Demoniac Intervention in the Thermal Electrocyclic Ring Opening of Cyclobutenes: $Fe(CO)_3$ Complexation of Pericyclic Transition Structures

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Dedicated to Professor *Edgar Heilbronner* on the occasion of his 80th birthday

Can metal complexation of organic π-systems alter the stereoselectivity of pericyclic reactions? We address this question for the $Fe(CO)_3$-templated electrocyclic ring opening of cyclobutene using hybrid HF-DFT calculations. These calculations show that the preferred pericyclic pathway in the presence of $Fe(CO)_3$ corresponds to the pathway that is orbital-symmetry-forbidden in its absence, validating predictions made previously based on extended *Hückel* calculations. The three-dimensional aromaticity of the preferred metal-complexed transition state is revealed by NICS calculations.

Demoniac Intervention? – Is it possible to reverse the stereoselectivity of a pericyclic reaction by selective complexation of an orbital-symmetry-forbidden transition structure? The ur-text on the subject [1] posited – some would say postured – that it would take (*Maxwell*) demoniac intervention to change what has been demonstrated clearly by both experiment and theory to be the allowed pathway for a given pericyclic reaction. But, from the beginning of the orbital-symmetry saga, there were experimental and theoretical hints that catalysis by complexation in discrete metal complexes might change the story [2]. Why not? One time-honored view of complexation of an organic molecule by an ML_n fragment is that forward and back donation create a molecule in a complex that is effectively in an excited electronic configuration.

We describe here calculations that show in detail how the $Fe(CO)_3$ group is indeed capable of reversing the stereoselectivity of the thermal electrocyclic ring opening of cyclobutene. This reaction normally proceeds (in the absence of metals) in an orbital-symmetry-allowed conrotatory fashion through a transition state that is favored over alternative disrotatory or diradical pathways by *ca.* 15 kcal/mol (for leading references, see [3])[4][5]. This is a formidible mountain to scale if a cyclobutene ring is to be compelled to open in a disrotatory fashion.

The prediction that disrotatory ring opening, with rotation of the breaking C−C bond towards the metal, should be the preferred mode of ring opening upon $Fe(CO)_3$ complexation of cyclobutene was made long ago based on qualitative orbital symmetry considerations and extended *Hückel* calculations [2][6]. It was predicted that conrotatory ring opening would be less favorable, and disrotatory ring opening away from the metal less favorable still[1]. Nonetheless, despite dogged attempts [8], the

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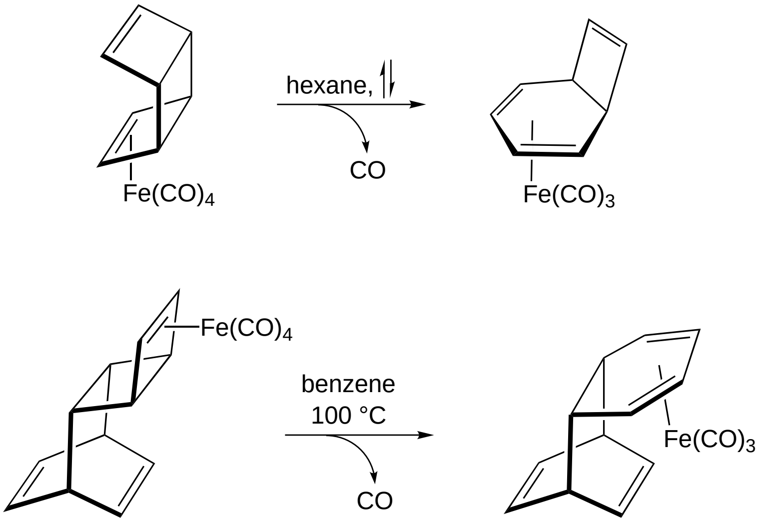
[1] This selectivity for a particular sense of disrotatory ring opening is related to the torquoselectivity predicted and observed previously for uncomplexed conrotatory ring-openings of substituted cyclobutenes [7].

stereoselectivity of $Fe(CO)_3$-promoted ring opening for geometrically unfettered cyclobutenes has not been determined. The ring-opening reactions of $Fe(CO)_4$ complexes of strained tricyclic cyclobutenes [9][10], which presumably lose CO to produce coordinatively unsaturated $Fe(CO)_3$-cyclobutene complexes [9][11], have been studied experimentally (representative examples are shown in the *Scheme*), but only disrotatory ring opening towards the metal is likely in these systems due to the geometric constraints imposed by the additional fused rings. We have investigated the ring opening of the parent $Fe(CO)_3$-cyclobutene model system²) using hybrid HF-DFT calculations to determine whether disrotatory ring opening towards the metal is in fact the preferred mode of ring opening in the absence of geometric constraints.

Scheme



Methods. – Calculations were performed using the GAUSSIAN 98 suite of programs [13] and the hybrid HF-DFT B3LYP method [14] with effective core potential (LANL2DZ [15]) and all-electron (DZVP2+ [16]) basis sets³). Full geometry optimizations⁴) and frequency calculations (to determine the nature of stationary points and obtain zero-point-energy corrections) were performed with the

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²) Additional aspects of the $Fe(CO)_4$-cyclobutene to $Fe(CO)_3$-butadiene reaction mechanism, including several competing non-pericyclic pathways, will be described elsewhere. A preliminary report on computations for a related Co-containing system can be found in [12].

³) The DZVP2 basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0 (http://www.emsl.pnl.gov:2080/forms/basisform.html), as developed and distributed by the *Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory*, which is part of the *Pacific Northwest Laboratory*, P.O. Box 999, Richland, Washington 99352, USA, and funded by the *U.S. Department of Energy* (contract DE-AC06-76RLO 1830). Contact *David Feller*, *Karen Schuchardt*, or *Don Jones* for further information. The basis set was augmented as described in [16].

⁴) Graphical depictions of structures were produced with *Ball & Stick 3.7.6*, a molecular graphics application for MacOS computers, *Norbert Müller* and *Alexander Falk*, Johannes Kepler University Linz, 2000.

former, and single-point energies were evaluated with the latter (for recent applications of this methodology, see [17]). All reported energies are those determined at the B3LYP/DZVP2+//B3LYP/LANL2DZ level and include zero-point-energy corrections (unscaled) from frequency calculations at the B3LYP/LANL2DZ level.

Ring-Opening Transition Structures. – Optimization of the orbital-symmetry-allowed conrotatory transition state for uncomplexed cyclobutene ring opening leads to a structure **1** (*Fig. 1*) that is in excellent accord with previously computed ones [3]. The computed barrier for ring opening (32.9 kcal/mol) is also in excellent agreement with previously computed values [3] and the experimental E_a of 32.9 ± 0.5 kcal/mol [18]. Not surprisingly, no disrotatory transition structure could be located at this level of theory[5]).

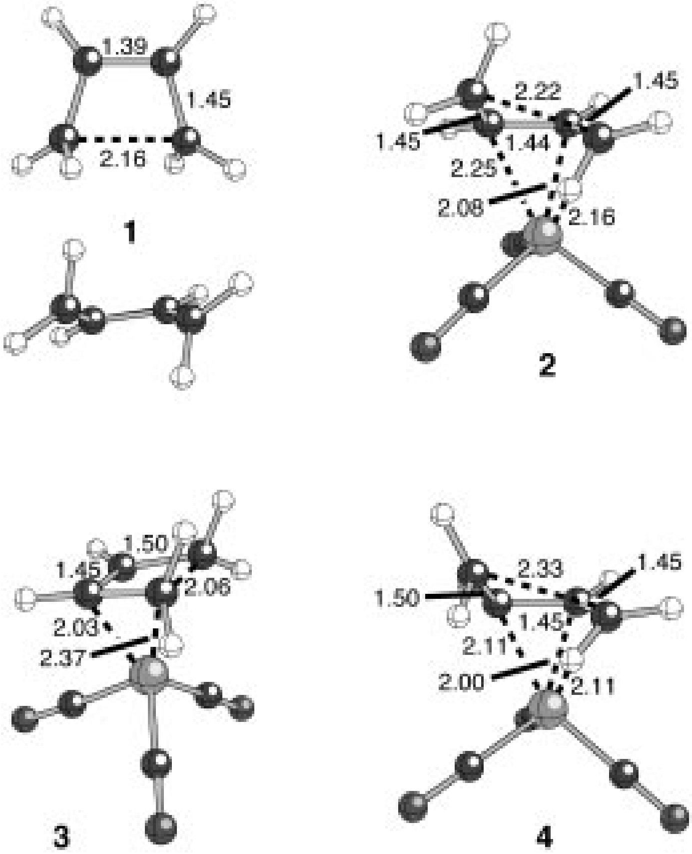

Fig. 1. *Ring-opening transition structures.* Selected interatomic distances are shown in Å.

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[5]) Although no disrotatory transition structure or second-order saddle point could be located, a single-point-energy calculation on the disrotatory geometry of the hydrocarbon fragment of the $Fe(CO)_3$-complexed transition structure shows it to be 54.6 kcal/mol less stable than optimized cyclobutene; from this energy, the preference for conrotatory ring opening is predicted to be 22 kcal/mol, in reasonable agreement with the ≥ 15 kcal/mol estimate from experiments [4] and calculations of *Breulet* and *Schaeffer* [5] on a disrotatory second-order saddle point at the TCSCF/DZ level of theory.

Unlike the uncomplexed case, both conrotatory and disrotatory ring-opening transition structures **2**–**4** were located when the $Fe(CO)_3$ group was included (*Fig. 1*). Complexation perturbs the geometry of the conrotatory transition structure only slightly (compare **2** with **1**). The internal C–C bond has the most double-bond character in the free transition structure, and this bond is slightly lengthened upon complexation to a value (1.44 Å) comparable to that of the elongated double bond in $Fe(CO)_3$-cyclobutene (1.45 Å). The breaking C–C bond is also slightly lengthened upon complexation. The Fe makes a fairly long contact with one of the methylene C-atoms (the Fe $\cdots$ C distance is 2.40 Å) and is even further from the C-atom in the other methylene group (Fe $\cdots$ C distance is 3.15 Å). Neither $CH-CH_2$ bond length is changed significantly upon complexation. There is a relatively short Fe $\cdots$ H contact of 2.16 Å, which could be an agostic interaction, except that the C–H bond is not significantly stretched.

In contrast to the conrotatory transition structure, the transition structure **3** for disrotatory opening towards the metal boasts direct interactions between Fe and all four C-atoms in the ligand. Cleavage of the C–C σ-bond has commenced in this structure, but is somewhat less advanced than in the conrotatory structure **2**.

The transition structure **4** for disrotatory ring-opening away from the metal is actually quite similar to the conrotatory structure **2**. It does not have C_s symmetry, and close Fe $\cdots$ C contacts are observed with only the two internal C-atoms (these are slightly shorter than those in **2**). The two $CH-CH_2$ bonds differ in length in **4**, and bond cleavage is more advanced in this structure than in either of the others.

The Stereoselectivity of Ring-Opening. – In stark contrast to the uncomplexed case, the complexed *disrotatory* transition structure **3** in which the σ-bond breaks towards the metal is more stable than the conrotatory transition structure **2** by 5.2 kcal/mol! The activation barrier from $Fe(CO)_3$-cyclobutene⁶) to disrotatory transition structure **3** is 30.6 kcal/mol, more than 10 kcal/mol lower than the experimental estimate for the uncomplexed disrotatory process [4], and even 2.3 kcal/mol lower than the barrier for the uncomplexed conrotatory pathway (see above). The transition structure **4** for disrotatory ring-opening away from the metal is 0.8 kcal/mol less stable than the complexed conrotatory transition structure **2**. This relative ordering of stabilities for the three possible modes of ring opening agrees with that predicted previously based on extended *Hückel* calculations [6].

Orbital Considerations and Aromaticity. – The rationale for predicting that disrotatory ring opening towards the metal should be preferred in this system [2][6] merits repeating here. Qualitative orbital-correlation diagrams for disrotatory ring opening in the absence and presence of $Fe(CO)_3$ are shown in *Figure 2*. As shown in the leftmost correlation diagram, the uncomplexed disrotatory ring opening is orbital-symmetry-forbidden [1]. However, when the frontier orbitals of the $Fe(CO)_3$ fragment [19] (only the two frontier orbitals most involved in bonding of the d^8 $Fe(CO)_3$

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6) $Fe(CO)_3$-cyclobutene can exist in either of two conformations, both of C_s symmetry, which involve rotation of the $Fe(CO)_3$ tripod – one in which a CO ligand is eclipsed with the ligand π-bond and the other in which the tripod is rotated by 60°. The former is more stable, but by only 0.8 kcal/mol, and the two conformers interconvert with a barrier of less than 1.5 kcal/mol²). Our reported barrier is from the lower-energy conformer.

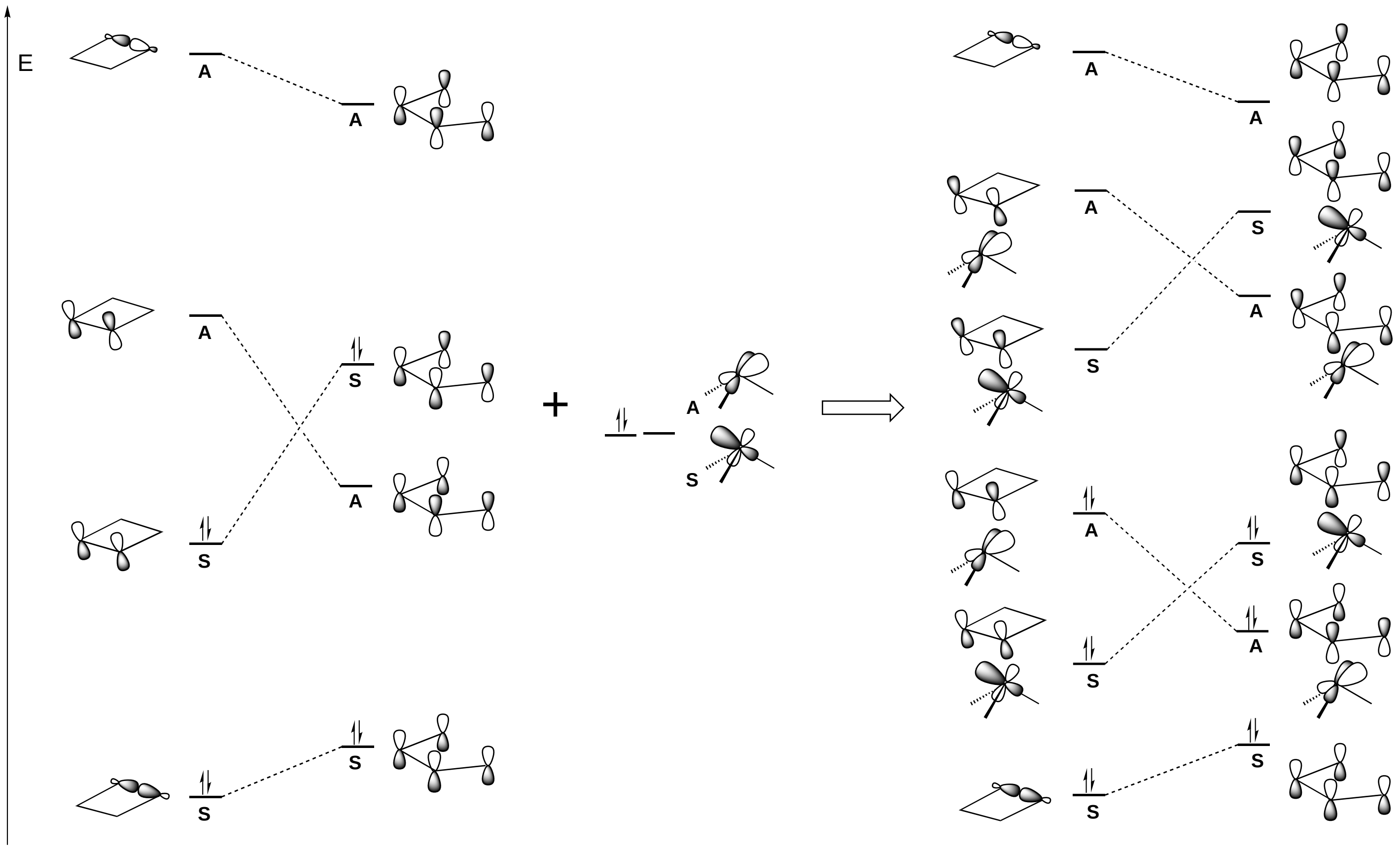

Fig. 2. *Correlation diagrams for uncomplexed and $Fe(CO)_3$-complexed cyclobutene ring opening*. The latter is constructed from the former and the frontier orbitals of $Fe(CO)_3$ shown. All orbitals are labeled as symmetric (S) or antisymmetric (A) with respect to the plane of symmetry maintained along the C_s reaction coordinate. No attempt is made to depict relative orbital coefficients explicitly.

fragment to the hydrocarbon ligand are shown; these orbitals contain two electrons) are allowed to interact with the cyclobutene/butadiene orbitals, the disrotatory ring opening becomes orbital-symmetry-allowed; the rightmost correlation diagram shows the most important metal-ligand interactions.

It has also been suggested that antiaromatic π-systems like cyclobutadiene can become aromatic when complexed to transition metals [20][21][22b]. The three-dimensional aromaticity [21][22b] of the ligand-metal array has been explained by favorable symmetry-allowed interactions between the frontier orbitals of the cyclobutadiene ligand, for example, and the metal (or organometallic fragment) that allow for delocalization of $4n+2$ electrons [20][21]. This explanation is similar to the rationale for the allowedness of disrotatory cyclobutene ring opening upon complexation by $Fe(CO)_3$ just discussed; the orbital interactions between the disrotatory transition state and the $Fe(CO)_3$ fragment are analogous to those between cyclobutadiene and $Fe(CO)_3$. In the case of $Fe(CO)_3$-cyclobutadiene, there would be six electrons (four from the ligand, two from the $Fe(CO)_3$ fragment) delocalized over five atoms (the four ligand C-atoms and Fe); by analogy, the four electrons involved in the cyclobutene ring-opening transition state (and also the butadiene product) could also interact with the two electrons in the frontier orbitals of the $Fe(CO)_3$ fragment, leading to three-dimensional aromaticity[7]).

Since the aromaticity of organometallic arene complexes has been correlated with nucleus-independent chemical shift (NICS) values [22], we have used this methodology to test for three-dimensional aromaticity along the reaction coordinate for ring-opening of $Fe(CO)_3$-cyclobutene. NICS Values (the negative of the absolute magnetic shieldings) at or above the centroids of rings have been used as a criterion of aromaticity in many systems; negative NICS values are found for aromatic systems, positive NICS values are found for systems with antiaromatic character, and NICS values close to zero are found for nonaromatic systems [22]. It has also been shown that, along reaction coordinates for pericyclic reactions, NICS values tend to be most negative at or near the transition structure [22c], consistent with pericyclic transition structures possessing aromatic character.

For the $Fe(CO)_3$-complexed disrotatory ring opening towards the metal, the NICS value at the center of the four C-atoms of the ligand (all NICS calculations were performed at the GIAO/B3LYP/DZVP2+//B3LYP/LANL2DZ level; the NICS values at the centers of benzene and singlet rectangular cyclobutadiene are -8 and $+27$, respectively, at this level of theory) decreases steadily (*Fig. 3*) from the reactant (-4) to transition structure **3** (-15) to the product (-27), implying that aromatic character in the ligand ring system increases along this reaction coordinate. A similar, although smaller, effect is observed for NICS values computed at 1 Å above the face of each ring system, which should reduce σ and metal effects [22b]. In contrast, the most negative NICS value for the uncomplexed conrotatory ring opening is found at the transition structure (-10)[8])

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[7]) Calculations on the acceleration of pericyclic reactions by main-group metal cations have been described previously in [23]. Although this study did address the aromaticity of complexed transition states, it focused only on the pathways that would be allowed in the absence of the cations and ascribed the predicted rate acceleration to electrostatic effects.

[8]) *Jiao* and *Schleyer* calculated a value of -12 at the GIAO-SCF/6-31G*//B3LYP/6-311+G** level [22c].

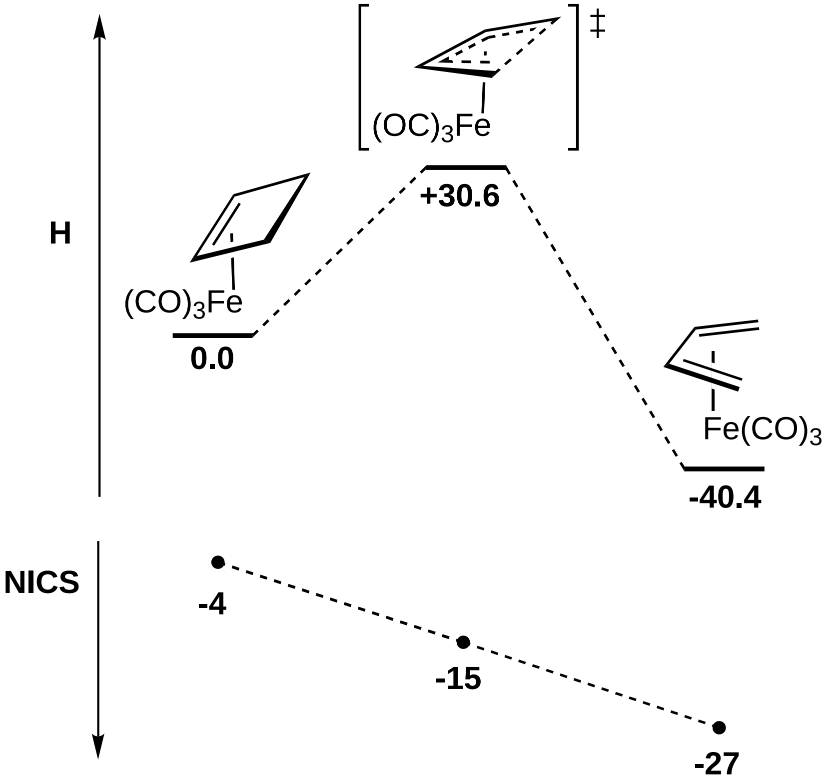

Fig. 3. *NICS Values for stationary points along the pathway for distrotatory ring opening towards the metal*

while the NICS values for cyclobutene and s-*cis*-butadiene are both close to zero. The very negative NICS value for the $Fe(CO)_3$-butadiene product (–27)[9]) indicates that this species does indeed exhibit three-dimensional aromaticity (as does the complexed disrotatory transition state, albeit to a lesser degree), consistent with steadily increasing orbital overlap along the reaction coordinate as the methylene groups of the σ-bond in the reactant rotate into conjugation with the remaining ligand π-system and the Fe.

The three-dimensional aromaticity of transition structure **3** is in sharp contrast to the nature of disrotatory species without the $Fe(CO)_3$ group. The NICS value at the center of a species constructed by removing the $Fe(CO)_3$ fragment from the complexed disrotatory transition structure is positive (+7), consistent with expectations that such a species should have antiaromatic character[10]).

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[9]) *Schleyer*, *Sorensen*, and co-workers report a value of – 20 at the IGLO/III//B3LYP/6-311 + G** level [22b].

[10]) A comprehensive account of the use of NICS calculations as a measure of antiaromatic character in orbital symmetry-forbidden pericyclic reactions will be reported in due course [24]. The NICS values for the complexed transition structures for conrotatory and disrotatory ring opening away from Fe are more difficult to interpret due to the asymmetry of these species. Nonetheless, the NICS value for the $Fe(CO)_3$-complexed conrotatory transition structure is considerably less negative than that for the disrotatory transition structure (– 8 compared to – 15).

Ligand Substitution Effects. – Are these observations restricted to the $Fe(CO)_3$ system? To address this question, we examined a system in which one CO ligand of $Fe(CO)_3$ was replaced by PH_3; this should make the $Fe(CO)_2X$ fragment more electron rich without changing the symmetry properties of its orbitals. The predicted activation barrier for disrotatory ring opening of $Fe(CO)_2PH_3$-cyclobutene (30.5 kcal/mol) was essentially the same as that for $Fe(CO)_3$-cyclobutene (30.6 kcal/mol), suggesting that the ligand substitution affects the reactant and transition state to the same extent. However, the preference for disrotatory opening towards the metal over the alternative conrotatory and disrotatory pathways was increased; the 'disrotatory-towards' transition structure is 6.4 kcal/mol more stable than the conrotatory structure (the energy difference in the $Fe(CO)_3$ case was 5.2 kcal/mol) and 11.2 kcal/mol more stable than the 'disrotatory-away' structure (the energy difference in the $Fe(CO)_3$ case was 6.0 kcal/mol). This suggests that these two transition structures are more sensitive to changes in the $Fe(CO)_2X$ fragment, which could allow for tuning of the stereoselectivity of the ring-opening reaction through ligand substitution.

Conclusions. – The disrotatory ring opening of cyclobutenes is normally symmetry-forbidden, but intervention by organometallic fragments such as $Fe(CO)_2X$ makes it the favored pathway (by more than 5 kcal/mol), consistent with predictions derived from qualitative orbital considerations [6]. NICS Calculations show that the stability of the complexed disrotatory transition state is correlated with a switch from antiaromatic to aromatic character.

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