observed suggests that the system does not proceed beyond the ion-cluster intermediate **2**: either the formation of the zwitterion intermediate **3** or the subsequent prototropic shift from **3** to **4** could present barriers that are inaccessible at thermal energies. The similarly negative result for dimethyl ether is also of interest because the reverse reaction, (12), is a major pathway for forming

$$(CH_3O)_2PO_2^- \rightarrow (CH_3)_2O + PO_3^- \qquad (12)$$
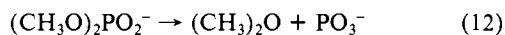
PO_3^- in the mass spectra of various phosphotriesters.[12] The sole reactions shown in Table II for PO_3^- are not chemical reactions at all but the physical clustering of polar molecules to a negatively charged ion. Such clustering reactions are third-order reactions involving collisional stabilization of the cluster by the buffer gas. The rate constants for forming $X^- \cdot HY$ clusters in Table II follow expected trends, correlating with the binding energy of the cluster, which, for a given X^-, depends on the heat of deprotonation of HY.[26]

We have verified the identity of the reactant ion (m/z 79) to be PO_3^- in several ways. A major ion in the ion source (m/z 125) suggests the formation of PO_3^- by reaction 12, which is a pathway already established for PO_3^- formation.[12] We have evidence for the collisional dissociation of PO_3^- to PO_2^- when PO_3^- is injected into the flow tube at high energy and this is confirmed by drift-tube experiments;[27] again, this pathway has been established previously.[12] Using trimethyl phosphate or dimethyl phosphite to produce PO_3^- gives identical results for reaction 2. Finally, at the highest pressure of HCl used, we see evidence that PO_3^- will bind a maximum of three HCl molecules.

On the basis of the thermodynamic and kinetic evidence presented here, we conclude that PO_3^-, *qua* PO_3^-, *is a highly stable and unreactive anion.* Consistently PO_3^- behaves as NO_3^- behaves, but with greater stability. Our very limited study has produced no evidence in the gas phase for the intriguing suggestion that PO_3^- is both an electrophile and an anion.[28] Such studies in the gas phase do test directly theoretical predictions of the properties of PO_3^-,[29] but the relationship of the gas-phase chemistry to the more interesting biochemical environment is less clear. The gas-phase results suggest that reactivity shown in solution cannot be due to PO_3^- per se but must reflect the environment as well. In this respect, it may be relevant to note that properties of phosphate ions in aqueous solution are influenced by hydrogen bonding.[30]

(26) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1971**, *93*, 7139.

(27) Smith, D.; Adams, N. G.; Paulson, J. F.; Dale, F., unpublished experiments at Birmingham University.

(28) Westheimer, F. H. *Adv. Chem. Ser.* **1980**, *No. 191*, 17.

(29) Loew, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 1630. Loew, L. M.; MacArthur, W. R. *Ibid.* **1977**, *99*, 1019.

(30) Kirby, A. J., private communication.

# Transient Ferracyclobutanes during Protonation of η³-Homoallyliron(0) Complexes

M. F. Semmelhack* and Hanh T. M. Le

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

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Nucleophile addition to $(\eta^4\text{-}1,3\text{-diene})Fe(CO)_3$ (**1**) produces the reactive intermediate $(\eta^3\text{-}3\text{-butenyl})$tricarbonyliron anionic complexes (**2**)[1–3] which rearrange to η^3-allyl complexes via carbon

Scheme 1

Series a: X = OMe
b: X = Me
c: X = Et

R = CHPh₂
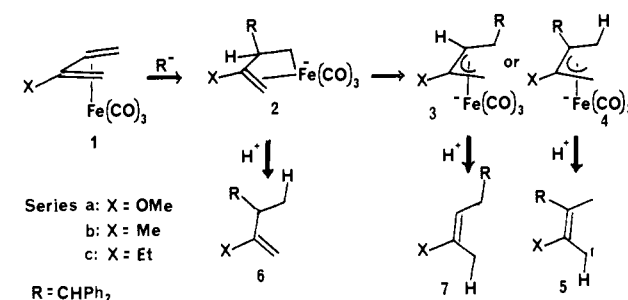
shift (to give **3**) or hydrogen shift (to give **4**).[3,4] The structures of the intermediate **2**–**4** are generally inferred from the simple products of protolytic cleavage.[4] Connected with the study of the hydrogen shift (**2a** → **4a**)[4] (Scheme I), we report in this paper a rearrangement process that was uncovered through the use of deuterium labels. The rearrangement appears to be quite general and can lead to skeletal changes; it is best understood in terms of a transient ferracyclobutane intermediate.[5]

Reaction of tricarbonyl(η^4-2-methoxy-1,3-butadiene)iron (**1a**) with diphenylmethyllithium (LiR) initially at –78 °C and then warmed at 25 °C for 2 h produced an intermediate (suggested to be **4a**). Cleavage with excess trifluoroacetic acid-*d* (–78 °C) gave primarily **5a** with deuterium exclusively at C-1 (66% yield), as expected.[6,7] The same reaction mixture held at –78 °C for 1 h and quenched in exactly the same way produced primarily the skeleton represented by **6a** (71% yield), as expected,[4] but ^2H NMR spectroscopy established that deuterium was located as indicated in A (Figure 1), with 20 ± 5% of the deuterium at the CH_3 group (C-4) and 80% at the C-1 vinyl positions (H_a, H_b; unresolved in the ^2H NMR spectrum).[6–8] In the ^1H NMR spectrum, the signals assigned to H_a (δ 3.7) and H_b (δ 3.6) are clearly resolved; they show equal areas (0.60 H relative to H_c as 1.0 H, δ 3.9) and patterns consistent with a mixture of unlabeled (H_a, H_b = H) and monolabeled compounds (H_a = H, H_b = D; H_a = D, H_b = H). The mass spectrum[9] allowed estimation of the number of deuterium atoms per molecule: 16% d_0, 71% d_1, 13% d_2. The main monodeuterated components in the mixture

(1) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15–C18.

(2) (a) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (b) Semmelhack, M. F.; Herndon, J. W.; Liu, J. K. *Organometallics* **1983**, *2*, 1885.

(3) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363.

(4) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715.

(5) We are aware of no simple ferracyclobutanes that have been characterized. However, such intermediates have been suggested as the key intermediates in the reaction of (alkylidene)tetracarbonyliron complexes with alkenes: (a) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750. With other metals, metallacyclobutane complexes have been implicated in important catalytic reactions and a few have been isolated. For leading references, see: Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 297.

(6) The structures of **5a** and **6a** were firmly established during general studies of nucleophile addition to **1a**, with proton quenching.[4]

(7) The presence of deuterium at the site(s) and in the relative amounts indicated is based on chemical shift assignments and integration of the ^2H NMR spectrum, assuming chemical shifts exactly parallel with the ^1H NMR chemical shift values for the unlabeled compound. For a discussion of the correlation of ^2H and ^1H chemical shifts, see: Harris, R. K.; Mann, B. E. "NMR and the Periodic Table", Academic Press: New York, 1978. For details of the experimental data see the supplementary material. Integration of the ^1H NMR spectrum and analysis of the ^2H shifts on the ^1H NMR chemical shift positions were entirely consistent with the assignment but less easily used for quantitation.

(8) Simple chromatography of **6a** on silica gel leads efficiently to the

ketone i. The unlabeled version has been fully characterized.[4] Deuterium appears primarily in the α-keto methyl group. Similarly, the mixture **18/19** has been cleaved with ozone to give the same ketone, i, in both the labeled and unlabeled series.
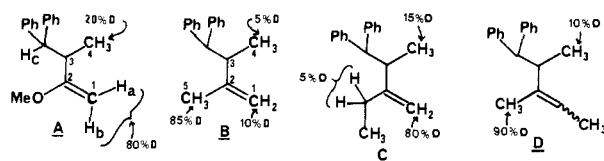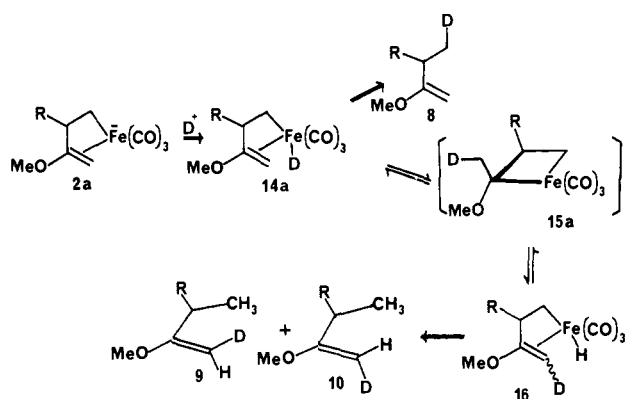
Figure 1. Deuterium distributions.
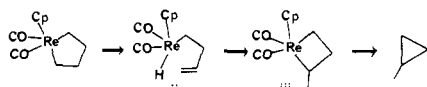
Scheme II

Scheme III

Scheme IV

are then assumed to be **8** (20%), **9** (40%), and **10** (40%), as shown in Scheme II.

In an exactly parallel way, (η^4-2-methyl-1,3-butadiene)tricarbonyliron (**1b**) reacted with diphenylmethyllithium at -78 °C, and the mixture was quenched with excess trifluoroacetic acid-*d* after 2 h. As usual,[4] the addition occurred at an internal position (leading to **2b** and then **6b**) and at a terminal position (leading to **3b** and **7b**) in a ratio **6b:7b** of ca. 6:1. The mixture of deuterium-labeled **6b** was isolated by chromatography (silica gel, AgNO₃) in 63% yield. Analysis by ^2H NMR[7] and ^1H NMR indicated the distribution of deuterium shown in B (Figure 1), with 10% D at C-1, 85% D at C-5, and 5% D at C-4. The ^1H NMR spectrum again indicates about equal distribution of deuterium at the *E* and *Z* position at C-1. The mass spectrum[9] suggested a mixture of 17% d_0, 70% d_1, and 13% d_2. The main monodeuterated components are then assumed to be **11** (5%), **12** (85%), and **13** (*E/Z*, 10%).

These results are easily accomodated by the parallel pathways shown in Schemes 2 and III. From complex **1a** (Scheme II), deuteration (D⁺) of intermediate **2a** is suggested to produce the iron(II) deuteride **14a**. Simple reductive elimination would give the minor product **8**. Addition across the alkene ligand leads to ferracyclobutane **15a**.[10] Then β-hydride elimination with a

substantial statistical and kinetic selectivity produces **16** (both *E* and *Z* deuterium) in preference to **14a**; reductive elimination from **16** gives a mixture of isomers with vinyl deuterium (**9, 10**).

In the pathway from **1:** (Scheme III), an additional pathway opens up, as ferracyclobutane **15b** can undergo β-hydride elimination toward the methyl group (C-5) to give **17** and lead to the major isomer **12**, which accounts for 85% of the deuterium label. The β-hydride elimination from **15b** is selective for the methyl group trans to the Ph₂CH unit, presumably due to conformational factors.

Scheme III suggests the possibility of skeletal rearrangements during anion addition/proton quenching with (η^4(2-ethyl-1,3-butadiene)tricarbonyliron (**1c**). Reaction of **1c** with diphenylmethyllithium and quenching at low temperature with trifluoroacetic acid, as before, produced three products, which were separated by chromatography: **18** and **19** (61% yield together; ratio 16:84)[8] and **20** (7% yield). The formation of rearranged products **18** and **19** is consistent with the general mechanism, shown specifically in Scheme IV. Similarly, quenching with trifluoroacetic acid-*d* produces a mixture of **18, 19,** and **20** (ratio 20:66:14 and 68% yield together) bearing deuterium. The patterns of deuterium labeling are presented in Figure 1 (structures C and D) and are consistent[7] with the results with isoprene and the pathway in Scheme IV. The ferracyclobutane **23** is the suggested intermediate, with β-hydride elimination toward the ethyl group in preference to the C-5 methyl.

In every experiment involving quenching with trifluoroacetic acid-*d*, the monodeuterated product was strongly preferred, but d_0 and d_2 products were significant (10-15%, typically). This pattern requires intermolecular H-D exchange, and we are seeking evidence to establish the mechanism of this exchange. We are continuing to probe for the generality of the ferracyclobutane formation and the consequences of the rearrangement pathways on product distributions.

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(9) The mass spectra were obtained on an AEI MS-9 instrument with EI ionization and careful scanning over the parent ion region. We are assuming no significant isotope effects on fragmentations which influence the relative ratio of peaks in the parent ion region. For the mass spectral data, see the supplementary material.

(10) It is difficult to predict the relative rates of the several insertion and reductive-elimination processes open to **14** and **25**. In a related study, Yang and Bergman[11] suggest that a metallacyclopentane involving CpRe(CO)₂ rearranges to a transient homoallylrhenium hydride (ii), then to the rhenacyclobutane (iii), and finally undergoes reductive elimination to a cyclopropane. Similarly, a tantalum metallacyclobutane is observed to undergo
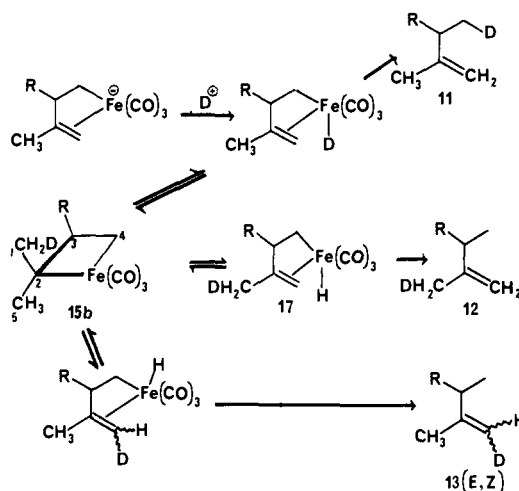

β-hydride elimination *into* the ring, and reductive elimination gives a simple alkene.[12] We have observed a similar β-hydride elimination process in a more general way from Fischer-type carbene iron complexes in addition to olefins, where ferracyclobutanes are again implicated.[5a]
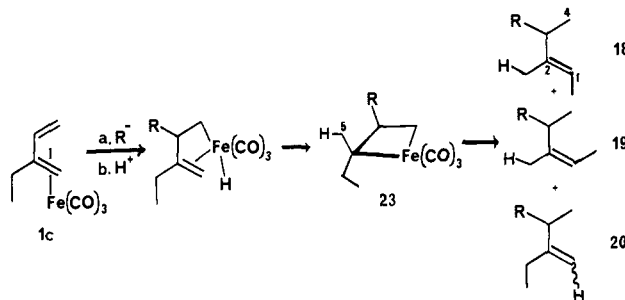
(11) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500-6501.

(12) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451-5453.

Supplementary Material Available: Detailed spectral and analytical data, and copies of the original spectra (^{1}H and ^{2}H NMR) for the mixture 18/19 in the labeled and unlabeled series (8 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Triplet Exciplex Formation in the External Heavy-Atom Effect [*J. Am. Chem. Soc.* **1982**, *104*, 1107]. MARIA C. TAMARGO and DWAINE O. COWAN*

The correct order of magnitude for all the entries in Table I: Summary of the First Order Decay Data should be 10^2 rather than 10^3, as shown. The text and the figure contain the correct numbers.

Structures and Stabilities of α-Hetero-Substituted Organolithium and Organosodium Compounds. Energetic Unimportance of Second Row d-Orbital Effects [*J. Am. Chem. Soc.* **1984**, *106*, 6467–6475]. PAUL VON RAGUÉ SCHLEYER,* TIMOTHY CLARK, ALEXANDER J. KOS, GÜNTHER W. SPITZNAGEL, CORNELIA ROHDE, DORIT ARAD, K. N. HOUK,* and NELSON G. RONDAN

The stabilization energy for X = PH$_2$ in Table II at 3-21+-G//3-21+G (third column) should be −19.9 instead of +15.9 kcal/mol.

In addition we neglected to mention that Professor F. Bernardi had informed us of his agreement with our conclusions (p 6474) that energetic effects of second-row substituents on the stabilization of carbanions is insignificant.

Chain-Folding Initiation Structures in Ribonuclease A: Conformational Analysis of *trans*-Ac-Asn-Pro-Tyr-NHMe and *trans*-Ac-Tyr-Pro-Asn-NHMe in Water and in the Solid State [*J. Am. Chem. Soc.* **1984**, *106*, 7946]. G. T. MONTELIONE, E. ARNOLD, Y. C. MEINWALD, E. R. STIMSON, J. B. DENTON, S.-G. HUANG, J. CLARDY, and H. A. SCHERAGA*

Page 7954: Footnote *b* of Table IV should read:
k_{ex} is given by eq 1 and $T_{1,mag}$ by eq 4. k_{ex} is in s^{-1} and $T_{1,mag}$ is in s.

Chain-Folding Initiation Structures in Ribonuclease A: Conformational Free Energy Calculations on Ac-Asn-Pro-Tyr-NHMe, Ac-Tyr-Pro-Asn-NHMe, and Related Peptides [*J. Am. Chem. Soc.* **1984**, *106*, 7959]. M. OKA, G. T. MONTELIONE, and H. A. SCHERAGA*

Page 7968: The first line of the legend of Figure 5 should read:
Minimum-energy conformations of Ac-Tyr-Pro-Ala-NHMe. (A)

Book Reviews

Dairy Chemistry and Physics. By Pieter Walstra (Agricultural University, Wageningen) and Robert Jenness (University of Minnesota). John Wiley & Sons, Inc.: New York. 1984. xviii + 467 pp. $59.95.

The authors have succeeded uncommonly well in producing "a reasonably complete and integrated picture of the chemistry and physics of milk". The book includes the usual chapters on composition of milk and the chemistry of milk carbohydrates, lipids, and proteins that one expects in a dairy chemistry text. But there are also chapters on milk secretion, the effect of heating on milk, physical properties of milk, colloidal and surface phenomena, interaction of milk with air bubbles, rheological properties, and properties of concentrated milk. H. T. Badings has contributed a chapter on flavors and off-flavors of milk. The book is not a comprehensive review but refers to key papers and reviews of various subjects at the end of each chapter. The chemistry and physics of dairy products other than milk are not treated directly.

The text is clear, the organization is well conceived, and the depth of treatment of each topic is consistent and appropriate for a college-level text. It will also be a very useful reference to those involved in the chemistry of milk and dairy products.

Earl G. Hammond, *Iowa State University*

Handbook of Chemical Microscopy. Volume One. Fourth Edition. By Clyde W. Mason (Cornell University). Wiley-Interscience Publishers: New York. 1983. XV + 505 pp. $75.00.

For those not familiar with the Third Edition, the Fourth Edition contains the following chapters. Chapters One and Two discuss the optical system of the microscope and the use of the microscope in the chemical laboratory. Chapters Three and Four describe the illumination of transparent and opaque objects. Chapter Five describes methods of preparing materials for microscopic study. Chapter Six discusses special methods for interpreting physical properties. Chapters Seven, Eight, and Nine deal with the topics ultramicroscopy, photomicrography, and electronmicroscopy. Chapters Ten and Eleven describe the study of

isotropic and anisotropic materials and the determination of the refractive indices of solids and liquids with use of the polarized light microscope. Chapter Twelve describes the optical properties of aggregates and crystals, Chapter Thirteen the preparation of crystals for study, Chapter Fourteen microscopic measurements, Chapter Fifteen particle size determinations, and Chapter Sixteen the quantitative analysis of heterogeneous mixtures. The new chapter, Chapter Seventeen, contains a brief summary of microscopic qualitative chemical analysis.

The Michel-Levy Color Chart included with the Fourth Edition is a color photograph representation and for the most part is an improvement over that found in the Third Edition. The reader should note that in the fourth order of this chart (the far right hand side of the chart), the color representation does not appear to be true.

In summary then, if you are an experienced microscopist who perhaps owns prior editions of Chemical Microscopy and wants to add to his or her library collection, this volume will not represent a significant addition. If, on the other hand, you are a beginner, a student who wants a solid, for the most part well written, tid-bit crammed but dated guide to chemical microscopy, then you will want the Fourth Edition of the classic!

W. W. McGee, *University of Central Florida*

Polymer Monographs. Volume 8. Poly(tetrahydrofuran). By P. Dreyfuss (The University of Akron). Series edited by M. B. Huglin (University of Salford). Gordon and Breach Science Publishers: New York. 1982. xiii + 306 pp. $59.50.

This is the eighth volume of the series of short "Polymer Monographs" each dealing with one specific polymer. These monographs, according to the editor's statement "cover equally basic scientific information on a polymer and information pertinent to its practical utilization". The following volumes have been published: "Poly(1-butene)", "Polypropylene", "Poly(vinyl chloride)", "Poly(vinyl alcohol)", "Poly(vinylidene chloride)", "Poly(N-vinyl carbazole)", "Heparin (and related polysacchardides)", and "Polytetrahydrofuran (PolyTHF)".