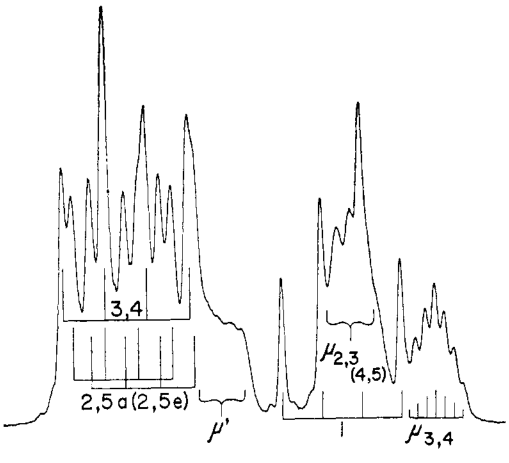

Figure 1. ^{1}H spectrum (220 MHz) of $^{11}B_5H_{11}$ containing 98% ^{11}B. The spectrum of normal isotopic content contains similar features but is less informative.

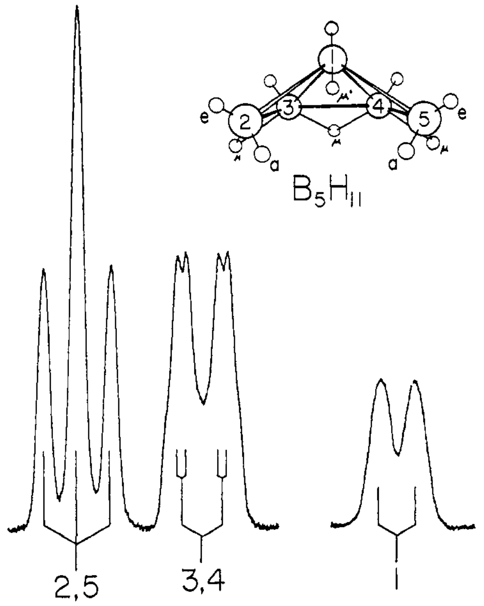

Figure 2. ^{11}B spectrum of (70.58 MHz) $^{11}B_5H_{11}$.

at $\delta - 2.09$ ppm, as a separate broad multiplet of intensity one.

A second new feature that appears in the higher field pmr studies is the resolution of peaks attributed to $-BH_2$ groups into magnetically nonequivalent sets of equatorial and axial protons. Although we are as yet unable to conclusively assign the two resonances, they display both different coupling constants and a chemical shift difference. We note that the lower field absorption of the $-BH_2$ set displays the smaller coupling constant (see Table I).

Table I

	δ, ppm	J, cps
220-MHz Proton Magnetic Resonance		
2,5e or a	-3.91^{a}	127
3,4	-3.82	160
2,5e or a	-3.47	135
μ'	-2.09	
1	$-.23$	153
Bridge 2,3(4,5)	$+.46$	
Bridge 3,4	$+1.64$	36^{b}
70.58-MHz Boron-11 Magnetic Resonance		
2,5	-7.44^{c}	132
3,4	-0.47	160 36^{b}
1	$+55.25$	152

[a] Relative to TMS. [b] Boron-11-bridge proton coupling. [c] Relative to $BF_3O(C_2H_5)_2$.

Features similar to the above appear in the spectra of B_4H_{10}, B_5H_9, B_6H_{12}, B_8H_{12}, B_8H_{18}, and n-B_9H_{15}. In addition, we have noted unusually shaped low-field quartets in the pmr spectra of B_6H_{10} and B_8H_{12}, but we cannot easily explain their skewed appearance at this time.

Finally, we are able to make gross structural inferences based on the general appearance of the pmr spectra. The pmr spectrum of B_8H_{18} can nearly be superimposed on that of B_4H_{10} except for the low-field quartet of the $-BH_2$ set, which has diminished intensity. This decrease in intensity and the presence of only one symmetric bridge proton resonance lead us to discount the beltline fragment model and to favor the bitetrabornyl structure (two B_4H_9 units joined with a boron–boron bond at the 2,2′ positions).[3] Also striking is the pmr spectrum of the recently discovered isodecaborane(16),[4] whose two quartets and symmetric bridge resonance in the ratio 6:2:8 almost perfectly overlay the pmr spectrum of B_5H_9. The formulation of this molecule as two B_5H_8 units boron–boron bonded through the 2,2′ positions is also supported by the 2:6:2 singlet, doublet, doublet pattern resolved in the 70.58-MHz ^{11}B nmr spectrum.

Reproductions of these spectra with complete tables of chemical shifts, coupling constants, and assignments will appear in full detail elsewhere.

Acknowledgments. The authors gratefully acknowledge the support of the National Science Foundation (Grant No. GP-4944). We are also indebted to Mr. A. O. Clouse for invaluable assistance in obtaining the ^{1}H and ^{11}B nmr spectra.

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(3) J. Dobson, D. Gaines, and R. Schaeffer, *J. Amer. Chem. Soc.*, **87**, 4072 (1965).

(4) J. Dobson, R. Maruca, and R. Schaeffer, *Inorg. Chem.*, in press.

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Received March 29, 1970

Catalysis of Symmetry-Restricted Reactions by Transition Metal Compounds. The Valence Isomerization of Cubane

Sir:

The subject of this communication is our discovery that certain transition metal compounds, notably of rhodium(I), are powerful catalysts for the valence isomerizations of cubane and its derivatives[1] to the corresponding *syn*-tricyclooctadienes, according to eq 1 and 2. We also wish to report some observations

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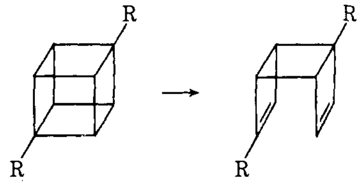
(1) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964). Rearrangement of the cubane compounds under the conditions of our experiments in the absence of a catalyst was negligible.

Table I. Rate Constants at 40°

Cubane	Solvent	Catalyst	k_1, M^{-1} sec^{-1}	k_4, M^{-1} sec^{-1}	k_1/k_4
Ia	CCl_4	$[Rh(IIa)Cl]_2$	1.7×10^{-1}		
Ia	CCl_4	$[Rh(NOR)Cl]_2$	2.6×10^{-1}		
Ia	$CDCl_3$	$[Rh(NOR)Cl]_2$	14	3.0×10^{-2}	4.6×10^{2}
Ib	CCl_4	$[Rh(COD)Cl]_2$	4.8×10^{-3}		
Ib	$CDCl_3$	$[Rh(COD)Cl]_2$	3.2×10^{-2}		
Ib	$CDCl_3$	$[Rh(NOR)Cl]_2$	11.4×10^{-2}	3.2×10^{-4}	3.6×10^{2}
Ib	$CDCl_3$	$[Rh(IIa)Cl]_2$	7.2×10^{-3}		
III	$CDCl_3$	$[Rh(NOR)Cl]_2$	8.8×10^{-1}	2.4×10^{-3}	3.6×10^{2}

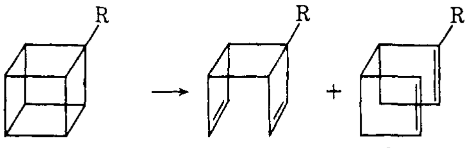
relating to the kinetics and certain other features of these reactions which serve to illuminate the mechanism of this interesting catalysis.



(1)

Ia, R = H
b, R = COOCH$_3$

IIa, R = H
b, R = COOCH$_3$



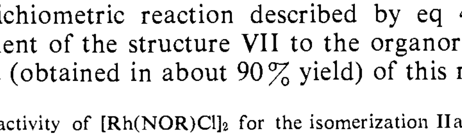
(2)

III, R = COOCH$_3$ IV (29%) V (71%)

The remarkable thermal stability of the highly strained cubane molecule presumably reflects the constraints of the Woodward–Hoffmann orbital symmetry conservation rules,[2] according to which the rearrangements represented by eq 1 and 2 are thermally "forbidden." The role of transition metals in catalyzing such symmetry-restricted processes is a subject of great current interest, and our results have an important bearing upon the interpretation of several other examples of such catalysis that have recently been reported.[3,4]

The isomerizations Ia → IIa,[5] Ib → IIb (mp 73–74°), and III → IV + V were found to proceed rapidly and quantitatively[6] in solvents such as chloroform and carbon tetrachloride in the presence of catalytic amounts ($\sim 10^{-3}$ M) of complexes of the type $[Rh(diene)Cl]_2(Rh^I)$, where diene = norbornadiene (NOR), cycloocta-1,5-diene (COD), or *syn*-tricyclooctadiene (IIa).[7] Kinetic measurements at 40°, using nmr to follow the reactions, yielded, in each case, the second-order catalytic rate law, $-d[\text{cubane}]/dt = k_1[\text{cubane}]\cdot[Rh_2(\text{diene})_2Cl_2]$. Values of k_1, illustrating the effects of several variables, are listed in Table I. Addition of up to a 20-fold excess of the free diene was found to be without effect on the rate, indicating that reversible displacement of the diene ligand from the catalyst by cubane is not a feature of the mechanism. The catalytic activity of $Rh(COD)Cl(PPh_3)$ for the reaction Ib → IIb was comparable to that of $[Rh(COD)Cl]_2$; on the other hand, $Rh(PPh_3)_3Cl$ and $Rh(CO)Cl(PPh_3)_2$ were virtually inactive.

A mechanistic theme of obviously great interest, whose elucidation was one of the principal objectives of our investigation, relates to the question of whether or not these catalytic transformations are concerted processes. The suggestion has previously been made that interaction with transition metals of appropriate configuration may result in relaxation of the constraints described by the Woodward–Hoffmann rules for the concerted pathways of 2 + 2 cycloadditions and related processes.[3,4] This concept, which has been applied to the interpretation of certain other rhodium(I)-catalyzed reactions such as the valence isomerization of quadricyclene to norbornadiene,[8] can also be extended to our reactions. However, an equally plausible interpretation is afforded by the nonconcerted mechanism depicted in eq 3. According to this, the rate-determining step involves the opening of only one carbon–carbon bond through an oxidative addition reaction of the type that rhodium(I) and other d^8 complexes are well known to undergo.[9,10] Because of the convincing support that it derives from the observations described below, we strongly favor the latter mechanism.



(3)

VI

The addition of a stoichiometric amount of $[Rh(CO)_2Cl]_2$ to a chloroform solution of cubane resulted not in a catalytic transformation, but instead in the stoichiometric reaction described by eq 4. The assignment of the structure VII to the organorhodium product (obtained in about 90% yield) of this reaction

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(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and references therein.

(3) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); F. D. Mango, *Advan. Catal.*, **19**, 291 (1969), and references therein.

(4) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969), and references therein.

(5) M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).

(6) The organic products were characterized by elemental analysis and by nmr, infrared, and mass spectroscopy. The compound X, which has not previously been described, was also synthesized for the purposes of this work by an independent route which will be described elsewhere.

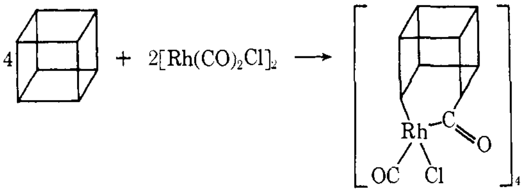
(7) The same rhodium complexes were also effective as catalysts for the further isomerization of the *syn*-tricyclooctadiene products to the corresponding cyclooctatetraenes. The second reaction, in each case, was about 1000-fold slower than the first and did not interfere with either the kinetic study of the cubane → tricyclooctadiene transformation or with the isolation of the intermediate tricyclooctadiene product. The catalytic activity of $[Rh(NOR)Cl]_2$ for the isomerization IIa to cyclooctatetraene is comparable to that of Ag$^+$ which has previously been reported to catalyze the same reaction.[4]

(8) H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967).

(9) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

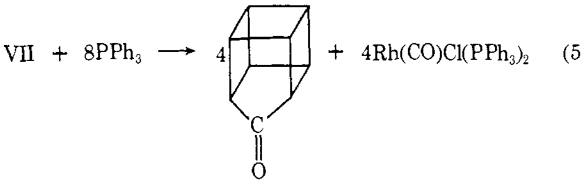
(10) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966); J. Halpern, *Advan. Chem. Ser.*, No. **70**, 1 (1968).

is based upon its elemental analysis, infrared spectrum (sharp bands at 2050 and 1703 cm^{-1} attributable to the terminal and acyl carbonyls), and molecular weight (1300 in chloroform).[11,14] Treatment of a methylene chloride solution of VII with a stoichiometric amount of triphenylphosphine gave, in about 90% yield, the cyclic ketone VIII,[16] together with a small amount (~5–10%) of cyclooctatetraene (eq 5).



(4)

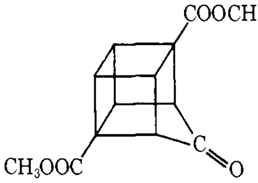
VII



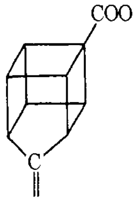
(5)

VIII

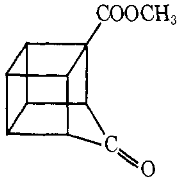
The acylrhodium compound VII presumably arises through the oxidative addition of cubane to $[Rh(CO)_2Cl]_2$ to form an adduct analogous to VI which undergoes the familiar "CO insertion" rearrangement[17] to the acyl compound.[18] Analogous reactions with $[Rh(CO)_2Cl]_2$ were observed also for the substituted cubanes. Although the resulting organorhodium products were not as fully characterized, treatment with triphenylphosphine yielded, in each case, the expected cyclic ketone, *i.e.*, IX (mp 112–113°), from Ib and a mixture (separated gas chromatographically) of 34% X (mp 69–70°) and 66% XI (mp 115–117°) from III. The reaction of $[Rh(CO)_2Cl]_2$ with each of the cubanes obeyed the second-order rate law, $-d[\text{cubane}]/dt = k_4[\text{cubane}][Rh_2(CO)_4Cl_2]$. Kinetic measurements yielded the values of k_4 which are listed, together with the corresponding k_1 values, in Table I.



IX



X (34%)

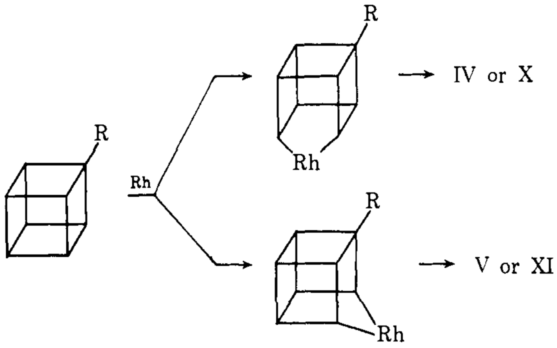


XI (66%)

These observations lead us to conclude that the $[Rh(\text{diene})Cl]_2$-catalyzed valence isomerization of cubane proceeds through the nonconcerted oxidative addition mechanism described by eq 3. This conclusion is reinforced by the following quantitative comparisons.

(1) The *ratio* of the rate constant (k_1) of the $[Rh(NOR)Cl]_2$-catalyzed isomerization to the rate constant (k_4) of the corresponding reaction with $[Rh(CO)_2Cl]_2$ is nearly constant ($4.1 \pm 0.5 \times 10^2$, Table I) for the three cubanes examined (Ia, Ib, III), despite the fact that k_1 and k_4 each varies by a factor of about 100.

(2) The distribution of isomeric products (34% X, 66% XI) from the reaction of III with $[Rh(CO)_2Cl]_2$ parallels that from both the $[Rh(COD)Cl]_2$- and $[Rh(NOR)Cl]_2$-catalyzed isomerization of III (29 ± 3% IV), (71 ± 3% V). This is readily reconciled with our conclusion that the product distribution in both cases is governed by the same (approximately statistical) competition between the two alternative sterically favored modes of oxidative addition of III, *i.e.*



Our observations and conclusions invite a reexamination of the interpretations that have been advanced for the observed catalysis by transition metal complexes of other symmetry-restricted reactions.[3,4] In particular we consider it likely (as Katz and Cerefice[19] have already concluded for the rhodium(I)-catalyzed rearrangements of *exo*-tricyclo[3.2.1.0.^{2,4}]octene) that other rhodium(I)-catalyzed reactions of this type, such as the valence isomerizations of quadricyclene,[8,19a] of hexamethylprismane,[20] and of hexamethyl(Dewar benzene),[21] also proceed through nonconcerted mechanisms involving oxidative addition steps. The applicability of such mechanisms may well extend also to other transition-metal-catalyzed processes such as the silver(I)-catalyzed cyclobutene–butadiene rearrangements described by Merk and Pettit,[4,22] the various cycloaddition reactions

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[11] Analogous acylrhodium complexes have previously been reported to arise from the reactions of $[Rh(CO)_2Cl]_2$ with cyclopropane[12] and with *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene.[13]

[12] D. M. Roundhill, D. N. Lawson, and G. Wilkinson, *J. Chem. Soc. A*, 845 (1968).

[13] H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeck, *J. Amer. Chem. Soc.*, **91**, 218 (1969).

[14] It seems likely that the structure of this tetrameric compound corresponds to a tetrahedral arrangement of Rh atoms, with triply bridging Cl$^-$ ions coordinated to each of the trigonal faces. Such a structure (analogous in some aspects to that of $[Fe(C_5H_5)S]_4$)[15] accommodates the attainment by each Rh^{III} of the presumably preferred coordination number of six.

[15] C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966).

[16] T. W. Cole, Jr., Ph.D. Dissertation, The University of Chicago, 1966.

[17] R. F. Heck, *Advan. Chem. Ser.*, **No. 49**, 181 (1965); K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, **7**, 345 (1968).

[18] The alternative possibility that VII derives from a reaction of II with $[Rh(CO)_2Cl]_2$ has been ruled out by direct demonstration that such a reaction does not occur under the prevailing conditions.

[19] T. J. Katz and S. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969).

[19a] NOTE ADDED IN PROOF. We have recently obtained further support for this conclusion by isolating an acylrhodium product, analogous to VII, from the reaction of quadricyclene with $[Rh(CO_2)Cl]_2$.

[20] H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).

[21] H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **86**, 830 (1967).

[22] W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4787, 4788 (1967).

of norbornadiene,[23] and the recently discovered olefin disproportionation reactions.[24]

Finally, we direct attention to a remarkable feature of the reactions described in this communication, namely the ability of the fully saturated cubane molecule to interact sufficiently strongly with a stable transition metal complex to experience the observed catalytic effects. Previous examples of the facile catalysis of hydrocarbon reactions by transition metals have involved molecules containing either unsaturated (*e.g.*, olefinic) bonds or cyclopropane rings which have been considered to play essential roles in the coordination of the substrates to the catalysts.[4,7,8,24a]

Acknowledgment. Support of this work by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Dr. Steven A. Cerefice for valuable discussions and assistance. One of us (L. C.) also thanks Montecatini Edison S.p.A. for a leave of absence and a fellowship.

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(23) T. J. Katz and N. Acton, *Tetrahedron Lett.*, 2601 (1967), and references therein. These authors have also interpreted the cycloaddition reactions of norbornadiene in terms of nonconcentrated mechanisms.

(24) N. Calderon, E. A. Ofstead, J. P. Ward, W. A. Judy, and K. W. Scott, *J. Amer. Chem. Soc.*, 90, 4133 (1968); W. B. Hughes, *ibid.*, 92, 532 (1970).

(24a) Note Added in Proof. Following submission of this manuscript two reports have appeared describing the silver(I)-catalyzed rearrangements of the homocubyl and 1,1'-bishomocubyl systems [W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, and D. L. Whalen, *Tetrahedron Lett.*, 787 (1970); L. A. Paquette and J. C. Stowell, *J. Amer. Chem. Soc.*, 92, 2584 (1970)]. Following this we have found that silver salts also catalyze the analogous rearrangements of cubane and its derivatives. The difference between the behaviors of the silver and rhodium catalysts in these systems is most striking and is being further examined.

(25) On leave from Montecatini Edison S.p.A., Centro di Chimica Organica Esplorativa, Novara, Italy.

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Received April 6, 1970

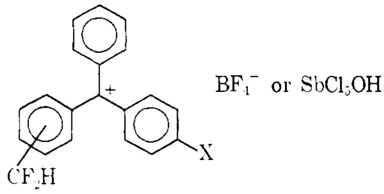
Nuclear Magnetic Resonance Studies of Chirality in Triarylmethyl Cations. Mechanism of Enantiomer and Diastereomer Interconversion

Sir:

The trityl cation, which derives its stability from charge delocalization to its equivalent phenyl rings, must assume a compromise conformation consistent with maximum coplanarity and minimum *ortho* steric interactions.[1] Evidence has accumulated that the ion has D_3 symmetry in solution[2] and the symmetrical propeller conformation in the solid state has been confirmed by an X-ray study.[3] Given a sufficiently high phenyl rotational barrier, suitably substituted trityl cations can give rise to both diastereomers and, as a consequence of the chirality inherent in the trityl propeller conformation, enantiomers. Interconversion of isomers must proceed *via* a transition state in which phenyl rings become either (a) perpendicular to or (b) coplanar with the trigonal plane.[4] Since the latter motion leads to increased steric interactions between neighboring *ortho* protons and the former leads to decreased charge stabilization by phenyl, studies of the energetics and mechanism for this exchange provide information on the relative importance of steric and electronic effects in this system.

The presence and magnitude of a barrier to the process which interconverts diastereomeric fluorines in di- and tri-*meta*-fluorotrityl cations have been elegantly demonstrated by the pioneering nmr study of Schuster, Colter, and Kurland (SCK).[5] However, such data in the absence of information on steric factors can be mechanistically compatible with a planar structure, and we have therefore chosen to detect the dissymmetry inherent in the trityl propeller by utilization of a *m*-difluoromethyl group as a diastereotopic[6] probe. The results, reported below, support a propeller conformation in which interconversion of enantiomeric propellers occurs *via* a two-ring flip (*i.e.*, two rings perpendicular) transition state, rather than the intuitively less satisfactory three-ring flip transition state proposed previously for a related system.[5]

The limiting ^{19}F nmr spectra of the *m*-difluoromethyltrityl cation are reproduced in Figure 1. The change from equivalent fluorines at ambient temperature (A_2X doublet, J_{HF} = 56 Hz) to nonequivalent fluorines at temperatures below −30° (ABX octet, $\Delta\nu_{FF}$ = 140 Hz, J_{FF} = 301.5 Hz) can be unambiguously attributed to the generation of diastereotopism in the CF_2H group as interconversion of the chiral trityl propellers becomes slow on the nmr time scale. Complete line shape analysis[7a] over the entire temperature range yields the activation data listed in Table I, the value $\Delta G^{\ddagger}$ = 12.7 kcal/mol being in reasonable agreement with the data of SCK,[5] as expected for these similar cations. Analogous data obtained with the $-CF_2H$ probe in a *para* position are also listed in Table I and confirm the trends exhibited by the *m*-CF_2H ions.



To obtain information on the mechanism of propeller interconversion, the effect of *para'*-donating substituents was examined. The reduced symmetry of these *m*-CF_2H,*p'*-X (X = CH_3 or OCH_3) trityl cations adds an additional element of complexity to the ^{19}F spectra; slow rotation now results in the formation of two equal energy diastereomers (*syn* and *anti* of Figure

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(1) G. N. Lewis and M. Calvin, *Chem. Rev.*, 25, 273 (1939); G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, 64, 1774 (1942).

(2) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, 37, 1402 (1959); R. Dehl, W. R. Vaughn, and R. S. Berry, *J. Org. Chem.*, 24, 1616 (1959).

(3) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta, Crystallogr.*, 18, 437 (1965).

(4) Four transition states are possible and have been referred to as zero-, one-, two-, and three-ring flip processes by SCK,[5] indicating the number of rings which become perpendicular. Their terminology has been adopted here.

(5) A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Amer. Chem. Soc.*, 87, 2278 (1965); R. J. Kurland, I. I. Schuster, and A. K. Colter, *ibid.*, 87, 2279 (1965); I. I. Schuster, A. K. Colter, and R. J. Kurland, *ibid.*, 90, 4679 (1968).

(6) For nomenclature and background of nmr spectroscopy of chiral compounds see: (a) M. van Gorkom and G. E. Hall, *Quart. Rev. Chem. Soc.*, 32, 14 (1968); (b) K. Mislow and M. Raban, *Top. Stereochem.*, 1, 22 (1967).