Complicated Goings-On in the Metal-Manipulated Ring-Opening of Cyclobutene

Dean J. Tantillo* and Roald Hoffmann

Contribution from the Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301

Abstract: Most reported examples of transition metal-mediated pericyclic reactions have been shown to proceed by nonpericyclic mechanisms. However, the conversion of $Fe(CO)_4$-cyclobutenes to $Fe(CO)_3$-butadienes and CO is thought to proceed through a mechanism involving an electrocyclic ring-opening step. We have examined this and possible alternative mechanisms for the parent $Fe(CO)_4$-cyclobutene complex using hybrid HF-DFT calculations. In this system there is an inherent preference for a pathway that avoids metal-templated electrocyclic ring-opening, but the pericyclic pathway is predicted to dominate for more elaborate substrates and under certain experimental conditions.

Introduction

Can the complexation of a metal or organometallic fragment with an organic π-system alter the rate or stereoselectivity of a pericyclic reaction without making it into a stepwise process? Although many reported metal-catalyzed pericyclic reactions have been shown to avoid pericyclic mechanisms,[1] it is thought that the ring-opening reactions of $Fe(CO)_4$ complexes of strained polycyclic cyclobutenes (representative examples are shown in Scheme 1)[2,3] may in fact involve truly pericyclic reactions.[1−4] Nonetheless, this matter remains unsettled.

To resolve this issue, we performed calculations on the ring-opening of a simple model system: unsubstituted cyclobutene complexed to $Fe(CO)_4$. Although ring-opening in this system has proven difficult to study experimentally,[5] it allows us to directly compare the energetics for pericyclic and nonpericyclic ring-opening pathways in the absence of geometric constraints. The proposed mechanism[2] for metal-templated ring-opening involves initial CO loss from $Fe(CO)_4$-cyclobutene complexes to produce coordinatively unsaturated $Fe(CO)_3$-cyclobutene complexes[6] that rapidly open to $Fe(CO)_3$-butadiene products (Scheme 2). Our goal was to characterize this and other possible mechanisms for metal-templated ring-opening to ascertain whether the preferred pathway is indeed pericyclic.

Several plausible mechanisms exist for transforming the $Fe(CO)_4$-cyclobutene complex (**1**) to the $Fe(CO)_3$-butadiene

Scheme 1
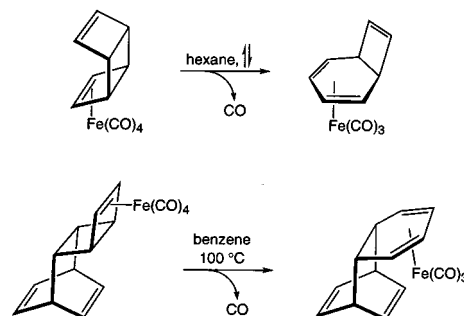
Scheme 2
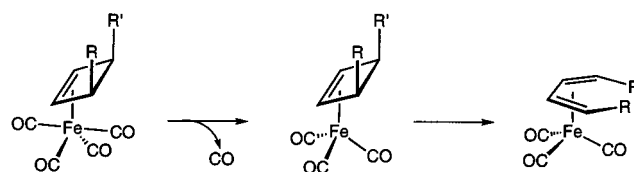
complex (**2**), including the pathway mentioned above (Scheme 3). These can be classified into three types based on the order of chemical events in each pathway: (A) CO loss to form **3** followed by ring-opening, (B) ring-opening to form **4** followed by CO loss, and (C) concomitant ring-opening and CO loss. Each of these pathways was examined computationally, and each is described in detail below.

Methods

Calculations were performed with the GAUSSIAN 98 suite of programs[7] and the hybrid HF-DFT B3LYP method[8] with effective core potential (LANL2DZ)[9] and all-electron (DZVP2+)[10] basis sets. Full geometry optimizations and frequency calculations (to determine the nature of stationary points and obtain zero point energy corrections) were performed with the former, and single point energies were evaluated with the latter.[11,12] 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.

(1) For leading references on transition metal-catalyzed pericyclic reactions which may or may not be truly pericyclic, see: Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109−205.

(2) Slegeir, W.; Case, R.; McKennis, J. S.; Petit, R. *J. Am. Chem. Soc.* **1974**, *96*, 287−288.

(3) Grimme, W.; Schneider, E. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 717−718.

(4) Related studies on Fe-promoted ring-openings of methylenecyclopropanes have also been reported: (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.

(5) Pinhas, A. R., Ph.D. Thesis, Cornell University, 1980.

(6) Knölker, H.-J. *Chem. Rev.* **2000**, *100*, 2941−2961.

Scheme 3
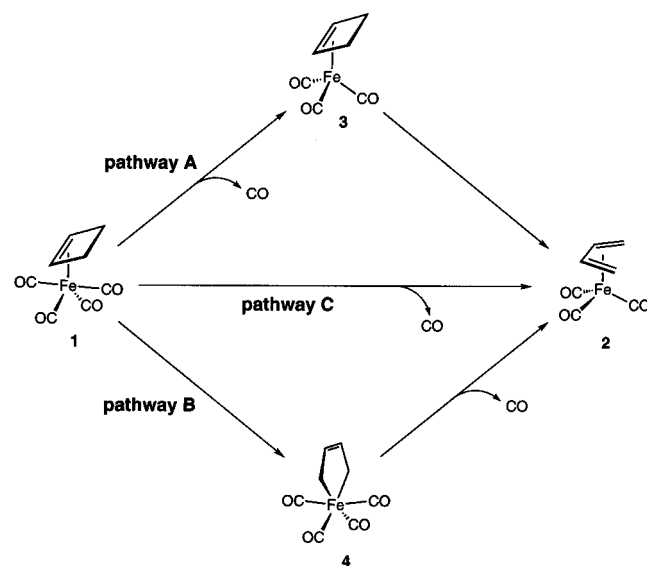
Reactants and Products

The overall conversion of $Fe(CO)_4$-cyclobutene (**1**) to separated $Fe(CO)_3$-butadiene (**2**) and CO is exothermic by 11.9 kcal/mol. Bond lengths in our optimized structures of **1** and **2** (Figure 1) agree (with a maximum deviation of 0.04 Å) with those reported previously for structures optimized at the B3LYP/6-311+G** level[13] and the X-ray crystal structure of **2**.[14] Rotating the $Fe(CO)_3$ tripod in **2** by 60° results in a transition structure that is 11.3 kcal/mol less stable than the rotamer shown in Figure 1. This predicted rotation barrier is in excellent agreement with that determined experimentally ($\Delta G^{\ddagger} = 9-13$ kcal/mol) and by previous calculations (9−14 kcal/mol).[15]

Pathway A: CO Loss Followed by Ring-Opening

The first step in this pathway (Figure 1, left) is dissociation of a CO ligand from $Fe(CO)_4$-cyclobutene (**1**). This requires overcoming a barrier of 31.5 kcal/mol. The barrier for this

process is comparable to bond dissociation energies in iron polycarbonyls, although substantially lower than that of $Fe(CO)_5$ itself.[16] The resulting 16-electron $Fe(CO)_3$-cyclobutene complex exists as a mixture of two tripod rotamers (Figure 1), both of C_s symmetry—one in which a CO ligand is eclipsed with the cyclobutene π-bond (**3b**) and the other in which the tripod is rotated by 60° (**3a**). These differ in energy only slightly (the former is more stable by 0.8 kcal/mol) and readily interconvert with a barrier of less than 1.5 kcal/mol. Since CO loss precedes the rate-determining step along this pathway (see below), incorporation of isotopically labeled CO under slight CO pressure should be experimentally observable.

$Fe(CO)_3$-cyclobutene **3b** can be converted directly to $Fe(CO)_3$-butadiene (**2**) through a pericyclic transition structure (**8**) involving disrotatory ring-opening (Figure 1, right), a proccess that would be orbital symmetry-forbidden in the absence of the $Fe(CO)_3$ fragment.[4a,17,18] The vibration corresponding to the imaginary frequency in this transition structure is dominated by disrotatory ring-opening, indicating that this motion precedes the rotation of the $Fe(CO)_3$ tripod that is necessary to produce the $Fe(CO)_3$-butadiene product (**2**). Transition structure **8** is 30.6 kcal/mol higher in energy than **3b**.

The oxidative addition of an allylic C−H bond in **3a** or **3b** is also possible (**3** → [**9**]‡ → **10**, Scheme 4). The oxidative addition transition structure **9** is only 16 kcal/mol higher in energy than **3a**, but this reaction would produce an $Fe(CO)_3$H-bound allyl species (**10**) that is 7 kcal/mol higher in energy than **3a** and that, in the absence of other reagents, could do little else than return its metal-bound hydrogen to the hydrocarbon ligand. Evidence for this process could possibly be obtained through deuterium labeling experiments, however.

Dimerization of 16-electron complexes such as **3a** or **3b** to form structures such as **11** is also a possibilty.[19] Although **11** is slightly lower in energy than two isolated molecules of **3a** (by

(7) (a) 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.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998. (b) Graphical depictions of structures were produced with *Ball & Stick 3.7.6*, molecular graphics application for MacOS computers, Norbert Müller and Alexander Falk, Johannes Kepler University Linz, 2000.

(8) (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.

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

(10) 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 basis set was augmented as described in: Braden, D. A.; Tyler, D. R. *J. Am. Chem. Soc.* **1998**, *120*, 942−947.

(11) Recent applications of this methodology include the following: (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.

(12) To further validate our choice of method we have performed test calculations using the CCSD method. CCSD/LANL2DZ single point energy calculations were performed on the B3LYP/LANL2DZ geometries of $Fe(CO)_3$-cyclobutene (**3b**) and transition structure **8**. Despite some multiconfigurational character in **3b** and **8** (as judged by the T_1 diagnostic test described by Lee and Taylor [Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199−207] and implemented through the "T1Diag" option in GAUSSIAN98; $T_1 = 0.046$ for **3b** and 0.054 for **8**), the activation barrier (**3b** → [**8**]‡) calculated at the CCSD/LANL2DZ//B3LYP/LANL2DZ level (27.7 kcal/mol) is not significantly different from that computed at the B3LYP/LANL2DZ (31.4 kcal/mol) and B3LYP/DZVP2+//B3LYP/LANL2DZ (30.6 kcal/mol) levels. Using identical hardware and software, the two CCSD/LANL2DZ single point calculations took >150 times longer to complete than B3LYP/LANL2DZ single point calculations on the same geometries. Other recent papers demonstrating that B3LYP performs as well or better than coupled cluster methods for related organometallic problems include the following: Niu, S.; Hall, M. B. *Chem. Rev.* **2000**, *100*, 353−406; Niu, S.; Hall, M. B. *J. Phys. Chem. A* **1997**, *101*, 1360−1365. Niu, S.; Hall. M. B. *J. Am. Chem. Soc.* **1999**, *121*, 3992−3999. Bartlett, K. L.; Goldberg, K. I.; Borden, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 1456−1465. Irigoras, A.; Mercero, J. M.; Silanes, I.; Ugalde, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5040−5043.

(13) Schleyer, P. v. R.; Kiran, B.; Simin, D. V.; Sorensen, T. S. *J. Am. Chem. Soc.* **2000**, *122*, 510−513.

(14) Mills, O. S.; Robinson, G. *Acta Crystallogr.* **1963**, *16*, 758−761. Additional calculations on this and related structures optimized at the B3LYP/LANL2DZ level are described in the following: Hietbrink, B. N., Ph.D. Thesis, University of California, Los Angeles, 2000.

(15) Donaldson, W. A. In *The Chemistry of Dienes and Polyenes*; Rappoport, Z., Ed.; John Wiley & Sons: New York, 2000; Vol. 2, pp 885−980 and references therein.

(16) González-Blanco, O.; Branchadell, V. *J. Chem. Phys.* **1999**, *110*, 778−783 and references therein.

(17) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970. See also: Hoffmann, R.; Woodward, R. B. *Acc. Chem. Res.* **1968**, *1*, 17−22.

(18) Details of this and other less favorable modes of electrocyclic ring-opening available to $Fe(CO)_2$X-cyclobutenes are described elsewhere. Tantillo, D. J.; Hoffmann, R. *Helv. Chim. Acta* **2001**, *84*, 1396−1404.
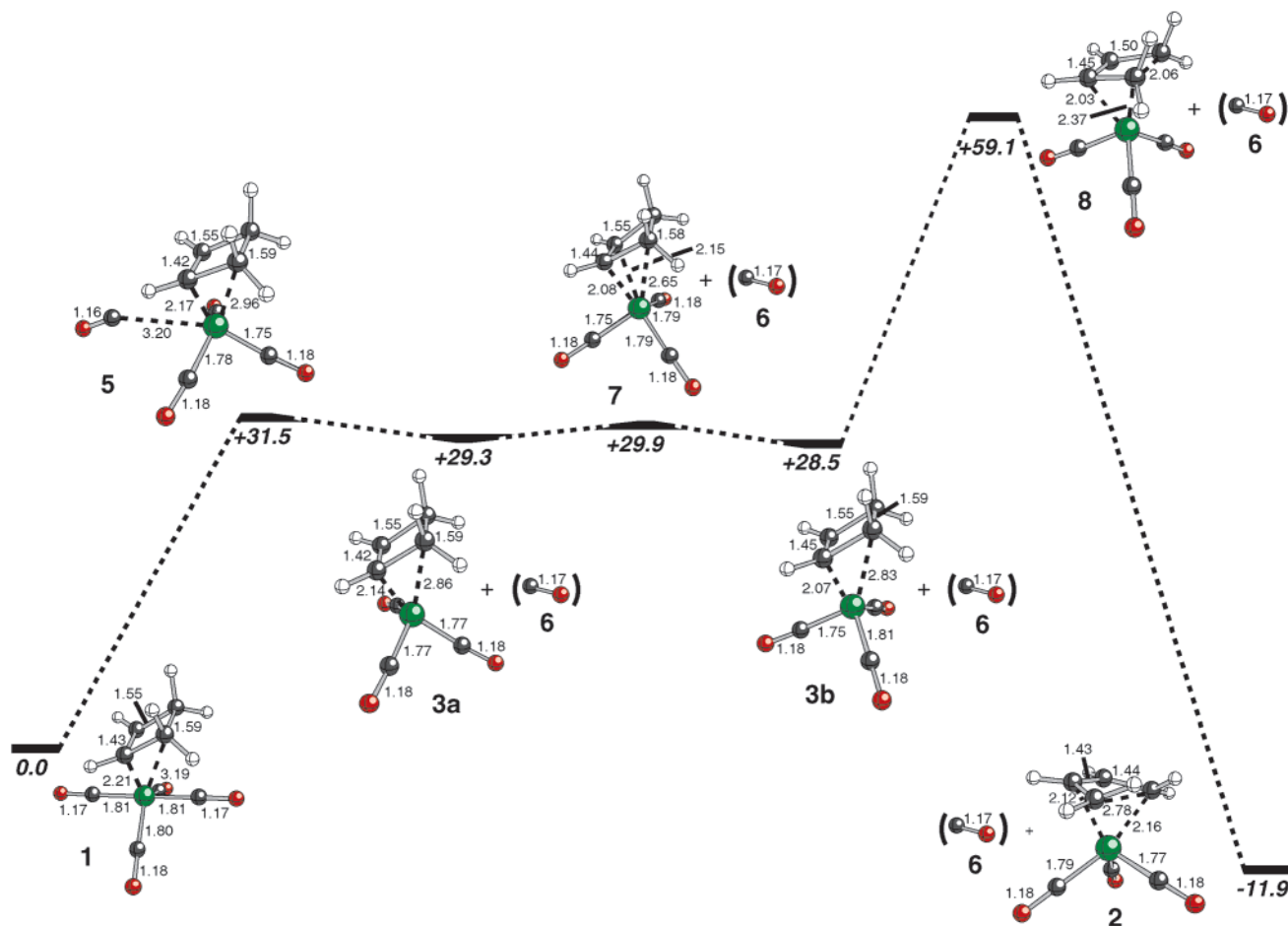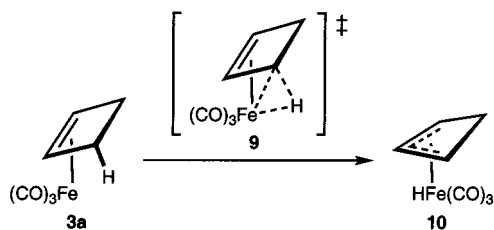
Figure 1. Structures and relative energies (kcal/mol) of stationary points along pathway A. All structures are C_s symmetric except for **7** which is C_1. Selected interatomic distances are shown in angstroms. In cases where CO is shown in parentheses, the reported energy is the sum of separated CO and Fe-bound species.

Scheme 4

2.9 kcal/mol), entropic effects and relatively low concentration conditions will discourage its formation, making it unlikely that such species disrupt the pathway from **3a** to **2**.
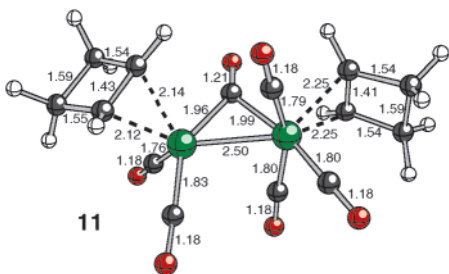
Pathway B: Ring-Opening Followed by CO Loss

The first step in this pathway (Figure 2, left) is an oxidative addition of the carbon−carbon single bond across the cyclobutene ring from the alkene to produce the octahedral, 18-electron metallacyclopentene complex **4**. In the transition structure for this reaction (**12**), the cyclobutene π-bond is shortened to a typical free alkene bond length as coordination to the Fe(CO)$_4$ fragment is lost, and the carbon−carbon single bond across from it is broken. The barrier for the reaction **1** → **4** (46.8 kcal/mol) is large compared to experimentally determined barriers for oxidative addition of carbon−carbon single bonds,[20] but this is likely a result of the loss of alkene coordination that accompanies ring-opening.

Metallacyclopentene **4** can then be converted to butadiene complex **2** (Figure 2, right). Despite attempts to locate a transition structure for CO loss that directly connects **4** and **2**, only a stepwise pathway could be found. First, a molecule of CO can dissociate from **4** to produce the square pyramidal metallacyclopentene **14**. This species is coordinatively unsaturated, and consequently, the Fe−C bonding in **14** is tighter than that in **4**. The barrier for CO loss from **4** (28.0 kcal/mol) is comparable to but slightly less than that for CO loss from **1**. The 16-electron metallacyclopentene **14** can then rearrange in an exothermic reaction to the 18-electron η^4-coordinated Fe(CO)$_3$-butadiene product (**2**). The transition state for this process (**15**) involves motion of the uncoordinated π-bond in **14** from one side of the Fe(CO)$_3$ tripod to the other to produce the favored rotamer of **2**.

(19) Although our optimization attempts consistently produced structure **11**, other dimers with different modes of CO bridging are theoretically possible.

(20) Gandelman, M.; Vigalok, A.; Konstantinovski, L.; Milstein, D. *J. Am. Chem. Soc.* **2000**, *122*, 9848−9849 and references therein.
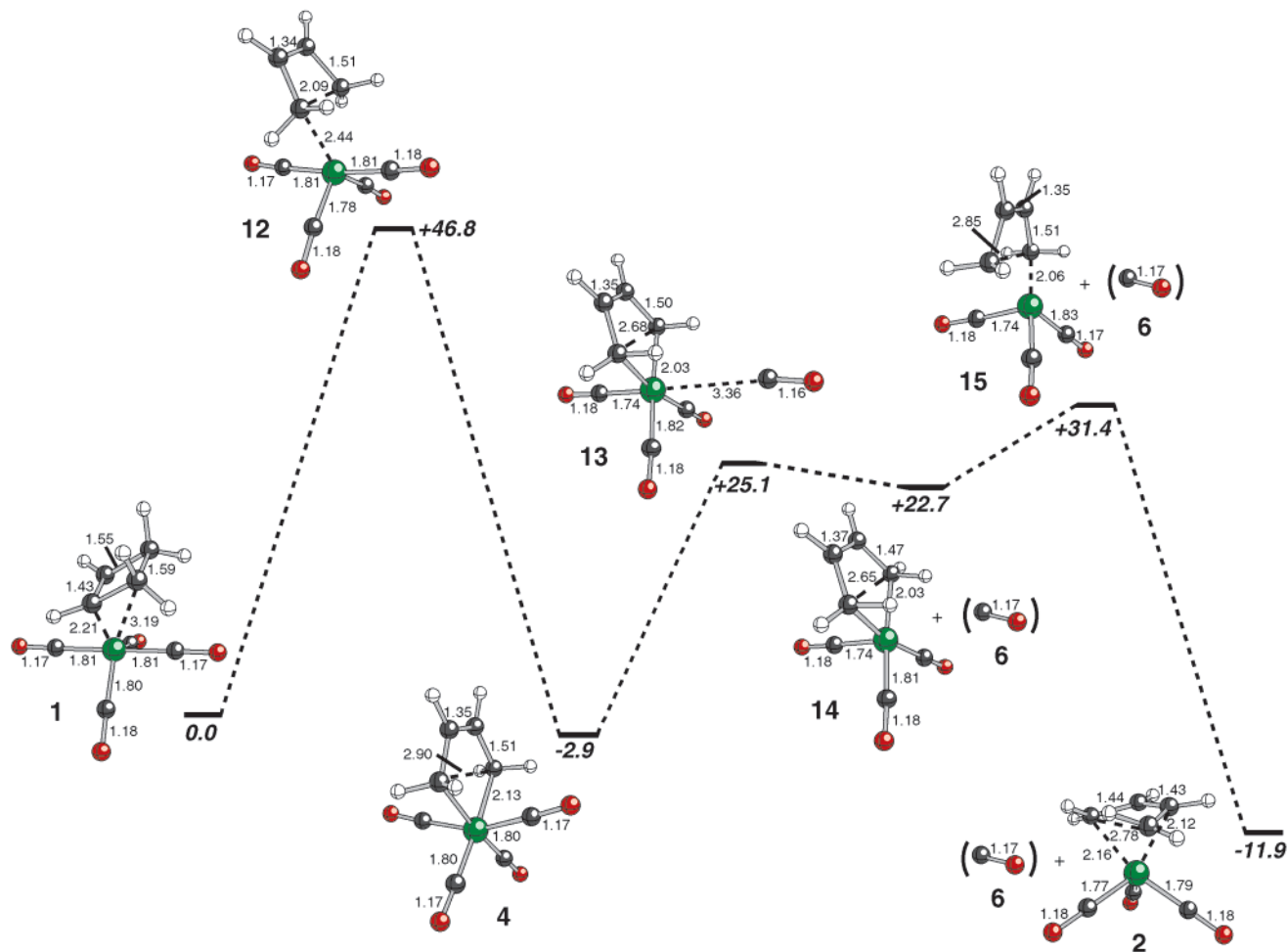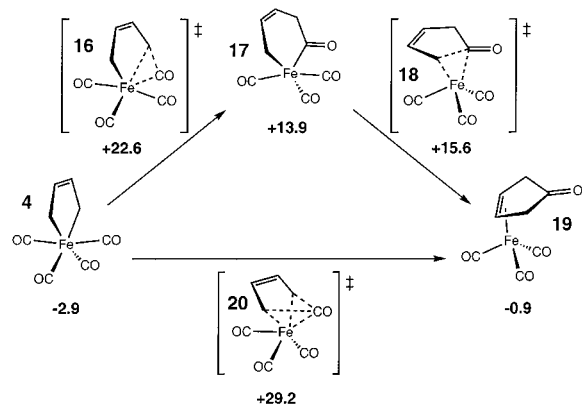
Figure 2. Structures and relative energies (kcal/mol) of stationary points along pathway B. All structures are C_s symmetric except for **4** which is C_{2v}. Selected interatomic distances are shown in angstroms. In cases where CO is shown in parentheses, the reported energy is the sum of separated CO and Fe-bound species.

Scheme 5

From **4**, several other reactions are also possible. These include CO insertion followed by reductive elimination (**4** → [**16**]‡ → **17** → [**18**]‡ → **19**, Scheme 5) and double reductive elimination (**4** → [**20**]‡ → **19**, which can also be thought of as a metal-templated cheletropic addition of CO and butadiene). Both routes ultimately lead to Fe(CO)₃-cyclopentenone **19**, which is 2.0 kcal/mol less stable than **4**. These processes are accompanied by barriers of 25.5 and 32.1 kcal/mol, respectively, from **4**. Although products such as **19** might be observable, the reversibility of these reactions would likely prevent cyclopent-3-en-1-ones from accumulating, especially when ring-opening

reactions are not run under CO pressure, since other pathways from **4** lead to CO loss.

**Pathway C: Concerted Ring-Opening and CO Loss**

A transition state for simultaneous ring-opening and CO loss would be reminiscent of the concerted ring-opening and leaving group dissociation observed for electrocyclic ring-openings of substituted cyclopropanes to produce allyl cations.[21] However, despite extensive effort, no transition state directly connecting **1** and **2** could be located. Models of this process were sought by using constrained optimizations, but in the resulting structures CO dissociation and cyclobutene ring-opening motions corresponded to separate imaginary frequencies. Optimizations without constraints tended toward transition states for CO loss from **1** such as **5**, or to weakly bound complexes of CO with the transition state for disrotatory ring-opening of **3**. At this level of theory, a direct route from **1** to **2** does not appear to exist.

The Overall Picture

As beautiful and useful as chemistry is, nothing chemical is likely to be simple; this reaction is no exception. The overall energetics for the competing pathways are summarized in Scheme 6. The rate-determining transition structure for pathway

(21) See, for example: Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 396−397. Schleyer, P. v. R.; Van Dine, G. W.; Schöllkopf, U.; Paust, J. *J. Am. Chem. Soc.* **1966**, *88*, 2868−2869.

Scheme 6
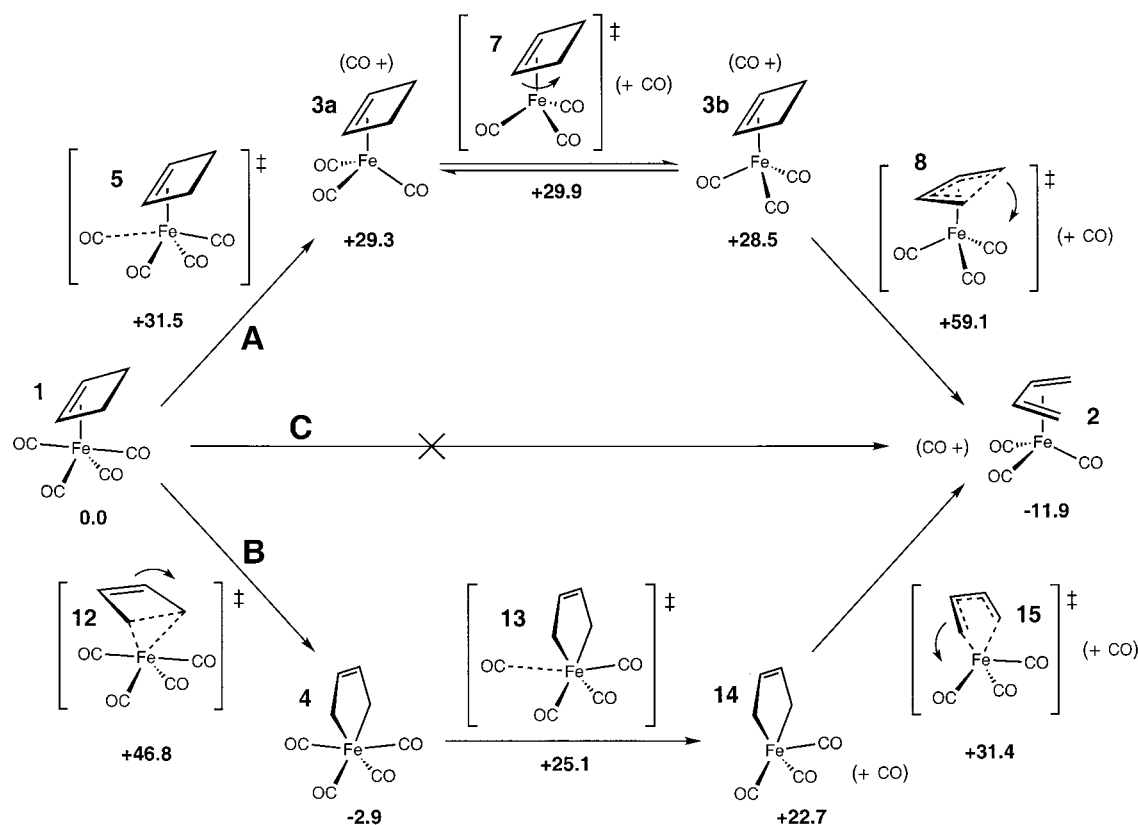
B (**12**) is approximately 12 kcal/mol more stable than that for the pericyclic ring-opening in pathway A (**8**). Clearly there is an inherent preference in this system for a nonpericyclic pathway.

In the actual experimental systems in which ring-openings of Fe(CO)$_4$-cyclobutenes have been observed (Scheme 1),[2,3] the situation is slightly different. In these systems, the Fe(CO)$_4$-complexed cyclobutene ring is fused to another four-membered ring. Rearrangement along pathway A should be facilitated in such systems, since the pericyclic ring-opening step will be accompanied by additional strain relief. The rate-determining transition state along pathway B, however (along with the Fe(CO)$_4$-metallacyclopentene intermediates to which it leads), will likely not profit as much as the pericyclic transition state; bridged derivatives of species such as **4** would be rather sterically crowded. Consequently, geometrically constrained systems likely proceed along pathways analogous to pathway A, utilizing a disrotatory electrocyclic ring-opening to reach Fe(CO)$_3$-butadiene products.

However, even for systems without geometric constraints, it is possible that the pericyclic pathway might be followed. Under conditions where CO loss is irreversible, barriers that are encountered after CO loss are not revelant to determining which pathway is followed. Dissociation of CO along pathway B requires 46.8 kcal/mol since the oxidative addition step must

occur before CO is lost. CO loss along pathway A, however, only requires 31.5 kcal/mol, since this occurs before ring-opening. Therefore, when CO loss is not reversible (and the Curtin–Hammett principle no longer applies), the pathway involving electrocyclic ring-opening should dominate.[22]

(22) Entropy contributions to free energies for each species were computed from their geometries and vibrational frequencies using statistical thermodynamics methods within the GAUSSIAN 98 framework.[23a,b] This involved several approximations (for example, low frequency ($\nu < 500$ cm^{-1}) modes were treated as vibrations[23c]), and our results are therefore mentioned only in passing. These methods suggest that the overall barrier for pathway A should be lowered upon inclusion of ΔS by approximately 8 kcal/mol, while that for pathway B should be lowered by only 1 kcal/mol when corrections for ΔS are included. This again is a result of the timing of CO loss and the rate-determining step on each pathway.

(23) (a) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, PA, 1996. (b) Ochterski, J. W. *Thermochemistry in Gaussian*, 2000, www.Gaussian.com/thermo.htm. (c) Ayala, P.; Schlegel, H. B. *J. Chem. Phys.* **1998**, *108*, 2314–2325.