$ core, with one notable exception.[9c] The Mössbauer spectrum of a polycrystalline sample at 4.2 K revealed a single quadrupole doublet with an isomer shift of 0.52 mm/s and a quadrupole splitting of 0.62 mm/s. Taken together, the geometry, Mössbauer, and magnetic properties of **1** are characteristic of high-spin iron(III) and do not appear to be significantly affected by the novel ring structure of the molecule.

A growing number of polynuclear iron and manganese compounds with predominantly oxygen donor ligands have been synthesized and structurally characterized as interest in related biological units, particularly those in ferritin[1,13] and the oxygen-evolving complex of photosystem II,[14] has increased. Included[15] are a variety of M_4,[15b] M_6,[15c] M_8 (M = Fe, Mn[15d]), Mn_9, Mn_{10}, Fe_{11}, Mn_{12}, and $Fe_{16}M'$ (M' = Fe[15e], Mn, Co) complexes. The present molecule, $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, is distinguished from this set by its high symmetry, simple empirical formula, and aesthetically pleasing circular structure. The last property is reminiscent of a cyclic toroidal iron–sulfur cluster having the formula $[Na_2Fe_{18}S_{30}]^{8-}$.[16] Other ligand-bridged polynuclear compounds with ring structures have been characterized, including M_4 (M = Ti, Ni, W),[17] M_5 (M = Cu, Ag),[18] M_6 (M = Ni, Cu, Mo),[19] and M_8 (M = V, Ni, Cu, Mo).[20] Of these, the iron decamer most closely resembles the recently reported octanuclear cluster, $[Cu_8(3,5\text{-dimethylpyrazolate})_8(OH)_8]$.[20d]

The nature of the soluble complexes formed by the polymerization of iron in aqueous or alcoholic media has remained obscure despite numerous studies. The novel arrangement of $\{Fe(OR)_2(O_2CR)\}$ units in **1** suggests new possible structural motifs for several such species.[21] A cyclic hexanuclear complex $[Fe_6(OH)_{12}](OH)_6$ has been postulated to exist in solution,[22] and a series of compounds having the same general empirical formula as **1** have been reported but not structurally characterized.[23] Efforts to prepare and elaborate further the structural patterns found in this interesting class of polynuclear iron compounds are continuing.

Acknowledgment. This work was supported by grants from the National Institutes of Health and the National Science Foundation. K.L.T. also thanks the National Science Foundation for a predoctoral fellowship. We are grateful to Drs. P. Poganiuch and S. Liu for assistance with the magnetic and X-ray structural studies and to Dr. G. C. Papaefthymiou for obtaining the Mössbauer spectrum.

Supplementary Material Available: Tables of atomic positional and thermal parameters for **1** (5 pages). Ordering information is given on any current masthead page.

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Genomic Direction of Synthesis during Plasmid-Based Biocatalysis

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Plasmid-based biocatalysis[1] potentially requires the preparation of a single plasmid in order to synthesize all the enzyme substrates intermediate in a biosynthetic pathway. The plasmid contains extrachromosomal copies of genes which encode enzymes that influence commitment of carbon resources in the cell. Elevated concentrations of these enzymes direct a surge of carbon flow into the targeted pathway. Which enzyme substrate is synthesized once plasmid-based biocatalysis has created a surge of carbon flow? If the plasmid is introduced into a microbial strain devoid of a particular catalytic activity due to a genomic mutation, the substrate synthesized may correspond to the substrate of the missing enzyme.[1] Alternatively, elevated carbon flow through the pathway may lead to synthesis of the substrate of a rate-determining enzyme intermediate in the biosynthetic pathway.

This report examines the substrate(s) synthesized by *aro*E mutants of *Escherichia coli* following transformation with plasmids which drastically increase the flow of carbon into the common

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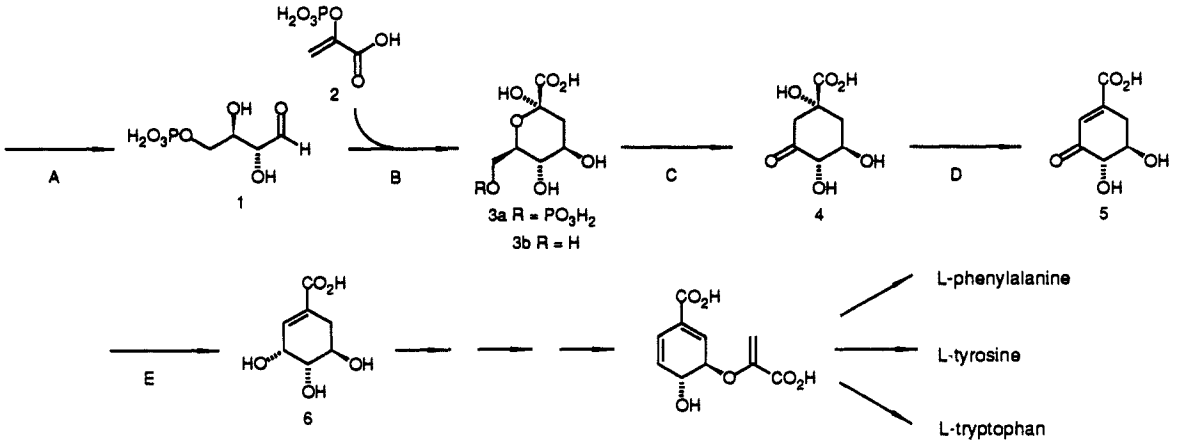
Scheme I[a]



[a] Enzyme (locus): (A) transketolase (tkt); (B) DAHP synthase (*aro*F); (C) DHQ synthase (*aro*B); (D) DHQ dehydratase (*aro*D); (E) shikimate dehydrogenase (*aro*E).

pathway of aromatic amino acid biosynthesis (Scheme I).[2] Catalytically viable shikimate dehydrogenase is missing from *E. coli aro*E. Choice of this mutation follows from a report that the rate of carbon flow through the shikimate pathway may be limited by the catalytic activity of DHQ synthase.[3] The plasmid-directed surge of carbon flow could therefore be directed toward the synthesis of 3-deoxy-D-*arabino*-heptulosonic acid (DAH, **3b**), the dephosphorylated substrate of rate-limiting DHQ synthase.[4] Alternatively, carbon flow might be directed toward synthesis of 3-dehydroshikimate (DHS, **5**), the substrate of shikimate dehydrogenase which is catalytically inactive due to a genomic mutation.

Analysis of the culture medium of *E. coli* AB2834 *aro*E[5] by ^{1}H NMR indicated that 3-dehydroshikimate was synthesized at concentrations of 9 mM with significant amounts of unidentified contamination (Figure 1A). *E. coli* AB2834 *aro*E was then transformed with plasmid pKD130A.[1] This plasmid encodes two enzymes, transketolase and DAHP synthase, which increase carbon flow into the common pathway.[1-3] Analysis by ^{1}H NMR of the culture supernatant of AB2834 *aro*E (pKD130A) (Figure 1B) revealed that while concentrations of DHS increased to 25 mM, DAH (Figure 1B, C-3 deoxy protons H_A, H_B) was also synthesized at concentrations of approximately 9 mM. The ratio of synthesized DHS and DAH indicates that neither the genomic *aro*E mutation nor the rate-limiting DHQ synthase completely dictates the direction of plasmid-based biocatalysis. However, the genomic *aro*E mutation determined the enzyme substrate which was synthesized in excess. Rate-limiting DHQ synthase primarily influenced the purity of the synthesized DHS.

To determine the consequences of removing the rate-limiting character of DHQ synthase, the *aro*B gene was inserted in plasmid pKD130A. A 1.65 kb fragment containing the *aro*B locus[6] was introduced into the *SphI* site of plasmid pKD130A to produce pKD136.[7] Plasmid pKD136 was transformed into *E. coli* AB2834 *aro*E. Analysis of the culture medium of AB2834 *aro*E (pKD136) (Figure 1C) indicated that 56 mM glucose was converted into 30 mM DHS. Increasing the concentration of DHQ synthase results in exclusive synthesis of the substrate of the enzyme which is catalytically inactive. On the basis of the complete removal of D-glucose from the culture medium and the concentration of synthesized DHS, 54% of the carbon consumed by *E. coli aro*E (pKD136) has been siphoned into aromatic amino acid biosynthesis.

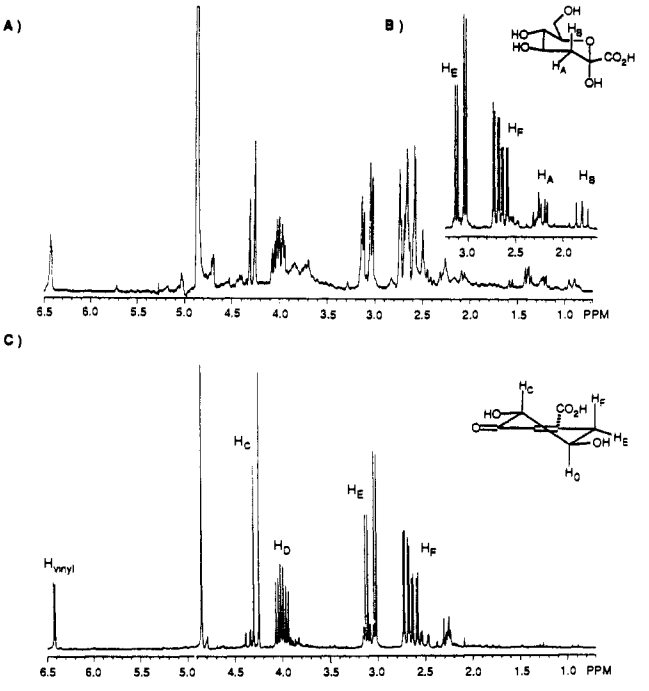


Figure 1. ^{1}H NMR spectra (D_2O) of crude culture supernatant: (A) AB2834 *aro*E; (B) AB2834 *aro*E (pKD130A); (C) AB2834 *aro*E (pKD136). Crude culture supernatant was concentrated from D_2O and dissolved in D_2O containing the sodium salt of 3-(trimethylsilyl)-propionic-2,2,3,3-d_4 acid (TSP). Concentrations of DAH were determined by comparison of the integrals of the C-3 deoxy protons (H_A, H_B) and TSP. Concentrations of DHS were determined by comparison of the integrals of the C-6 deoxy protons (H_E, H_F) and TSP.

Substrates of enzymes in the common pathway are already being exploited as starting materials in the synthesis of enzyme inhibitors.[8,9] Such uses for biosynthetic enzyme substrates will

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likely multiply as the diversity of available substrates expands. The concentration and purity of DHS synthesized by AB2834 *aro*E (pKD136) is a step in this direction. At the same time, microbial syntheses of DHS warn that plasmid-directed surges of carbon flow create a set of regulatory tenets beyond those originally selected by microbial evolution. Partially rate limiting DHQ synthase influenced only the purity of the DHS synthesized by *E. coli aro*E (pKD130A). For enzyme substrates situated after the common pathway and end products of aromatic amino acid biosynthesis, genomic factors could severely dissipate plasmid-directed surges in carbon flow. Surmounting these limitations has a direct bearing on the ultimate utility of microbial syntheses of prephenic acid, L-phenylalanine, and L-tryptophan which are essential to the assembly of (respectively) antibiotic bacilysin,[10] the artificial sweetener aspartame,[11] and indigo dyes.[12]

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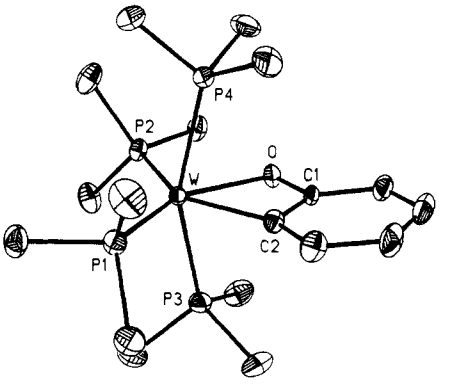


Figure 1. Molecular structure of $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$.

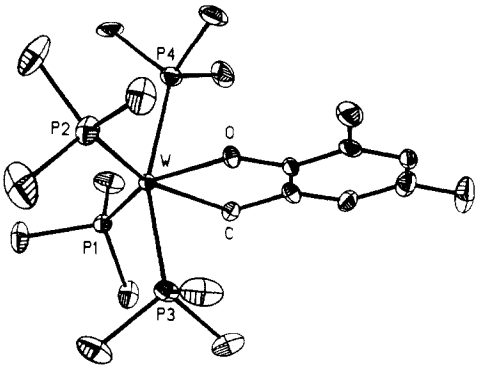
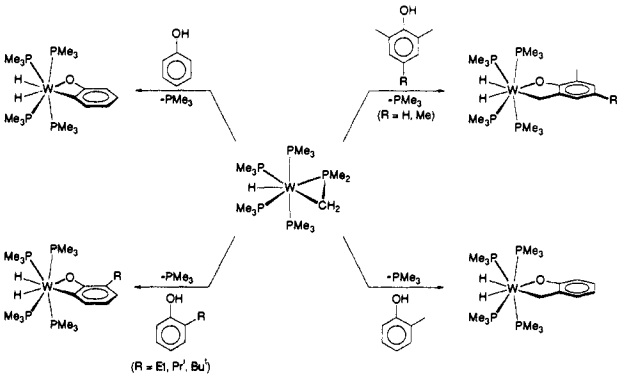


Figure 2. Molecular structure of $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$.

Scheme I



Competitive sp^3 and sp^2 C-H Bond Activation of Phenols by $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$: Formation of Four- and Five-Membered Oxametallacycles

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The susceptibility of the electron-rich complexes $W(PMe_3)_6$[1] and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$[2] toward oxidative addition suggests that these complexes may be candidates for selective C-H bond activation reactions.[3] Here we report that the reactions of both $W(PMe_3)_6$ and $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with alkyl-substituted phenols result in selective C-H bond activation and formation of novel four- and five-membered oxametallacycles, in preference to the more commonly observed six-membered derivatives.

The reactions of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with phenols giving four- and five-membered oxametallacycles are summarized in Scheme I.[4] Identical products are also obtained from the analogous reactions with $W(PMe_3)_6$. The mechanism for the formation of the oxametallacycle derivatives most probably involves cyclometalation of an aryloxy-hydride intermediate (eq 1). Cyclometalation of the aryloxy ligand may occur at either

$$W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H \xrightarrow{HArOH} [W(PMe_3)_5H(OArH)] \xrightarrow{-PMe_3} \overbrace{W(PMe_3)_4H_2(OAr)} \quad (1)$$

the aryl ring or alkyl substituent. Thus, whereas phenol reacts to form the four-membered oxametallacycle $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$ as a result of sp^2 C-H bond activation at one of the ortho positions, the reaction with 2,6-dimethylphenol gives the five-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_3Me(CH_2)\}$ derived from sp^3 C-H bond activation at one of the methyl groups. Similarly, 2,4,6-trimethylphenol gives the five-membered oxametallacycle $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$. The presence of the four- and five-membered oxametallacycle rings in the complexes $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$[5] and $W(PMe_3)_4H_2\{\eta^2\text{-}OC_6H_2Me_2(CH_2)\}$[6] has been confirmed by X-ray diffraction

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(4) All new compounds have been characterized analytically and spectroscopically.

(5) Crystal data for $W(PMe_3)_4H_2(\eta^2\text{-}OC_6H_4)$: monoclinic, $P2_1/n$ (No. 14), a = 9.713 (2) Å, b = 16.008 (5) Å, c = 16.283 (2) Å, β = 93.51 (1)°, V = 2527.1 (9) Å^3, Z = 4, ρ_{calcd} = 1.53 g cm^{-3}, μ(Mo Kα) = 51.0 cm^{-1}, λ(Mo Kα) = 0.71073 Å (graphite monochromator); 2364 unique reflections with $3° < 2\theta < 40°$ were collected of which 1981 with $F > 6\sigma(F)$ were used in refinement; R = 0.0262, R_w = 0.0356, GOF = 1.055.

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