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THEORETICAL ASPECTS OF THE COORDINATION OF MOLECULES TO TRANSITION METAL CENTERS

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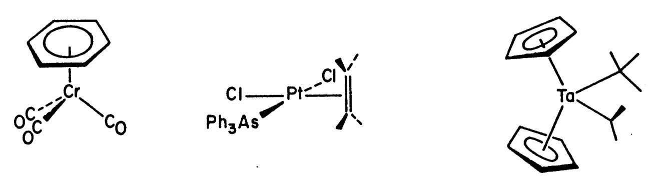
Abstract - When bound in transition metal complexes, organic molecules such as olefins, acetylenes, polyenes, cyclopolyenes and carbenes exhibit a variety of equilibrium geometries. The range of observed barriers to a conformational change as simple as rotation around the metal-ligand coordination axis is impressively large, from 0 to >40 kcal/mole. Clearly it is electronic factors that are operative in setting the preferred geometries in these molecules and in controlling the magnitude of the conformational barriers. In this lecture several specific examples of the theory of these conformational phenomena will be presented.

Uncomplexed organic molecules display a wide range of barriers to internal rotation, from near zero six-fold barriers in toluene, through a typical torsional barrier of 3 kcal/mole for ethane, to barriers in the range of 10-20 kcal/mole for torsion about the C-N bond in amides, to large values of the order of 65 kcal/mole for twisting ethylene to a D_{2d} geometry. The very lowest barriers are symmetry conditioned -- it would be a peculiar molecular potential that would oscillate so violently as to make a six- or higher-fold barrier attain a large magnitude. The barriers of the ethane type we may very loosely call steric, being painfully aware through our own work of the fundamental lack of distinction between steric and electronic effects. While steric effects can be reinforced and cumulated to create substantial barriers (Ref. 1), the very largest barriers, such as those for twisting an ethylene or squashing a methane to planarity, are clearly electronic. In these there is a great loss of bonding in one conformation over another.

When an organic molecule is bound as a ligand in a transition metal complex while retaining its general atomic connectivity, a new internal rotation problem arises, that of rotation around the metal-ligand axis. The range of observed barriers is impressively large, from near zero in benzene-$Cr(CO)_3$, 1 (Ref. 2), to 12 kcal/mole in the complexed ethylene, 2 (Ref. 3), to >21 kcal/mole in the carbene complex, 3 (Ref. 4).



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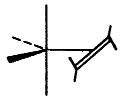
What makes for the variability of these barriers? We think it is fair to say that in the organometallic realm we often lack the intuitive feeling that characterizes the organic side for those electronic determinants of molecular geometry which would allow us to predict equilibrium conformations and approximate barrier sizes. Over the past few years our research group has been engaged in a broad theoretical attack on inorganic and organometallic problems. In the process we have gained some understanding of the electronic factors governing rotational barriers in organometallic compounds, which is the subject of this lecture.

THE FRAGMENT AND SUBSTITUTIONAL APPROACHES. A CASE STUDY OF $Fe(CO)_4$(ETHYLENE).

No theory of chemical bonding has a monopoly on explanation. There are many ways of reaching the same conclusion. Indeed, if one is dealing with approximate calculations, it is best to have in one's interpretative armament an assortment of qualitative methods to check the seductive numbers that emerge from a computer. Two protocols of analysis that we have found useful in studies of conformational preferences are what could be called a whole-molecule or substitutional approach, and a fragment or reconstructional analysis. The two procedures are best illustrated on a specific case, the equilibrium conformation of $Fe(CO)_4$(ethylene) which is 4 rather than 5.



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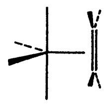

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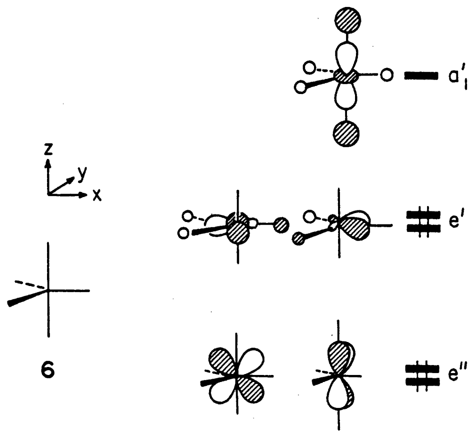
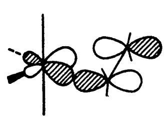
In the whole molecule or substitutional approach as applied to this problem (Ref. 5) we first consider a general ML_5 species, beginning with ligands that carry no orbitals of π symmetry, e.g. that theoreticians' delight, the hydride. We then compare the π bonding capability of the various d orbitals. The d level splitting scheme for a trigonal bipyramid is a familiar one (Ref. 6), shown in 6 below.



Lowest lies the e″ set composed of pure metal d functions, xz and yz. Above is the e′ orbital, metal x^2-y^2 and xy. This equatorial set is now hybridized by an admixture of metal x and y. The sign of the mixing (Ref. 5) is such that the e′ set overlaps better with p orbitals on the equatorial ligands than it would have done in the absence of metal p orbitals. It follows that a d^8 ML_5 complex, with e′ and e″ occupied, will have greater π donating capability in the equatorial plane. The specific controlling interaction with an ethylene π^* is shown in 7.



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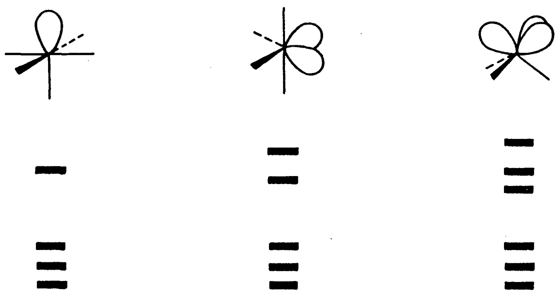
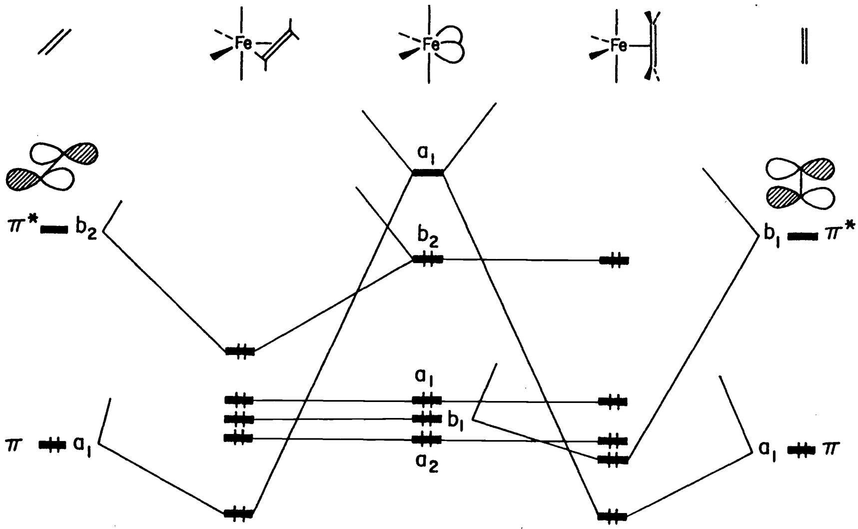
The fragment or reconstructional procedure would approach the same problem by building up the orbitals of the two alternative conformations, 4 and 5, from those of $Fe(CO)_4$ and ethylene pieces. There is no problem in getting the orbitals of the organic moiety. Crucial to this approach is a thorough understanding of the molecular orbitals of a variety of transition metal fragments, ML_n. To achieving this end we have devoted considerable effort (Ref. 7). The complete description is a molecular orbital one, sensitive to changes in fragment geometry. However, an adequate simplified picture may be obtained as follows for important ML_n species in geometries close to those which are octahedral fragments.

There are 9-n valence orbitals in ML_n, of which 3, descended from the octahedral t_{2g} set, are at lower energy. Higher lying are 6-n orbitals, which can be viewed as the proper symmetry-adapted linear combinations formed from 6-n localized hybrids pointing toward the missing ligands that would complete the octahedron. These upper orbitals often will be significantly split in energy among each other, but the general pattern is that given in 8-10.



8 9 10

The $Fe(CO)_4$ fragment in our complex is a cis-octahedral one, with C_{2v} symmetry. The two upper hybrids combine to give a_1 and b_2 molecular orbitals, b_2 at lower energy. The d^8 configuration forces formal occupation of the b_2 level. A schematic reconstruction of 4 and 5 is shown in 11 below.



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The ethylene π level interacts with $Fe(CO)_4$ a_1 approximately to the same extent in the two conformations. The differential is set by the ethylene acceptor function, the π^* orbital, of b_2 symmetry in 4, b_1 in 5. Orbital interactions are governed by the usual perturbation theoretic expression.

$$\Delta E = \frac{|H_{ij}|^2}{E_i - E_j} \qquad (1)$$

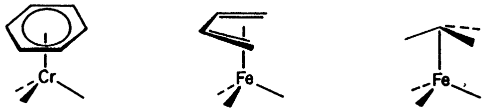
The equatorial orientation 4 is favored both by the smaller energy gap between the b_2 orbitals and their greater overlap, compared to b_1 in 5.

We have seen that both qualitative approaches lead to the same geometrical prediction. Getting a reliable number for the barrier is another story. Theoreticians are especially prone to overselling their pet methodology. The procedure that we have used in our work, the extended Hückel method, has the merit of being on the low end of a quality scale of approximate MO calculations. Since all other methods are superior to it, it inculcates in its user a feeling of humility and forces him or her to think about why the calculations come out the way that they do. The method is widely applicable and transparent, but it has limited quantitative reliability. The consumer of theory is cautioned not to believe any numbers given here by us to within a factor of three or so. For a rigid octahedral fragment $Fe(CO)_4$ and a planar ethylene we calculate a rotational barrier of 32.0 kcal/mole (Ref. 8).

The experimental magnitude of this barrier is not clear. A Berry pseudorotation sets in prior to or in concert with a simple rotation (Ref. 9). The observed barrier for intramolecular carbonyl interchange in $Fe(CO)_4$ complexes of substituted ethylenes is 11-15 kcal/mole. Our calculated surface for the coupled rotation-pseudorotation itinerary has a 10 kcal/mole activation energy.

ROTATIONAL BARRIERS IN POLYENE AND CYCLOPOLYENE-ML_3 COMPLEXES

We have recently completed a study of rotational barriers in polyene and cyclopolyene-ML_n complexes, n = 2,3,4 (Ref. 8, 10). The problem may be put into focus by noting the experimentally observed barriers for carbonyl interchange in 12 - 14; near zero



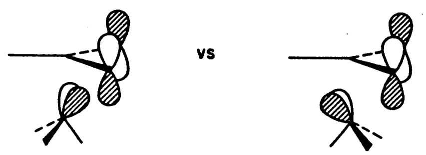
12 13 14

in benzene-$Cr(CO)_3$ (Ref. 2); 9.5 kcal/mole in butadiene-$Fe(CO)_3$ (Ref. 11); 19-20 kcal/mole in trimethylenemethane-$Fe(CO)_3$ (Ref. 12.) The high symmetry of the benzene complex accounts for its low barrier. But it is not at all obvious why the trimethylenemethane (TMM) complex 14 should have a three-fold barrier nearly an order of magnitude greater than ethane.

The analysis begins with the orbitals of $Fe(CO)_3$, which we must examine in considerably greater detail than that implied in the previously given schematic 10. Contour diagrams of the six valence orbitals are shown in Fig. 1 (see next page). $1a_1$ and $1e$ are the lower set of three, $2a_1$ and $2e$ the upper.

There is significant tilting or left-right asymmetry in these orbitals. This is a consequence of the descent of the fragment from an octahedron, and proves to be crucial in setting the conformational preferences and barriers in complexes of this fragment. To see how this occurs consider the reconstruction of the electronic structure of 14 from its components, in the observed staggered geometry (Fig. 2, see next page).

Figure 2 shows that the primary bonding interaction in the complex is that between the 2e set on the $Fe(CO)_3$ fragment and e″ on TMM. However, upon rotation about the iron-TMM axis by 60° into an eclipsed geometry the interaction of these orbitals is decreased because the overlap between them decreases. This is shown below for one member of the degenerate set.



Therefore the energy of the HOMO in the molecule increases in the eclipsed form, and this is the main but, as we discuss next, not the only factor behind the barrier.

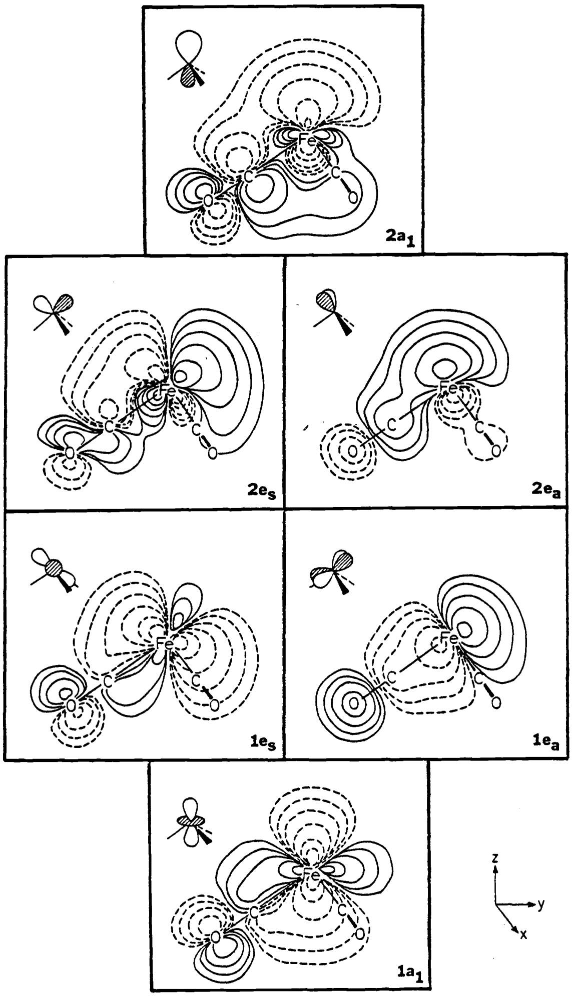


Fig. 1 (right). A plot of the valence orbitals of an $M(CO)_3$ fragment. The orbitals are plotted in the yz plane, except for those which have a node in that plane. Those were plotted in a parallel plane displaced 0.5Å in the x direction.

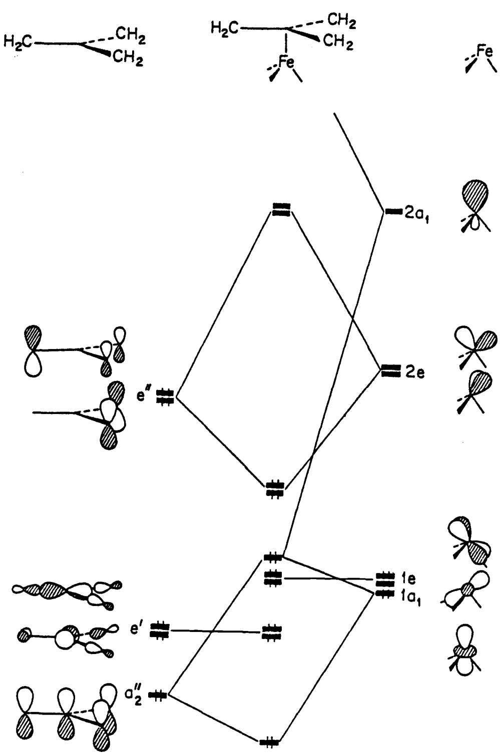
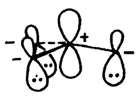


Fig. 2 (left). Orbital interaction diagram for a planar trimethylene-methane and $Fe(CO)_3$.

In the staggered geometry the overlap between the 1e set and e″ is almost zero since that portion of 1e pointing up towards TMM lies in the nodal region of e″. However, upon rotation to the eclipsed geometry the overlap increases by an order of magnitude, while still remaining considerably smaller than the 2e - e″ overlap. The interaction between 1e and e″ is a four-electron repulsive one -- the greater the interaction, the less stable the structure. This is then another factor contributing to the overall preference for the staggered conformation.

Our extended Hückel calculations give a barrier of 21 kcal/mole using a planar TMM ligand and carbonyl-iron-carbonyl angles of 90°. If we allow the TMM fragment to approach its experimental puckered geometry, the computed barrier rises slightly to 24 kcal/mole, both values being in reasonable agreement with experiment.

There are two seemingly different but in fact equivalent ways to think about this substantial barrier. First, as discussed above, the barrier arises from maximizing two-electron bonding (2e - e″) and minimizing four-electron destabilizing (1e - e″) interactions. Second, one could think of the TMM^{2-} ligand as being in an unpopular charge distribution, 16, and through its



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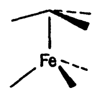

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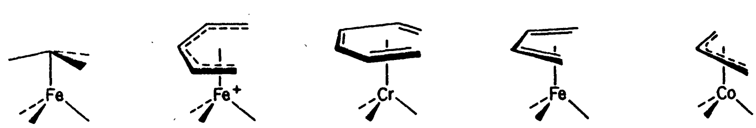
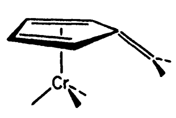
three electron pairs completing an octahedron around the iron. The internal rotation problem, 17 ⇄ 18, is transformed into the problem of a trigonal twist of an octahedron into a trigonal prism. That deformation is expected to cost a great deal of energy for most d^6 complexes; for instance, for a specific model compound $(CH_3)_3Fe(CO)_3^-$ we compute a barrier of 50 kcal/mole.

In fact it can be shown that both ways of analyzing the problem merge. The tilt of both the 1e and 2e sets and the matching asymmetry of their organic ligand partners is all-important in setting the interaction pattern. Each point of view has its advantages. For instance, focusing on the balance of attractive and repulsive interactions with e″ allows one to rationalize why the barriers fall in the series TMM-$Fe(CO)_3$, pentadienyl-$Fe(CO)_3^+$ (Ref. 13), hexatriene-$Cr(CO)_3$ (Ref. 14), butadiene-$Fe(CO)_3$ (Ref. 11), allyl-$Co(CO)_3$ (Ref. 15) (observed barriers



19-20 kcal/mole 13 11-12 9.5 ≤5

below structures), why a fulvene-$Cr(CO)_3$ complex, 19, assumes a different orientation, and tilts the exocyclic double bond in a different way from a cyclopentadienone-$Fe(CO)_3$, 20



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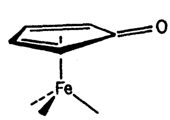

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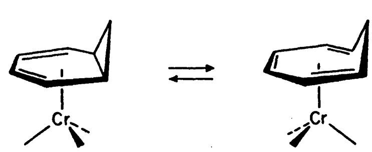
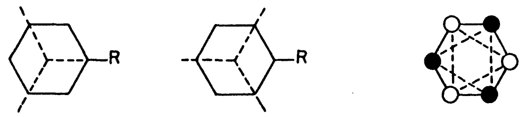


21 22

(Ref. 16), or how $Cr(CO)_3$ orientations interact with the norcaradiene-cycloheptatriene equilibrium, 21 ⇄ 22 (Ref. 16). Either mode of analysis rationalizes the preference in substituted benzene-$Cr(CO)_3$ complexes for 23 over 24 when R is a π-donor and the reverse for an ac-



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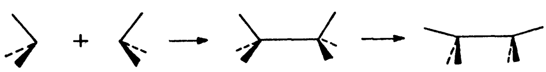
ceptor. The octahedral viewpoint of the same arene complexes leads in a transparent way to the concept of two interpenetrating trios in the benzene ring, 25. The maximal perturbation of the tiny barrier in the parent complex may be achieved by selective substitution of donors, acceptors, or heteroatoms in separate trios. We believe that this particular rotational barrier, benzene-$Cr(CO)_3$, is tunable over a 30-40 kcal/mole range by appropriate substitution tactics.

BINUCLEAR $M_2(CO)_6$(LIGAND) COMPLEXES

We have recently carried out a systematic molecular orbital study of the electronic structure of complexes containing the $M_2(CO)_6$ binuclear transition metal fragment bonded to a variety of ligands, including acetylene, two carbonyls, C_4R_4 (ferroles), C_6R_6 (flyover bridges), cyclobutadiene, dienes, azulene, cyclooctatetraene, hexatrienes, tetramethyleneethane, pentalene, and others (Ref. 17). Many conformation questions arise along the way, a selection of which will be mentioned here.

It is evident that a reconstructional approach is natural for this large group of interesting compounds. The orbitals of the $M_2(CO)_6$ moiety can be constructed in step-wise fashion by first bringing together two $M(CO)_3$ units in an eclipsed D_{3h} geometry, 26, and then bending the



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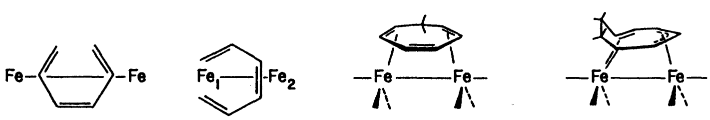
$M(CO)_3$ groups back to achieve the lower-symmetry C_{2v} sawhorse geometry common in these fragments.

As an example of the conformational problem that we can treat, consider the hexatriene ligand, which can choose between conformations 28 and 29. We calculate minima for both, with a



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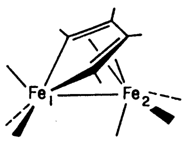
1-2 eV barrier to rotation between the two. Structural examples of both equilibrium conformations are known in 30 (Ref. 18) and many structures of type 31 (Ref. 19) whose geometry resembles 29. The fluctionality of complexes of eight-membered rings of type 31 has been studied in great detail by Cotton and coworkers (Ref. 19, 20). The rotation process discussed does not occur on the NMR time scale. Incidentally, we have studied the barriers to carbonyl interchange in 29, a model for 31, and in (azulene)$Mo_2(CO)_6$ and were able to predict correctly that the carbonyls at Fe_2 in 29 would interconvert easier than those at Fe_1, and that those under the five-membered ring of the complexed azulene would interchange more readily than those at the metal atom under the seven-membered ring.

Not quite a rotational barrier, but an interesting conformational question is posed by the known ferrole and flyover bridge structures, 32 and 33. Why doesn't 33 assume a structure 34 analogous to the ferrole? Why doesn't 32 take on a flyover bridge structure 35, or even 36 or 37? The last structure is a triple-decker, and we have discussed the electronic structure



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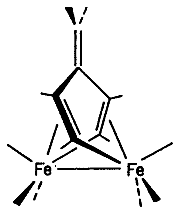

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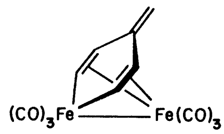

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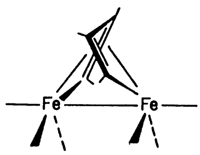

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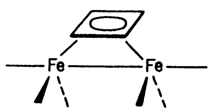

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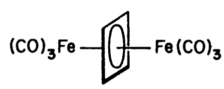

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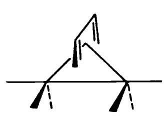
of these complexes elsewhere (Ref. 21). The choice between 33 and 34, or between 32 and 35, is approached by putting either complex into a symmetrical C_{2v} structure, 38 or 39, and



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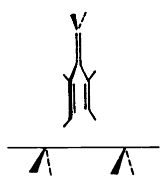

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watching it fall over to a ferrole or twist to a flyover bridge, motions of b_2 or a_2 respectively. The results are revealing with respect to the equilibrium geometries and the barrier necessary to achieve the symmetrical structure, which itself can serve as a transition state for isomerization.

The above examples form a most brief sample of the variety of conformational problems that we have studied. A still greater set remains to be explored. The factors that determine molecular geometry in typical organometallic complexes are generally electronic. The equilibrium geometries are usually well-defined, that is substantial rotational barriers separate conformers. The understanding that is achieved of these conformational problems is a necessary prerequisite to a systematic analysis of the reactivity of organometallic and inorganic molecules.

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