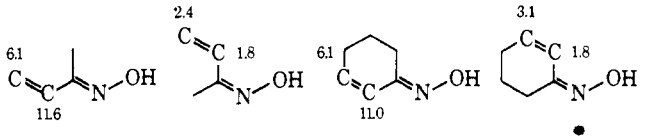
Table II. INDO MO Calculations of J_{CN}

Oxime	$^1J_{CN}$ Exptl	$^1J_{CN}$ Calcd	$^2J_{CN}$ Exptl	$^2J_{CN}$ Calcd	$^3J_{CN}$ Exptl	$^3J_{CN}$ Calcd
Acetaldehyde (*Z*)[a]	2.3	1.80	1.8	1.76		
Acetaldehyde (*E*)[a]	4.0	1.57	9.0	−3.11		
Pyridine[a,b]	0.4	−1.54	2.4	6.03	3.6	−6.60
Pyridinium ion[a,b]	12.0	−27.5	2.1	7.38	5.3	−8.72
Quinoline[c]	1.4	−2.2 (C_2)	2.7	8.64 (C_3)	3.5	−10.74 (C_4)
	0.6	−1.24 (C_9)	9.3	−2.58 (C_8)	0	−4.32 (C_5)
			2.1	6.32 (C_{10})	3.9	−7.36 (C_7)
Quinolinium ion[c]	15.9	−27.3 (C_2)	1	7.37 (C_3)	4.6	−9.35 (C_4)
	13.8	−20.9 (C_9)	1	4.42 (C_8)	0	−4.73 (C_5)
			1	5.46 (C_{10})	2.7	−5.73 (C_7)

[a] Based on geometries described in R. Wasylishen and T. Schaefer, *Can. J. Chem.*, **50**, 2989 (1972). [b] Data from ref 11. [c] Data from ref 12.

2-cyclohexenone oxime (**2**) while the reverse order ob-



tains in the *Z* isomers. These are precisely the structural relationships in quinoline[12] between $^2J_{N8}$ and $^3J_{N7}$ on the one hand, and $^2J_{N3}$ and $^3J_{N4}$ on the other. Hence it is unlikely that the differences in the quinoline values are ascribable to the apparent differences in dihedral angle; more likely, enhancement of $^2J_{N8}$ over $^2J_{N3}$, and their corresponding values in **1** and **2**, are associated with proximity of the lone pair. Whether agreement in values between corresponding isomers of **1** and **2** reflects a conformation in **1** similar to that in **2** remains open.

The range of $^1J_{CN}$ values in Table I falls well below that expected (~13 Hz) based on the simple dependence on s characters of the coupled nuclei (eq 1) proposed by Binsch, *et al.*,[13] predicated on the assumption that the

$$S_N S_C = 80 J_{NC} \qquad (1)$$

Fermi contact term is the dominant spin–spin coupling mechanism; however, lack of agreement with eq 1 does not necessarily exclude dominance of this mechanism. The values calculated on this basis (Table II) using finite perturbation theory in the INDO approximation,[15,16] while displaying poor quantitative agreement with experimental values, nonetheless reproduce several trends, although the absence of experimental sign determinations prevents any detailed comparison. The protonation-induced increases of $^1J_{CN}$ in pyridine and quinoline are apparent, and the larger magnitude of $^2J_{CN}$ in *E*- compared to *Z*-acetaldoxime accords with the negative sign calculated for the latter value, which suggests that experimentally $^2J_{CN}$ is negative, at least in the *E* isomer. This is consistent with the demonstration that lone-pair proximity makes a positive contribution to the *reduced* coupling constant ^2K ($=4\pi^2 J/h\gamma_N\gamma_C$) in phosphorus-[17] and nitrogen-containing[3a] systems. The same parallelism exists between experimental and calculated values of $^2J_{CN}$ and $^3J_{CN}$ in free and protonated pyridine and quinoline, particularly when the sign dependence on lone-pair proximity is considered.

Finally, it should be noted that $^1J_{CN}$ differences in isomeric pairs may reflect more subtle differences in bond lengths or angles; C–N bond lengths in aromatic nitrogen heterocycles are about 0.05 Å longer than in nonconjugated compounds;[18] values of $^1J_{CN}$ are consistently smaller in the former class than in geometrically analogous members of the latter. Indeed, preliminary calculations show that numerical values of the coupling constants are very sensitive to changes in these parameters, although the trends remain unaffected.

Further work is in progress to determine the signs of the couplings and the effect of protonation in order to more definitively assess the theoretical results.

Acknowledgments. For support of this work at Hunter College, gratitude is expressed to the City University of New York Faculty Research Award Program, the Research Corporation, and the American Philosophical Society. We are indebted to Dr. V. J. Bartuska of JEOL for his kind hospitality and skillful assistance during determination of some of the spectra. R. W. thanks the National Research Council of Canada for a Postdoctoral Fellowship.

(15) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 11 (1970).
(16) (a) A. D. C. Towl and K. Schaumberg, *Mol. Phys.* 22, 49 (1971); (b) A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, **55**, 950 (1971).
(17) (a) M. P. Simonnin, R. M. Lequan, and F. W. Wehrli, *J. Chem. Soc., Chem. Comm.*, 1204 (1972); (b) S. Sorenson, R. S. Hansen, and H. J. Jakobsen, *J. Amer. Chem. Soc.*, **94**, 5900 (1972).
(18) C. Sandorfy, in ref 6, Chapter 1.

Robert L. Lichter*
Department of Chemistry
Hunter College of the City University of New York
New York, New York 10021

Douglas E. Dorman
Bell Telephone Laboratories
Murray Hill, New Jersey 07974

Rod Wasylishen
National Institute of Arthritis, Metabolism, and Digestive Diseases
National Institutes of Health
Bethesda, Maryland 20014

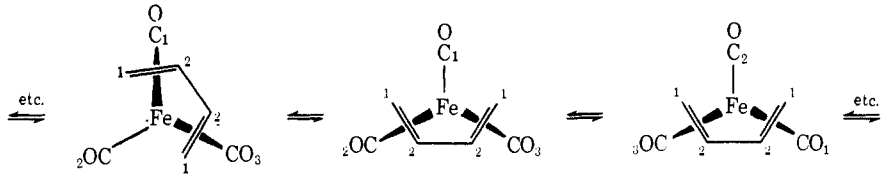
Received September 26, 1973

Fluxional Behavior of (Diene)iron Tricarbonyl Type Complexes

Sir:

During our investigation on the chemistry of tricarbonyl(1,4-η-cycloheptatriene)iron and its cycloheptatriene substituted analogs, we were somewhat puzzled to find that the ^{13}C nmr spectra of the complexes showed only one resonance for the three carbonyl

Scheme I. Possible Mechanism to Account for Basal–Apical Carbonyl Exchange in (1,3-Diene)Fe(CO)$_3$



Ia I Ia

Table I.[a,b] ^{13}C Nmr Data for (Diene)Fe(CO)$_3$

	Apical CO	Basal CO	T, °K	ΔE_a,[c] kcal/mol
(1,3-Hexadiene)Fe(CO)$_3$	212.7		272	
				7.4 ± 0.2
	215.5	210.9	180	
(Butadiene)Fe(CO)$_3$	212.8		272	
				9.5 ± 0.2
	216.9	210.1	195	
(Cycloheptatriene)Fe(CO)$_3$	211.7		272	
				11.6 ± 0.3
	214.8	210.9	200	

[a] The table shows only the behavior of the carbonyl groups, in the temperature range studied the resonances due to the ligand atoms remained essentially unchanged. [b] Chemical shifts, ppm downfield from internal TMS spectra, were run on a Bruker HFX-10 machine in 50% carbon disulfide–50% deuterioacetone. [c] Activation energies obtained by recording spectra at 3–4° intervals over the exchange region (typically −40 to −80°), fitting the observed spectra to computer generated spectra (DNMR3, by G. Binsch, QCPE, Indiana University, Bloomington, Ind.), and then plotting log K *vs.* $1/T$ to obtain a least-squares fit (adapted from EXCHSYS by G. M. Whitesides (MIT)) to the Arrhenius expression.

groups. The structure of these molecules should be based on a square-pyramidal geometry[1] and it follows that one should see at least two resonances in a ratio of 2:1 for the basal and apical CO groups, respectively.[2] Indeed, as expected, the carbon atoms of the ring show seven well-separated resonances. Such findings can be explained in two ways: fortuitous chemical shift equivalence or time-averaged equivalence resulting from rearrangement within the complexes.[3] To resolve the ambiguity we decided to investigate the variable-temperature cmr of cycloheptatriene- and the related butadiene- and (1,3-cyclohexadiene)Fe(CO)$_3$ (the latter two complexes also show only one ^{13}C resonance for the three carbonyl groups at room temperature[6]). The results of our studies are summarized in Table I. It is vividly apparent that the molecules are fluxional. The limiting spectrum, which is reached in each case,[7] shows the two expected[2] resonances (basal/apical) in the ratio 2:1. The simplest mechanism that can explain the interchange of the basal and apical carbonyl groups (Scheme I) consists of an independent or simultaneous rotations of the carbonyl groups[8] and diene moiety. However, lack of local c_3 symmetry for the three carbonyl fragments demands that the rotations of the ligating groups be also accompanied by small bending motions. The independent permutation of the three carbonyl groups is similar to the mechanism suggested by Clark[5] to account for the fluxional behavior of his PF_3 substituted diene iron carbonyl complexes. We should like to point out that the above scheme is related to the well-known Berry pseudorotation and turnstile mechanism[10] that is us used to explain nonrigidity in other five-coordinated molecules. However, since the required trigonal-bipyramidal intermediate would be severely distorted due to the small bite size of the 1,3-diene moiety,[11] we do not feel that such idealized mechanism is warranted for the complexes of this study. It is pertinent to point out in this connection that with nonconjugated 1,4- and 1,5-dienes, which span axial–equatorial sites of a trigonal bipyramid more easily, the fluxionality of the complexes increases drastically; indeed no broadening of the carbonyl resonance is observed down to −110°,[12] indicating perhaps that for these molecules, pseudorotation is indeed the *modus operandi for* the rearrangement. Although our studies do not allow an unambiguous assignment for the mechanism, the observation that similar fluxional behavior also operates in other (diene)Fe(CO)$_3$ complexes (diene: bicyclo[4.2.0]octa-2,4-diene, tetrakis(trifluoromethyl)cyclopentadienone, 1,3,5-cyclooctatriene, 4-phenyl-3-buten-2-one (benzalacetone), benzylideneacetophenone (chalcone), cinnamaldehyde)[13] does establish a general phenomenon for this class of compounds[14] and identifies, possibly, the largest group of fluxional five-coordinated molecules. The study also provides but an additional demonstration of the

(1) F. A. Cotton, V. W. Day, B. A. Frenz, K. I. Hardcastle, and J. M. Troup, *J. Amer. Chem. Soc.*, **95**, 4522 (1973), and references within.

(2) Strictly speaking in this molecule all three carbonyls are nonequivalent, C_1 symmetry; however, the chemical shift difference for the two basal CO groups could be very small.

(3) This is a very real possibility since five-coordinate complexes are known to undergo facile rearrangement;[4] moreover, Clark[5] has shown that the molecules (butadiene)Fe(CO)$_{3-x}$(PF$_3$)$_x$ and (1,3-cyclohexadiene)Fe(CO)$_{3-x}$(PF$_3$)$_x$, x = 1, 2, 3, are fluxional.

(4) J. R. Shapley and J. A. Osborn, *J. Amer. Chem. Soc.*, **92**, 6976 (1970).

(5) (a) J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970); (b) J. D. Warren, M. A. Busch, and R. J. Clark, *ibid.*, **11**, 452 (1972).

(6) (a) H. G. Preston and J. C. Davies, *J. Amer. Chem. Soc.*, **88**, 1585 (1966); (b) H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *ibid.*, **88**, 2710 (1966); (c) this work.

(7) It is perhaps surprising to find such "high" limiting temperatures for pentacoordinated molecules (see, however, ref 4); however, Clark[5] has already made the interesting observation for (1,3-cyclohexadiene)Fe(CO)$_{3-x}$(PF$_3$)$_x$ that as the PF_3 substitution increases so does the rate of rearrangement. Our results corroborate this observation.

(8) A similar type of carbonyl exchange in tricarbonyl (1,6-η-cycloheptatriene)chromium and molybdenum was recently observed by Kreiter.[9]

(9) C. G. Kreiter and M. Lang, *J. Organometal. Chem.*, **55**, C27 (1973).

(10) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960); (b) P. Gillespie, P. Hoffman, H. Klusacek, D. Marguarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and Ivan Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

(11) The angle, double bond-Fe-double bond, is about 62° in a series of related iron complexes.[1]

(12) L. Kruczynski, unpublished observations on norbornadiene-, tetrafluorobenzabicyclo[2.2.2]octatriene, and 1,5-cyclooctadiene(Fe)-(CO)$_3$.

(13) L. Kruczynski and Li Shing Man, work in progress.

(14) We note with interest that in the variable-temperature cmr study of (1-4-η-cyclooctatetraene)Fe(CO)$_3$ Rigatti, *et al.*,[15] have concluded that the "carbonyl exchange process rate is independent of the ring-atom exchange process." Clearly, the evidence that we have presented for the fluxional behavior of (diene)Fe(CO)$_3$ clarifies the nature of the two processes.

(15) G. Rigatti, G. Boccalon, A. Ceccon, and G. Ciaconnetti, *J. Chem. Soc., Chem. Commun.*, 1165 (1972).

tremendous potential of cmr spectroscopy as a structural tool in organometallic chemistry.

Acknowledgment. We thank the University of Alberta, the National Research Council of Canada, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

Leonard Kruczynski, Josef Takats*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada
Received September 11, 1973

The Role of the Symbiotic Algae of *Plexaura homomalla* in Prostaglandin Biosynthesis

Sir:

The startling announcement by Weinheimer[1] that *Plexaura homomalla* contains A-type prostaglandins in high concentration (up to 1.8% by weight) has instigated a variety of studies on this interesting species of "soft" coral.[2] We have reported recently that under suitable conditions enzymic conversion of 8,11,14-eicosatrienoic acid or arachidonic acid to PGA_1 or PGA_2, respectively, can be effected by homogenates of *Plexaura homomalla*.[3] Unfortunately, the enzyme preparations which were obtained did not bring about sufficiently high conversion to be preparatively useful. Our initial studies did not touch on the question of whether prostaglandin biosynthesis occurs in the coral cells or in the algae which coexist with *Plexaura homomalla* in a symbiotic relationship. This report deals with the isolation and culture of the algae to determine what contributions, if any, they make to prostaglandin biosynthesis. There are two possible roles for the algae to play: the synthesis and subsequent release of PGA_2 to the coral or the synthesis and release of a fatty acid precursor, arachidonic acid. The former role coupled to a method for culturing the algae could lead to a highly useful process for the production of PGA_2. The latter possibility, which seems quite reasonable in view of the widespread occurrence of C_{20} polyunsaturated acids in marine algae,[4] would be of special interest in connection with the nature of the biochemical events in the symbiosis.

Plexaura homomalla, collected off New Providence, Bahamas, was transported to Cambridge in sea water at 20°.[5] Examination revealed that the algae were found as single cells imbedded in the tissue of the coral. To free the cells, the coral was scraped with a razor under sterile sea water at 4°. The minced tissue was a viscous slime which was filtered through four layers of cheese cloth. The filtrate was centrifuged at 1500*g* for 4 min to collect the algae. After several washings of the cells by suspension in fresh sea water followed by centrifugation, the cells, in a minimum of sea water, were layered on a discontinuous sucrose gradient consisting of 20, 30, and 40% layers. After 7 min of centrifugation at 1600*g*, the algae were found at the 30–40% interface and in the 40% layer. These fractions were combined and washed with sterile sea water. To remove other contaminating cells, this pellet was applied to a continuous 20–40% sucrose gradient. After 3 min at 900*g*, the algae formed a green band midway down the gradient. This fraction was collected and washed repeatedly with sterile sea water. From 15 g of coral approximately 50–100 mg of clean algae cells were obtained.

These cells were transferred to flasks containing sterile Gonyaulox medium.[6] The algae grew best at 24–26° when exposed to alternating 12-hr light and dark periods. The algae first formed green clusters and finally a thin film covering the bottom of the flasks. Agitation of the mixtures under incubation did not enhance growth. It is possible that the algae are dependent on the coral for nutrients since growth was not as pronounced in the medium F/2[7] which contained fewer vitamins than the Gonyaulox medium.

To determine the fatty acid distribution, 5 g of packed algae cells were repeatedly extracted with 1:1 $CHCl_3$–MeOH and with ethyl acetate until all color was removed from the cells. The combined organic extracts were concentrated and then hydrolyzed under argon using 1 *N* aqueous alcoholic potassium hydroxide at 25°. After removal of the neutral material, the acids were esterified with ethereal diazomethane at 0°. This material, after separation by preparative tlc (two developments using 25% $CHCl_3$–hexane), yielded 16 mg of fatty acid methyl esters.

This mixture was analyzed with a gas chromatograph equipped with an electron capture detector using a 6-ft glass column packed with 12% DEGS at 165°. To confirm assignment of the components, a gas chromatograph–mass spectrometer combination was employed.[8] As can be seen in Table I, 39% of the esters were C_{16}, 54% were C_{18}, and only 1% were C_{20} fatty acids. Since arachidonic acid constitutes only 0.7% of the mixture, it would appear that if the algae is the source of the arachidonic acid used by the coral, it is not stored in quantity by the algae but passed on directly to the coral.

Table I

Fatty acid	% of total fatty acids	Fatty acid	% of total fatty acids
14:0	0.3	18:2	12
16:0	2	18:3	42
16:1	3	20:3	0.3
16:2	12	20:4	0.7
16:3	22		

In order to test for prostaglandin biosynthesis in the algae, it was necessary to rupture the cells. Significantly, a more vigorous procedure was found to be required than that needed to prepare the enzymically

(1) A. J. Weinheimer and R. L. Spraggins, *Tetrahedron Lett.*, 5186 (1969).
(2) See, *e.g.*, (a) W. P. Schneider, R. D. Hamilton, and L. E. Rhuland, *J. Amer. Chem. Soc.*, **94**, 2122 (1972); and (b) R. J. Light and B. Samuelsson, *Eur. J. Biochem.*, **28**, 232 (1972).
(3) E. J. Corey, W. N. Washburn, and J. C. Chen, *J. Amer. Chem. Soc.*, **95**, 2054 (1973).
(4) See (a) R. F. Lee and A. R. Loeblich III, *Phytochemistry*, 10, 593 (1971); (b) G. R. Jamieson and E. H. Reid, *ibid.*, **11**, 1423 (1972).
(5) The total elapsed time between collection in the sea and isolation of the algae was ~7 hr. At no time before use was the coral exposed to air.
(6) M. Fogel and J. W. Hastings, *Arch. Biochem. Biophys.*, **142**, 310 (1971).
(7) R. R. L. Guillard and J. H. Ryther, *Can. J. Macrobiol.*, **8**, 229 (1962).
(8) We wish to thank Professor Klaus Biemann of MIT for making available the mass spectrometer.