hydride ligand bridges each of the two metal-metal bonds.

The details of the nature of the delocalized bonding in clusters such a I remains to be established, but this bonding could have an important influence on the reactivity of the compounds and could lead to the development of new reaction processes that are characteristic of multinuclear metal centers.

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Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters, interatomic distances, angles and structure factor amplitudes are available for structures I and II (26 pages). Ordering information is given on any current masthead page.

Remarkable, Contrasteric, Electrocyclic Ring Opening of a Cyclobutene[1]

William R. Dolbier, Jr.,* and Henryk Koroniak

Department of Chemistry, University of Florida
Gainesville, Florida 32611

Donald J. Burton,* A. R. Bailey, G. S. Shaw, and S. W. Hansen

Department of Chemistry, University of Iowa
Iowa City, Iowa 52242

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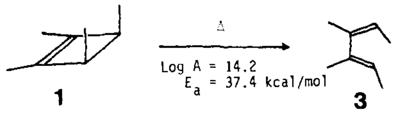
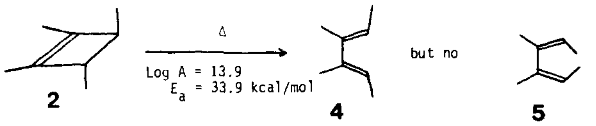
The earliest examples of electrocyclic cyclobutene ring opening, which demonstrated unambiguously the orbital symmetry control of such reactions, derived from Criegee's elegant studies of the *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes (**1** and **2**).[2] In the case of the cis isomer, **1**, the *E*,*Z*-diene **3** was the only product





that could have been formed by conrotatory ring opening. On the other hand, conrotatory ring-opening of the trans isomer, **2**, could have formed either the observed *E*,*E*-isomer **4** or the unobserved *Z*,*Z*-isomer **5**. The exclusive formation of **4** has been uniformly attributed to probable repulsive steric interactions that would be present in the transition state for formation of **5** due to the two methyl substituents rotating simultaneously inward. This argument has been uniformly applied to rationalize similar results in virtually all electrocyclic ring-opening reactions of cyclobutenes.

We wish to report kinetic and thermodynamic studies of the *cis*- and *trans*-perfluoro-3,4-dimethylcyclobutene system (**6** and **7**), which open this interpretation to serious doubt since the trans isomer, **7**, ring opens to the *Z*,*Z*-diene **9** with an activation energy ~18 *kcal less* than it ring opens to the *E*,*E*-diene **10** ($k_{ZZ}/k_{EE} = 1.9 \times 10^9$ at 111.5 °C).

Table I. Thermodynamic Parameters[a]

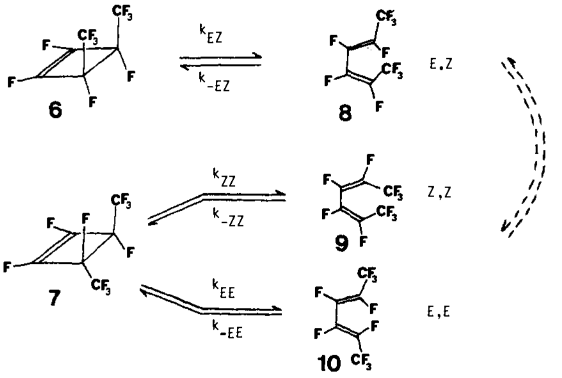
	6 (cis)	7 (trans)	8 (*E,Z*)	9 (*Z,Z*)	10 (*E,E*)
$\Delta H°$ [b]	2.5	0	7.7	7.2	8.3
ΔS [c]	0.5	0	12.8	11.0	12.1

[a] All thermodynamic parameters are given relative to 7. [b] In kcal/mol. [c] In cal/deg.

Table II. Kinetic Parameters

	Log *A*	E_a [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	mean *T*, °C
k_{ZZ}	12.6 (0.3)	30.5 (0.5)	29.8	−3.1	93.8
k_{-ZZ}	10.2 (0.3)	23.2 (0.5)	22.5	−14.0	93.8
k_{EE}	14.2 (0.4)	49.7 (0.8)	48.6	3.5	257.8
k_{-EE}	11.6 (0.4)	41.4 (0.8)	40.4	−8.6	257.8
K_{EZ}	14.6 (0.2)	39.6 (0.4)	38.7	5.5	207.8
k_{-EZ}	11.9 (0.1)	34.4 (0.3)	33.5	−6.9	207.8

[a] In kcal/mol. [b] In cal/deg.



The thermal equilibrations **6** ⇄ **8**, **7** ⇄ **9**, and **7** ⇄ **10** were examined kinetically over the temperature ranges 199.25–217.0, 76.5–111.5, and 240.75–272.5 °C, respectively, yielding the thermodynamic and kinetic parameters in Tables I and II. All equilibria were actually examined starting from the respective dienes[3] since in each case the cyclobutenes were strongly favored thermodynamically. Rate data for the *leakage* process from the **7**, **9**, **10** system to the **6**, **8** system could not be determined with great precision, but the approximated E_a (42 kcal/mol) is consistent with the process involving a double-bond isomerization process (**10** ⇄ **8**).[6]

The contrast of these results with those of the methyl-substituted cyclobutenes is both dramatic and remarkable. Moreover there is not a simple explanation for this anomaly. Since the results are clearly contrary to expectations based upon the oft-quoted "steric" argument, the whole use of steric effects to explain the methyl-derivative results must be called into question. Theoreticians have projected a probable cisoid but skewed geometry, with

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[1] Taken in part from: Shaw, G. S. Ph.D. Thesis, University of Iowa, Iowa City, Ia, 1981. Reported in part (D. J. Burton, G. S. Shaw, and S. W. Hansen) at the 6th Winter ACS Fluorine Conference, Daytona Beach, Florida, Feb 1983.

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[3] Dienes **8**, **9**, and **10** were synthesized by coupling of (*E*)- and (*Z*)-perfluoroprop-1-enylcopper reagents with (*E*)- and (*Z*)-perfluoro-1-iodopropene.[4] They were characterized by their ^{19}F NMR, IR, and UV spectra, with the unambiguous *E* vs. *Z* determination deriving from the well-precedented[5] and distinctive 145 and 5.1 Hz $J_{F_2F_3}$ values obtained for **10** and **9**, respectively.

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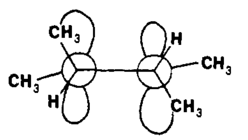

Figure 1. Pyramidalization of 1,2,3,4-tetramethylcyclobutene.

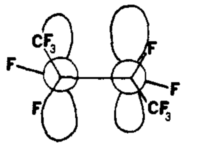

Figure 2. Pyramidalization of perfluoro-3,4-dimethylcyclobutene.

deviations from planarity calculated to be from 20° to 40°, for the conrotatory ring opening of cyclobutenes.[7] It is not apparent that the steric factors in such a transition state should be so significant as to give rise to the specificity observed for the **2** → **4** conversion. It appears moreover that there have been *no* theoretical examinations of such competitive conrotatory processes.

Freedman, in an interesting study of 1,2,3,4-tetraphenylcyclobutenes,[8] attempted to correlate ground-state conformational geometry with rates of electrocyclic ring closure. While there is little doubt that the ground-state geometry of *Z*,*Z*-diene **9** is skewed (the UV $\lambda_{\max}$'s for **9**, **8**, and **10** are 207, 214, and 219 nm, respectively), and perhaps closer to the required transition-state geometry than the *E*,*E*-isomer **10**, there is no reason to believe that a significant energy would be required for **10** to reach a similar reactive conformation[9] or that ground-state energy differences could thus give rise to the observed dramatic kinetic results.

One should consider the possibility that the specificity of cyclobutene **2** ring opening to diene **4** is only fortuitously in accord with steric prejudices and that the driving force for that stereospecific electrocyclic process, as well as for the contrary observations in the case of cyclobutene **7**, is a nonsteric substituent effect on the cyclobutenes. Houk has predicted the effect of allylic substituents on the tendency for double bonds to pyramidalize wherein pyramidalization is maximized for electron-deficient, eclipsing allylic σ-bonded substituents.[11] It was hypothesized, moreover, that such pyramidalization "reflects interactions in the ground state of molecules which are related to much larger energetic effects in transition states".[12]

Consistent, then, with Houk's generalizations is our hypothesis that the differences observed in the hydrocarbon cyclobutene (**2**) and the perfluorocyclobutene (**7**) systems may be due to a difference in their directions of pyramidalization as shown in Figures 1 and 2.

Theoretical and experimental probes of this hypothesis are under way.

Acknowledgment. We gratefully acknowledge the National Science Foundation (W.R.D., D.J.B) and the Air Force Office of Scientific Research (D.J.B.) for their generous support of this research.

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Stereocontrolled Lactone Synthesis Using Diene-Molybdenum Chemistry

Anthony J. Pearson* and Md. Nazrul I. Khan

Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

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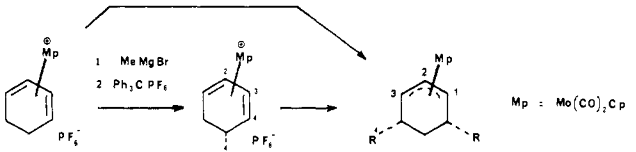
We recently showed that the $Fe(CO)_2L$ moiety (L = CO, PPh_3, $P(OPh)_3$) bound to a cyclic dienyl cation may be used to direct stereochemistry during the attachment of two substitutents, giving 1,2-stereocontrol in the six-membered ring[1] and 1,3-stereocontrol in the seven-membered ring.[2] Other transition metals can be expected to show analogous and complementary stereocontrol. Arene-manganese complexes have been used to establish 1,2-stereocontrol in the six-membered ring.[3] Faller et al.[4] showed that the molybdenum complex **1** is converted to **2** in very high yield and that **2** is stereospecifically methylated (MeMgBr) to give **3**. This offers a useful complementarity to the cyclohexadienyl-$Fe(CO)_3$ cations,[1] but currently available methods for demetalation of π-allyl complexes such as **3** use harsh conditions ((i) $NOPF_6$; (ii) $NaBH_4$; (iii) O_2), less useful when sensitive functional groups are present. We have investigated potentially milder methods for decomplexation, recognizing that **2** might be useful for generating the relative stereochemistry at C(5), C(6), and C(8) in compounds such as tylosin (**4**) and magnamycin B

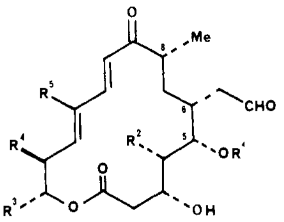


1

2

3, R = R' = Me
6a-l

6a, R = H; R' = $CH(CO_2Me)_2$
b, R = H, R' = $CH(SO_2Ph)CO_2Me$
c, R = H; R' = $CH(COMe)CO_2Me$
d, R = Me; R' = $CH(CO_2Me)_2$
e, R = Me; R' = $CH(SO_2Ph)CO_2Me$
f, R = Me; R' = $CH(COMe)CO_2Me$
g, R = H; R' = $CH(CO_2Me)CO_2H$
h, R = Me; R' = $CH(CO_2Me)CO_2H$
i, R = H; R' = CH_2CO_2Me
j, R = Me; R' = CH_2CO_2Me
k, R = H; R' = CH_2CO_2H
l, R = Me; R' = CH_2CO_2H



4, R^1 = sugar residue;
R^2 = Me; R^3 = Et;
R^4 = CH_2Omycinase;
R^5 = Me
5, R^1 = sugar; R^2 = OMe;
R^3 = Me; R^4 = R^5 = H

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