

In the crystal, the cobalt(II) corrin **2** is found to contain a pentacoordinate<sup>18</sup> low-spin<sup>14</sup> Co(II) center, bound equatorially by the four corrin nitrogens and ( $\alpha$ -)axially by a benzimidazole nitrogen (Figure 2). The Co(II) center is displaced by 0.12 Å from the plane of the corrin N's toward the axial base (in **1** and **4**, the deviations of Co(III) from the plane of the four corrin N's are within experimental error<sup>17</sup>). The equatorial Co-N bond lengths in **2** (average: 1.89 Å) are within experimental error of the corresponding bond lengths of **1** (1.90 Å)<sup>17c</sup> and of **4** (1.92 Å).<sup>17d</sup> The axial Co-N bond in the cobalt(II) corrin **2** (2.13 Å) is shorter than in the two cobalt(III) corrins **1** (2.24 Å) and **4** (2.19 Å).<sup>17</sup>

The structure of the cobalt(II) corrin **2** is strikingly similar to that of the corrin moiety of coenzyme B<sub>12</sub> (**1**, Figure 1) and of methylcobalamin (**4**). In particular, the "upward folding"<sup>8</sup> of the corrin ligand in **2** (16.3°) compares to that in **1** (13.3°) and in **4** (15.8°).<sup>8,17</sup> Position and orientation of the nucleotide base with respect to the corrin ring are virtually unchanged in **1** and **2** as well, as the shorter axial bond is compensated for by the downward movement of the cobalt center in **2**. Significant differences in ligand structure between **1** and **2** are only evident for the D ring and its substituents, the nucleotide bearing f side chain and the g acetamide group: The peripheral ring-D substituents are displaced upward, as a consequence of a change in the tilt of ring D with respect to the corrin ring plane, which accompanies the downward axial shift of the Co(II) center in **2**. In the nucleotide loop, this results in considerable conformational changes in the ribophosphate segment.<sup>19</sup>

If the concept of activation of the bound coenzyme B<sub>12</sub> by protein-induced deformation<sup>4-12</sup> is meaningful, we expect a deformation of **1** toward the structure of the homolysis products to be relevant, i.e., to **2** and to a 5'-deoxyadenosyl radical. As concerns the corrin fragment, our data give little support to the major modes of deformation considered, an increase of the "upward folding" of the corrin ligand<sup>4a,8,10</sup> and a movement of the benzimidazole base.<sup>10e,f</sup> On the other hand, the cobalt corrin core of **2** differs from that of **1** mainly by an upward deflection of the ring-D periphery and downward movement of the Co center. A corresponding deformation of **1** would result in increased strain between the adenosyl group and the corrin ligand.<sup>8b,c</sup> This could lead to "sterically induced labilization" of the Co-C bond of the type predicted<sup>9b-d</sup> for activation of the coenzyme.

However, protein-induced activation of coenzyme B<sub>12</sub> does not necessarily require steric deformation of the bound starting material, but will result from differential binding of the coenzyme **1** and of the homolysis products (**2** and the 5'-deoxyadenosyl radical) to the apoenzyme.<sup>20</sup> Cobalt corrin based potential contributors to the protein-induced activation of the homolysis are provided by the structural differences between the unstrained **1** and **2**. In the crystal, these are noted at the nucleotide loop in particular, which has a high density of groups capable of strongly interacting with a protein.

In conclusion, the crystallographic data point at a remarkable similarity of the structures—including the "upward folding"<sup>8</sup>—of the corrin part of the coenzyme B<sub>12</sub> (**1**) and the homolysis fragment cob(II)alamin (**2**). In view of the structural information presented, the interactions (apoenzyme/coenzyme) at the corrin moiety of the coenzyme **1** appear insufficient to provide by themselves the major means<sup>21</sup> for a protein-induced activation of the bound **1** toward homolysis of its Co-C bond. Instead, the organometallic

bond of the bound **1** may be labilized largely by way of apoenzyme (and substrate) induced separation of the homolysis fragments, made possible by strong binding<sup>5,6</sup> of both separated fragments to the protein. On the other hand, the structural similarity between the corrin part of **1** and **2** presumably is an important factor for lowering the activation barrier in the Co-C bond homolysis of **1** and in the radical trapping reactions of **2**.

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**Supplementary Material Available:** X-ray structural data for cob(II)alamin (**2**), including crystal data, atomic positional and thermal parameters, anisotropic temperature coefficients, observed and calculated hydrogen atom coordinates, bond lengths and bond angles, least squares plane analyses, and stereoscopic crystal packing diagrams, and a comparison of distances of equivalent atoms in the crystal structures of **1** and of **2** (15 pages). Ordering information is given on any current masthead page.

### Tetrakis(trifluoromethyl)cyclopentadienyl Ligands for Transition Metals<sup>†</sup>

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The introduction of substituents into the cyclopentadienyl (Cp) backbone is well-known to dramatically affect the reactivity of transition metals containing these ligands.<sup>1</sup> While complexes of electron-rich derivatives such as pentamethylcyclopentadienide have been extensively studied, metal centers that contain cyclopentadienyl groups bearing electron-withdrawing substituents<sup>2</sup> remain relatively unexplored. Recently, Gassman and Winter demonstrated the effects of placing one trifluoromethyl group on a Cp ring.<sup>3</sup> Our objective has been to develop general routes to highly electron withdrawing cyclopentadienyl ligands containing multiple trifluoromethyl substituents. Such ligands should lead to electrophilic, yet nonoxophilic, late-transition-metal complexes with potentially useful properties such as oxidation resistance and fluorocarbon solubility. We report the preparation and properties of several transition-metal complexes containing the tetrakis-(trifluoromethyl)cyclopentadienyl ligands,  $\eta^5$ -C<sub>5</sub>(CF<sub>3</sub>)<sub>4</sub>X (X = H, OSiEt<sub>3</sub>).

Our initial efforts focused on establishing the coordinating ability of the known<sup>4</sup> tetrakis(trifluoromethyl)cyclopentadienide salt, [C<sub>5</sub>(CF<sub>3</sub>)<sub>4</sub>H]<sup>-</sup>Me<sub>4</sub>N<sup>+</sup> (**1**). No reaction occurred between **1** and metal halides, probably owing to the low nucleophilicity of this anion. Reaction with the solvated metal cation [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(MeCN)<sub>3</sub>]<sup>+</sup>O<sub>3</sub>SCF<sub>3</sub><sup>-</sup>,<sup>5</sup> however, resulted in essentially

<sup>†</sup> We dedicate this paper to Dr. George W. Parshall on the occasion of his 60th birthday.

(1) (a) King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. (b) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1. (c) Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470 and references therein.

(2) (a) Bruce, M. I.; Skelton, B. W.; Wallis, R. C.; Walton, J. K.; White, A. H.; Williams, M. L. *J. Chem. Soc., Chem. Commun.* **1981**, 428. (b) Bruce, M. I.; Humphrey, P. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1989**, *361*, 369. (c) Young, K. M.; Wrighton, M. S. *Organometallics* **1989**, *8*, 1063. (d) Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 4008. (e) Heimann, W.; Huber, M. *Chem. Ber.* **1978**, *111*, 3124.

(3) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.

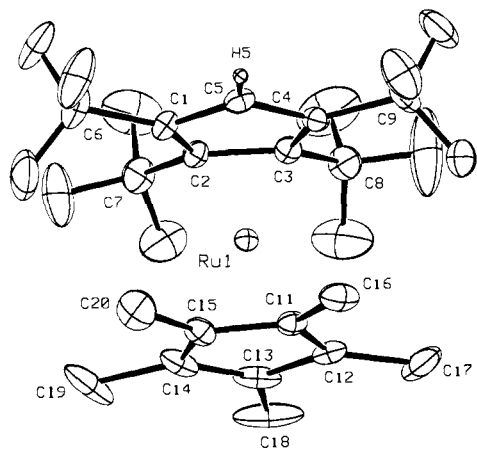
(4) Janulis, E. P., Jr.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1983**, *105*, 3563.

(18) An ill-defined solvent molecule produces electron density near the second axial coordination site, but ca. 3.42 Å from the metal center.

(19) The ribose ring assumes a C2'-exo conformation in **2** and a C3'-endo conformation in **1**. Dihedral angles along the nucleotide side chain differ by up to 20°, leading to positional discrepancies of up to 2.1 Å for the phosphate oxygens. Apart from that, the b and e carboxamide termini differ in position (by up to 4.8 Å), due to adaptation (trans vs gauche) of the side-chain conformations to the particular H-bonding pattern in the crystals (see, e.g., ref 8b).

(20) See, e.g.: Fersht, A. *Enzyme Structure and Mechanism*, 2nd ed.; W. H. Freeman & Co.: New York, 1985; pp 311-346.

(21) Potential minor contributors are discussed in the previous two paragraphs.



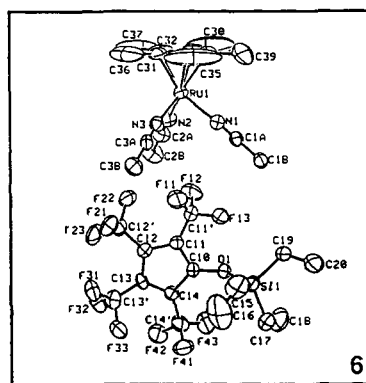
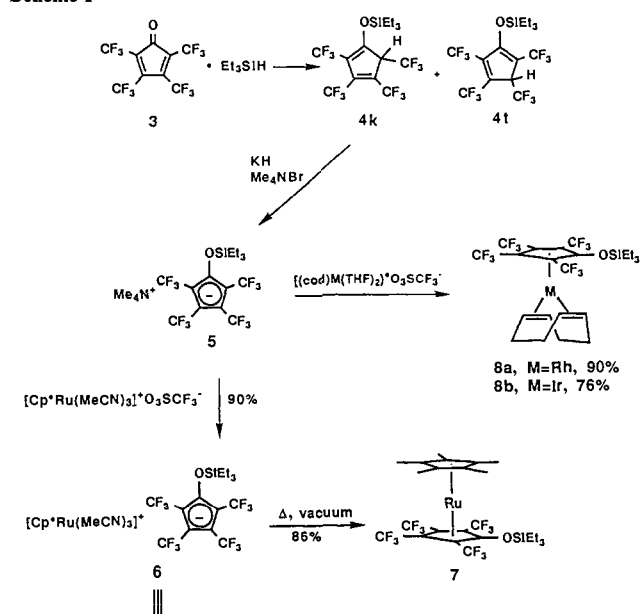
**Figure 1.** ORTEP drawing of mixed ruthenocene **2**, with thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) are as follows: Ru1-C(1-4)<sub>avg</sub> = 2.168 (5), Ru1-C5 = 2.203 (6), Ru1-C(11-15)<sub>avg</sub> = 2.183 (6), C5-H5 = 0.62 (9); Ru1-C1-C6 = 130.3 (5), Ru1-C4-C9 = 127.9 (4), Ru1-C2-C7 = 128.7 (5), Ru1-C3-C8 = 130.6 (5), Ru1-C5-H5 = 141.0 (8). Hydrogen atoms on the C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub> ligand and fluorine atom labels are omitted for clarity.

quantitative formation of a new complex containing **1** as a ligand. Spectroscopic studies<sup>6</sup> along with X-ray crystallography<sup>7</sup> (Figure 1) established the structure as the mixed ruthenocene [(η<sup>5</sup>-C<sub>5</sub>-(CF<sub>3</sub>)<sub>4</sub>H)Ru(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)] (**2**). Of interest is the staggered arrangement of the two rings, this being the first example of a staggered ruthenocene derivative to our knowledge. Such an arrangement probably derives from steric repulsion between the two rings rather than electronic effects, since the electronically analogous (η<sup>5</sup>-Cp)Ru(η<sup>5</sup>-C<sub>5</sub>(CO<sub>2</sub>Me)<sub>5</sub>) is eclipsed in the solid state.<sup>2a</sup> In solution, the barrier to ring rotation in **2** is immeasurably low by <sup>1</sup>H NMR down to -80 °C. The nearly equivalent bond distances between the Ru center and the two different Cp rings in **2** (C<sub>5</sub>Me<sub>5</sub>(centroid)-Ru = 1.813 (6) Å, C<sub>5</sub>(CF<sub>3</sub>)<sub>4</sub>H-(centroid)-Ru = 1.804 (6) Å) demonstrates the ability of **1** to act as a covalent ligand for transition metals.

We have found that ligand systems similar to **1** are easily obtained by reduction of the readily available tetrakis(trifluoromethyl)cyclopentadienone,<sup>8</sup> **3**. For example, reaction with triethylsilane proceeds smoothly without a catalyst and affords the siloxy dienes **4** as a regioisomeric mixture (80% isolated yield). Deprotonation with KH in the presence of excess Me<sub>4</sub>NBr gives rise to the new cyclopentadienide salt **5** in 75% yield (Scheme I).

Reaction between **5** and [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ru(MeCN)<sub>3</sub>]<sup>+</sup>O<sub>3</sub>SCF<sub>3</sub><sup>-</sup> initially yields the product of anion metathesis (**6**) with the cyclopentadienide as the counterion. Heating **6** in vacuo (80 °C, 0.01 Torr) affords the mixed ruthenocene **7** as a white sublimate. The structures of both **6**<sup>9</sup> and **7**<sup>10</sup> have been confirmed by X-ray

## Scheme I



crystallography. The ruthenocene **7** was found to be fluorocarbon soluble to the extent of 12 mg/mL (17.1 mM) in perfluorohexane; the nonfluorinated analogue (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ru is essentially insoluble in this solvent.

Rhodium and iridium complexes of **5** have been prepared via the in situ generated solvated cations [(cod)M(THF)<sub>2</sub>]<sup>+</sup>O<sub>3</sub>SCF<sub>3</sub><sup>-</sup> (Scheme I). Intermediates analogous to **6** were not observed, and the products (**8**) were isolated as thermally sensitive yellow/orange oils. The <sup>13</sup>C NMR spectrum of **8a** displays coupling between rhodium and all five cyclopentadienyl ring carbons, confirming that the ligand **5** is bound in an η<sup>5</sup> fashion. We have been able to prepare up to 50 mM (35 mg/mL) solutions of **8a** in perfluorohexane; dynamic light scattering measurements indicate that these solutions are essentially free of particles or aggregates (detection limit ca. 5-Å radius).

The electrochemical oxidation potentials of **2** and **7** illustrate the strong electron-withdrawing power of the ligands **1** and **5**. For example, the irreversible oxidation of **7** in methylene chloride occurs at E<sub>1/2</sub> = 1.62 V vs Ag/AgCl (1.58 V vs SCE), which is ca. 1.03 V more positive than the corresponding potential for (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Ru (E<sub>1/2</sub> = 0.55 V vs SCE).<sup>11</sup> Similarly, the half-wave potential for **2** in CH<sub>3</sub>CN is even more positive, E<sub>1/2</sub> = 1.77 V vs Ag/AgCl (1.73 V vs SCE), and again irreversible. These results suggest that the ligands **1** and **5** substantially lower the metal-based HOMO and are in accord with a recent report on a series of mixed-ruthenocene derivatives.<sup>12</sup>

(5) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(6) <sup>1</sup>H NMR (THF-d<sub>6</sub>): δ 1.90 (s, 15 H), 5.58 (s, 1 H). <sup>19</sup>F NMR (relative to CFC1<sub>3</sub>): δ -56.5 (m, 6 F), -53.9 (m, 6 F). <sup>13</sup>C NMR: δ 124.8 (q, J<sub>CF</sub> = 270 Hz, CF<sub>3</sub>), 124.75 (q, J<sub>CF</sub> = 270 Hz, CF<sub>3</sub>), 82.0 (overlapping q, J<sub>CF</sub> = 41 Hz, CCF<sub>3</sub>), 94.2 (CCH<sub>3</sub>), 76.0 (J<sub>CF</sub> = 3.8 Hz, CH), 10.5. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>F<sub>12</sub>Ru: C, 39.80; H, 2.81. Found: C, 39.88; H, 2.79.

(7) The X-ray diffraction analysis of **2** was performed by Oneida Research Services, Inc. Crystal data for C<sub>19</sub>H<sub>16</sub>F<sub>12</sub>Ru (**2**): orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), a = 10.548 (2) Å, b = 13.154 (5) Å, c = 14.799 (9) Å, T = -30 °C, V = 2053 Å<sup>3</sup>, Mo Kα radiation, μ<sub>calcd</sub> = 8.6 cm<sup>-1</sup>, d<sub>calcd</sub> = 1.85 g cm<sup>-3</sup>, Z = 4, FW = 573.39. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to residuals of R = 0.042, R<sub>w</sub> = 0.046, GOF = 1.46 for 3226 unique reflections with I > 2.0σ(I) and 292 variables. Full structural details are given as supplementary material.

(8) Dickson, R. S.; Wilkinson, G. *J. Chem. Soc.* **1964**, 2699.

(9) Crystal data for C<sub>31</sub>H<sub>40</sub>F<sub>12</sub>N<sub>3</sub>OSiRu (**6**): orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (No. 19), a = 12.162 (4) Å, b = 13.951 (2) Å, c = 21.790 (2) Å, T = 0 °C, V = 3697.1 Å<sup>3</sup>, Mo Kα radiation, μ<sub>calcd</sub> = 5.33 cm<sup>-1</sup>, d<sub>calcd</sub> = 1.487 g cm<sup>-3</sup>, Z = 4, FW = 827.87. The structure was solved by automated Patterson analysis (PHASE) and refined by a full-matrix least-squares procedure to residuals of R = 0.046, R<sub>w</sub> = 0.040, GOF = 1.23 for 3231 unique reflections with I > 3.0σ(I) and 442 variables. Full structural details are provided as supplementary material.

(10) Preliminary X-ray data indicates that **7**, like **2**, exists in the staggered form in the solid state. Further details are given in the supplementary material.

(11) Ward, M. D. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, 1989; Vol. 16, p 181.

(12) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.

Ligand substitution studies indicate that the trifluoromethyl-substituted Cp moiety of **7** is surprisingly resistant to nucleophilic displacement. No reaction was observed upon treating **7** with excess MeCN, CO, or  $\text{PMe}_3$  at 80 °C. The apparent inertness of **7** may derive from kinetic effects associated with steric bulk around the Ru center, rather than inherent bond strengths. Heating the less hindered systems **8** (50 °C, 5 h) in the presence of  $\text{PPh}_3$  (2 equiv) resulted in clean displacement of **5** rather than cod from the metal center, generating the stable adducts  $[(\text{cod})\text{M}(\text{PPh}_3)_2]^+\text{5}^-$  (**9a**, M = Rh; **9b**, M = Ir).

This work demonstrates that tetrakis(trifluoromethyl)cyclopentadienyl ligands are strongly electron withdrawing and can lead to relatively stable, fluorocarbon-soluble transition-metal complexes. Further studies on these and related systems are in progress.

**Acknowledgment.** We thank Dr. Michael D. Ward for performing the electrochemical experiments and Dr. Richard B. Flippen for the light scattering measurements. We are grateful to Dr. E. P. Janulis, Jr., whose work provided the initial sample of **1**. We also acknowledge John E. Feaster, William Marshall, and Patricia M. Trask for skilled technical assistance.

**Supplementary Material Available:** Full experimental details, including preparations and spectral and analytical data, for compounds **2** and **4-9**, X-ray diffraction data for **2** and **6**, including tables of crystal data, atomic coordinates, thermal parameters, bond distances, and bond angles, and ORTEP and packing diagrams of **2** (Figure 2) with full atom labels (17 pages). Ordering information is given on any current masthead page.

### Difluoromaleic Anhydride as a Source of Matrix-Isolated Difluoropropadienone, Difluorocyclopropenone, and Difluoroacetylene

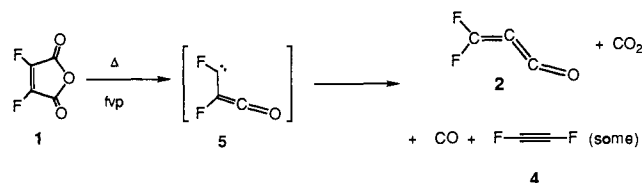
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We wish to report some remarkably clean thermal and matrix-isolated photochemical transformations of difluoromaleic anhydride (**1**), which have led to a new synthesis of difluoropropadienone (**2**), the first synthesis and characterization of difluorocyclopropenone (**3**), and the first infrared characterization of difluoroacetylene (**4**).

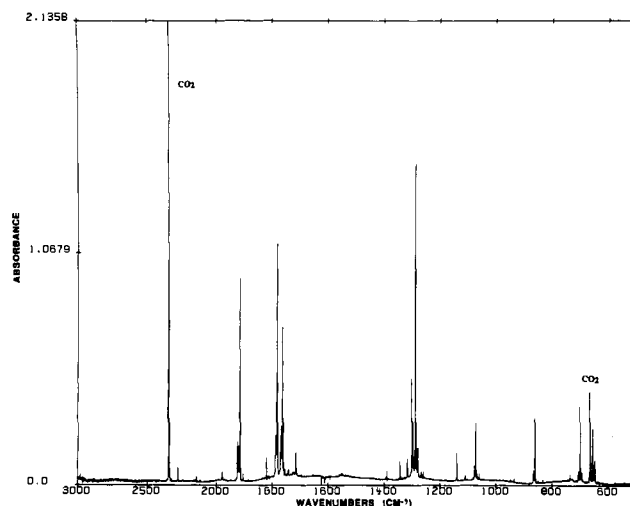
Pyrolysis of difluoromaleic anhydride<sup>1</sup> is reported to yield fluoropropynoyl fluoride and small amounts of difluoroacetylene.<sup>2</sup> In our hands, flash vacuum pyrolysis (825 °C at  $5 \times 10^{-5}$  Torr) of a mixture of **1** in argon (1:500) and deposition of the pyrolysate on a cesium iodide window cooled to 22 K cleanly produced difluoropropadienone<sup>3</sup> and carbon dioxide along with a negligible amount of difluoroacetylene (1341  $\text{cm}^{-1}$ ). At much higher temperatures (975 °C), larger amounts of difluoroacetylene are produced, but **2** is still present. The reaction presumably proceeds via the ketene carbene **5**, which undergoes fluorine atom migration to yield **2**.



(1) Raasch, M. S.; Miegel, R. E.; Castle, J. E. *J. Am. Chem. Soc.* **1959**, *81*, 2678-2680.

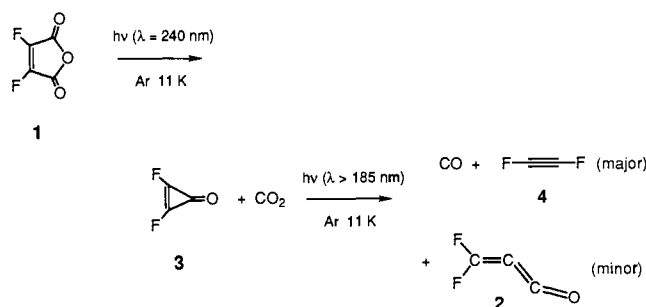
(2) Middleton, W. J. U.S. Patent 2,831,835, April 22, 1958; *Chem. Abstr.* **1958**, *52*, P14658f.

(3) Brahm, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 3071-3073.



**Figure 1.** Infrared spectrum of matrix-isolated difluorocyclopropenone and carbon dioxide in argon at 12 K generated by photolysis of difluoromaleic anhydride.

When an argon matrix of **1** is irradiated at 11 K with 240-nm light from a grating monochromator<sup>5</sup> for 1 h, the infrared bands for **1** completely disappear and in their stead arise bands corresponding to carbon dioxide (2344 and 665  $\text{cm}^{-1}$ ) and a species that we assign as difluorocyclopropenone<sup>6</sup> (**3**) (Figure 1). This compound is stable to prolonged irradiation at 240 nm, but irradiation with the full mercury arc through quartz ( $\lambda > 185$  nm) leads to the rapid decomposition of **3** and the appearance of bands corresponding to carbon monoxide (2138  $\text{cm}^{-1}$ ), difluoroacetylene (1341  $\text{cm}^{-1}$ ), and difluoropropadienone.<sup>7</sup> The exact ratios of the photolysis products are difficult to quantify, but qualitatively the major photochemical process is decarbonylation.<sup>8</sup> Control experiments reveal that difluoropropadienone is photochemically inert under these conditions.



As an aid in understanding this system, we have carried out ab initio calculations<sup>9</sup> for several  $\text{C}_3\text{F}_2\text{O}$  potential energy minima using the 6-31G\* basis set and complete geometry optimization.<sup>10</sup>

(4) IR (Ar, 11 K): 1819 (s), 1809 (s), 1767 (m), 1757 (m), 1390 (s), 1140 (s), 1060 (s), 936 (s), 736 (m), 673 (w)  $\text{cm}^{-1}$ .

(5) An L-1 illumination system (Photon Technologies) with a 75-W mercury-xenon lamp and grating monochromator was used as the light source.

(6) For the preparation of another dihalocyclopropenone, dichlorocyclopropenone, see: West, R.; Chickos, J.; Osawa, E. *J. Am. Chem. Soc.* **1968**, *90*, 3885-3886.

(7) Similar photolysis of matrix-isolated maleic anhydride yields acetylene, carbon monoxide, and carbon dioxide; see: Dunkin, I. R.; MacDonald, J. G. *J. Chem. Soc., Chem. Commun.* **1979**, 772-773.

(8) Photolysis of matrix-isolated cyclopropenones is a general method for the preparation of strained acetylenes; see: Chapman, O. L.; Gano, J.; West, P. R.; Regitz, M.; Maas, G. *J. Am. Chem. Soc.* **1981**, *103*, 7033-7036.

(9) The calculations employed Gaussian 88: M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Ragavachari, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA.

(10) The optimized geometries and total energies are available as supplementary material.