the absolute stereochemical assignments were determined by deoxygenation[14] of the aldol adducts **3a** and **3b** and subsequent correlation with the α-methyl-substituted carboxylic acids of known absolute configuration.

It is clear that the erythro specificity of zirconium enolates is due to steric interactions in the transition state between the substituents on the enolate and the bulky cyclopentadienyl ligands of the metal.[1,15] One possible model for these interactions is shown in Scheme III. We speculate that the interaction of the cis-methyl group of the enolate with the cyclopentadienyl ligands and the influence of the side arm of the chiral pyrrolidyl ring generate a chiral pocket on the metal into which the aldehyde must fit in order for bond formation to occur. The absolute configuration of all products so far determined is consistent with this conjecture. The absolute requirement of a Z-substituent, such as methyl or n-alkyl, on the chiral enolate has been demonstrated, and the analogous acetate enolates lacking this substituent exhibit virtually no aldol diastereoface selection. Related trends have been noted in this laboratory for chiral boron enolates.[16]

Acknowledgment. This research has been supported by the National Institutes of Health.

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Electronic States of 2-Methylenecyclopentane-1,3-diyl and Trimethylenemethane

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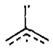
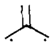
Table I. Energies for the Electronic States of Trimethylenemethane and 2-methylenecyclopentane-1,3-diyl

Trimethylmethane[a]

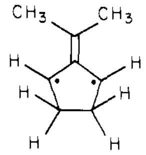
state		SOGVB	MCSCF
$^3A_2'$ (1)		0.0	0.0
$^1B_1$ (2)	 [b]	15.2	15.2
$^1A_1$ (3)		29.0	21.2
$^1B_2$ (4)	 [c]	22.1	22.1

2-Methylenecyclopentane-1,3-diyl[d]

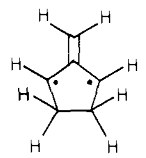
state	MCSCF/SOGVB
$^3B_2$	0.0
$^1A'$ (C_s)	10.3
$^1B_1$	15.5
$^1A_1$	18.7
$^1B_2$	23.9

[a] Energies in kcal/mol relative to the triplet state, E (MCSCF) = -153.03095 au = E (SOGVB). [b] Orthogonal unique CH_2 group. [c] Planar unique CH_2 group. [d] Energies in kcal/mol relative to the triplet state, E (SOGVB) = -229.04382 au.

The nature of open-shell systems, such as diradicals, are important in understanding a variety of chemical processes. These systems are being widely studied by both theory[1] and experiment.[2,3] One of the best studied diradicals is trimethylenemethane (TMM) for which a number of low-lying electronic states are known (see Table I). The energy differences between the triplet ground state **1** and various excited singlet states are of great interest.[4-27] The generally accepted theoretical value for the energy difference between **1** and **2** is ~14 kcal/mol while that between **2** and **4** is 2-3 kcal/mol, with **2** being more stable. Recent experimental work has suggested, contrary to theoretical predictions, that the singlet-triplet splitting is quite small, falling between 1 and 4 kcal/mol.[26,27] This experimental work was done on a system with the TMM moiety incorporated in a five-membered ring (**5**). We



5



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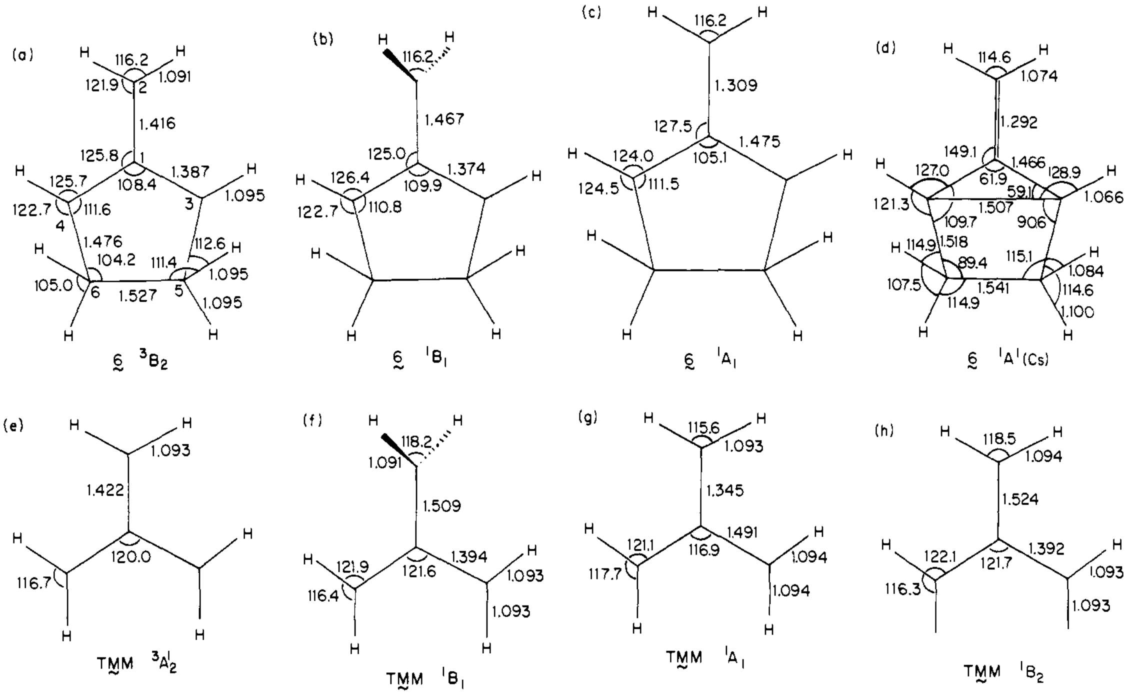

Figure 1. Geometries obtained from PRDDO optimizations employed in the ab initio calculations on TMM and **6**. The calculations on TMM were done with Slater exponents and those on **6** with STO-3G exponents.[31] (a) $^3B_2$(**6**), full optimization; (b) $^1B_1$(**6**), partial optimiation; (c) $^1A_1$(**6**), partial optimization; (d) $^1A'$(**6**), full optimization, C_s symmetry; (e) $^3A'_2$(TMM), full optimization; (f) $^1B_1$(TMM), full optimization; (g) $^1A_1$(TMM), full optimization; (h) $^1B_2$(TMM), full optimization.

have examined the low-lying states of 2-methylenecyclopentane-1,3-diyl (**6**) using molecular orbital theory in order to provide a better comparison between theory and experiment. In order to develop our computational method for treating the electronic states of **6**, we reexamined the electronic states of TMM for comparison as this system is somewhat easier to understand.

The calculations were carried out with two methods for evaluating the integrals and a variety of means for solving the SCF equations. The initial calculations were carried out by using the PRDDO approximation,[28] with exponents on C set at the values of Hehre, Stewart, and Pople[29] and the exponent on H set at 1.2. Complete geometry optimizations of the appropriate electronic states of TMM were carried out by using the above basis and with a basis employing Slater exponents on C.[30,31] Complete geometry optimizations of the $^3B_2$ state and the closed-shell $^1A'$ state (C_s geometry) of **6** were performed. Partial geometry optimization for the remaining states of **6** was done in the following manner. For the $^1A_1$ and $^1B_1$ states of **6**, the coordinates for carbons 3–6 (see Figure 1) and the hydrogens attached to carbons 5 and 6 were not varied. These coordinates were obtained from the optimized structure for the $^3B_2$ state. All of the remaining hydrogen distances were kept constant as was the HCH angle on the exocyclic methylene group. The remaining geometric parameters were then chain optimized. The coordinates for the $^1B_2$ state were taken from those of the $^1B_1$ state except for a 90° rotation about the C–CH$_2$ (exocyclic) bond. The PRDDO calculations on the $^3A'_2$ ($^3B_2$ for **6**), $^1B_1$, $^1B_2$, and closed-shell $^1A_1$ ($^1A'$) states employed a restricted Hartree–Fock (RHF) formalism. The calculations on the open-shell $^1A_1$ state were done by using a generalized valence bond perfect-pairing (GVB (pp)) wave function,[32] since this state cannot be described at the RHF level. The geometries determined as described above and used in the subsequent ab initio calculations are shown in Figure 1.

Ab initio calculations were done using the geometries in Figure 1 for the various states of TMM and **6** and the STO-3G basis sets.[29] Initially, GVB (pp) calculations splitting either one orbital [$^3A'_2$ ($^3B_2$), $^1B_1$, $^1B_2$ states] and treating the two open-shell orbitals consistently or splitting two orbitals ($^1A_1$ states) were carried out. Full multiconfiguration SCF (MCSCF) calculations for the π space of the states of TMM were done starting from the localized GBV (pp) wave functions.[33] As an aid for understanding these results, strongly orthogonal GVB (SOGVB) calculations were also performed on these states.[34] For the states of **6**, SOGVB calculations on the $^1B_1$, $^1B_2$, and $^3B_2$ states were done while the $^1A_1$ states were treated at the MCSCF level (see below). The relative energies for the electronic states of TMM and **6** at the MCSCF/SOGVB levels are summarized in Table I.

A test of the adequacy of the calculation for treating the states of TMM is the energy for the two symmetry components of the $^1E'$ state, $^1A_1$ and $^1B_2$ (in our case, at the optimum $^3A'_2$ geometry). These two states only become degenerate at the MCSCF level of calculation giving an energy of 30.2 kcal/mol relative to the $^3A'_2$ state. The $^1A_1$ state is always lower at the RHF or GVB(pp) level of calculation which leads to an overestimation of the stability of this state; at the SOGVB level, this is reversed and the $^1A_1$ state lies above the $^1B_2$ state. At the MCSCF level and for the optimimum geometries, the $^1A_1$ state actually lies above the $^1B_1$ state but is slightly below the $^1B_2$ state. This result confirms the work of Davidson and Borden[12] and, indeed, our $^3A'_2$–$^1B_2$ energy difference is in quantitative agreement with their result. Our study is more complete as we allow for a full relaxation of the sigma core in the MCSCF calculation while the π-CI calculations of Davidson and Borden were done by using a core taken from an

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(31) In the PRDDO approximation, the bond distances using the exponents of ref 29 tend to be somewhat shorter (~0.02–0.03 Å) than those using the Slater exponents for these types of compounds. For TMM, the geometries using Slater exponents agree better with the values obtained by using a double zeta basis set (ref 8 and 9). Since only very small differences in the relative energies for the electronic states of TMM were found with the two basis sets, the geometries obtained with the Slater basis set were used in our ab initio study of TMM.

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RHF triplet calculation. Our results demonstrate that the assumption by Davidson and Borden[12b] of a frozen σ core obtained from a calculation on the triplet state is extremely good for the low-lying electronic states of TMM. Since these workers[12b] employed a π CI, they could not treat the $^1B_1$ state except at the RHF level; we can, however, treat the $^1B_1$ state at the same level as the other electronic states.[35] We predict a $^3A'_2$–$^1B_1$ energy splitting that is in good agreement with the SCF–CI calculations of Hood, Schaefer, and Pitzer who employed a double zeta basis. We note that the rotation barrier, i.e., the $^1B_1$–$^1B_2$ energy difference, is predicted to be 7 kcal/mol, significantly higher than previous estimates.

SOGVB calculations on the states of TMM were done to provide a better physical understanding of the energetics. For the $^1B_1$ state, the SOGVB and MCSCF calculations are formally identical, since they incorporate the same configurations. For the $^3A'_2$ state the SOGVB–MCSCF energy difference is $<10^{-2}$ mhartree, while for the $^1B_2$ state, the difference is $<10^{-1}$ mhartree. In contrast, the SOGVB–MCSCF energy difference for the $^1A_1$ state is 12.70 mhartree, and the energy of the $^1A_1$ state must be determined at the MCSCF level. Since the SOGVB and MCSCF calculations are in such good agreement and because the SOGVB calculations are more computationally efficient, the final calculations for the $^3B_2$, $^1B_1$, and $^1B_2$ states of **6** were done at the SOGVB level, and only the energies of the $^1A_1$ and $^1A'$ states were obtained by using the MCSCF method.

The SOGVB calculations provide further information about the physical nature of these states. The calculations show that only two configurations besides the Hartree–Fock configuration are required to determine the energies for the $^3A'_2$ ($^3B_2$), $^1B_1$, and $^1B_2$ states. The $^1A_1$ state requires more configurations. The Hartree–Fock configuration for the $^1B_2$ of TMM can be written as *2011* where the first two orbitals are the bonding and antibonding orbitals of the allylic fragment and the final two orbitals are the singly occupied nonbonding allylic orbital and the singly occupied lone pair on the unique methylene group. This configuration enters with a coefficient of –0.9450. The GVB (pp)-like configuration corresponds to promoting two electrons from the allylic bonding orbital to the antibonding orbital, *0211*, and enters with a coefficient of 0.1736. Besides the Hartree–Fock configuration, the most important configuration, however, is the configuration *1111* where the first two electrons are coupled into a triplet as are the final two electrons; these two triplet pairs are then coupled overall into a singlet. This configuration has a coefficient of –0.2770. Similar results are observed for the other states of TMM and the appropriate states of **6**. In order to determine why this last configuration is so important, we carried out calculations on the cations generated by removing an open-shell electron from the $^1B_2$ state of TMM. This leads to a $^2A_2$ state (removal of an electron from the lone pair orbital on the unique methylene) or a $^2B_1$ state (removal of an electron from the nonbonding orbital of the allyl radical). The GVB (pp)–SOGVB energy difference for the $^2A_2$ cation (allyl-like fragment) is 0.04232 au, while for the $^1B_2$ state of the neutral this difference is 0.04129 au. In contrast, the energy difference for the $^2B_1$ cation (allyl-cation-like fragment) is only 0.00239 au. This result suggests that the dominant error in treating most of the states at the GVB (pp) (or RHF) level is an improper treatment of the allylic moiety due to neglect of the spin recoupling term.

Comparison of the energy results given in Table I shows that the energies of the states of **6** are similar to those of TMM. The major changes are that the $^1A_1$ state of **6** is significantly lower in energy than the $^1B_2$ state, in contrast to the TMM results where the two states are of comparable energy. Furthermore, for **6** another form of the $^1A_1$ state is present which has the diradical electrons paired in a bond to form a bicyclic system with C_s symmetry. (This state is equivalent to methylenecyclopropane (MCP) in the case of TMM). The energy of this bonded $^1A'$ state is 10 kcal/mol above the $^3B_2$ state. In comparison, MCP is 25–30 kcal/mol more stable than the $^3A'_2$ state of TMM. The energy of this closed-shell form of the $^1A'$ state of **6** should show the largest basis set error since it has the most strain. Consequently, its energy relative to the $^3B_2$ ground state could be somewhat lower. It is possible that this closed-shell $^1A'$ state can be invoked to explain the low value for the singlet–triplet splitting observed in the trapping experiments of Berson and Platz.[26] Experimental estimates of the rotation barrier about the C–CH_2 (unique methylene) bond in substituted trimethylenemethanes range from ~2–4 kcal/mol. Our value for this barrier on the basis of the $^1B_1$–$^1B_2$ splitting is 7 kcal/mol for TMM and 8 kcal/mol for **6**. If the $^1B_1$–$^1A_1$ splitting is employed, the rotation barriers are 6 kcal/mol for TMM and 3 kcal/mol for **6**. These latter values agree somewhat better with the experimental results. We note, however, that an exact comparison between theory and experiment is difficult, since substituent effects could easily affect the experimentally determined rotation barriers by 1–3 kcal/mol and there is a likely error of 1–2 kcal/mol in the calculations. Thus an exact comparison must await more detailed calculations and experimental studies.

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[35] We employed only the p–π orbitals in determining the configurations for the MCSCF calculations on the $^1B_1$ state. These orbitals correspond to the three allyl π orbitals and the lone p orbital on the rotated methylene group. The GVB (pp) calculations employed as the starting guess for the MCSCF calculations were already highly localized and did not include a significant contaminant from the "π-type" CH_2 orbital on the unique methylene group. The wave functions for the $^1B_1$ and $^1B_2$ states were very similar which demonstrated that the two states, $^1B_1$ and $^1B_2$, were being treated in the same manner. The SOGVB calculations on the $^1B_1$ and $^1B_2$ states rigorously gave only the three configurations described below. Since the SOGVB and MCSCF results are in excellent agreement, this provides further evidence that we are treating the two states in a comparable fashion.

Metal–Metal Bonded Complexes of the Early Transition Metals. 2. Synthesis of Quadruply Bonded Tungsten(II) Trifluoroacetate Complexes

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Twenty years ago Wilkinson and co-workers reported the synthesis of molybdenum(II) carboxylate complexes[1] which were subsequently shown to be dimeric,[2] quadruply bonded[3] molecules. Numerous efforts, published and unpublished,[4] have been made since that time to prepare tungsten analogues but without any conclusive success. Attempts to mimic the original Wilkinson synthesis (eq 1) by substituting $W(CO)_6$ for $Mo(CO)_6$ have

$$2Mo(CO)_6 + 4HO_2CR \xrightarrow{\Delta} Mo_2(O_2CR)_4 + 12CO + 2H_2 \quad (1)$$

produced an interesting series of trinuclear tungsten(IV) cluster compounds, but no binuclear tungsten(II) species were isolated from the reactions of tungsten hexacarbonyl with acetic, propionic, or pivalic acids.[5] Metathetical reactions between preformed

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