termittently sealing the cavity entrance.

In conclusion, molecular recognition is demonstrated to occur in the gas phase, not only in solution and in solids. The dependence of complexation on various parameters can be studied easily. Since experiments are described in terms of bimolecular interactions, without involvement of solvating species, fundamentally important information on host–guest structures and thermochemistry is potentially accessible.

Supplementary Material Available: Chemical ionization mass spectra of reagent gases, recorded under the same experimental conditions adopted in the experiments reported in Table I and Figure 1 (1 page). Ordering information is given on any current masthead page.

A Rigorous Test for Orbital Symmetry Control in Cation Radical/Neutral Cycloadditions

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Two potentially distinct mechanistic role senses have been recognized for the cation radical Diels–Alder reaction.[1,2] The mechanism in which the cation radical component reacts as the dienophile is classified as a [4 + 1] cycloaddition and is formally symmetry allowed. The alternate reaction mode in which the cation radical component reacts in the s-cis diene role is classified as a [3 + 2] cycloaddition and is formally symmetry forbidden. In the preponderance of the cases thus far observed of cation radical Diels–Alder cross additions between two conjugated dienes, the more ionizable component is exclusively incorporated into the adduct as the dienophilic moiety (e.g., Scheme I), in apparent agreement with orbital symmetry considerations.[2–4] However, since cation radical cyclobutanation, another orbital symmetry forbidden cation radical cycloaddition, is extremely facile, it is probable that any symmetry-imposed barrier to [3 + 2] cycloaddition must be much more modest than analogous barriers to forbidden cycloadditions of neutrals. The feasibility of [3 + 2] cycloadditions, first as a minor reaction channel in competition with cyclobutanation in the reaction of relatively more ionizable dienes with electron-rich alkenes[5] and then as the major reaction channel where the less ionizable component, a styrene, is unable to function effectively in the dienic role,[6] has more recently been established. The fundamental question of whether orbital symmetry (or other) effects favor the [4 + 1] cycloaddition in systems in which both reaction components are comparably amenable to the dienic role remains to be rigorously addressed.

In Diels–Alder cycloadditions to neutral dienes, dienic aptitude is, of course, strongly correlated with the s-cis conformational population of the diene. The same should be true of the [4 + 1] reaction. The [3 + 2] reaction, however, is even more acutely affected by diene conformation since the barrier to conformational equilibration in a diene cation radical is prohibitively high. Therefore, to the extent that dienes exist in the s-trans conformation and are ionized to the s-trans cation radical, [3 + 2] cycloaddition is precluded and either [4 + 1] or [2 + 1] cyclo-
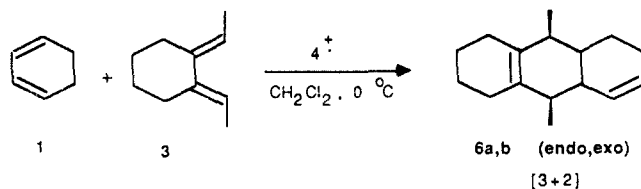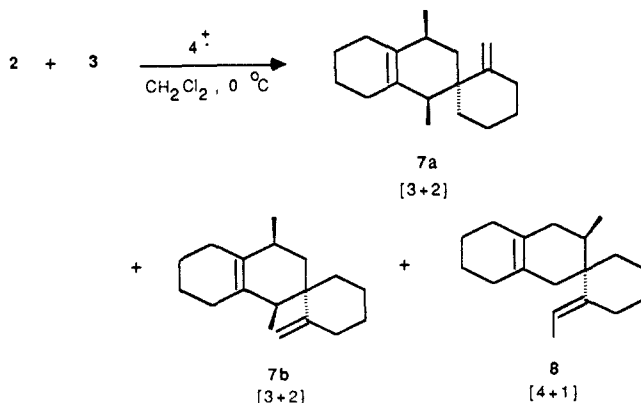
Scheme I
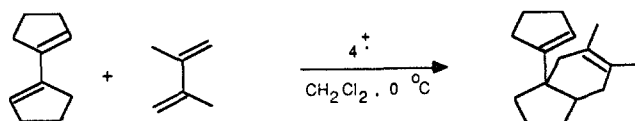
Scheme II
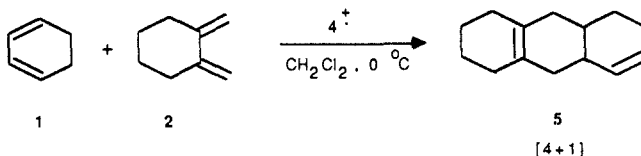
Scheme III

Scheme IV

addition must result (as in Scheme I). It was therefore critical to this study to involve only rigidly s-cis dienes. Further, to render mechanistic role assignments unequivocal, diene pairs were selected for which the oxidation potential differences are sufficiently large that the more ionizable diene can be reliably assumed to be the hole-carrying species. This assumption is scrutinized in a subsequent paragraph. The reactant pair selected for initial study was 1,3-cyclohexadiene (1; E_{ox} = 1.53 V) and 1,2-dimethylene-cyclohexane (2; E_{ox} = 1.85 V).[7] The tris(4-bromophenyl)aminium hexachloroantimonate (4$^{\bullet+}$) initiated cycloaddition of 1 and 2 in dichloromethane at 0 °C yielded, as a cross adduct, essentially only 5 (Scheme II; 45% yield). The mechanistic classification of the reaction leading to 5 is [4 + 1] (i.e., 1$^{\bullet+}$/2), based in part upon the previously stated assumption. The 1,4-dicyanobenzene photosensitized reaction of 1 and 2 in acetonitrile also yields 5 as the sole cross adduct.

The closely analogous reaction of 1 and 3 (E_{ox} = 1.36 V)[8] was then studied. In this case, 1 is the less ionizable component. The observed adducts (6a,b; Scheme III) now reflect a selective [3 + 2] cycloaddition (3$^{\bullet+}$/1). In agreement with this assignment, the dimer of 3 is a major coproduct of the reaction but that of 1 is produced in only minor amounts when 1 and 3 are used in a 1:1 ratio. Once more, the 1,4-dicyanobenzene photosensitized reaction gives the same cross adducts (6a,b) as in the aminium salt reaction and no others.

Finally, the reaction of 2 and 3 was studied in order to examine a case in which the [3 + 2] and [4 + 1] adduct structures are

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closely similar (Scheme IV). Whichever mechanistic classification may be followed, the reaction must involve **3**·⁺/**2**, given the gross difference in ionization potentials and the difficulty of ionizing **2**. The [3 + 2] reaction could produce two diastereoisomeric adducts (**7a,b**), while the [4 + 1] cycloaddition should produce a single diastereoisomer (**8**). In fact, both the aminium salt initiated and photosensitized cross additions of **2** and **3** produce all three isomers in the ratios **7a:7b:8** = 0.5:0.7:1.0. The [3 + 2]:[4 + 1] ratio is therefore 1.2:1.

The assumption that the more readily ionized diene is the hole-carrying species in these reaction systems can be justified quantitatively. The rate constant for the cyclodimerization **1**·⁺/**1** has been measured (3 × 10⁸ mol L⁻¹ s⁻¹).[9] The analogous reaction **1**·⁺/**2** is estimated to have a rate constant of at least 1.5 × 10⁸ on the basis that even the relatively more stabilized (more selective) *trans*-anethole cation radical adds (in the Diels–Alder mode) to **1** and **2** at the relative rate of only 2:1. A species of higher hole energy, such as **1**·⁺, would be presumed to react with **1** and **2** even less selectively. The corresponding role-inverted reaction **2**·⁺/**1** requires the generation of **2**·⁺, which is qualitatively indicated to be quite difficult by the observation that **2** is essentially inert under the aminium salt conditions. Given the measured oxidation potentials of **1**, **2**, and **3**, the rate of generation of **2**·⁺ must be a factor of 10⁵ slower than the rate of generation of **1**·⁺ at 0 °C.[10] For the overall rate of the **2**·⁺/**1** reaction to compete with that of the **1**·⁺/**2** reaction, the rate constant for the cycloaddition **2**·⁺/**1** would then have to be at least 10¹³, or 10³ faster than the maximum diffusion-controlled rate. In the case of the **2**·⁺/**3** reaction, the even larger difference in ionization potentials (0.49 V) and the correspondingly greater ratio of the rates of formation of **3**·⁺ relative to **2**·⁺ (10⁷) would require a **2**·⁺/**3** cycloaddition rate of 10¹⁵. The virtual absence of the dimer of **2** as a product of any of these reactions also independently supports the proposed mechanistic role assignments. Since **2**·⁺ has high hole energy and is not sterically stabilized, its reactions with **2** vs **1** or **3** should be quite rapid and unselective. The amount of dimer formation is therefore an approximate measure of the amount of cross adduct formed via the **2**·⁺/**1** or **3** mechanism.

These studies suggest that orbital symmetry allowedness/forbiddenness has no discernible effect on role selectivity in the cation radical Diels–Alder reaction. Although the factors that determine adduct selectivity are not as yet completely defined, they appear to correlate with product development control (e.g., adduct strain energies) and to vanish for adduct structures that are quite similar. The apparent irrelevance of orbital symmetry effects is consistent with the facility of such formally symmetry forbidden cation radical reactions as cyclobutanation (*S/S* stereochemistry) and the cation radical vinylcyclobutane rearrangement (*S/R* stereochemistry). The failure of orbital symmetry to exert even a small effect on role selectivity is interesting theoretically, and the following factors may be involved: (i) activation energies for cation radical cycloadditions generally are miniscule in comparison with neutral cycloadditions; differential effects may thus be vanishingly small; (ii) cation radical cycloadditions are highly nonsynchronous; orbital symmetry effects on such reactions should be minimal.

Supplementary Material Available: Experimental details for the cycloaddition reactions of **1** and **2**, **1** and **3**, and **2** and **3** by both the aminium salt procedure and the photosensitized electron-transfer procedure (3 pages). Ordering information is given on any current masthead page.

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(10) From the Marcus equation, $\Delta G^* = \Delta G_0^*(1 + \Delta G_0'/4\Delta G_0^*)^2$, using $\Delta G_0^* = 7$ kcal/mol and $\Delta G_0'$ from the difference in oxidation potentials of **4** (1.05 V) and the appropriate diene (1.85, 1.53, 1.36 V). The above value of ΔG_0^* was experimentally derived for the aminium salt/diene endoergic hole transfers and is in accord with other measurements.[11,12]

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Synthesis, Structure, and Magnetic Properties of the Stable Triangular [Mn$^{IV}_3$O$_4$]$^{4+}$ Core

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The structure of the oxygen evolving center (OEC) in photosystem II of plants and the mechanism of water oxidation are still unknown. Recent biological results have been reviewed in ref 1. Chemists can contribute to this study by synthesizing new manganese clusters and studying the electronic properties of those complexes; then useful comparisons can be made with the spectroscopic properties of the natural system. This approach led, for instance, to the synthesis of [Mn$_4$O$_3$Cl]$^{6+}$ cores[2,3] and of adamantane-like [Mn$_4$O$_6$]$^{4+}$ cores.[4,5] Chemical results have been reviewed in ref 6. We report here the synthesis and magnetic studies of a new type of manganese cluster made of a triangular [Mn$_3$O$_4$]$^{4+}$ core with two mono-μ-oxo bridges and one di-μ-oxo bridge.

Synthesis was carried out under argon. A solution of MnCl$_2$ (1.8 mmol) in 4 mL of DMF[10] and a solution of bipy (4 mmol) and TsOH (3.2 mmol) in 4 mL of DMF were mixed. Before any precipitate appeared, this solution was added to a solution of NEt$_4$MnO$_4$ (1.2 mmol) in 8 mL of DMF; a dark brown solution was obtained. After 16 h, addition of (NEt$_4$)$_2$MCl$_4$ (1 mmol) (M = Mn or Cd) in 14 mL of DMF afforded brown powders of stoichiometry [Mn$_3$O$_4$(bipy)$_4$Cl$_2$]MCl$_4$·3DMF after washing with acetonitrile (M = Mn (**1**), Cd (**2**)).[7] Crystals of **1** were obtained

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(7) Anal. Calcd for **1** (C$_{49}$H$_{53}$Cl$_6$Mn$_4$N$_{11}$O$_7$): C, 43.90; H, 3.99; N, 11.49; Cl, 15.87; Mn, 16.39. Found: C, 42.91; H, 3.83; N, 11.1; Cl, 16.51; Mn, 16.19. Anal. Calcd for **2** (C$_{49}$H$_{53}$CdMn$_3$Cl$_6$N$_{11}$O$_7$): C, 42.10; H, 3.82; N, 11.02; Cl, 15.21; Mn, 11.79; Cd 8.04. Found: C, 41.83; H, 3.55; N, 10.72; Cl, 15.11; Mn, 11.43; Cd, 7.75. Yield around 60 % based on bipy.

(8) X-ray analysis of **1**: orthorhombic, space group *Pbca*, $a = 17.137$ (3) Å, $b = 23.917$ (5) Å, $c = 27.786$ (7) Å, $V = 11\,388$ Å^3, $Z = 8$; $R = 0.070$ for 319 variables and 2644 observed [$I > 2\sigma(I)$] diffractometer-collected reflections (Mo Kα radiation, 293 K). The DMF molecules were found disordered, and the disorder could not be solved. Difference-Fourier peaks not inconsistent with solvent molecule atoms were introduced in calculations as statistically distributed C atoms with partial site occupancies (atoms C(d) in table of positional parameters in supplementary material).

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(10) Abbreviations used: DMF = dimethylformamide, TsOH = *p*-toluenesulfonic acid, NEt$_4$⁺ = tetraethylammonium cation, bipy = bipyridine, OEC = oxygen evolving center, EPR = electron paramagnetic resonance, zFS = zero-field splitting.