402 nm, $\epsilon \sim 15{,}400$) closely similar to that of *C. acidi-urici* Fd_{ox}[10] (per active site). Pmr studies (FT, 60 MHz) in DMSO-d_6 further substantiate incorporation of Ac-L-cys-NHMe into the tetramer, resulting in formation of the Fe–S–CH_2–CH– unit in common with the proteins.[5,6] At, *e.g.*, a 7.7/1 ratio (initial tetramer 1.9×10^{-2} M), signal integration indicates complete substitution by added thiol, and isotropically shifted signals are observed at 13.0 ppm (CH_2, $\Delta\nu_{1/2}$ 160 Hz) and at 5.3 ppm (CH, $\Delta\nu_{1/2}$ 24 Hz) downfield of TMS. These data provide the first independent corroboration of β-CH_2 cysteinyl proton assignments in the pmr spectra of HP_{red} and Fd_{ox} proteins.[11] Pmr experiments also indicate the feasibility of forming tetramers linked by substitution reactions with dithiols. At (1,4-ben-zenedithiol)/(tetramer) ratios up to 1.3/1 in DMSO-d_6, *t*-BuSH but no free dithiol signals are observed. At a 0.5/1 ratio a broad feature at 5.9 ppm is evident and is tentatively assigned to dithiolate protons in [(S-*t*-Bu)$_3$S$_4$-Fe$_4$-SC$_6$H$_4$S-Fe$_4$S$_4$-(S-*t*-Bu)$_3$]$^{4-}$.

These results suggest the feasibility of several experiments which further explore the utility of [Fe$_4$S$_4$-(SR)$_4$]$^{2-}$ as active site analogs. These include (i) protein reconstitution from the apoprotein and preformed cluster, (ii) extrusion of the intact Fe$_4$S$_4$ active site core from the holoprotein, and (iii) variable separation linkage of clusters thereby allowing examination of coupled redox and electronic interactions such as may exist between the two sites in 8-Fe ferredoxins. Further investigation of ligand substitution reactions is in progress.

(10) J.-S. Hong and J. C. Rabinowitz, *J. Biol. Chem.*, **245**, 4982 (1970).
(11) These assignments refer to signals in the $\sim$10–20 ppm downfield range: (a) W. D. Phillips, M. Poe, C. C. McDonald, and R. G. Bartsch, *Proc. Nat. Acad. Sci. U. S.*, **67**, 682 (1970); (b) M. Poe, W. D. Phillips, C. C. McDonald, and W. Lovenberg, *ibid.*, **65**, 797 (1970); (c) M. Poe, W. D. Phillips, C. C. McDonald, and W. H. Orme-Johnson, *Biochem. Biophys. Res. Commun.*, **42**, 705 (1971); (d) C. C. McDonald, W. D. Phillips, W. Lovenberg, and R. H. Holm, *Ann. N. Y. Acad. Sci.*, in press; (e) W. D. Phillips, C. C. McDonald, N. Stombaugh, and W. H. Orme-Johnson, *Proc. Nat. Acad. Sci. U. S.*, in press.

M. A. Bobrik, L. Que, Jr., R. H. Holm*
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Disrotatory Ring Opening of Cyclobutene–Iron Carbonyl Complexes

Sir:

Several examples of facile transition metal catalyzed rearrangements of organic species, leading to products which would be "forbidden" by any concerted process in the absence of the metal, are now known. It is clearly of importance to determine whether the organic moiety, presumably now a ligand coordinated to the metal, is undergoing concerted rearrangement under these conditions. One such reaction is the facile disrotatory ring opening of strained cyclobutenes catalyzed, *inter alia*, by silver and cuprous ions.[1] Theo-

(1) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967); J. Wristers, L. Brener, and R. Pettit, *ibid.*, **92**, 7499 (1970); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969).

retical arguments have been produced indicating that the concerted disrotatory ring opening of a cyclobutene–Ag$^+$ olefin complex to a butadiene–Ag$^+$ complex is an "allowed" process;[1,2] however, the reality of this process has been brought into question.[3] We report now an analogous noncatalyzed reaction of cyclobutene–iron carbonyl complexes for which a concerted process is indicated.

Treatment of *syn*-tricyclo[4.2.0.0^{2,5}]octa-3,7-diene with Fe$_2$(CO)$_9$ affords *syn*-tricyclooctadiene–iron tetracarbonyl (**1**); the nmr spectrum of this complex clearly indicates that the organic ligand is attached to the metal by means of the standard olefin–metal interaction.[4]

In refluxing hexane, complex **1** is readily converted to bicyclooctatriene–iron tricarbonyl (**2**),[5] presumably
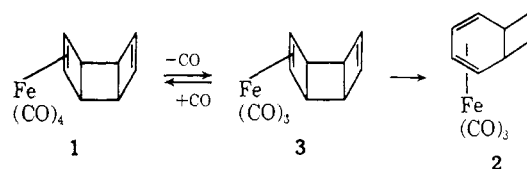
having the anti configuration indicated. The rate of conversion of complex **1** to complex **2** is not significantly affected upon changing the solvent from hexane to methanol; hence, an ionic process is not indicated. The conversion is strongly inhibited by CO and added olefins such as dimethyl maleate and excess *syn*-tricyclooctadiene. Accordingly, we propose that the formation of **2** involves thermal loss of CO from complex **1** to yield the monoolefin–Fe(CO)$_3$ complex (**3**) in which the effective atomic number of iron is now two less than that of krypton. The organic ligand in **3** then undergoes concerted disrotatory ring opening of the coordinated ring to yield the butadiene–Fe(CO)$_3$ complex **2** in which the electronic inert gas structure about iron is regained. Added potential ligands such as CO and olefins would reduce the concentration of complex **3** and provide the observed inhibitory effect.

In an analogous manner *anti*-tricyclooctadiene and *syn*-tricyclooctene react with Fe$_2$(CO)$_9$ to produce the corresponding olefin–Fe(CO)$_4$ complexes **4** and **5**, respectively.[6] These latter complexes react in refluxing hexane giving *syn*-bicyclooctatriene–Fe(CO)$_3$ (**6**)[7] and *anti*-bicyclooctatriene–Fe(CO)$_3$ (**7**),[8] respectively. In refluxing hexane the extrapolated half-lives for the ring opening of the complexes **1** and **4** are 2.5 and 2 hr,[9] respectively, whereas for the free ligands, under

(2) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).
(3) (a) L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); F. D. Mango, *Tetrahedron Lett.*, 1509 (1973). (b) In accordance with a referee's suggestion we stress that the use of the term "concerted" in these processes is directed only to that part of the overall reaction pathway in which the carbon framework is undergoing rearrangement to that which is finally observed.
(4) The nmr spectrum (acetone-d_6) exhibits absorption at τ 3.57 (t, 2), 6.07 (d, 2), and 6.7–7.1 (m, 4).
(5) This compound as well as all new compounds gave satisfactory analyses. The nmr spectrum (acetone-d_6) exhibits absorption at τ 3.78 (s, 2), 4.35 (m, 2), 6.65 (m, 2), and 6.9 (m, 2).
(6) As in the case of *syn*-tricyclooctadiene a bisiron tetracarbonyl complex can also be obtained from *anti*-tricyclooctadiene. The nmr spectrum (acetone-d_6) of **4** exhibits absorption at τ 3.54 (t, 2), 5.8 (d,2), 6.8 (m, 2), and 7.2 (m, 2).
(7) The nmr spectrum (acetone-d_6) of **6** possesses absorption at τ 3.95 (s, 2), 4.56 (m, 2), 6.5 (m, 2), and 7.4 (br s, 2).
(8) E. O. Fischer, C. Palm, and H. Fritz, *Chem. Ber.*, **92**, 2645 (1959).
(9) There also occurs some thermal degradation of the complexes **1** and **4** to liberate the free organic ligands which then inhibit the formation of the bicyclooctatriene complexes. The estimated half-lives of

Fe
(CO)₄

4

→

Fe
(CO)₃

6

Fe
(CO)₄

5

→

Fe
(CO)₃

7
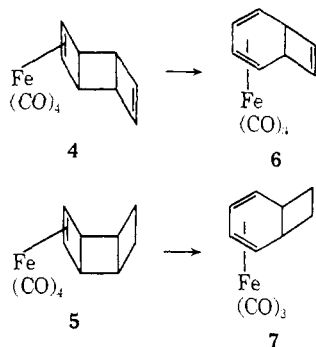
the same conditions the half-lives for the thermal ring opening are approximately 16 hr and 3 weeks, respectively. The metal atoms are clearly assisting the ring opening process, especially since the slow step in the metal reactions may well be the initial loss of CO.

The data provide for the first time experimental evidence supporting the hypothesis that cyclobutene-metal complexes, in which the metal is bound to the olefin, can undergo facile, disrotatory, concerted ring opening of the ligand to yield butadiene–metal complexes; in the absence of any experimental evidence to the contrary, we consider that this provides a satisfactory explanation of the analogous silver ion catalyzed reactions mentioned above.

A further point of interest concerns the pronounced stability of the bicyclooctatriene complexes **2** and **6** compared to bicyclooctatriene **8** itself. Whereas the latter system readily converts to cyclooctatetraene at 0° (half-life 14 min),[10] complex **2**, on the other hand, shows no sign of rearrangement to cyclooctatetraene–Fe(CO)₃ upon heating for 10 hr in refluxing hexane. We attribute this to the fact that the isomerization of the free ligand presumably proceeds *via* a Cope type rearrangement as indicated in formula **8**.[11] A similar type of rearrangement of the ligand in complex **2** would lead to the *dihapto*cyclooctatetraene–Fe(CO)₃ complex (**9**) in which the inert gas structure about iron is now lost. The isomerization which would lead directly to *tetrahapto*cyclooctatetraene–Fe(CO)₃ (**10**), with the

8

Fe
(CO)₃

9

Fe
(CO)₃

10
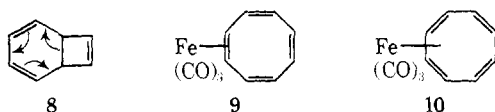
inert gas structure about iron maintained, would involve disrotatory ring opening of the four-membered ring in the complex **2** and this is of course "forbidden," the metal atom not now being in a position to render it an "allowed" process.

the reactions leading to the complexes 2 and 6 are based on data points obtained for initial low conversions.
(10) E. Vogel, H. Kiefer, and W. R. Roth, *Angew Chem., Int. Ed. Engl.*, **3**, 442 (1964).
(11) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

W. Slegeir, R. Case, J. S. McKennis, R. Pettit*

Department of Chemistry, University of Texas at Austin
Austin, Texas 78712
Received September 15, 1973

Photoelectron Spectroscopic Study of Cyclic Amines. The Relation between Ionization Potentials, Basicities, and s Character of the Nitrogen Lone Pair Electrons

Sir:

Photoelectron spectroscopy (PES) has recently been proved to be potentially useful for structural studies of organic molecules.[1] Much attention has been paid to the studies of electronic interactions such as π,π, n,π, and n,n interactions in a molecule.[2] However, there has been no report on the systematic PES studies of amines with attention to the ionization potentials (IP) of the lone pair electrons.[3] Here we wish to report the relation between IP's, basicities, and the hybridized nature of lone pair electrons for cyclic amines. We are concerned with the effect of the ring size on the physicochemical properties of cyclic amines with much attention to the IP's of the lone pair electrons as a probe for elucidation of the intrinsic nature of cyclic molecules. We have studied here the PES of three- to seven-membered cyclic amines. The measured vertical ionization potentials (IP's) are shown in Table I. All of the first

Table I. Vertical Ionization Potentials (eV) for Cyclic Amines[a]

Compound	R = H	R = CH₃
△NR	9.85, 11.90	
CH₃—△NR	9.57	
CH₃/CH₃ △NR	9.29, 11.07	8.68, 10.58
◇NR	9.04, 11.50	
⬠NR	8.77, 11.49	8.41, 11.19
⬡NR	8.64, 10.75	8.29, 10.59
⬦NR	8.41, 10.85	8.29, 10.68

[a] He(I) photoelectron spectra were recorded on a JASCO PE-1 spectrometer. Vertical IP values are accurate to ±0.02 eV.

IP's of these amines are readily assigned to the ionizations from lone pair orbitals. A remarkable feature of this table is that the values of the IP's of lone pair electrons in N–H derivatives fall in the order of increasing ring size, *i.e.*, aziridine > azetidine > pyrrolidine > piperidine > hexamethylenimine. The similar trend in IP is also the case for N-methyl homologs, *i.e.*, N-methylpyrrolidine > N-methylpiperidine ≈ N-methylhexamethylenimine, although the data for three- and four-membered imines are lacking. It is, there-

(1) For example, (a) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, New York, N. Y., 1970; (b) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).
(2) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973); D. A. Sweigart and D. W. Turner, *J. Amer. Chem. Soc.*, **94**, 5592, 5599 (1972); S. F. Nelsen, J. M. Buschek, *ibid.*, **95**, 2011, 2014 (1973); A. D. Bain, J. C. Bünzil, D. C. Frost, and L. Weiler, *ibid.*, **95**, 291 (1973).
(3) Though Gallegos, *et al.*, reported 9.94, 9.1, and 9.0 eV for the IP's of aziridine, azetidine, and pyrrolidine, respectively, by using electron impact spectroscopy, these data seem to contain considerable experimental error: E. Gallegos and R. W. Kiser, *J. Phys. Chem.*, **65**, 1177 (1961); **66**, 136 (1962).