

Modes of Rearrangement in Substituted Octahedral Complexes

Jeremy I. Musher* and William C. Agosta

Contribution from the Belfer Graduate School of Science, Yeshiva University, New York, New York 10033, the Department of Organic Chemistry, Hebrew University, Jerusalem, Israel, and The Rockefeller University, New York, New York 10021. Received August 25, 1973

Abstract: The modes of rearrangement and the observable processes for octahedral dihydro complexes containing no, one, and two chelating rings are presented. The last of these can be used to indicate the actual rearrangement for such complexes when appropriate conditions regarding the effect of chelation are satisfied. The modes and OP's for a square pyramidal molecule, an octahedral molecule containing a single lone pair, are also presented. Some observations on related systems are developed.

Intramolecular rearrangements in five- and six-coordinate systems have been discussed recently by several authors.¹⁻⁵ The three problems considered extensively in the literature concern the trigonal bipyramidal phosphoranes,⁶⁻⁹ the octahedral cis-dihydro iron and ruthenium tetraphosphine complexes,¹⁰⁻¹² and the tris-M(AB)₃ complexes for varieties of metal atoms and choices of ligands.¹³⁻²¹ A fundamental difficulty in analyzing the rearrangements in these systems is that in most cases for each rearrangement $A \rightleftharpoons B$ there exists a rearrangement $A \rightleftharpoons B^*$, where B^* is the mirror image of B . It is thus impossible to determine the stereochemistry of the rearrangement precluding any discussion about the mechanism of the rearrangement.

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We consider here the problem of the cis-dihydro iron complexes. We cyclize the phosphine ligands first with a single cycle and then with two cycles. This permits us to observe the rearrangement without greatly modifying the stereochemistry of the uncyclized complex. The bicyclic complex permits a definitive choice of the stereochemistry involved in the rearrangement. A brief discussion of some of the simple rearrangement mechanisms is also given. In the following section the modes of rearrangement about a square pyramidal molecule, related to the octahedral complex by replacing one ligand with a so-called lone pair, are considered. The article is concluded with a discussion of some of the implications for related studies.

Cis-Dihydro Octahedral Complexes

We consider now the rearrangements of cis-dihydro octahedral complexes, the first one of which is *cis*-H₂Fe[P(OEt)₃]₄, **1**, with no chelating ligands. For the purpose of the analysis all hydrogen and phosphorus ligands are considered to be distinguishable, and it is assumed that the trans isomer is not attainable under the conditions involved; therefore, only the 24 isomers which contain the cis-dihydro substituents are considered. The modes of rearrangement for these 24 isomers are given by

$$\begin{aligned} M_0(1) &= I & M_3(6) &= ccc \\ M_1(10) &= cc & M_4(6) &= ccxc \\ M_2(1) &= tt \end{aligned}$$

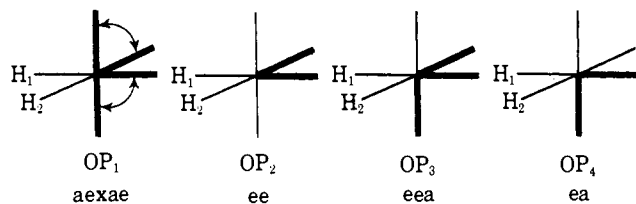
following the notation given previously for a general octahedral complex.⁴ When observable processes are considered these modes are split and it is convenient to introduce the notation using a's and e's for axial and equatorial relative to the plane defined by the two cis hydrides which remain fixed. The numbers in parentheses indicate, as before, the multiplicity of the rearrangements involved. The OP's are

$$\begin{aligned} \text{OP}_0: I &= aa (M_0, M_2) \\ \text{OP}_1: aexae(2) &= aeae(2) (M_3, M_4) \\ \text{OP}_2: ee &= eexaa (M_1) \\ \text{OP}_3: eea(4) &= eaaa(4) (M_3, M_1) \\ \text{OP}_4: ea(4) &= eaa(4) (M_1) \end{aligned}$$

and the 24 stereochemical rearrangements are reduced

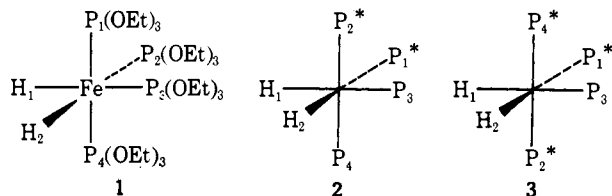
to 12 OP's. These OP's are exemplified by the four processes indicated in Scheme I which, with the ex-

Scheme I



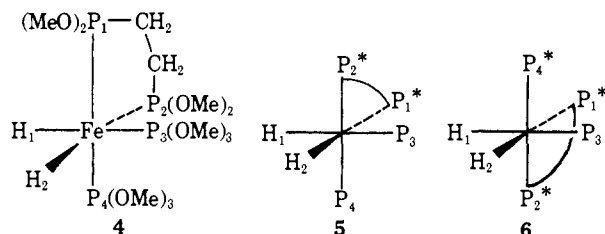
ception of the unique OP₂, give one example of the possible operationally equivalent rearrangements. The alternative processes leading to the mirror-image series could be similarly depicted. This would include the aa rearrangement of OP₀. These are further divided into those involving cc processes with only phosphine ligands, the ae and ee rearrangements, those involving cc processes with one phosphine and one hydride ligand, the aae rearrangements, and that involving the cc process exchanging the two hydrides, the aaxee rearrangement.

The nmr experimental results are consistent with the observable process OP₄.^{4,10} This cannot distinguish between the rearrangement taking **1** into **2** via an ae process or that taking **1** into **3** via an aae process. The rearranging nuclei are indicated with an asterisk. This entire discussion illustrates the important point, which is not always sufficiently appreciated, that only rarely do all rearrangements according to a given mode possess the same energy of activation. A similar analysis follows for the rearrangements in OP₀, OP₁, and OP₃.



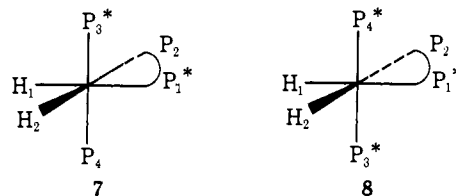
We consider now an as yet unknown monochelated octahedral complex $H_2Fe[P(OR)_3]_2[(R'O)_2PCH_2CH_2P(OR')_2]$, with $R = R' = CH_3$, in which the five-membered FePCCP ring is not expected significantly to modify intramolecular rearrangements except for those in which the chelate itself is involved. We consider only the rearrangements in OP₄, as these are the ones shown experimentally to occur in complexes containing only monodentate ligands.¹⁰

There are three ae processes and three corresponding aae processes. The activation energies for all of the ae rearrangements are different as are those for all of the aae rearrangements, and this obviates the necessity for studying in detail the temperature-dependent nmr through the transition region if the rearrangement is dominated by a single process.

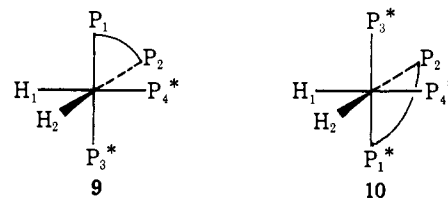


The ae rearrangement $4 \rightleftharpoons 5$ exchanges the chelating phosphorus ligand while keeping the $P(OMe)_3$ groups nonequivalent. This reduces the four OCH_3 peaks (which are actually further split into doublets by the phosphorus) to two while preserving the two different $P(OCH_3)_3$ peaks. Something similar occurs for the more complex CH_2CH_2 spectrum. The nmr spectrum of **5** cannot, however, be distinguished from that of **6**, its mirror image, which is obtained from **4** via the completely different aae rearrangement, once again illustrating the difficulty in obtaining a unique stereochemical analysis of the rearrangement. It is convenient to view **6** by placing it underneath **5** so that the plane of symmetry is easily observed.

The symmetrical molecule **7**, in which the PCH_2CH_2P ring is coplanar with the two hydrides, is obtained from **4** via an ae process, and the mirror image **8** is obtained via an aae process. It is easy to see that the nmr spectra of these two molecules, **7** and **8**, are not only indistinguishable but give rise to only one peak for the $P(OMe)_2$ methyls, one for the $P(OMe)_3$ methyls, and one hydrogen peak for the CH_2CH_2 protons, split, perhaps into a triplet, by the two phosphorus atoms via virtual coupling.



The only rearrangements which give unique nmr spectra are the ea $4 \rightleftharpoons 9$ and eaa $4 \rightleftharpoons 10$ processes. The first of these preserves the four OMe peaks and four distinguishable hydrogens while equilibrating the two sets of $P(OMe)_3$ peaks. The second of these, however, takes **4** into the mirror image of **9**. Not only does this equilibrate the two sets of $P(OMe)_3$ peaks but it equilibrates the two equatorial OMe groups, coplanar with the two hydrides, and the two axial OMe groups, along with the ring hydrogens. This reduces the four OMe peaks to two and will also simplify the CH_2CH_2 peaks. The ea and eaa rearrangements are therefore distinguished by the number of OMe peaks observed as well as the complexity of the CH_2CH_2 spectrum. Notice that the two hydrides, H_1 and H_2 ,



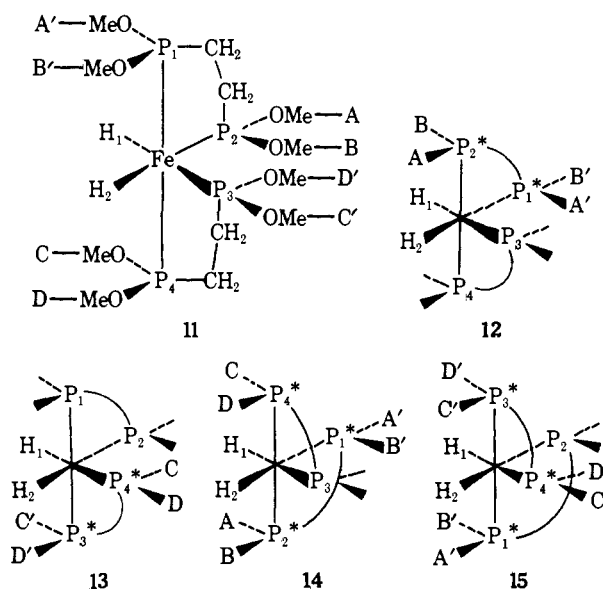
remain distinguishable as they were in the rearrangements to **5** and **6** and contrary to the result in the rearrangements to symmetrical **7** and **8**. The results are tabulated in Table I.

We consider now the bis chelate **11**. This compound can rearrange by only two ea processes taking **11** into **12** and **13** and by only two eaa processes taking **11** into **14** and **15**. An examination of the ea rearrangement $11 \rightleftharpoons 12$ shows that the methoxyl groups on P_1 and P_2 are exchanged according to $A \rightleftharpoons B'$ and $B \rightleftharpoons A'$ and similarly for **13**. There are thus two distinguish-

Table I. Number of Methoxyl Nmr Peaks for the Six Rearrangements in a Monochelated Complex^a

	ae			aac	
	P(OMe) ₃ (2)	P(OMe) ₂ (4)		P(OMe) ₃ (2)	P(OMe) ₂ (4)
4 ⇌ 5	2	2	4 ⇌ 6	2	2
4 ⇌ 7	1	1	4 ⇌ 8	1	1
4 ⇌ 9	1	4	4 ⇌ 10	1	2

^a The numbers in parentheses are the number of peaks in the nonrearranging compound.



able methoxyl groups when the rearrangement is carried out in this way. An examination of the eaa rearrangement $11 \rightleftharpoons 14$ shows that while the A and B methoxyls exchange along with the A' and B' methoxyls, the D and D' methoxyls in the other cycle exchange along with the C and C' methoxyls. This implies that when **14** rearranges in the same way but holding P₁ fixed the A, A', B, and B' ligands all equilibrate as do the C, C', D, and D' ligands.

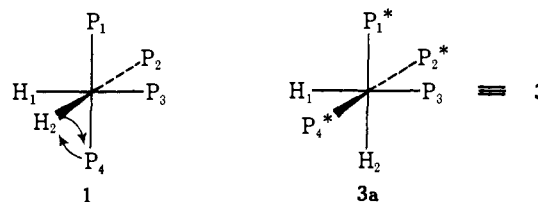
We have now a way to distinguish among the rearrangements. If the four different low-temperature methoxyl peaks coalesce to two peaks then this occurs *via* an ae rearrangement, whereas if the four different low-temperature methoxyl peaks coalesce to a single peak then this occurs *via* an aae rearrangement. If the doublet coalesces to a singlet on further raising of the temperature, this would imply the existence of an aae rearrangement following the ae process. This distinction now permits us to describe intramolecular rearrangements uniquely, just as the inclusion of diastereotopic groups in M(AB)₃ complexes (called M(A*B)₃ complexes) permits a uniquely determined rearrangement. If both rearrangements are occurring at the same time, the spectrum in the transition region will not correspond to the simple spectra expected for the appropriate single process, and analysis of these intermediate spectra can determine the rates of both processes. It is, of course, in principle also possible for rearrangement of monocyclic and bicyclic systems to take place preferentially *via* any of the other possible OP's. Similarly, the rearrangement taking the cis dihydride into the trans dihydride could also occur.

Three examples of compounds similar to **11** have been mentioned briefly in the literature,¹² H₂FeR₂, with

R = (CH₃)₂PCH₂CH₂P(CH₃)₂, (C₆H₅)₂PCH₂CH₂P(C₆H₅)₂, and (C₂H₅)₂P-*o*-phenylene-P(C₂H₅)₂. The first two of these are reported as being purely cis although no details were given. The third at low temperature is purely trans with the higher temperature spectrum interpreted as being due to a slightly higher state attainable *via* a relatively low barrier. This spectrum, which shows a low-temperature quintet broadening and becoming a (slightly shifted) high-temperature quintet, could also be interpreted as arising from the low temperature rigid trans molecule with an A₂A'₂ phosphorus spectrum converting to a high-temperature rearranging system with an A₄ spectrum. The trans orientation could be due to the interaction between the two aromatic rings.

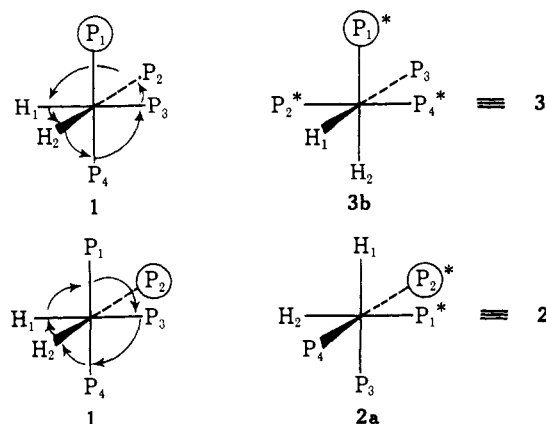
It seems of interest to make a few remarks concerning possible mechanisms for the rearrangements observed, be it the ae rearrangement or the aae rearrangement. Out of the large variety of possible mechanisms we find three to be easily envisaged and not energetically unlikely. Motion is only permitted from a site to a cis-oriented neighbor, and the pairwise exchange of two bulky phosphorus ligands is avoided as being energetically unlikely. We continue to use a and e to refer to the location of the four phosphorus ligands, although the actual motions can of course involve all ligands. As above we consider only the cis-dihydro complexes.

The first mechanism would exchange one of the hydrogens with a cis phosphorus, as in **1** → **3a**. This is



a reasonable rearrangement since site exchange between the small hydrogen atom and phosphorus is easily envisaged. While this is mechanistically a cis exchange of phosphorus and hydrogen, it is an aae rearrangement, and the phosphorus ligands formally rearranged are indicated with an asterisk.

The second and third rearrangements are c⁵ processes⁴ and involve the motion of five ligands including three of the bulky phosphorus groups but in a rather gentle manner, since all migrating groups move to vacant cis sites. The first of these, **1** → **3b**, carries one of the hydrogens into a position trans to the stationary ligand, which is circled, and is an aae rearrangement. The second of these, **1** → **2a**, carries a hydrogen away from



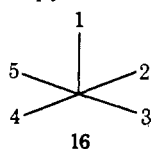
a position oriented trans to the stationary atom and is an ae rearrangement. The energy required for each of these processes will clearly be different, but there seems to be no obvious way to choose between them.

The remaining mechanisms taken from c^5 rearrangements keep one of the hydrogens fixed. Such processes are also reasonable but are not treated explicitly here. It should be noted that we have considered here only mechanisms based on an octahedral or distorted-octahedral geometry in the belief that anything more complex would too closely approach the speculative limit.

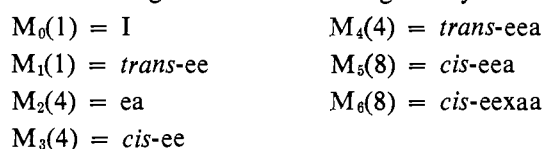
Modes of Rearrangement for a Square Pyramid

Square pyramidal complexes, which have been viewed as octahedral complexes with a lone pair occupying the sixth site, are considerably rarer than are trigonal bipyramidal and octahedral complexes. The central atom which is not specified here is not, in general, coplanar with the four planar ligands.

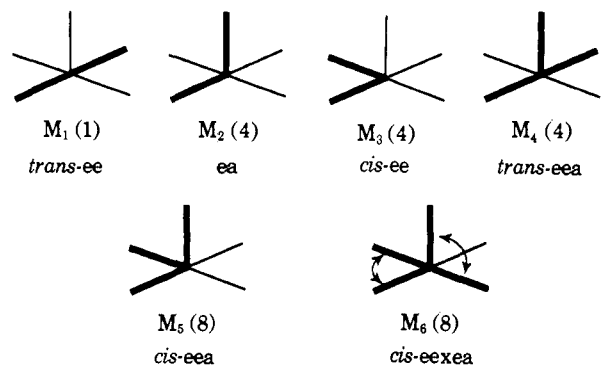
Consider the square pyramidal molecule **16** where



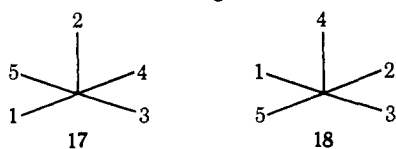
the numbers 1-5 indicate specific substituents which may, or may not, be all different. There are 30 different labeled isomers since there are six different ways of placing the four numbers in the basal plane and five different choices of apical atoms, or $5 \times 6 = 30$. The basal atoms are denoted by e for equatorial where it will be necessary to indicate whether a pair of such atoms is cis or trans. As for trigonal bipyramidal and octahedral complexes, it is straightforward to work out the modes of rearrangement. These are given by



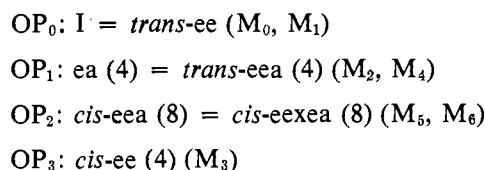
As before we indicate in parentheses the number of rearrangements that occur according to the given mode, all of which are indicated in Scheme II. For simplicity



we do not specify the corresponding equivalent rearrangements. A *trans-eea* rearrangement takes **16** into **17** while a *cis-eea* rearrangement takes **16** into **18**.



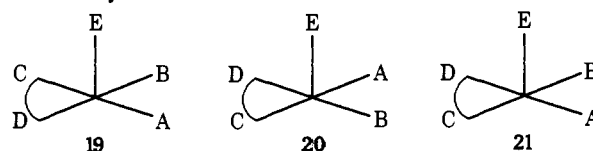
When the ligands 1-5 are monatomic, mirror image symmetry permits the reduction of the seven modes to four observable processes



Notice that OP_3 comes from a single mode while all the others come from modes in pairs. Except for OP_3 , it will be necessary to utilize bidentate ligands as discussed above in attempts to describe experimental results in terms of unique rearrangements.

Very recently Brunner and Herrmann²² have given the first convincing demonstration of an intramolecular rearrangement in a chelated square pyramidal molecule. They studied the compounds **19** with $M = Mo$ or W , $A = B = CO$, $E = h^5-C_5H_5$, and $CD = o-NC_5H_4CNCH(CH_3)(C_6H_5)$. The stable structure of the complex has the cyclopentadienyl group in the axial position. It is experimentally observed that the stereoisomer **19** rearranges thermally to its diastereomer **20** via an M_3 rearrangement, or **21** via an M_1 rearrangement. A distinction between **20** and **21** would be effected were $A = CO$ and $B = N_2$.

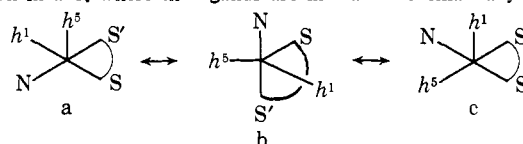
These authors have proposed that **19** rearrange to **20** or **21** by a series of transformations whose stereo-



chemistry corresponds to that of a reverse Berry pseudorotation in which the square pyramidal molecules rearrange through a trigonal bipyramidal intermediate. When such a rearrangement is considered it can be seen that the effective enantiomer **21** is obtained by passing through a three fold barrier, the minima of which corresponds to *trans-eea*, *cis-eea*, and *cis-ee* rearrangements, respectively. Were the true enantiomer, **20**, required, the process would go through a six-fold barrier. In both cases, the various square pyramidal intermediates do not all have the same energies. The simpler three fold barrier description is illustrated in Scheme III.^{22a}

(22) H. Brunner and W. A. Herrmann, *Chem. Ber.*, **106**, 632 (1973).

(22a) NOTE ADDED IN PROOF. The recent study of W. G. Kita, M. K. Lloyd, and J. A. McClevery [*Chem. Commun.*, 420 (1971)] on $Mo(C_5H_5)_2(NO)(S_2CNMe_2)$ and $Mo(C_5H_5)_2(NO)[S_2C_2(CN)_2]$ should also be mentioned. These authors showed that at intermediate temperatures the $h^5-C_5H_5$ and the $h^1-C_5H_5$ groups equilibrate while the two methyl groups remain distinguishable. They interpret this as arising from the axial (SP) C_5H_5 group becoming axial in the intermediate and then going to an equatorial (SP) site in the rearranged molecule. This mechanism also requires the *trans* S-Mo-NO linkage to be stronger than the *cis* S-Mo-NO linkage. A more suitable hypothesis would allow only those square pyramids possessing an axial $h^5-C_5H_5$ group to occur in the rearrangement. This then permits *only* the rearrangement with *both* C_5H_5 groups equatorial (TBP) in the intermediate as shown in a-b, where the ligands are indicated schematically and the



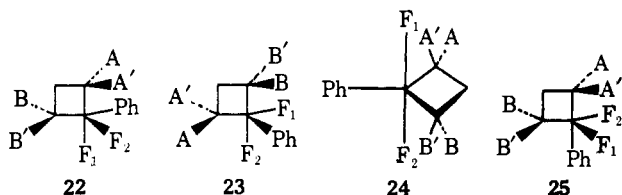
labels h^1 and h^5 are retained only for purposes of identification, it being assumed that the axial (SP) and equatorial (SP) ligands are h^5 and h^1 ,

Discussion

In the above examples we have shown how stereochemical problems can be simplified by the introduction of bidentate ligands. Other methods exist which, in principle, might be used in such stereochemical analyses. Among the most suitable of these are the incorporation of prochiral and chiral ligands into the molecular structure.²³ Replacement of the ethoxyl groups by optically active *sec*-butoxyl substituents might well lead to useful information, but there are no examples of such compounds as yet in the literature.

Some related examples of intramolecular rearrangements both in sulfur and in phosphorus chemistry are worthy of notice here.

The rearrangements in the difluoro²⁴ and diethoxyphosphorus²⁵ compounds **22** and **26** have been interpreted as involving the four-membered rings in the equatorial plane. The nmr spectrum of the difluoro compound, which is exceptional in showing two separate isomers at low temperature, has been interpreted as evidence for **22** \rightleftharpoons **23** and **24** in a ratio of 2.4 to 1. The rearranging pair of isomers accounts for the presence of only two methyl peaks before phosphorus spin splitting, and the equatorial four-membered ring accounts for the single methyl peak of lower intensity. An attractive alternative interpretation of the spectra is that the minor component is **25**, with the two fluorine



atoms equatorial, and that this is in rapid equilibrium with its mirror image **25*** through the intermediacy of **24**. This is a little more satisfactory than the previous proposal, since here **24** with its unfavorable diequatorial C-P-C bond angle of near 90° is a high-energy intermediate, several kilocalories per mole above **25**, rather than the stable, observed conformer, only 0.6 kcal/mol above **22**. Another possibility is to consider **25** as the nonrearranging lower energy structure with **22** and **23** having the dip with **24** in it. This would more satisfactorily account for the J_{PF} splittings²⁶ with the 932 Hz corresponding to a pure equatorial fluorine and 770 Hz corresponding to an equatorial-axial

respectively. This is an M_4 , *trans-eea*, rearrangement. All other rearrangements require passing through a square pyramid with *both* of the C_5H_5 groups equatorial. Such isomers cannot benefit from the stability in the favorable orientation of the *haptocyclopentadienyl* group. Notice, however, that the product could equally well be the isomer obtained by taking the mirror image of a in the $hNSS'$ quasi-plane, although we have not considered a mechanism for it. This would be an M_2 , *ea*, rearrangement.

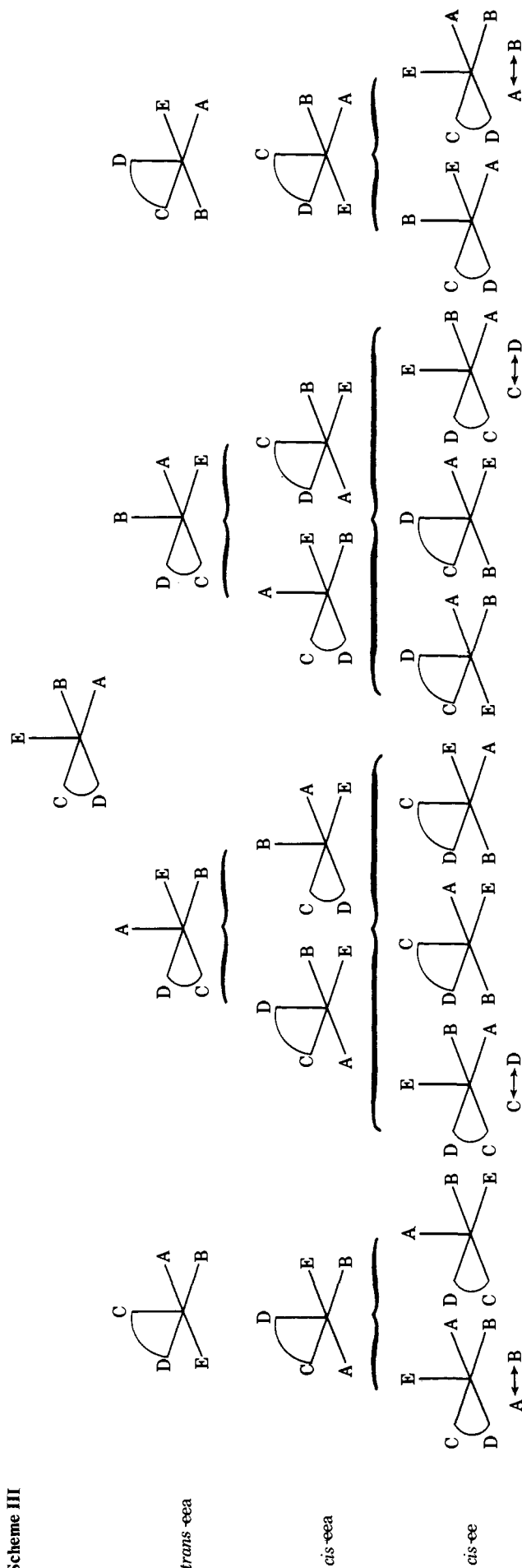
Rearrangements in square-pyramidal molecules have also been discussed by J. W. Faller and A. S. Anderson [*J. Amer. Chem. Soc.*, **92**, 5852 (1970)]. The equilibration of the two methyl groups in Figure 9, which is a particular *cis-ee* rearrangement keeping the CO groups fixed, could also be described by the three-step reverse-Berry-pseudorotation of Scheme III. Analogous rearrangements have been studied by P. Kalck, R. Pince, and R. Poilblanc [*J. Organometal. Chem.*, **24**, 445 (1970)] and R. J. Mawby and G. Wright [*ibid.*, **21**, 169 (1970)].

(23) R. Freeman, K. McLauchlan, J. I. Musher, and K. G. Pachler, *Mol. Phys.*, **5**, 321 (1962).

(24) N. J. De'Ath, D. Z. Denney, and D. B. Denney, *J. Chem. Soc., Chem. Commun.*, 272 (1972).

(25) D. Z. Denney, D. W. White, and D. B. Denney, *J. Amer. Chem. Soc.*, **93**, 2067 (1971).

(26) L. C. Duncan and G. H. Cady, *Inorg. Chem.*, **3**, 1045 (1964).



Scheme III

trans-eea

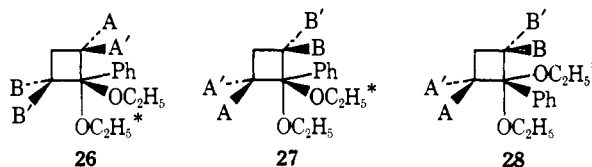
cis-eea

cis-ee

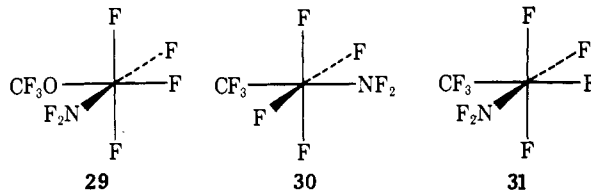
(averaged) fluorine. In structures 22–28, A, A', B, and B' indicate distinguishable methyl groups.

The diethoxy compound 26 shows three different temperature regions.²⁶ First, below -68° , there are only two ring methyl groups and this is interpreted as evidence for the same aexae process as in $22 \rightleftharpoons 23$. Above -20° , the two methyl peaks coalesce while the ABM_3X spectrum of the CH_3CH_2OP group remains unchanged, a result which is interpreted as evidence for the rearrangement going through the analog of 25. The high-temperature equilibration of all the protons is interpreted as going through the analog of 24. The low-temperature experiment can also be interpreted as evidence for the analog of 25 with the intermediate result the same as above except that now the excitation is to the analog of $22 \rightleftharpoons 23$. Another interpretation of the high-temperature experiment would describe the rearrangement as an aexae process taking 26 to 27. Since the low-temperature nmr spectrum shows rearrangement of $26 \rightleftharpoons 28$, the combination of the two rearrangements aexae and aexae would serve to equilibrate all the CH_2 peaks as is observed.

Most examples of $RR'SF_4$ compounds show R and R' to be cis as in²⁶ 29 and the only reported example,



which shows identical fluorine atoms, can be interpreted not only as a rigid molecule²⁷ with trans substituents as in 30 but also as the cis complex 31 under-



going rearrangement to the higher energy 30 under the conditions utilized in the experiment.

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Localized Molecular Orbitals and Chemical Reactions.

II. A Study of Three-Center Bond Formation in the Borane–Diborane Reaction

David A. Dixon, Irene M. Pepperberg, and William N. Lipscomb*

Contribution from the Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138. Received September 21, 1973

Abstract: Comparison of the symmetric (C_{2h}) approach of two BH_3 molecules to form B_2H_6 with the unsymmetric (C_s) approach in which only a single hydrogen bridge is formed leads to strong preference for the C_{2h} transition state having two very unsymmetrical hydrogen bridges. This symmetric state lies 2.6 kcal/mol of B_2H_6 higher than $2BH_3$ in a self-consistent field calculation extended by inclusion of all 14 single and 210 double excitations from the valence shells of a minimum Slater basis. The two equivalent unsymmetrical bridges have a long $B \cdots H$ interaction with a B–B distance of 3.0 Å in the transition state. The formation of the three-center BH_3B bond is investigated by examining the properties of the localized molecular orbitals along the symmetric pathway. A covalent three-center (bent) $B-H \cdots B$ forms as the $B \cdots B$ distance closes to about 2.1 Å, corresponding to a $H \cdots B$ distance of 1.65 Å.

The diborane molecule has been the object of much theoretical work¹ since it is the prototype boron hydride. The dimerization of two boranes to form diborane



is the simplest reaction involving the formation of B–H–B three-center bonds from B–H two-center terminal bonds. The small size of the molecules involved in reaction 1 and the considerable theoretical work done on the system² make it attractive for a

theoretical study of the reaction pathway. The reverse of reaction 1, which we shall call 1b, is of substantial experimental importance^{3–5} as the generally accepted first step in the diborane pyrolysis (except for the proposal of Long⁶). Most of the higher boranes are generated *via* a chain mechanism from the initial decomposition of diborane (reaction 1b).

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