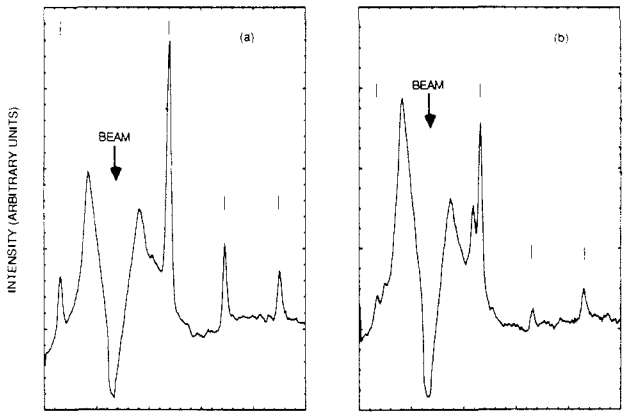

Figure 2. Radially integrated diffraction patterns for **1**. (a) Diffraction at 10 °C and 50% relative humidity; tic marks indicate the expected reflections for a lamellar lattice with basis length $d = 31.5$ Å. The arrow indicates the position of the main beam, blocked by a beam stop. (b) Diffraction at 10 °C and 80% relative humidity; tic marks indicate expected reflections for lamellar lattice of $d = 33.5$ Å. Note the appearance of the second lattice peak as described in the text.

recovery, without trailing of **1** on the column. These gel filtration results infer the presence of a nonvesicular component in the initial dispersion. Vesicles derived from **1** were stable for more than 48 h at ambient temperature (light scattering).

X-ray diffraction was used to demonstrate that dried, sedimented pellets of **1** form a lamellar phase when moistened in a stream of humidified gas. Specimens were prepared by depositing a drop of the vesicle dispersion onto a 12.5 μm thick mylar substrate, followed by overnight dehydration at 20% relative humidity at room temperature. This procedure is known to enhance macroscopic orientation and pseudoperiodic stacking of lamellae.[10] Specific methods used for sample preparation, humidity control, and X-ray analysis were similar to those previously described.[11-14] In the temperature range of −30 °C to 10 °C (20–50% relative humidity), a single lamellar lattice is clearly indicated (Figure 2a); above 50% humidity, a second lattice appears. However, too few diffraction lines are present to establish its structure. Figure 2b shows the diffraction pattern seen at 10 °C and 80% relative humidity, which clearly indicates a 33.5 ± 1.5 Å lamellar lattice coexisting with the second lattice. As the humidity is raised further, diffraction from the second lattice increases in intensity, while the original lamellar lattice loses intensity. Qualitatively, similar results were obtained at room temperature. Bulk (unoriented) dispersions of **1** also show two closely spaced lines, suggestive of two coexisting phases. In this case, a definitive phase assignment cannot be made because of the lack of higher orders of diffraction. In combination with the oriented specimen and electron microscope data, it appears likely that at least one of the phases is lamellar.

Studies which are now in progress are aimed at characterizing the permeability properties of these bilayers and at preparing analogous membranes from mixtures of single- and double-chain surfactants.[15] Results of these efforts will be reported in due course.

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A Model for the Chromophoric Site of Purple Acid Phosphatases

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The active sites of the purple acid phosphatases from bovine spleen and porcine uterus consist of a binuclear iron complex with two accessible oxidation states—a catalytically inactive, purple Fe(III)–Fe(III) form and an enzymatically active, pink Fe(II-I)–Fe(II) form.[1-8] The visible chromophore in these enzymes is associated with a tyrosinate-to-Fe(III) charge-transfer transition;[4,9] its persistence in both oxidation states and the similar extinction coefficients found for the chromophore in both states implicates a binuclear complex where tyrosine is coordinated to only one of the iron centers, the redox-inactive chromoporic site. Evidence for histidine coordination to both iron centers has been found in NMR[10] and pulsed EPR[11] studies. The oxidized Fe(II-II)–Fe(III) forms exhibit strong antiferromagnetic coupling[3,4,7,8] and Fe–Fe distances of 3.0–3.2 Å estimated from EXAFS studies.[2,6,12] Together, these observations suggest the presence of oxo and carboxylato units which bridge the iron atoms, as found for methemerythrin[2,13] and ribonucleotide reductase.[2,14,15] However, the absence of spectral features in the resonance Raman[4] and EXAFS[2,6] spectra that would corroborate the presence of the oxo group is troubling. We have therefore initiated an effort to model the active site of the purple acid phosphatases; our initial results are reported herein.

Treatment of a methanolic solution of $Fe(NO_3)_3 \cdot 9H_2O$ with the tripodal ligand *N*-(*o*-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine[16] (L) and an equivalent of Et_3N gives rise to a

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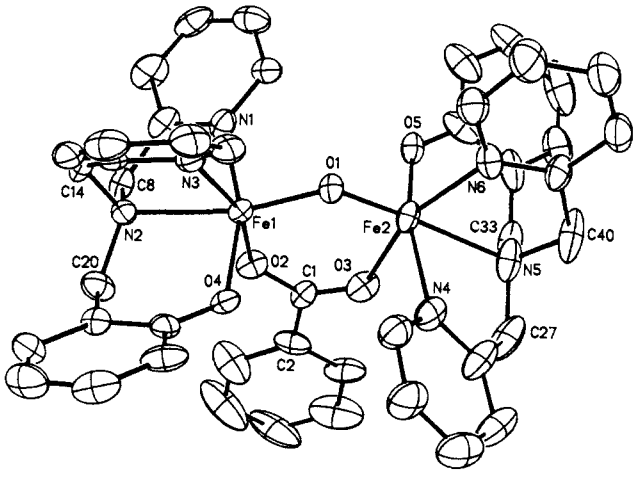

Figure 1. Plot of the structure of $[Fe_2L_2O(OBz)]^+$ (50% probability ellipsoids). Hydrogen atoms omitted for clarity. Selected distances (Å) and angles (deg): Fe1–O1, 1.777 (6); Fe1–O2, 2.059 (6); Fe1–O4, 1.924 (6); Fe1–N1, 2.158 (8); Fe1–N2, 2.266 (7); Fe1–N3, 2.165 (8); Fe2–O1, 1.799 (6); Fe2–O3, 2.082 (7); Fe2–O5, 1.931 (7); Fe2–N4, 2.185 (9); Fe2–N5, 2.277 (9); Fe2–N6, 2.156 (8); Fe1–O1–Fe2, 128.3 (3); O1–Fe1–O2, 102.2 (3); O1–Fe2–O3, 100.4 (3).

purple solution; subsequent addition of an equivalent of sodium benzoate results in the formation of a purple solid. Metathesis with $NaBPh_4$ and recrystallization from CH_3CN/ethyl acetate affords a complex that analyzes satisfactorily as $[Fe_2L_2O(OBz)]BPh_4$[17] (**1**). Analogous complexes can be prepared by using acetate and propionate.

The structure[18] of **1** (Figure 1) reveals a μ-oxo-μ-benzoato-diferric core with the tetradentate ligand completing the coordination sphere of each iron center. The iron–oxo bonds average 1.79 (1) Å, as expected,[2,19,20] and the Fe–Fe separation is 3.218 (2) Å, resulting in an Fe–O–Fe angle of 128.3 (3)°. The two halves of the binuclear unit are related by an approximate noncrystallographic 2-fold axis defined by the vector connecting O1 and C1. The phenolic oxygen atom occupies a coordination site trans to one pyridine nitrogen atom of L and cis to the other, while the tertiary amine nitrogen atom is trans to the bridging oxo ligand. It is clear from this structure that a single carboxylate bridge is sufficient to constrain the Fe–Fe distance and the Fe–O–Fe angle to values similar to those found in the recently characterized (μ-oxo)bis(μ-carboxylato)diiron(III) complexes.[20,21]

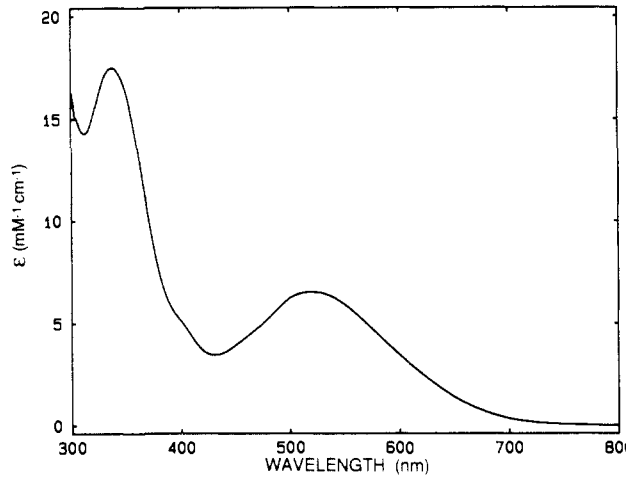

Figure 2. Electronic spectrum of $[Fe_2L_2O(OBz)]BPh_4$ in CH_2Cl_2.

Complex **1** exhibits a UV–vis spectrum (Figure 2) with features at 336 (ϵ 8900 M^{-1} cm^{-1}/Fe), 400 (sh, ϵ 2400 M^{-1} cm^{-1}/Fe), and 522 nm (ϵ 3300 M^{-1} cm^{-1}/Fe). By analogy to previously studied iron(III)–phenolate[22] and oxodiiron(III) complexes,[19] the lower energy band is associated with a phenolate-to-Fe(III) charge-transfer transition, while the higher energy band probably arises from both phenolate- and oxo-to-Fe(III) charge-transfer transitions. The 522-nm band has an extinction coefficient larger[23] than any previously observed for synthetic iron(III)–phenolate complexes, which, in general, have extinction coefficients of 1000–2000 M^{-1} cm^{-1} per iron(III)–phenolate bond.[22] The Mössbauer spectrum of **1** shows one quadrupole doublet with values (δ, 0.49 mm/s; ΔE_Q, 1.40 mm/s) consistent with an oxo-bridged diiron(III) unit.[2,19] The oxo bridge also mediates strong antiferromagnetic coupling between the iron(III) centers, as indicated by the small isotropic shifts observed in the ^1H NMR spectrum of the complex.[24]

We have synthesized **1** to serve as a model for the chromophoric iron(III) site of oxidized purple acid phosphatases. This site is associated with a chromophore that has an absorption maximum near 550 nm and a molar extinction coefficient of 4000 M^{-1} cm^{-1}.[25] On the basis of the extinction coefficient, two tyrosines were suggested to be coordinated to this iron.[4,10] However, oxo-bridged bis(phenolato)iron(III) complexes such as $[Fe(salen)]_2O$,[19] $[Fe(N\text{-propsal})_2]_2O$,[19] and $[Fe(2\text{-mequin})_2]_2O$[26] exhibit charge-transfer features only in the near UV region (300–400 nm), which do not match those of the enzymes. The spectral properties of **1** demonstrate that an oxo-bridged diiron(III) complex with only one phenolate per iron can give rise to a purple chromophore with a substantial extinction coefficient, properties comparable to those found for the enzymes. What still remains to be explored are the consequences of such a coordination environment on Raman and EXAFS properties; such spectroscopic studies on **1** paralleling similar studies on the proteins should clarify whether the purple acid phosphatases can have a diiron site bridged by oxo and carboxylate groups.

(16) L was synthesized by the reaction of *o*-acetoxybenzyl bromide with *N*,*N*-bis(2-pyridylmethyl)amine in the presence of triethylamine in refluxing methanol. Subsequent treatment of the reaction mixture with NaOH removed the acetyl group. After acidification, the solution was evaporated to dryness, and the resulting solid was extracted with THF to yield a solution of L, which was used without further purification. *o*-Acetoxybenzyl bromide was prepared according to the following procedure: Harris, W. R.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1975**, *14*, 974–978.

(17) Abbreviations used: OBz, benzoate; salen, *N*,*N*′-ethylenebis(salicylideneamine); *N*-propsal, (*N*-propyl)salicylideneamine; mequin, 2-methyl-8-hydroxyquinoline.

(18) The compound crystallized in the orthorhombic system, space group $P2_12_12_1$, with a = 17.728 (3) Å, b = 18.204 (4) Å, c = 19.383 (4) Å, Z = 4, and V = 6255 Å^3 at −115 °C. The intensity data were collected in the θ–2θ scan mode with a variable scan rate (2–30 deg min^{-1}). The original crystal shattered after collection of approximately half the data; a second crystal was used to complete the data set. The data from the two crystals were appropriately scaled and merged before use. The structure was solved by interpretation of the Patterson map (5385 of 6270 reflections with I(obsd) > $1.25\sigma(I)$, Mo Kα radiation (λ = 0.7107 Å), 4° ≤ 2θ ≤ 50°, Nicolet R3m diffractometer). All non-hydrogen atoms were refined with anisotropic thermal parameters. The enantiomorph was established by refinement of a multiplicative factor on the imaginary components of the anomalous dispersion correction terms. A final difference Fourier electron density map revealed low level residual electron density, which may ultimately be modeled as disordered, fractional CH_3CN molecules from the crystallization medium. Current residual indices: R = 0.086, R_w = 0.132, GOF = 2.19.

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(23) The corresponding tris(2-pyridylmethyl)amine complex, $[Fe_2L'_2O(OBz)](ClO_4)_3$, has also been synthesized and exhibits no intense absorption features in the 500-nm region.

(24) Prominent features are observed at 15.6, 14.8, 13.7, 10.6, 8.8, 7.4, 6.9, 3.3, 2.9, and −1.8 ppm.

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Supplementary Material Available: Tables of atomic positional and thermal parameters for $[Fe_2L_2O(OBz)]BPh_4$ (6 pages). Ordering information is given on any current masthead page.

Diastereofacialselectivity in Intramolecular Pauson-Khand Cycloaddition: Highly Stereoselective Synthesis of Pentalenene

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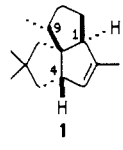
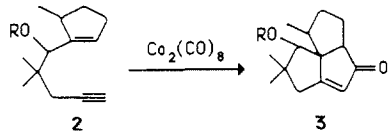
Our interest in expanding the scope of the intramolecular Pauson-Khand cyclopentenone synthesis recently led to our successful demonstration of this reaction's viability in the preparation of the angularly fused triquinane ring system.[1] In order to test the degree of stereocontrol available in this process we sought an efficient route to an enyne system which would be suitable for elaboration via cycloaddition into triquinane natural products. Herein we describe a synthesis of (±)-pentalenene (**1**)[2,3]



1

which makes use of (1) a novel approach to the generation of the quaternary center via conjugate addition-alkylation, (2) an efficient application of dissolving metal reduction to remove an otherwise intractable protecting group, and (3) a gratifyingly large kinetic diastereofacialselectivity in the Pauson-Khand cycloaddition itself, utilizing only the methyl group at the lone stereocenter in the precursor enyne to direct ring-closure in the required direction.

In our previous study the then unavoidable presence of an extraneous protected alcohol in the cycloaddition precursor (**2**, R = CH_2OCH_3) had two unfavorable effects: the products of

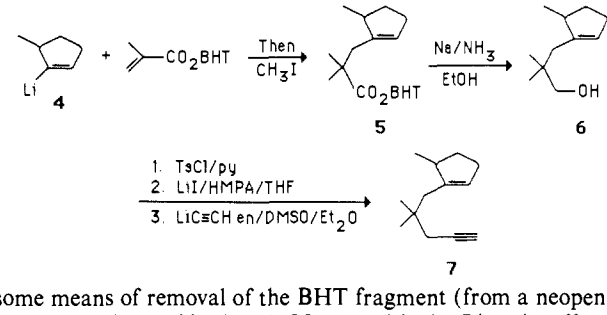


2 **3**

cycloaddition (**3**) were chemically unstable with respect to fragmentation reactions, and steric interference involving the protected alcohol overwhelmed any stereocontrol that the methyl group might have imparted to the cycloaddition process, resulting mostly in products with the undesired stereochemistry at C-9 (exclusively so for one of the diastereomers of **2**).

As a result we turned to conjugate addition of the readily available 5-methylcyclopentenyllithium (**4**)[4] to methacrylate as a possible approach to the deceptively simple enyne required. Attempts to form and utilize either an organocopper[5] or organocuprate[6] derivative of **4** were, however, unsuccessful. Cooke's report of conjugate addition resulting from the reaction of organolithium reagents with BHA and BHT esters of α,β-unsaturated acids[7] then attracted our attention. Due to the availability of simple oxidative methods for subsequent removal of the BHA moiety, it is the preferred group for protection of an ester from 1,2-addition. Unfortunately, **4** fails entirely to add to BHA methacrylate.

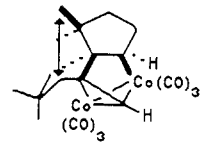
Reaction of **4** with BHT methacrylate is extremely efficient, however, and in situ methylation of the resulting enolate gives **5** in 90% overall yield. This result would be of little value unless



4 **5** **6** **7**

some means of removal of the BHT fragment (from a neopentyl ester, no less!) could be found. Not surprisingly, **5** is quite effective at resisting attack by nucleophiles: it is recovered unchanged after reaction with either $LiAlH_4$ for 5 h in refluxing THF or "Super-Hydride" ($LiEt_3BH$) for 18 h in THF at 25 °C. Fortunately, **5** succumbs to attack by solvated electrons; treatment with 10 equiv of Na in liquid NH_3 containing 4 equiv of ethanol affords alcohol **6** in a modest but usable 45% yield.[8] The sequence **4** → **6** is unprecedented in its simplicity, especially considering that the Sakurai approach[9] is inapplicable here due to the need to control the regiochemistry of the alkene. Conversion of **6** to enyne **7** is achieved in 34% overall yield as shown.[10]

The control of stereochemistry at C-9 in syntheses of angularly fused triquinanes in general and pentalenene in particular has been achieved with varying success. It has generally been found that greater success has resulted from sequences that set the stereochemistry in a ring-forming step.[3c,e,g,l] We hoped that the $Co_2(CO)_6$ complex of alkyne **7** would similarly display a preference for reaction on the face of the alkene opposite to the methyl substituent. Examination of models of the presumed intermediate made it far from obvious, however, that any single interaction would be capable of directing the cycloaddition in the desired direction. The only likely candidate appeared to be a 1,3-pseudodiaxial interaction that develops between the endo substituent at C-9 and the propargylic methylene group (arrow, below).



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