Disrotatory and Conrotatory Transition Structures for the Fe(CO)₃-Templated Rearrangement of Methylenecyclopropane to Trimethylenemethane

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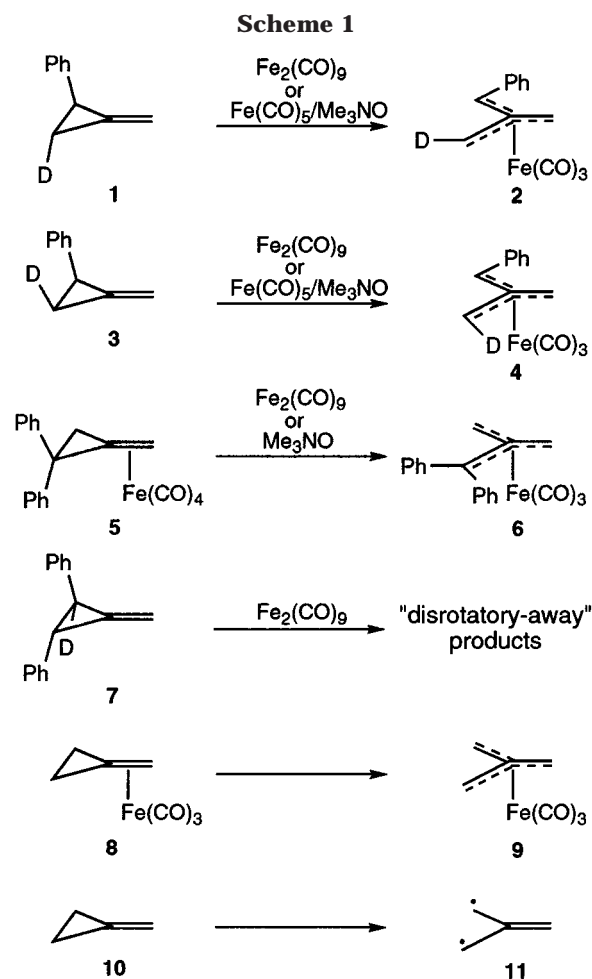*Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301*

Hybrid HF-DFT calculations were used to compute the structures and relative energetics of competing disrotatory and conrotatory transition states for ring-opening of Fe(CO)₃-complexed methylenecyclopropanes.

Introduction

Experiments[1b–d] have shown that the conversion of methylenecyclopropanes to Fe(CO)₃-trimethylenemethane (Fe(CO)₃-TMM) complexes by the action of Fe₂(CO)₉ or Fe(CO)₅/Me₃NO (Scheme 1) most likely involves the formation of Fe(CO)₃-methylenecyclopropane complexes, which then ring-open in a disrotatory fashion.[2] The disrotatory nature of the ring-opening is evident from the observation that deuterium-labeled 2-phenylmethylenecyclopropanes **1** and **3** produce isomeric TMM complexes **2** and **4**, respectively.[1b–d] If it is assumed that initial complexation of the alkene in **1** and **3** occurs on the face *anti* to the phenyl group, then these experiments also show that bond-breaking occurs by rotation of the methylene groups so that the maximum of electron density is away from the metal.[1b–d,3] These experiments support the prediction,[1a] arrived at based on considerations of orbital symmetry, perturbation theory, and extended Hückel calculations, that the disrotatory ring-opening of Fe(CO)₃-methylenecyclopropanes should involve bond-breaking "away" from the metal rather than "toward" it.

It could be argued that disrotatory ring-opening of **1** and **3** could not have occurred "toward" the metal since that would require that the phenyl group rotate inward into a sterically unfavorable environment, yet the ring-opening of isolated Fe(CO)₄-2,2-diphenylmethylenecyclopropane (**5**) also produces a TMM product (**6**).[1c] In addition, ring-opening of Fe(CO)₃ complexes of **7**, in which one phenyl group must rotate inward for either disrotatory mode, produces "disrotatory-away" products preferentially.[1d] Mechanisms in which Fe(CO)₄-meth-

Scheme 1

ylenecyclopropanes are converted to TMM complexes without the intermediacy of Fe(CO)₃-methylenecyclopropanes are also unlikely in light of the observation that **5** produces **6** only when reagents that promote CO loss, such as Me₃NO or Fe₂(CO)₉, are added.[1c]

We have now reexamined the ring-opening of the parent Fe(CO)₃-methylenecyclopropane **8** using hybrid HF-DFT calculations in order to clarify the energetics of the competing disrotatory and conrotatory ring-opening pathways in the absence of sterically demanding substituents.
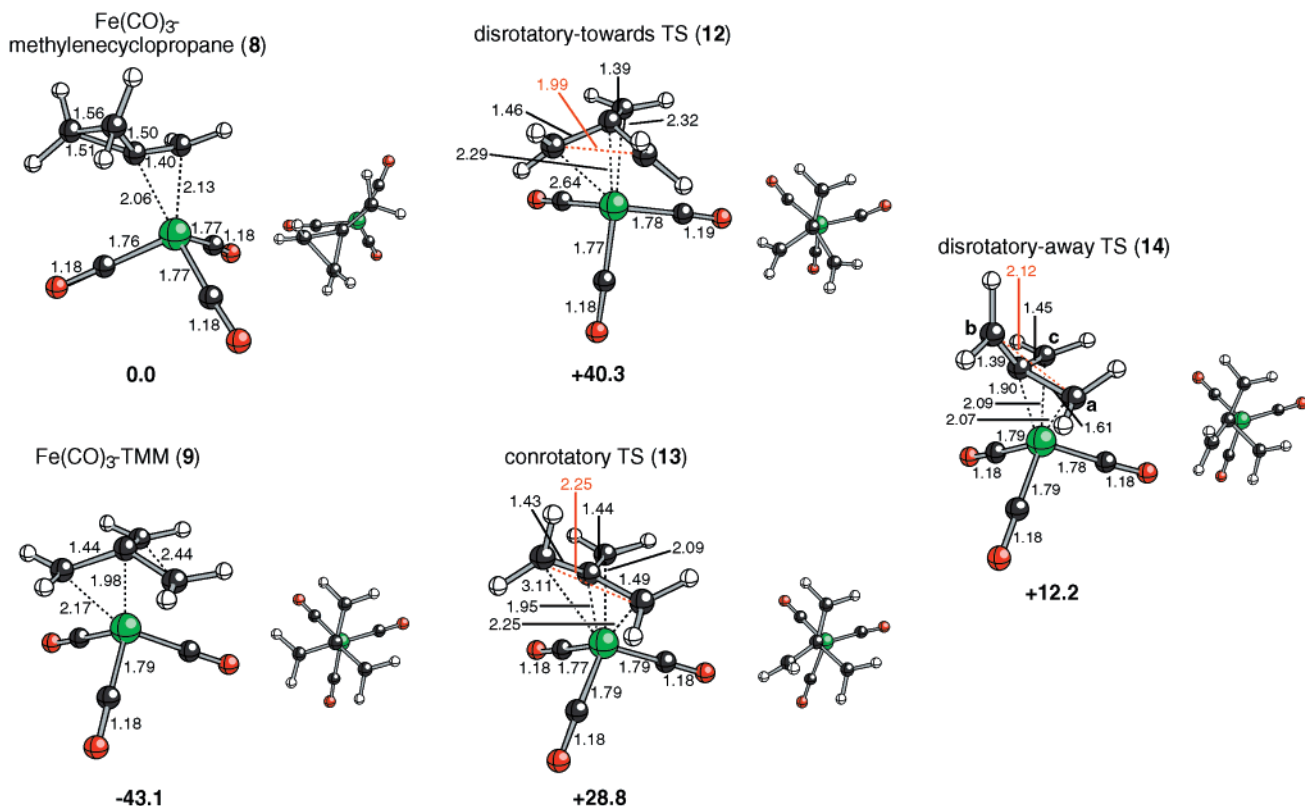
(1) (a) Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15–17. (b) Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 17–19. (c) Pinhas, A. R.; Samuelson, A. G.; Risemberg, R.; Arnold, E. V.; Clardy, J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 1668–1675. (d) Samuelson, A. G.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1981**, 354–356.

(2) In addition to Fe(CO)₃-TMM products, Fe(CO)₃-butadiene biproducts are also observed. These likely result from initial oxidative addition of an allylic C–H bond in the coordinatively unsaturated Fe-(CO)₃-methylenecyclopropane complexes. See ref 1c for details.

(3) 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: Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471–477.

Figure 1. Geometries and relative energies of $Fe(CO)_3$-methylenecyclopropane (**8**), $Fe(CO)_3$-TMM (**9**), and ring-opening transition structures **12–14**.[13] Selected interatomic distances are shown in Å, and energies (below each structure in boldface type) are in kcal/mol. Top views are shown to the right of each structure.

Methods

Calculations were performed using the GAUSSIAN 98 suite of programs[4] using the hybrid HF-DFT B3LYP method[5] with effective core potential (LANL2DZ)[6] and all-electron (DZ-VP2+)[7] basis sets. Full geometry optimizations and frequency calculations—to determine the nature of stationary points and obtain zero-point energy corrections (which were used unscaled)—were performed with the former, and single-point energies were evaluated with the latter.[8] Thus, all reported

energies were derived from calculations at the B3LYP/DZVP2+//B3LYP/LANL2DZ+ZPE(B3LYP/LANL2DZ) level. There is extensive precedent for using DFT—and the B3LYP method in particular—to treat organometallic systems.[8,9] All transition structures were further characterized by analysis of the vibrational modes corresponding to their imaginary frequencies.

Results and Discussion

It has been shown previously[10] that the conversion of uncomplexed methylenecyclopropane (**10**) to a TMM biradical (**11**) is endothermic by approximately 35 kcal/mol and has a barrier to ring-opening of approximately 40 kcal/mol.[11] The transition state for this reaction, located by Borden and co-workers at the (4/4)CASSCF/6-31G* level of theory,[10,11] is dominated by rotation of one methylene group of the breaking bond, since the TMM singlet biradical produced has one methylene group twisted out of conjugation to avoid excessive electron repulsion. The TMM group in $Fe(CO)_3$-TMM complexes such as **9**[12] is tightly bound to $Fe(CO)_3$, which results in a very exothermic reaction for the metal-

(4) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I. R.; Gomperts, R.; Martin, L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M. P.; Gill, M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998; Revision A. 9.

(5) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. (d) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.

(6) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.

(7) 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, WA 99352, 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 original DZVP2 basis set (Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571) was augmented as described in: Braden, D. A.; Tyler, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 942–947.

(8) Recent applications of this methodology include: (a) Merlic, C. A.; Walsh, J. C.; Tantillo, D. J.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 3596–3606. (b) Tantillo, D. J.; Hietbrink, B. N.; Merlic, C. A.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 7136–7137 (additional note: *J. Am. Chem. Soc.* **2001**, *123*, 5851). (c) Creary, X. *Org. Lett.* **2000**, *2*, 2069–2072.

(9) For recent reviews on DFT applied to transition metals, including comparisons with more expensive multiconfigurational methods, see: (a) Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353–406. (b) Niu, S.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 1360–1365. (c) Koch, W.; Hartwig, R. H. In *The Encyclopedia of Computational Chemistry*; Schleyer, P. v. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaeffer, H. F., III., Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, 1998; p 689.

(10) Lewis, S. B.; Hrovat, D. A.; Getty, S. J.; Borden, W. T. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 2339–2347, and references therein.

complexed system (Figure 1). Upon complexation, the hydrocarbon framework becomes slightly pyramidalized rather than twisted, and its C−C bonds are equalized.

The geometries and relative energies of the competing transition structures (**12**−**14**) for ring-opening of **8** are also shown in Figure 1. As expected, disrotatory ring-opening toward the metal is accompanied by a large activation barrier of approximately 40 kcal/mol, comparable to the barrier in the absence of $Fe(CO)_3$.[10] Based on extended Hückel calculations,[1a] it was unclear whether the conrotatory or "disrotatory-away" pathway would be the preferred alternative to this "disrotatory-toward" pathway. The experiments described above[1b−d] suggest that the "disrotatory-away" pathway should be favored, however, and this is also borne out by our calculations. While the barrier for conrotatory ring-opening (28.8 kcal/mol) is significantly less than that for disrotatory ring-opening toward the metal, it is signifcantly higher than the barrier for disrotatory ring-opening away from the metal (12.2 kcal/mol).

While the disrotatory-toward transition structure (**12**) retains C_s symmetry, the disrotatory-away transition structure (**14**) is very unsymmetrical, perhaps even more so than the conrotatory transition structure (**13**). In **12**, the two methylenes of the breaking bond both interact only weakly with the Fe (Fe−C distances of 2.64 Å), while in **13** and **14** one methylene of the breaking bond interacts strongly with the Fe (Fe−C distances of 2.25 and 2.07 Å for **13** and **14**, respectively) while the other does not. Interactions with the third methylene (Fe−C distances of 2.32, 2.09, and 2.09 Å) and the central carbon atom of the hydrocarbon fragment (Fe−C distances of 2.29, 1.95, and 1.90 Å) increase in strength from **12** to **14** as well.

The asymmetry of transition structure **14**, its relatively low energy, and the presence in it of a most unusual long bond (between the central carbon and C_a, Figure 1) prompt us to think about the bonding in it in two alternative ways. First, imagine breaking the long bond. One could then view transition structure **14** as an 18-electron complex of Fe with three carbonyls, methylene (C_aH_2), and one double bond of an allene (consisting of the central carbon, C_bH_2, and C_cH_2), shown schematically in two ways below (**15**). The methylene empty p-orbital is pointing directly at the uncomplexed "allene" double bond, a classical situation for methylene/ethylene interactions.

Alternatively, one recognizes in the geometry of the hydrocarbon fragment an allylic anion (including C_a, C_c, and the central carbon), substituted at its central carbon by a methyl cation (C_bH_2), shown schematically below (**16**). The $Fe(CO)_3$-allyl anion fragment in this complex

allene/methylene
15
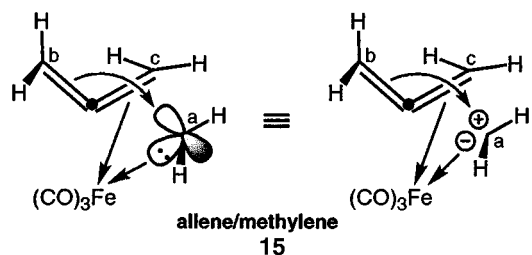
of a zwitterionic, singly rotated form of trimethylenemethane would again be 18-electron. The adjacent long and short bonds between the central carbon and C_a and C_b, respectively, are consistent with hyperconjugative stabilization of a carbocationic center at C_b by the appropriately oriented C_a-central carbon bond. This hyperconjugation would be smaller in **13** due to the less favorable orientation of the methylene groups in its breaking bond, which is consistent with the observed differences for the carbon−carbon bond lengths in **13** and **14** (Figure 1).

alkyl cation/allylic anion
16
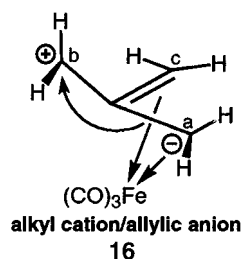
These two formulations—$Fe(CO)_3$ complexes of alkyl cation/allylic anion and allene/methylene—correspond to the limiting "bond/no bond" resonance structures for the hyperconjugative interaction described above. However one chooses to view **14**, close Fe−C contacts are tighter in this transition structure than the others, suggesting that, as a result of the orientations of its parting methylenes, this transition structure can best accommodate the stabilizing interactions available upon deviating from C_s symmetry.[14]

Like the electrocyclic ring-opening of $Fe(CO)_3$-cyclobutenes,[1a,15] the ring-opening of $Fe(CO)_3$-methylenecyclopropanes appears to be another case in which the inherent stereochemical predilections of a carbocyclic framework are overwhelmed by metal−ligand interactions.

(11) At the B3LYP/DZVP2+//B3LYP/LANL2DZ+ZPE(B3LYP/LANL2DZ) level, the ring-opening of uncomplexed methylenecyclopropane (**10**) is endothermic by 28.0 kcal/mol and has a barrier of 36.5 kcal/mol. At this level of theory, however, the TMM product is not twisted (although it does have two short and one long C−C bond of 1.41 and 1.48 Å, respectively), and the ring-opening transition structure is disrotatory rather than monorotatory. The singlet diradical TMM and transition structure suffer from spin contamination, however; their ⟨S^2⟩ values are 1.01 and 0.63, respectively. (The utility of ⟨S^2⟩ values for asssessing spin contamination in DFT calculations is still in debate; see, for example: Gräfenstein, J.; Cremer, D. *Mol. Phys.* **2001**, *99*, 981−989.) Although this level of theory appears to be inadequate for accurate descriptions of the diradical species involved in the uncomplexed ring-opening, the metal-complexed reactions do not involve such species, and this level of theory has been shown to be appropriate for characterizing related closed-shell species.[9a,b,15]

(12) C−C and Fe−C distances in **9** are in excellent agreement with analogous distances computed by Koch and co-workers for a methylated derivative of **9** using an all-electron basis set for optimization. Their C−C distances are all 1.44 Å, and their Fe−C distances range from 1.96 to 2.17 Å. See: Pfletschinger, A.; Schmalz, H.-G.; Koch, W. *Eur. J. Inorg. Chem.* **1999**, 1869−1880.

(13) Graphical depictions of structures were produced using: Müller, N.; Falk, A. *Ball & Stick 3.7.6*, a molecular graphics application for MacOS computers; Johannes Kepler University: Linz, 2000.

(14) C_s-symmetric models for the disrotatory-away process possess two imaginary frequencies: one corresponding to the disrotatory-away motion, and the other to a rocking motion of the hydrocarbon fragment relative to the $Fe(CO)_3$ fragment that breaks the C_s symmetry.

(15) Tantillo, D. J.; Hoffmann, R. *Helv. Chim. Acta* **2001**, *84*, 1396−1404.