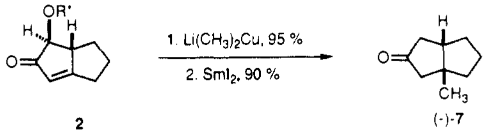
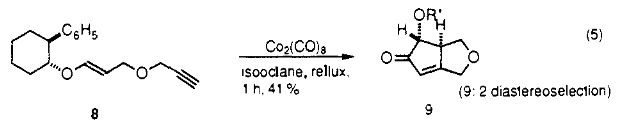
below, in 86% yield. Significantly, the chiral auxiliary could be recovered in 92% yield.[14]



(4)

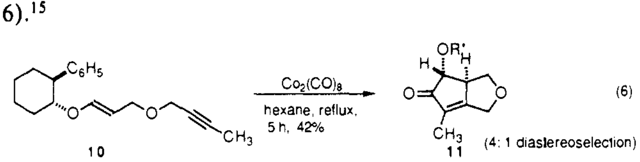
The Pauson–Khand products **2** and **5** presumably arise from the dicobalt hexacarbonyl complexes of the enol ethers **1** and **4** through the indicated *s-trans* conformation (eqs 2 and 3). This exposes the C_α-re face of the double bonds to intramolecular attack by the C_2Co_2 group, while positioning the C_α-si face so as to be shielded by the phenyl group.

This asymmetric version of the Pauson–Khand reaction appears to be notably broad in scope. An oxygen atom can be accommodated in the chain (eq 5).[15]



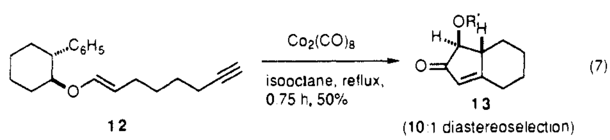
(5)

Furthermore, a terminal alkyl substituent is also tolerated (eq 6).[15]



(6)

Preliminary results indicate that diastereoselection may be even greater in the formation of bicyclo[4.3.0]nonenones; bicyclic enone **13**, for example, is obtained from enyne **12** with 10:1 diastereoselectivity (eq 7).[11]



(7)

The considerable potential of this approach is illustrated by an enantioselective formal total synthesis of hirsutene (**19**), the proposed biogenetic precursor of the hirsutanes (Scheme I).[16]

Homochiral diyne **16** was conveniently prepared through a novel copper-mediated coupling procedure[17] that involved the zinc reagent derived from bromide **14** and the iodoacetylene **15**. Conversion of **16** to the corresponding *E* enol ether could be selectively accomplished with $LiAlH_4$ in THF. The key bicyclization occurred smoothly under unusually mild conditions (exposure to 1.1 equiv of $Co_2(CO)_8$ in hexane, followed by warming at 42 °C for 12 h)[11,18] to produce diastereoselectively (5–6:1) enone **17**, mp 96–97 °C, easily purified by simple chromatography.[19] Birch reduction or, less efficiently, catalytic hydrogenation[20] delivered the dihydro derivative, mp 44–46 °C, from which the auxiliary could readily be cleaved[21] (91% recovery) to give **18**, $[\alpha]^{24}{}_D$ −68° (*c* 1.5, CH_2Cl_2). In that the bicyclic ketone **18**, in racemic form, has previously been converted to hirsutene, the present work constitutes an enantioselective approach to this substance.[16]

The results described in this paper establish both the feasibility and the practicality of chiral auxiliary-directed asymmetric Pauson–Khand bicyclization. Further investigation is warranted and is actively being pursued in our laboratories.

Acknowledgment. We thank Prof. J. Lhomme and Dr. J. L. Luche for their interest in our work, Prof. G. Magnusson for the spectra of racemic **18**, and the DGICYT (Grant PB86-0510) and the CNRS (UA 332) for financial support. Fellowships from Ministerio de Educación y Ciencia (to J.C.) and the Swedish National Board for Technical Development (to H.S.) are gratefully acknowledged.

Registry No. **1**, 130121-38-9; **2**, 130121-39-0; **3**, 130194-15-9; **4**, 130194-16-0; **5**, 130121-40-3; **6**, 130194-17-1; (−)-**7**, 102849-89-8; **8**, 130121-41-4; **9**, 130121-42-5; **9** (diastereomer), 130194-19-3; **10**, 130121-43-6; **11**, 130121-44-7; **11** (diastereomer), 130121-45-8; **12**, 130195-29-8; **13**, 130121-46-9; **13** (diastereomer), 130195-30-1; **14**, 130121-47-0; **15**, 130121-48-1; **16**, 130121-49-2; **16** ((*E*)-enol ether), 130121-51-6; **17**, 130121-50-5; **17** (diastereomer), 130194-20-6; **17** (dihydro derivative), 130121-52-7; **18**, 130194-18-2; **19**, 59372-72-4.

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(13) Greene, A. E.; Charbonnier, F. *Tetrahedron Lett.* **1985**, *26*, 5525–5528. Ketone (−)-**7** displayed at 300 nm the expected negative maximum in its CD spectrum. An optical purity of >99% was established by ^{13}C NMR. See: Hiemstra, H.; Wynberg, H. *Tetrahedron Lett.* **1977**, 2183–2186.

(14) In addition, it was found that diastereomers **2** ($Li(CH_3)_2Cu$) and **6** ($Li(CH_3)_2Cu$; equilibration with $t\text{-}C_4H_9OK$) gave the same 4-alkoxy-1-methylbicyclo[3.3.0]octan-3-one, as did **3** and **5**. SmI_2 converted that derived from **2** and **6** to (−)-**7** and that from **3** and **5** to (+)-**7**.

(15) Diethers **8** and **10** were prepared in 51–72% yield by sequential treatment of *trans*-2-phenylcyclohexanol with KH, $Cl_2C{=}CHCl$, C_4H_9Li, and CH_2O (one pot), followed by exposure to KH and $BrCH_2C{\equiv}CH$ or $MsOCH_2C{\equiv}CCH_3$, and then reduction. The absolute configuration of **9** was assigned on the basis of the positive CD maximum of the derived 1-methyl-7-oxabicyclo[3.3.0]octan-3-one ($Li(CH_3)_2Cu$; SmI_2) and can also be rationalized by assuming an *s-trans* conformation (analogous to that indicated for **1**) of the dicobalt hexacarbonyl complex of enol ether **8**.

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The $g = 4.1$ EPR Signal of the S_2 State of the Photosynthetic Oxygen-Evolving Complex Arises from a Multinuclear Mn Cluster

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Received July 30, 1990

The process of water oxidation and dioxygen evolution by the photosystem II (PSII) component of plant photosynthesis is cyclic, with intermediate states of the oxygen-evolving complex (OEC) designated S_0 through S_4.[1] Two electron paramagnetic resonance (EPR) signals have been assigned to the S_2 state of the complex. A "multiline" EPR signal centered at the $g = 2$ region of the spectrum shows 16 or more partially resolved Mn hyperfine

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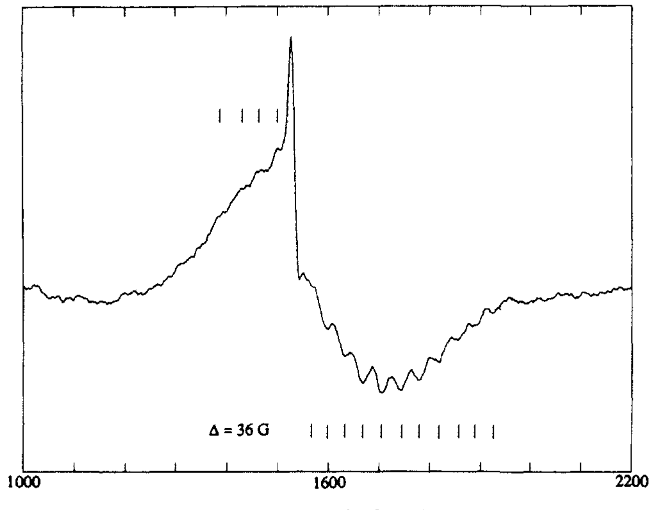

Figure 1. EPR spectra of oriented PSII membranes treated with 100 mM NH_4Cl at pH 7.5 in the presence of 400 mM sucrose. The membrane normal is oriented parallel to the applied magnetic field (0°). The solid line displays the $g = 4.1$ signal recorded following 5-min illumination with a 400-W tungsten lamp at a temperature of 195 K. The dotted line displays the EPR signal remaining in this field range following an "annealing" step in which the sample is warmed to 0 °C for 1 min. This annealing step results in the formation of the ammonia-altered multiline signal at the expense of the $g = 4.1$ signal.[8,11,14] The sharp feature at $g = 4.3$ observed in both illuminated and annealed spectra is due to rhombic Fe^{3+} present in these preparations. Mn hyperfine features are not observed when the membrane normal is oriented 90° with respect to the magnetic field. Spectrometer conditions are as follows: microwave frequency, 9.22 GHz; microwave power, 20 mW; field modulation amplitude, 10 G; sample temperature, 7.5 K.

transitions and arises from a cluster with a minimum of two exchange-coupled mixed-valence Mn atoms.[2] The other S_2 EPR signal occurs in the $g = 4.1$ region of the spectrum.[3,4] The lack of resolved Mn hyperfine couplings has prevented conclusive assignment of the $g = 4.1$ EPR signal to a Mn center. However, a shift of the Mn X-ray K edge to higher energies is correlated with the appearance of the $g = 4.1$ signal in PSII membranes illuminated at 140 K.[5] A considerable body of experimental work, including measurements of the temperature dependence of the EPR signals[6,7] and observations of the interconversion between the multiline and the $g = 4.1$ signals,[4,8] has given rise to two different models involving $S = {}^3/_2$ Mn origins for the $g = 4.1$ signal. Hansson et al.[7] have suggested that the $g = 4.1$ signal arises from an isolated Mn(IV) ion in an axially distorted octahedral environment and that this mononuclear Mn site is in redox equilibrium with a binuclear Mn site that gives rise to the multiline signal. Brudvig and co-workers[6,8-10] have proposed a different model, in which the two EPR signals arise from two different conformations of a single tetranuclear Mn site.

In this communication, we present direct spectral evidence of a multinuclear Mn origin for the S_2 $g = 4.1$ signal. The $g = 4.1$ EPR signal obtained from oriented PSII membranes under conditions of ammonia inhibition of oxygen evolution shows at least 16 Mn hyperfine lines with a regular spacing of approximately 36 G. Ammonia-treated PSII membranes were prepared as previously described.[11] PSII membrane samples were oriented by using a modification of the method described by Rutherford.[12] In our procedure, PSII membranes were rapidly dried (1 h) onto Mylar films under a flow of N_2 gas in the dark at 4 °C. The membranes were determined to be highly oriented by measurements of the anisotropy of EPR signals arising from the cytochrome b_{559} complex and the D^+ tyrosine radical.[12,13] Figure 1 displays the $g = 4.1$ signal obtained by illumination at a temperature of 195 K of a sample with the membrane normal oriented parallel to the applied magnetic field (solid line). The background signal (dotted line) is obtained after "annealing" the sample for 1 min at 0 °C, a process that converts the $g = 4.1$ S_2 signal into the ammonia-altered form of the multiline EPR signal.[8,11,14] The sharp feature at $g = 4.3$ originates from rhombic Fe^{3+} in the preparation and is not affected by illumination. At this orientation, with the membrane normal parallel to the magnetic field, approximately 16 Mn hyperfine features are partially resolved on the light-induced $g = 4.1$ signal. These lines are regularly spaced, with an average splitting of approximately 36 G. As the angle between the magnetic field and the membrane normal is incremented from 0° to 90°, we observe a dramatic decrease in the resolution of the Mn hyperfine features. We note that Diril et al.[15] have demonstrated that only the z component of the g tensor gives rise to resolved Mn hyperfine couplings in some binuclear Mn(II)Mn(III) systems. The x and y components are potentially unresolved due to strain effects associated with the g and/or hyperfine tensors. It is likely that we resolve Mn transitions at the 0° orientation because of the fortuitous orientation of a specific principal axis of the effective g tensor along the membrane normal. The lack of resolved Mn hyperfine structure at 90° may be due to the complex superposition of transitions corresponding to the other two axes, which lie near the plane of the membrane. We do not observe Mn couplings associated with the $g = 4.1$ signals of oriented samples prepared without ammonia treatment, a result consistent with the findings of Rutherford.[12] Ammonia binding to a Cl^- competitive OEC site has been found to stabilize the $g = 4.1$ signal.[8,16] Clearly more investigation is needed to understand the role of ammonia binding in providing resolution of Mn hyperfine features on this signal. However, the highly anisotropic nature of the resolution of Mn hyperfine lines does explain why such structure has not been observed in previous studies of the $g = 4.1$ signal in nonoriented ammonia-treated preparations.[8,16]

The observation of partially resolved Mn hyperfine structure on the $g = 4.1$ signal allows us to assess critically the possible origins for the $g = 4.1$ signal. In this analysis both the number of hyperfine lines and the spacings between lines are important. Specifically, we can rule out the possibility of a monomeric Mn(IV) origin for the $g = 4.1$ EPR signal. The ^{55}Mn nucleus has a nuclear spin of $I = {}^5/_2$, and a monomeric Mn(IV) with an isotropic g tensor would be expected to give rise to six hyperfine lines with a separation of approximately 75 G.[17] Although g or hyperfine anisotropy could increase the number of lines, it would

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be quite remarkable for the lines to be as evenly spaced as we observe on the $g = 4.1$ signal.[18] In addition, as discussed above, we favor a model where the resolved components all arise from a single principal component on the g tensor.

Furthermore, the $g = 4.1$ signal cannot arise from an isolated binuclear Mn complex. The $g = 4.1$ signal appears to arise from an $S = {}^3/_2$ ground-state doublet.[6,7] Antiferromagnetic coupling within either a Mn(III)Mn(IV) or a Mn(II)Mn(III) binuclear complex will produce an $S = {}^1/_2$ ground state. Even if the $g = 4.1$ signal arose from an excited state, one would expect to observe an associated $S = {}^1/_2$ $g \approx 2$ signal whose intensity at a given temperature would be directly proportional to the intensity of the $g = 4.1$ signal. However, such an associated $g \approx 2$ signal is not observed, and in fact, there appears to be an interconversion between the $g = 4.1$ and $g = 2$ multiline EPR forms.[4,8]

On the other hand, an exchange-coupled tetranuclear Mn complex could have either an $S = {}^3/_2$ ground state or an $S = {}^1/_2$ ground state.[6c,10] Additionally, the reduced hyperfine couplings observed in the $g = 4.1$ spectra are consistent with a tetranuclear origin for the signal. The measured ^{55}Mn hyperfine interaction for each ion will scale to the mononuclear hyperfine couplings of the ion by the projection of each individual ion spin on the total spin.[2] To illustrate the reduction of hyperfine couplings that will occur in an $S = {}^3/_2$ tetranuclear complex, we consider as an example a "dimer-of-dimers" model consisting of two dimeric complexes with antiferromagnetic couplings as well as magnetic couplings between the two dimers. Using a simplified vector coupling model in which the interdimer exchange couplings are set equal, we can calculate the predicted values for the Mn hyperfine couplings. Consider the case of a $\mathrm{Mn_1(III)Mn_3(IV)}$ tetramer in which a $\mathrm{Mn_A(III)}$ and a $\mathrm{Mn_B(IV)}$ are strongly antiferromagnetically coupled to give an $S_{AB} = {}^1/_2$ ground state, and the $\mathrm{Mn_C(IV)}$ and $\mathrm{Mn_D(IV)}$ ions are antiferromagnetically coupled to give an $S_{CD} = 1$ first excited state. Ferromagnetic coupling between the dimers can then give rise to a total spin $S = {}^3/_2$ ground state.[6b,c,10] Calculation of the projected hyperfine couplings gives $A_A = {}^2/_3A_{(III)}$, $A_B = -{}^1/_3A_{(IV)}$, and $A_C = A_D = {}^1/_3A_{(IV)}$, where $A_{(III)}$ and $A_{(IV)}$ are the hyperfine coupling constants for monomeric Mn(III) and Mn(IV), respectively. This reduction in line spacing and the approximately 2:1 ratio in the magnitude of the effective hyperfine couplings are consistent with our experimental observation of a regular spacing of 36 G between lines. We are commencing EPR simulations of this and other tetranuclear models. At present, we cannot rule out the possibility that different conformations of a Mn trimer could also give rise to both the $g = 4.1$ and multiline signals. However, this would leave a "voyeur" Mn that is always EPR silent in the OEC. With a monomeric origin for the $g = 4.1$ signal discounted by this work, the motivation for considering separate mononuclear and trinuclear centers in the OEC is decreased. Our new observations of resolved hyperfine structure on the $g = 4.1$ signal are strongly suggestive that, under conditions of ammonia inhibition of oxygen evolution, the multiline and $g = 4.1$ EPR signals arise from a common tetranuclear mixed-valence Mn cluster that can present either an $S = {}^1/_2$ or an $S = {}^3/_2$ ground state, depending on slight configurational differences.

Acknowledgment. This work was supported by a grant from the National Science Foundation (DMB-8804526) and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Energy Biosciences of the U.S. Department of Energy, under Contract DE-AC0376SF00098. D.H.K. gratefully acknowledges the receipt of a University of California President's Undergraduate Fellowship (1989–1990). R.D.B. gratefully acknowledges support from the Camille and Henry Dreyfus Foundation.

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(18) From the measured pattern of Mn hyperfine lines on the oriented $g = 4.1$ signal, we could describe it as another "multiline" signal. We note that the $g = 4.1$ signal resembles the ammonia-altered multiline form (see ref 11, Figure 2) in that both signals have better resolution of Mn hyperfine features in the higher field regions.

Molecular Engineering in the Design of Short-Range Ferromagnetic Exchange in Organic Solids: The 1,3,5-Triphenylverdazyl System

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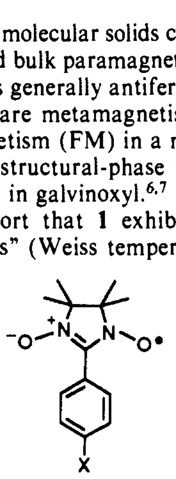
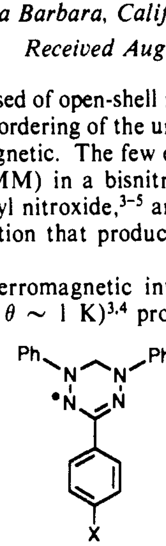
Received August 20, 1990

Organic molecular solids composed of open-shell molecules, as a rule, yield bulk paramagnets. If ordering of the unpaired spins occurs, it is generally antiferromagnetic. The few exceptions to the above are metamagnetism (MM) in a bisnitroxy,[1,2] weak ferromagnetism (FM) in a nitronyl nitroxide,[3-5] and weak FM prior to a structural-phase transition that produces antiferromagnetism in galvinoxyl.[6,7]

The report that **1** exhibits "ferromagnetic intermolecular interactions" (Weiss temperature $\theta \sim 1$ K)[3,4] prompted us to determine if introduction of a nitro group in the isoelectronic position of triphenylverdazyl; e.g., **2N**, would also lead to an FM or short-range ferromagnetic (SRFM) organic solid. Here we report the magnetic properties and crystal structures of **2N** and **3** and the rationale for the design of **3**, an organic solid exhibiting SRFM with $\theta = +1.6$ K.



1, X = NO$_2$



2, X = H; **2N**, X = NO$_2$

1,3,5-Triphenylverdazyl (**2**) is an unusually stable organic free radical that has been studied extensively.[8,9] Magnetic susceptibility measurements[9] showed it to be an AF coupled system. Electron spin resonance spectroscopy (ESR)[8] and NMR[8] spectroscopy had been performed on a number of verdazyls and multiple verdazyls.[10] In general, the preponderance of spin density is on the four nitrogen atoms,[11,12] which is also observed in **2N** and **3**.[13]

Compounds **2N** and **3** were prepared according to literature procedures.[8,14] In Figure 1a we show that the solid-state structure[15] of **2N** consists of stacks and that the tetraazapentadienyl moieties are arranged for good intermolecular "overlap" within the stacks. Since these are the regions of maximum spin density, it follows from McConnell's model[16] that this solid should exhibit antiferromagnetism. In Figure 2a we show the results of static magnetic susceptibility measurements,[17] which, contrary

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