(50%); 4-octene (**d**) 15/85 (50%); 5-decene (**e**) 15/85 (63%)].[11]

In view of the trapping experiments described above and the widely accepted mechanism of the stoichiometric reactions between ylides and the chalcogen elements sulfur[12] and oxygen,[8] it is likely that selenoaldehydes **2** serve as key intermediates in this *catalytic* olefin forming ylide cleavage reaction.[13,14] In this case, the product-forming step in the catalytic cycle is a Wittig olefination-type reaction of a selenoaldehyde. The rather high trans selectivity observed here contrasts with the Wittig olefination of aldehydes RCHO under similarly salt-free conditions.[15] This might originate from a more facile reversal of the formation of a selenaphosphetane from RCHSe and $Ph_3P{=}CHR$ as compared to the oxaphosphetane analogue[16,17] or a preferred reaction path through a thermally unstable trans disubstituted episelenide stereoselectively decomposing under the reaction conditions.[18]

Acknowledgment. We thank Dr. G. Schomburg for helping us with the GC analyses. Generous financial support of the Fonds der Chemischen Industrie and the Alfried Krupp von Bohlen und Halbach-Stiftung is gratefully acknowledged.

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An Unusually Stable $Mn^{II}Mn^{III}$ Complex with Novel EPR Spectra: Synthesis, Structure, Magnetism, and EPR Analysis[†]

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Xiaohua Zhang,[2] Joseph A. Potenza,*[2] Harvey J. Schugar,*[2]
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Well-characterized polynuclear Mn complexes that catalytically oxidize H_2O to molecular oxygen are of intense current interest as models for the polynuclear Mn center in photosystem II.[3] The protein center exhibits a rich, hyperfine-structured EPR spectrum in its S_2 state whose interpretation could be facilitated by examining the corresponding spectra of suitable low molecular weight complexes. Earlier, we reported the first structural characterization of valence-trapped $Mn^{II}Mn^{III}$ complexes and demonstrated that the development of Mn hyperfine structure in the low-temperature EPR spectra is related to the strength of the Mn–Mn coupling.[4]

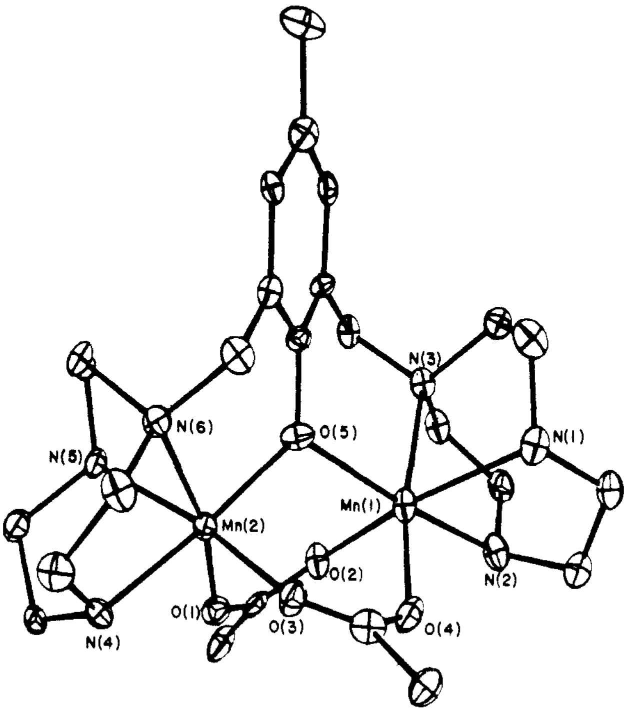

Figure 1. ORTEP plot of the $[Mn_2(bcmp)(\mu\text{-}OAc)_2]^{2+}$ cation in **1**. Selected interatomic distances and angles are as follows: Mn(1) –O(2), 2.135 (9); –O(4), 2.09 (1); –O(5), 2.17 (1); –N(1), 2.26 (1); –N(2), 2.22 (1); –N(3), 2.23 (1); Mn(2)–O(1), 2.01 (1); –O(3), 2.056 (9); –O(5), 1.957 (9); –N(4), 2.11 (1); –N(5), 2.23 (1); –N(6), 2.18 (1); Mn(1)···Mn(2), 3.422 (3) Å; Mn(1)–O(5)–Mn(2), 112.1 (4)°.

We report here the preparation and characterization of a new binuclear $Mn^{II}Mn^{III}$ complex (**1**), $[Mn_2(bcmp)(\mu\text{-}OAc)_2](ClO_4)_2{\cdot}CH_2Cl_2$, that exploits the special thermodynamic and kinetic stability associated with the binucleating 1,4,7-triazacyclononane[5] (tacn) ligand bcmp (**2**). We also report a novel

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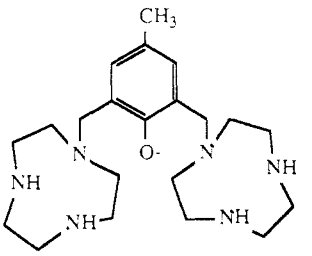
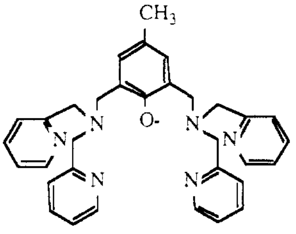


bcmp, (2)



bpmp

interpretation of the rich EPR spectra of the binuclear complex (1) as well as that of the open chain analogue $[Mn_2(bpmp)(\mu\text{-}OAc)_2]^{2+}$ (3) described previously.[4] Notable in this regard is the work of Wieghardt et al. on mononuclear, binuclear, and tetranuclear oxo-bridged manganese complexes with tacn and its derivatives.[6]

Ligand **2** was prepared by the reaction of *N*,*N'*-bis(*p*-tolylsulfonyl)-1,4,7-tacn[7] with 2,6-bis(chloromethyl)-*p*-cresol followed by deprotection.[8] The addition of LiOAc and $NaClO_4$ to an ethanolic solution containing the 2:1 complex of $Mn(OAc)_2 \cdot 4H_2O$ and (**2**), followed by air oxidation, caused complex **1** to precipitate as a green-black solid which was recrystallized from CH_2Cl_2.

X-ray analysis[9] of (**1**) (Figure 1) revealed a valence-trapped $Mn^{II}Mn^{III}$ cation in which Mn(1) is the Mn^{II} site and Mn(2) is the Mn^{III} site Jahn–Teller distorted along the N(5)–Mn(2)–O(3) ("*z*") direction. Both Mn atoms show pseudooctahedral coordination similar to that observed for **3**.

Electrochemical measurements of **1** in acetonitrile showed one-electron oxidation and reduction to $Mn^{III}Mn^{III}$ and $Mn^{II}Mn^{II}$ species ($E_{1/2}$ = +0.35 and −0.13 V, respectively, vs Fc^+/Fc). The oxidation/reduction wave of **1** corresponding to $Mn^{II}Mn^{III} \rightarrow Mn^{III}Mn^{III}$ is more reversible than for the open chain analogue **3** as measured by cyclic voltammetry (peak heights and separation of oxidation and reduction waves).

Magnetic susceptibility data for **1** (μ_{eff}/complex = 7.15 μ_B at 301.2 K to 1.81 μ_B at 5.0 K) are consistent with isotropic magnetic exchange between high-spin Mn^{II} and Mn^{III} ions with $J = -7.7$ cm^{-1}. Corresponding data for **3** gave $J = -6.0$ cm^{-1}.

When cooled to 8 K, the EPR spectra of **1** develop complicated ^{55}Mn hyperfine structure (Figure 2) similar to that observed for **3**. The three components of the $S = 1/2$ g tensor overlap at X band. While they do not completely separate out at Q band, the Q-band spectra are indicative of a system with a nearly axial g tensor with resolved hyperfine structure for the z component. We surmised that only the hyperfine structure for the z component was resolved in the X- and *Q*-band spectra and that hyperfine structure for g_x and g_y components had broadened to the point of not contributing significantly to the observed EPR spectra. Successful simulation of the EPR spectra using the g, hyperfine, and line width parameters shown in Figure 2 support this hypothesis. The observation of hyperfine structure for the z component is due to a narrowing of the line width which is M_I dependent. This hyperfine structure may arise from reduced nitrogen

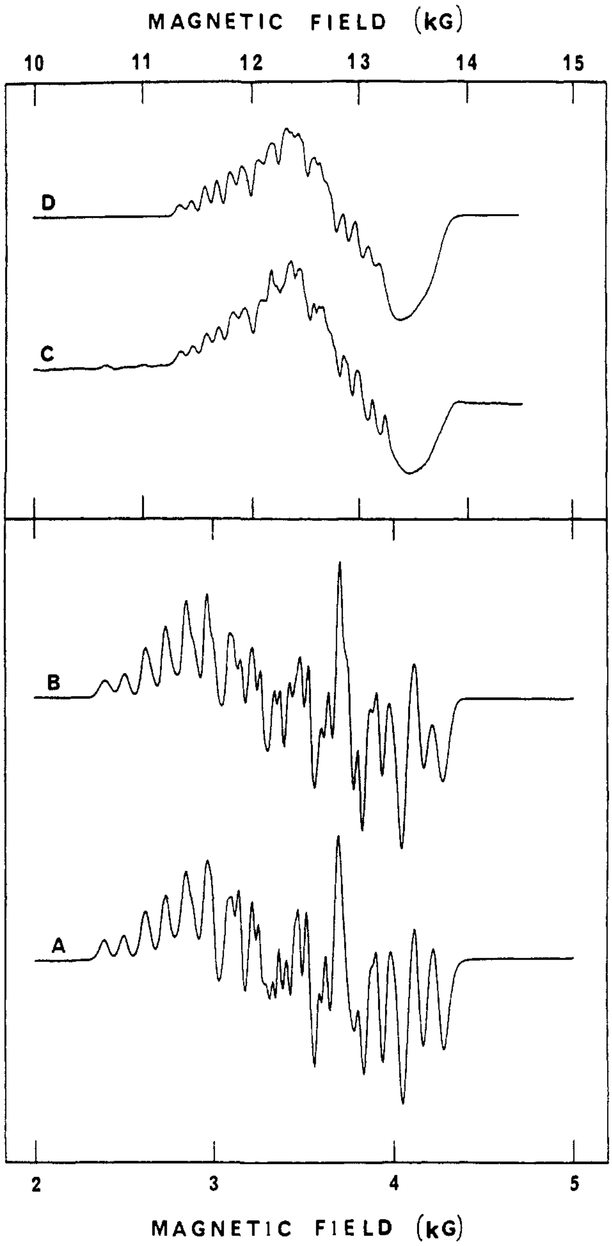


Figure 2. Simulated and observed 8.0-K X-band and ~20-K Q-band EPR spectra for an acetone/toluene/ethanol (2:1:2) glass of **1**. Spectrum A is the observed X-band spectrum; B is simulated by using $g_z = 2.022$, $g_x \simeq 1.905$, $g_y \simeq 1.905$, line widths of $W_x = W_y \simeq 175$ MHz and M_I − dependent $W_z = 38 + 2.5(M_I^{(1)} + M_I^{(2)})^2$ (MHz) where $M_I^{(i)}$ is the nuclear spin projection on the *i*th Mn ion, and the hyperfine parameters are as follows: A_z = 736 MHz ($Mn^{(1)}$) and 318 MHz ($Mn^{(2)}$); $A_x = A_y \cong 460$ MHz ($Mn^{(1)}$) and 220 MHz ($Mn^{(2)}$). Spectrum C is the observed Q-band spectrum; D is simulated by using the same parameters as for the X-band spectrum except $W_z = 61 + 2.5(M_I^{(1)} + M_I^{(2)})^2$ (MHz) and $W_x = W_y \simeq 280$ MHz. Unfortunately, the Q-band magnet only operated up to ~14 kG.

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(8) We have recently developed a new, easier method for preparing ligand **2**. Details will be published elsewhere.

(9) Crystallography: $Mn_2Cl_2O_{13}N_6C_{25}H_{43} \cdot CH_2Cl_2$, orthorhombic, $Pca2_1$, a = 19.273 (1) Å, b = 15.155 (2) Å, c = 13.749 (3) Å, V = 4016 (1) Å^3, d_{calcd} = 1.503 g cm^{-3}, d_{obsd} = 1.54 (1) g cm^{-3}, $Z = 4$. The structure was solved by direct methods by using 2324 unique reflections ($I > \sigma(I)$) collected at 296 (1) K with Mo Kα radiation (λ = 0.71073 Å) to $2\Theta = 45°$ on an Enraf-Nonius CAD-4 diffractometer. All atoms of the perchlorate anions and the dimanganese cation refined smoothly with the perchlorate O atoms showing somewhat large thermal parameters (8.7 (3) < B < 15.6 (6) Å^2). The solvate molecule was difficult to locate and refine, and it appears to be severely disordered. Refinement, with solvate and $O(ClO_4)$ atoms isotropic, yielded $R_F = 0.074$, $R_{wF} = 0.085$, and GOF = 2.50. The largest peak in a final difference map was 0.60 e/Å^3.

superhyperfine splitting associated with the elongated Mn(2)-N(5) distance ("*z*" for Mn^{III}) relative to those for Mn(2)-N(4) and Mn(2)-N(6) ("*x*, *y*" for Mn^{III}, Figure 1). The EPR spectra of 3 have also been simulated by using the same principles.

Acknowledgment. We are thankful for support from NIH Grants HL 13652 (D.N.H.), 1510 RRO 1486 01A1 (crystallographic instrumentation at Rutgers, H.J.S.), and the Rutgers research council (S.S.I.).

Supplementary Material Available: Tables of positional and thermal parameters for $[Mn_2(bcmp)(\mu\text{-}OAc)_2]\cdot CH_2Cl_2$ (6 pages). Ordering information is given on any current masthead page.

Exclusion of a 1,4-Cyclohexenediyl as a Metastable Intermediate in the [3,3] Sigmatropic Rearrangement of a 1-Hexen-5-yne

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Although semiempirical calculations[1,2] suggest that the much discussed[3,4] 1,4-cyclohexanediyl species **1** (R_1–R_3 = H) is a true intermediate on the reaction coordinate of the thermal Cope ([3,3] sigmatropic) rearrangement of 1,5-hexadienes (Scheme I), ab initio calculations,[5] thermochemical kinetic arguments,[6] and a study[7] of the rearrangement's stereospecificity (when R_1, R_3 = Me, R_2 = Ph) do not bear out this result. As the first stage in an effort to give the hypothetical biradical pathway a chance to manifest itself, we now have examined the mechanism of the eneynic–enallenic [3,3] sigmatropic process which interconverts a 1-hexen-5-yne and a 1,2,5-hexatriene (**3** → **4**, Scheme I).

The biradical corresponding to **1** in this case would be a 1,4-cyclohexenediyl, **2**. By using the 1981[6] (or 1976[8]) values of bond energies, one may estimate that species **2** lies only 3.6 (or 1.2) kcal/mol higher in energy than the transition state (E_a = 32.7 kcal/mol[9]) and hence might be a better candidate than is **1** for the role of a true intermediate.

In a formal sense, the distinction between **2** as an intermediate and **2** as a transition state is that, in the latter case, cleavage of the C_5–C_6 bond must occur at the rate of $\kappa RT/Nh$ (about 1×10^{13} s^{-1} at 200 °C). We propose to use a ring conformational change as an internal clock by which to measure the bond cleavage rate. There is good reason to believe that the rate of ring inversion in **2** will be much greater than in **1** (see below), thereby providing a faster clock and again increasing the chance for the intermediate to make its existence known.

The content of stereochemical information of starting material **3** will be transferred intact to product **4** if the rearrangement occurs by a concerted pathway either exclusively "allowed" or exclusively "forbidden" (see Figure 1). The same result is predicted for a biradical mechanism via **2**, but only if bond cleavage (k_1) is much faster than ring inversion (k_2, Scheme II). However, this stereospecificity will be degraded if **2** is an intermediate that lives long on the time scale of its own conformational inversion or if both "allowed" and "forbidden" pathways are followed. Moreover, if this occurs, the reversibility of the sigmatropic rearrangements guarantees that all of the sigmatropically related species ultimately will be racemized.

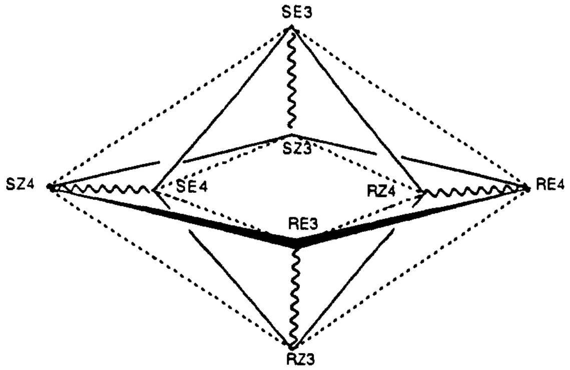
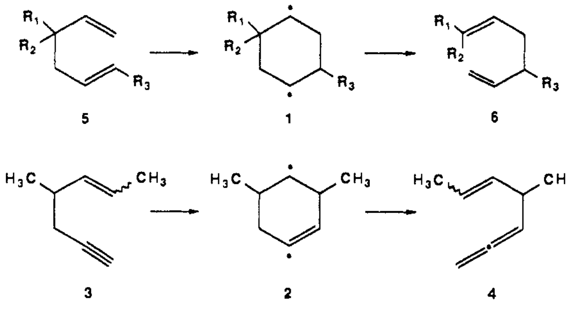
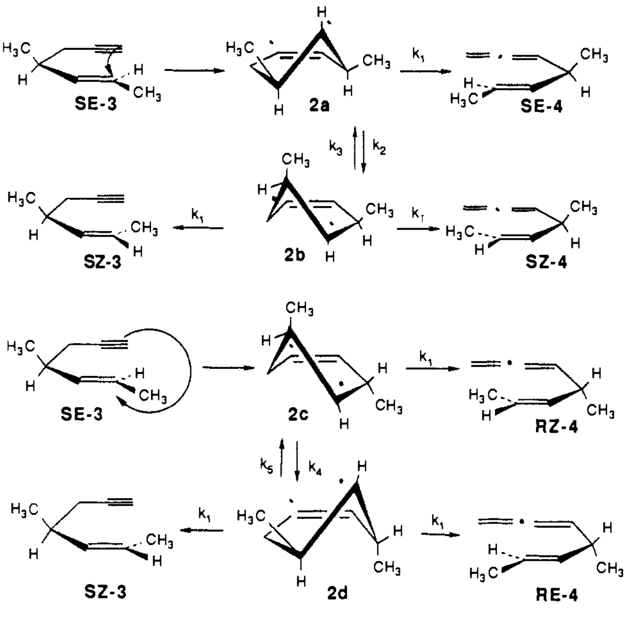


Figure 1. Interconversion paths among acetylenes **3** and allenes **4**. The stereochemical descriptors are indicated before the numerals. Solid and dashed lines, respectively, represent "allowed" and "forbidden" sigmatropic rearrangements; wiggly lines represent stereomutation about the olefinic bond by the mechanism of Scheme II. Hypothetically interconverting biradicals (not shown) are to be imagined as connecting adjacent "allowed" and "forbidden" pathways in Figure 1 (see Scheme II).

Scheme I



Scheme II



The compound (−)-(*S*,*E*)-**3** of 62.2 ± 2% ee was obtained in four synthetic steps from the known[10] ethyl (−)-(*S*,*E*)-3-

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