tion properties from each other. The calculations on the ground state of $CpMn(CO)_3$, however, indicate that the characters should be quite similar, and ab initio calculations on positive ions formed by removal of a d electron from ferrocene indicate that the positive ions have more similarly localized d orbitals than ferrocene itself. Interactions with other orbitals and higher-order effects have also been assumed to be small in this analysis. In any event, the bulk of the evidence indicates that ionizations from orbitals which are primarily metal d in character occur close in energy, and that ionization from the a_1-type orbital probably follows ionization from the e-type orbitals by no more than a few tenths of an electron volt.

References and Notes

(1) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.
(2) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, **47**, 112 (1969).
(3) D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, **8**, 2544 (1969).
(4) B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **69**, 1659 (1973).
(5) I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **27**, 215 (1974).
(6) D. L. Lichtenberger, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **12**, 702 (1973).
(7) D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, **13**, 486 (1974).
(8) S. Cradock, E. A. V. Ebsworth, and A. Robertson, *J. Chem. Soc., Dalton Trans.*, 22 (1973).
(9) B. R. Higginson, D. R. Lloyd, J. A. Connor, and I. H. Hillier, submitted for publication.
(10) J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Hussain, and K. Siegbahn, *J. Chem. Phys.*, **57**, 1185 (1972).
(11) S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1847 (1972).
(12) S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **70**, 356 (1974).
(13) S. Evans, M. F. Guest, I. H. Hillier, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, **70**, 417 (1974).
(14) S. Evans, J. C. Green, and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 2*, **68**, 249 (1972).
(15) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
(16) For a review, see R. F. Fenske, *Prog. Inorg. Chem.*, **21**, 179 (1975).
(17) I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **22**, 1025 (1971).
(18) I. H. Hillier and V. R. Saunders, *Mol. Phys.*, **23**, 449 (1972).
(19) M. F. Guest, M. B. Hall, and I. H. Hillier, *Mol. Phys.*, **25**, 629 (1973).
(20) M. B. Hall, M. F. Guest and I. H. Hillier, *Chem. Phys. Lett.*, **15**, 592 (1972).
(21) (a) A. Viellard, *Chem. Commun.*, 1022, 1427 (1969); (b) *J. Chem. Soc., Chem. Commun.*, 250 (1973).
(22) M. Coutiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, **27**, 281 (1972).
(23) For example, see R. B. King, "Transition Metal Organometallic Chemistry", Academic Press, New York and London, 1969, and references therein.
(24) (a) T. H. Whitesides, D. L. Lichtenberger, and R. A. Budnik, *Inorg. Chem.*, **14**, 68 (1975); (b) J. Müller, K. Fenderl, and B. Mertschenk, *Chem. Ber.*, **104**, 700 (1971).
(25) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 768 (1972).
(26) J. J. Eisch and R. B. King, "Organometallic Syntheses", Academic Press, New York and London, 1965.
(27) POLYATOM (Version 2), D. B. Neumann, H. Basch, R. L. Kornegay, L. C. Snyder, J. W. Moskowitz, C. Hornbeck, and S. P. Liebmann, Program 199, Quantum Chemistry Exchange, Indiana University, Bloomington, Ind.
(28) R. F. Fenske, *Pure Appl. Chem.*, **27**, 61 (1971).
(29) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).
(30) R. F. Stewart, *J. Chem. Phys.*, **50**, 2485 (1969).
(31) A. F. Berndt and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).
(32) (a) P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 1696 (1970); (b) R. F. Bryan, *J. Chem. Soc. A*, 192 (1967); (c) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **8**, 1936 (1969); (d) T. Toan and L. F. Dahl, *J. Am. Chem. Soc.*, **93**, 2654 (1971).
(33) R. F. Bryan, P. T. Greene, and A. R. Manning, Abstracts of American Crystallographic Association, Seattle, Wash., March 1969, No. M6.
(34) V. G. Andianov, B. P. Biryukov, and Y. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 1129 (1969).
(35) D. J. Darensbourg, *Inorg. Chem.*, 11, 1606 (1972).
(36) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 11, 1619 (1972).
(37) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965).
(38) W. G. Richards, *Int. J. Mass. Spec. Ion Phys.*, **2**, 419 (1969).
(39) H. Preuss and G. Diercksen, *Int. J. Quantum Chem.*, I, 349 (1967).
(40) H. Preuss and R. Janoschek, *J. Mol. Struct.*, **3**, 423 (1969).
(41) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968).
(42) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **9**, 1053 (1970).
(43) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 315 (1956).
(44) D. L. Lichtenberger and R. F. Fenske, *J. Chem. Phys.*, in press.
(45) N. Rosch and K. H. Johnson, *Chem. Phys. Lett.*, **24**, 179 (1974).
(46) J. S. Griffith, "The Theory of Transition Metal Ions", University Press, Cambridge, 1971.
(47) M. B. Hall, *J. Am. Chem. Soc.*, **97**, 2057 (1975).
(48) D. L. Lichtenberger, *Diss. Abstr.*, submitted for publication.
(49) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds. Volume II, The Transition Elements", Methuen and Co., London, 1968.
(50) O. A. Gansow, D. A. Schexnayder, and B. V. Kimura, *J. Am. Chem. Soc.*, **94**, 3406 (1972).
(51) M. Jungen, *Chem. Phys. Lett.*, **21**, 68 (1973).

Thermolysis of Diene Iron Tricarbonyl Complexes. Cis–Trans Isomerization and Hydrogen Scrambling Reactions in Cyclic and Acyclic Complexes

Thomas H. Whitesides* and James P. Neilan

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

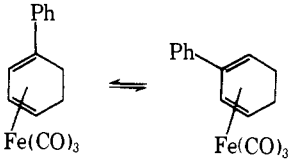
Received March 24, 1975

Abstract: The thermolysis of several cyclic and acyclic diene iron tricarbonyl complexes has been investigated. On heating (*trans,cis*-1,5-diphenylpentadiene)iron tricarbonyl (*cis*-**3**) in benzene two competing reactions were observed: metal epimerization (leading to racemization and exo-endo scrambling) and isomerization to the trans,trans isomer (*trans*-**3**). On the basis of kinetic and labeling studies a mechanism for these reactions involving a coordinatively unsaturated dihapto iron tricarbonyl complex is proposed. Only 1,3-shifts of hydrogen were detected, presumably due to the formation of a π-allyl metal hydride intermediate. When the cyclic species were subjected to the same reaction conditions, 1,5-hydrogen shifts were observed. When the cyclic complex contained an aromatic substituent, metal epimerization was observed as well. These reactions are postulated to involve consecutive 1,3-hydrogen migrations and coordination of the iron to the aromatic ring, respectively. As suggested by earlier work, there is no necessity to postulate any concerted [1,*n*], $n = 3, 5$, sigmatropic migration of hydrogen; all of the reactions can be consistently explained on the basis of known intermediates.

The question of the mechanism of hydrogen migrations catalyzed by transition metals is of substantial practical and theoretical interest. Hydrogen migration reactions can either be a limitation on the synthetic usefulness of a given catalytic process, leading to mixtures of products,[1] or a powerful synthetic tool,[2] allowing novel transformations not

readily carried out by other techniques. On the other hand, the labilization of hydrogen on ligands bound to transition metals is one of the fundamental ways in which coordination affects reactivity, and thus the study of reactions involving migration may yield insight into such reactions as hydrogenation, β-elimination, and ligand insertion reactions.

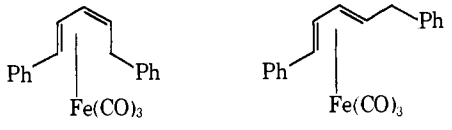
One of the questions which the research described herein was designed to answer is that of the role of orbital symmetry in controlling the reactions of transition metal complexes.[3] The particular reaction involved here is the suprafacial [1,5] sigmatropic shift, which has been amply demonstrated[4] to involve an orbital symmetry controlled pathway in the uncatalyzed systems. We had previously discovered that certain diene iron tricarbonyl complexes undergo thermal isomerizations resulting from a formal [1,5] shift at a temperature considerably lower than that involved in the absence of a metal. A brief communication[5] reported evidence that the mechanism of the conversion of **1** and **2** did



1 2

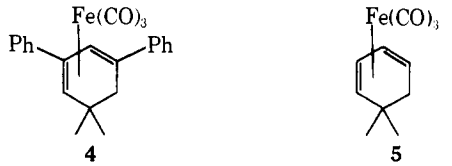
not involve a concerted migration; in fact, further work[6] indicates that, at least in the cyclopentadiene system, the [1,5] migration pathway is considerably retarded by a metal. This paper amplifies and extends our preliminary conclusions. Closely related work has been carried out by several workers on the isomerization of simple olefins by iron carbonyls.[7] A similar rearrangement of cycloheptatrienemolybdenum[8a] and -chromium[8b] tricarbonyl has also been reported and shown to involve a [1,5] shift of hydrogen.[8b]

The apparent absence of [1,5] migrations in the phenyl cyclohexadiene system led us to investigate acyclic diene complexes, in particular *cis*-**3**, in the hopes that the diminished steric constraints in **3** would allow more favorable or-



cis-3 *trans*-3

bital interactions, and thus permit the concerted pathway to operate. At the same time, in order to study isomerization pathways due to the aromatic ring, which had complicated the investigation of **1** and **2**, we also synthesized and studied the thermolysis of **4** and **5**.

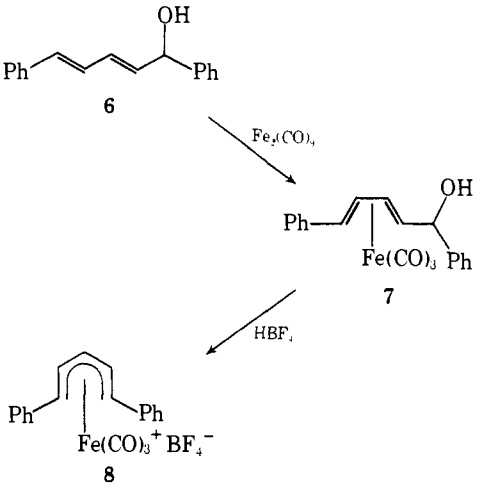


4 5

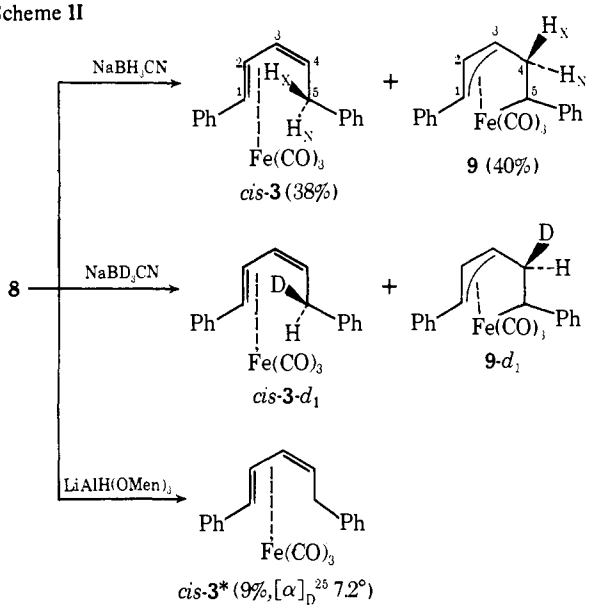
Results

Synthetic Aspects. Acyclic Compounds. The synthesis of **3** was accomplished via reduction of (diphenylpentadienyl)iron tricarbonyl cation **8**, which was available by the route shown in Scheme I. When *trans,trans*-1,5-diphenyl-2,4-pentadien-1-ol[9] was allowed to react with diiron nonacarbonyl, the diene complex **7** could be isolated in 85% yield. Treatment of the alcohol complex with anhydrous

Scheme I



Scheme II

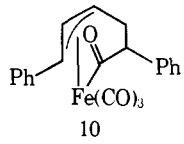


fluoboric acid in acetic acid gave the orange salt **8** in 75% yield. The structure of this species was confirmed by elemental analysis, ir (ν_{CO} 2104, 2060, and 1970 cm^{-1}, typical of dienyl iron tricarbonyl salts[10]), and NMR. In addition to a ten proton multiplet at δ 7.7, the NMR showed only three resonances, at δ 7.3 (1 H, t, J = 7 Hz, H_3), 6.7 (2 H, dd, J = 7, 12 Hz, H_2, H_4), and 4.7 (2 H, d, J = 12 Hz, H_1, H_5), in keeping with the symmetrical nature of the compound.

Reduction of **8** with cyanoborohydride led to the formation of *cis*-**3**, together with a second species, assigned structure **9**, in approximately equal quantities. The trans,cis diene complex (mp 132–133.5°) was a yellow crystalline solid, with acceptable elemental analysis and consistent ir and mass spectra. In the NMR spectrum, in addition to the aromatic absorptions, resonances at δ 6.0 (1 H, dd, J_{23} = 5 Hz, J_{12} = 10 Hz, H_2), 5.2 (1 H, t, $J_{23} \simeq J_{34} \simeq$ 5 Hz, H_3), 3.4 (1 H, d, J_{12} = 10 Hz, H_1), 2.8 (1 H, dd, J_{45N} = 4 Hz, J_{gem} = 14 Hz, H_5 endo), 2.6 (1 H, ddd, J_{45N} = 4 Hz, J_{34} = 5 Hz, J_{45X} = 11 Hz, H_4), and 2.3 (1 H, dd, J_{45X} = 11 Hz, J_{gem} = 14 Hz, H_{5X}) were observed. The resonances due to H_4, H_{5X}, and H_{5N} could be resolved adequately only at 270 MHz; the assignments are based on coupling constants, together with the results of the reduction with sodium cyanoborodeuteride.[11] In this case, the peak at δ 2.3 had disappeared, together with the 11 and 14 Hz couplings to H_4 and H_{5N}. Since hydride donors are expected[12] to attack the ligand from the side away from the metal, this signal is at-

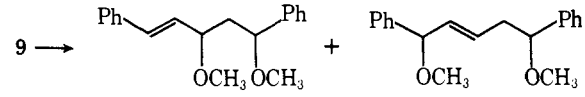
tributed to the exo proton at C_5. The cis stereochemistry of the C_3–C_4 linkage is confirmed by the relatively small coupling between H_3 and H_4 (5 Hz) and by comparison to the trans,trans complex (see below).

Species **9**[13] was obtained as an unstable, air-sensitive yellow oil, and satisfactory elemental analysis was not obtained. In the ir, metal carbonyl bands were observed at 2058, 1988, and 1981 cm^{-1}, consistent with a neutral tricarbonyl group. No bands attributable to a metal acyl structure could be detected, ruling out **10** as a possible



10

structure. The NMR of the compound showed resonances at δ 4.6 (1 H, dd, J_{12} = 12 Hz, J_{23} = 7 Hz, H_2), 4.2 (1 H, d, J_{12} = Hz, H_1), 3.6 (1 H, m, H_3), 2.9 (1 H, J_{34N} = 10 Hz, J_{gem} = 14, J_{4N5} = 10 Hz, H_{4N}), 2.65 (1 H, J_{34X} = 3 Hz, J_{gem} = 14 Hz, J_{4X5} = 10 Hz, H_{4X}), and 1.1 (1 H, $J_{54X} \sim J_{54N}$ = 10 Hz, H_5). In the deuterated compound, the resonance at δ 2.65 disappeared, and those at δ 3.6 (H_3) and 2.9 (H_{4N}) and 1.1 (H_5) became a triplet, triplet, and doublet, respectively. On this basis, with the assumption that hydride again is donated from the side of the ligand remote from the metal, the signal at δ 2.65 is assigned to H_{4X} and that at δ 2.9 is assigned to H_{4N}. In addition, degradation of the complex with Ce(IV) in methanol led to the formation of equal amounts of the dimethoxy compounds **11** and **12** in 34% overall yield. The ethers were separated by

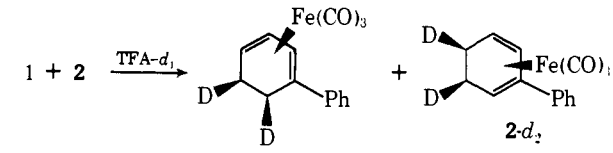


11 12

column chromatography and identified by a combination of high resolution mass spectrometry, NMR, and ir spectra. The NMR of **11** showed absorptions at δ 7.2 (10 H, aromatic H), 6.5 (1 H, d, J = 16 Hz, C_1H), 5.9 (1 H, dd, J = 16, 8 Hz, C_2H), 4.2 (1 H, m, C_3H), 3.9 (1 H, m, C_5H), 3.2 (3 H, s, $-OCH_3$), 3.1 (3 H, s, $-OCH_3$), and 1.7 (2 H, m, C_4H). The NMR spectrum of **12** showed absorptions at δ 7.2 (10 H, m, aromatic CH), 5.5 (1 H, m, H_3), 4.4 (1 H, d, J = 6 Hz, H_1), 4.0 (1 H, t, J = 8 Hz, H_5), 3.2 (3 H, s, $-OCH_3$), 3.1 (3 H, s, $-OCH_3$, and 2.4 (2 H, q, J = 8 Hz, C_4H). The ir spectrum exhibited a C–O stretch at 1100 cm^{-1}. Absorptions due to organic carbonyl were not seen in either species, and high resolution mass spectral studies confirmed their elemental composition. The isolation of these compounds is strong evidence for the proposed structure for **9**.

In addition to the labeled species **3**-d_1, the mechanistic studies described below required **3** in optically active form. After several trials, it was found that this goal could be accomplished, albeit in poor yield, by asymmetric induction using lithium tris(menthoxy)aluminum hydride, prepared in situ by the reaction of 3 equiv of *l*-menthol ($[\alpha]^{25}D$ −50°) with 1 equiv of lithium aluminum hydride in ether at −44° for 14 hr. A 9% yield of optically active **3** was isolated, with a rotation of +7.2°. The enantiomeric purity of this material was not determined.

Cyclic Compounds. Several substituted cyclohexadiene iron tricarbonyl complexes were prepared in the course of this study, with stereochemically specific deuterium labeling. The 1- and 2-phenylcyclohexadiene iron tricarbonyl species **1** and **2** are prepared by photochemical reaction of a mixture of 1- and 2-phenylcyclohexadiene[14] with iron pentacarbonyl. The isomers could be separated by careful column chromatography on alumina. The 2-phenyl isomer **2** was obtained as an oil and characterized by NMR, ir, and high resolution mass spectrum, while the 1-phenyl isomer **1**, a crystalline solid (mp 53–55°), gave a satisfactory elemental analysis as well. The NMR spectra in particular served to distinguish clearly between the two isomers. Complex **2**, with only one "internal" olefinic proton, shows a doublet at δ 5.3 in the normal olefinic region for H_3, together with two "outside" complexed olefinic protons at δ 3.4 (H_1) and 2.7 (H_4). In contrast, complex **1** has two downfield signals (δ 5.3 (H_2) and 4.7 (H_3)), but only one upfield (δ 2.8 (H_4)). In addition, both species showed a series of complex multiplets between δ 2.4 and 1.0 for the four methylene protons. On treatment of the mixture of **1** and **2** with deuterated trifluoroacetic acid (TFA-d_1), a mixture of **1**-d_2 and **2**-d_2 was obtained which was separated as before. Consistent with

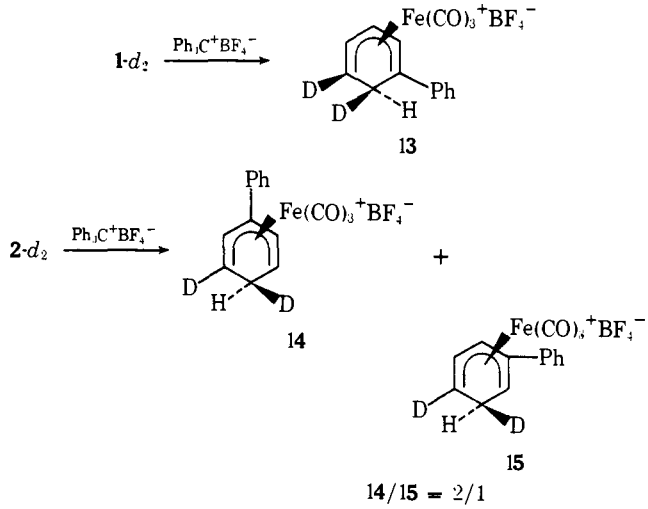


1-d_2 2-d_2

(1/2 = 73/27) (1/2 = 21/79)

our previous work,[12] only the endo methylene protons exchanged, as shown by reaction with triphenylmethyl fluoborate. In both cases, only hydride was lost. Thus, **1**-d_2 gave only one hexadienyl salt **13**, whose NMR spectrum showed the presence of two deuterium atoms as indicated, while **2** under similar conditions gave a mixture of the two salts **14** and **15**. These salts could not be separated, but the NMR of the mixture was consistent with the presence of deuterium as indicated in Scheme III (see experimental section). The

Scheme III

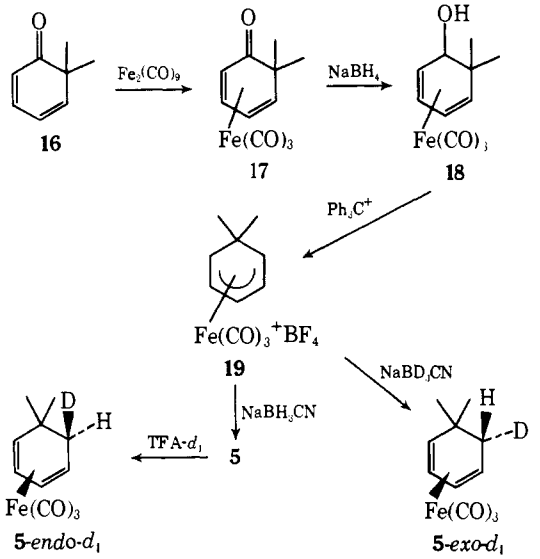


14/15 = 2/1

absence of **15** from the reaction mixture derived from **1**-d_2 is presumably a reflection of the steric requirements for abstraction of hydride by the triphenylmethyl cation; only the hydrogen farther from the substituent is removed. This sensitivity to steric factors is a serious limitation on the utility of this reaction for preparative purposes.

While our initial work[5] on hydrogen migration reaction was performed on the phenylcyclohexadiene system, the NMR spectra of these species were complex, and rendered the quantitative analysis of the thermolysis experiments quite difficult. For this reason several other species, with simpler spectra, were synthesized and subjected to the thermolysis conditions. Complex **5**, 5,5-dimethylcyclohexadi-

Scheme IV

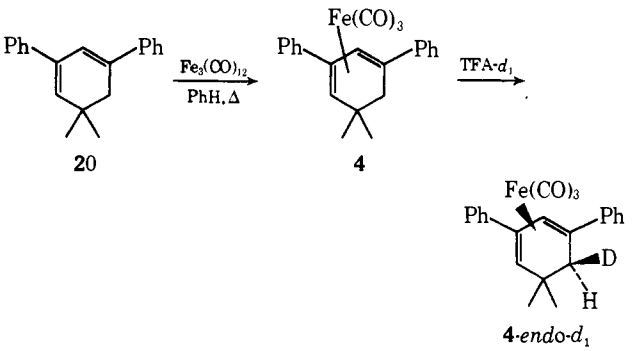


eneiron tricarbonyl, and the stereospecifically deuterated compounds **5**-*exo*-d_1 and **5**-*endo*-d_1 were prepared as shown in Scheme IV. Dimethylcyclohexadienone (**16**), prepared by the method of Alder et al.,[15] was allowed to react with diiron nonacarbonyl in pentane to give a 62% yield of the iron complex **17**. Reduction of this species with sodium borohydride in methanol gave the alcohol complex **18** (55%). The crude product of the reduction was treated with triphenylmethyl cation in methylene chloride. Addition of ether resulted in the precipitation of the salt **19** (75%); NMR (TFA) δ 7.1 (1 H, t, J = 6 Hz, H_3), 5.7 (2 H, t, J = 6 Hz, H_3, H_5), 4.3 (2 H, d, J = 6 Hz, H_2, H_6), 1.6 (3 H, s, CH_3), and 0.9 (3 H, s, CH_3). Reduction of **19** to the diene complex **5** was accomplished using $NaBH_3CN$ in a two-phase system (H_2O–pentane) in 55% yield; a similar reaction in D_2O–pentane using $NaBD_3CN$ gave the exo deuterated **5**-*exo*-d_1. The endo deutrated compound was obtained by exchange of **5** with TFA-d_1.[12] These species and the position of the labels were characterized by elemental analysis and spectral data. Unfortunately, fortuitous overlapping of several signals made it necessary to run NMR's in both benzene and carbon disulfide in order to obtain separate measures of all the protons in the molecule; even then, the diastereotopic protons of the methylene group at C_6 were insufficiently resolved at 100 MHz for accurate integration. In benzene-d_6, **5** showed peaks at δ 4.7 (2 H, m, H_2, H_3), 2.6 (2 H, m, H_1, H_4), 1.5 (downfield half (A) of ABX pattern, H_{6N}), 1.3 (upfield half (B) of ABX, H_{6X}; J_{AB} = 15, J_{AX} = J_{BX} = 2.5 Hz), 0.9 (3 H, s, CH_3), and 0.8 (3 H, s, CH_3). In the spectrum of the exo deuterated (86% d_1 by mass spectrometry) material, the signal at 1.3 had disappeared, and that at 1.5 appeared as a broad multiplet. With the endo labeled compound (95% d_1), the reverse was true; the signal at δ 1.5 could not be seen, and that at 1.3 was a broad multiplet. With CS_2 as a solvent, the C_6 methylene protons could not be resolved, and appeared as a multiplet at δ 1.4. However, it was possible in this solvent to resolve H_1 and H_4; these protons gave rise to two multiplets at δ 2.8 (H_1) and 2.6 (H_4). The assignments are based on the broader multiplet observed for the downfield signal; H_1 is subjected to splittings by the C_6 methylene protons not experienced by H_4.

Complex **4**, η^4-(1,3-diphenyl-5,5-dimethylcyclohexadiene)iron tricarbonyl, was prepared in 76% yield directly from the diene[16] **20** by reaction with $Fe_3(CO)_{12}$ in refluxing benzene. The compound was obtained as a yellow solid, mp 114–115°, and characterized by its high resolution mass

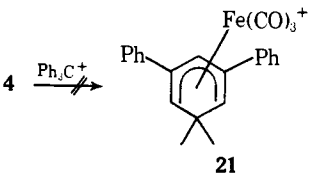
Table I. First-Order Rate Constants for the Conversion of *cis*-3 to *trans*-3 (benzene-d_6 solution)

Temp, °C	10^5k_1, sec^{-1}	
100.0	5.30 ± 0.14	
110.0	17.1 ± 0.9	E_a = 33 kcal/mol
120.0	53.5 ± 2.6	log A = 14



spectrum and physical properties. In this case, all of the protons gave well-resolved resonances in benzene-d_6. In addition to a ten proton multiplet for the aromatic protons, signals were observed at δ 6.2 (1 H, brs, H_2), 3.4 (1 H, d, J = 1.5 Hz, H_4), 2.4 (1 H, d, J = 15 Hz, H_{6N}), 1.6 (1 H, d, J = 15 Hz, H_{6X}), 1.2 (3 H, s, CH_3), and 0.9 (3 H,, CH_3). Preparation of the endo labeled material **4**-*endo*-d_1 was accomplished by exchange with TFA-d_1 as before; in the spectrum of this compound, the peak at δ 2.4 had disappeared as had the 15 Hz coupling to the signal at δ 1.6.

Attempts to prepare the pentadienyl salt **21** from **4** by hydride abstraction with triphenylmethyl cation were unsuccessful, presumably as a result of the sterically congested environment of the H_6 proton. As a result, we were unable to prepare the compound with the exo label in this series.



Thermolysis Studies. Acyclic Complexes. Thermolysis of the trans,cis diene complex *cis*-**3** was carried out in benzene-d_6 solution in sealed NMR tubes at temperatures between 100 and 120°. With the unlabeled material, irreversible, first-order conversion to the trans,trans complex *trans*-**3** occurred. The progress of the reaction was followed by periodic examination by NMR, with the results shown in Table I. The complex *trans*-**3** could be isolated from these reaction mixtures or, more easily, by acid-catalyzed isomerization of *cis*-**3**.[17] The trans,trans complex was characterized principally by its NMR spectrum, which showed peaks at δ 7.2 (10 H, m, arom H), 5.6 (1 H, dd, J_{12} = 9 Hz, J_{23} = 5 Hz, H_2), 5.2 (1 H, dd, J_{23} = 5 Hz, J_{34} = 8 Hz, H_3), 2.9 (2 H, d, J_{45} = 8 Hz, H_5), 1.9 (1 H, d, J_{12} = 9 Hz, H_1), and 1.4 (1 H, q, J_{34} = J_{45} = 8 Hz, H_4). The upfield shift of H_4 relative to the corresponding value in *cis*-**3** (δ 1.4 vs. 2.6) and the larger coupling to H_3 (8 vs. 5 Hz) demonstrate the trans configuration at the C_3–C_4 bond.

Thermolysis under similar conditions (100°, sealed tubes) of the deuterated complex *cis*-**3**-d_1 (85.9 ± 0.5% d_1 at H_{5X}) gave two detectable reactions: isomerization to the trans complex, and exo,endo scrambling of deuterium between the diastereotopic methylene protons in the cis complex. The results obtained are summarized in Table II.

Table II. Percent Isomerization and Deuterium Distribution in the Thermolysis of *cis*-3-d_1[a] at 100.0°

Time (hr)	% isom[b]	*cis*-3[c,d] H_1	H_2	H_3	H_4	H_5N	H_5X	*trans*-3[c,d] H_1	H_2	H_3	H_4[e]	H_5
0	0	1.01	1.07	0.98	0.97	0.98	0.13	—	—	—	—	—
1	22 ± 1	1.00	1.00	1.00	0.98	0.77	0.40	0.94	1.01	0.65	(1.0)	1.52
3	49 ± 2	0.98	1.02	0.93	0.97	0.67	0.55	0.95	1.03	0.68	(1.0)	1.46
6	72 ± 3	0.93	1.02	0.93	0.94	0.64	0.67	0.95	1.02	0.66	(1.0)	1.50
							Av	0.95	1.02	0.66	(1.0)	1.49

[a] 85.8 ± 0.5% d_1 by mass spectrometry. [b] Percent *trans*-3 formed. [c] Integrated relative intensities of the indicated resonance in the 270-MHz NMR of the isolated species, normalized to 5.16 protons. [d] Estimated error ±10%. [e] A persistent impurity derived from the silica gel used for separation overlapped with this peak, and renders these values considerably less precise (estimated error ±20%).

Table III. Thermolysis of *cis*-3* (100.0°)

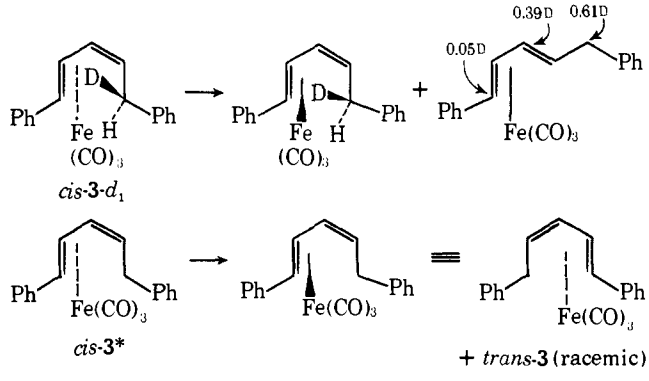
Time (hr)	% isom[a]	$[\alpha]^{23}D$ *cis*-3[b]	$[\alpha]^{23}D$ *trans*-3[c]
0	0	7.2 ± 0.3	
0.5	11	5.9 ± 0.3	
1.0	28	3.4 ± 0.2	
3.0	49	1.3 ± 0.2	0.0 ± 0.3

[a] Percent isomerization to *trans*-3, determined by NMR. [b] Specific rotation (in deg) of recovered *cis*-3, toluene solution, C = 14–19 mg/ml. [c] Specific rotation (in deg) of isolated *trans*-3; C = 15 mg/ml. Insufficient material was obtained prior to the 3 hr sample for a rotation to be measured.

Mass spectral studies of recovered *trans*-3 indicated no loss of deuterium (85.7 ± 0.5% d_1).

Since migration of the hydrogen endo to the metal would result in the incorporation of deuterium into the one position (see below), the data in Table II rule out any substantial amount of 1,5 migration of this hydrogen. They do not, however, allow any firm conclusion to be drawn concerning migration of the exo isotope, since a suprafacial shift is degenerate in *cis*-3-d_1. In order to detect migrations of the exo isotope, optically active *cis*-3* was also subjected to the thermolysis conditions. Since simple 1,5-migration by any route would result in loss of optical activity, racemization of the optically active species is a way to detect this reaction. The results are shown in Table III. It can be seen that *cis*-3* does loose optical activity, and that the trans complex formed is, to within detectable limits, racemic. Three observations can be made concerning these data. First, the only scrambling detectable in *cis*-3 is exo–endo scrambling of the C-5 methylene protons; no visible hydrogen migration occurs under our conditions. Note that this reaction would also result in racemization of the optically active complex (Scheme V). Second, the exo–endo scrambling is sufficient

Scheme V. Observed Reactions in the Thermolysis of *cis*-3



to explain all of the racemization occurring. This fact is more clearly seen by examination of Table IV, which compares the amount of epimer formation measured by the two independent methods. Thus, no 1,5 migration of hydrogen or deuterium is occurring. Third, the deuterium distribution

Table IV. Comparison of Epimerization of *cis*-3 Measured by Deuterium Scrambling and by Racemization

Time, hr	% epimer formation: From deuterium scrambling	From racemization
1	30 ± 6	26 ± 2
3	44 ± 8	41 ± 8

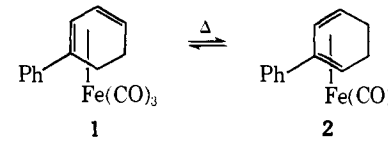
Table V. Thermolysis of 1-d_2 and 2-d_2

Time (hr)	1-d_2[a]	H_{ali}/H_3	% isom[b]	2-d_2[a]	H_{ali}/H_3
0	100	2.24 ± 0.05			
3	62 ± 4	2.51 ± 0.09	46 ± 7	38 ± 4	3.09 ± 0.25
24	45 ± 4	2.51 ± 0.30	70 ± 4	55 ± 2	3.32 ± 0.15
0	0			100	2.27 ± 0.5
8	15 ± 1	2.42 ± 0.7	63 ± 10	85 ± 1	2.45 ± 0.06
24	23 ± 2	3.11 ± 0.16	100	77 ± 2	2.56 ± 0.07

[a] Percent isomer in reaction mixture. [b] Based on K_{eq} = 3.4 ± 0.1.

in *trans*-3 is indicative of exclusive 1,3-shifts and is invariant with time.

Cyclic Compounds. As previously reported,[5] thermolysis of cyclohexadieneiron tricarbonyl complexes results in isomerization reactions which overall are the result of hydrogen migration. The original discovery of this phenomenon was the equilibration of compounds **1** and **2** at 145°.



K_{eq} = **2**/**1** = 3.4 ± 0.1

1 **2**

The thermolysis of **1**-d_2 and **2**-d_2, deuterated specifically endo to the metal in the methylene groups, was examined to probe the mechanisms of this process. Xylene solutions were sealed under vacuum in Pyrex tubes and heated in an oil bath at 145 ± 3°. The tubes were removed at intervals, and the composition of the mixtures was analyzed by NMR spectroscopy. The isomers were separated by careful preparative TLC, and the deuterium distribution was analyzed by NMR spectroscopy. The extent of deuterium scrambling was determined by measuring the ratio of the aliphatic protons to the olefinic proton at C_3. As seen in Table V, substantial scrambling of the deuterium into the vinyl positions occurs during the course of the reaction. In addition, a mixture of **1**-d_2 and **1**-d_0 (d_0/d_2 = 1.05 ± 0.03) was isomerized under the same reaction conditions to the extent of 8 ± 2% conversion. Species **2** was isolated and the ratio of d_0/d_2 material was found to be 1.28 ± 0.05, indicating a small but measurable isotope effect on the disappearance of **1**.

The isomerization of **1** is affected by the presence of triphenylphosphine. When **1** was heated with a tenfold excess of triphenylphosphine at 145 ± 3° for several hours, only 5% of isomerized product (free ligand + **2**) could be detect-

Table VI. Thermolysis of 5-*endo*-d_1 and 5-*exo*-d_1 (145 ± 3°, xylene solvent). Relative Integral Values[a] (NMR)

Time (hr)	Compound	H_1	$H_2 + H_3$	H_4	$H_{5X} + H_{5N}$
0	5-*exo*-d_1[a,b,d]	1.01	2.00	1.01	1.12
20		0.78	2.03	1.09	1.24
40		0.58	2.00	1.05	1.52
0	5-*endo*-d_1[c,e]	1.01	2.00	1.01	1.02
20		1.00	2.02	1.00	1.03
40		1.01	2.02	0.99	1.03

[a] Relative error: ±10%. [b] 85.7 ± 0.5% d_1 by mass spectrometry. [c] 95.0 ± 0.5% d_1 by mass spectrometry. [d] Values normalized to 5.14. [e] Values normalized to 5.05.

Table VII. Thermolysis of 4-*endo*-d_1 (benzene, 145°, sealed tubes). Composition[a] as a Function of Time

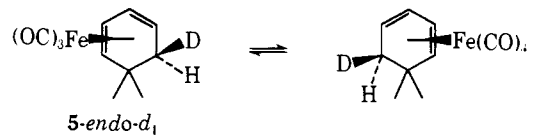
Time (hr)	4-*endo*-d_1 (%)	4-*exo*-d_1 (%)	4-*1*-d_1 (%)
0	100	0	0
1	76 ± 5	10 ± 5	0 ± 5
2	76	7	0
5[b]	57	26	3
5	54	29	6
10	50	40	14
23	40	29	22
25	40	34	29

[a] See experimental section. [b] Thermolysis carried out in the presence of an equimolar concentration of 20.

ed by NMR spectroscopy and high pressure liquid chromatography. In addition, a 71% yield of $Fe(CO)_3(PPh_3)_2$ was isolated. Under the same conditions, but in the absence of triphenylphosphine, 35% isomerized product was formed. Examination of the data in Table V shows that extensive scrambling of deuterium into all the positions on the ring occurs. However, as noted above, the NMR spectra of **1** and **2** were sufficiently complex that the data on the scrambling process were not very precise. In order to study the process in a compound with a more tractable NMR, and also to probe the role that the aromatic rings played in the isomerization and scrambling processes, the thermolysis of the dimethyl species **5** and its stereospecificially labeled analogues, 5-*endo*-d_1 and 5-*exo*-d_1, was investigated. Samples of the compounds were heated in sealed tubes as before. Periodically, a tube was removed, the complex recovered by chromatography, and the deuterium distribution determined by NMR. The results are shown in Table VI. Inspection of these values indicates that, within experimental error, 5-*endo*-d_1 does not scramble deuterium with any other position in the molecule. Its isomer 5-*exo*-d_1, on the other hand, readily incorporates deuterium at C-1. Confir-

5-*exo*-d_1

incorporation at C–1



5-*endo*-d_1

degenerate

mation of the stereochemically homogeneous nature of 5-*endo*-d_1 after heating was obtained by washing out the deuterium with TFA-d_0 in a sample which had been heated for 40 hr at 145°. The mass spectrum of the reexchanged material showed it to be 99.2 ± 1% d_0. Thus, while 1,5-migrations are occurring, as shown by the results on the exo labeled material, only those hydrogens on the same side of the ring as the metal can move, and there is no mechanism in this series for epimerization of the metal.

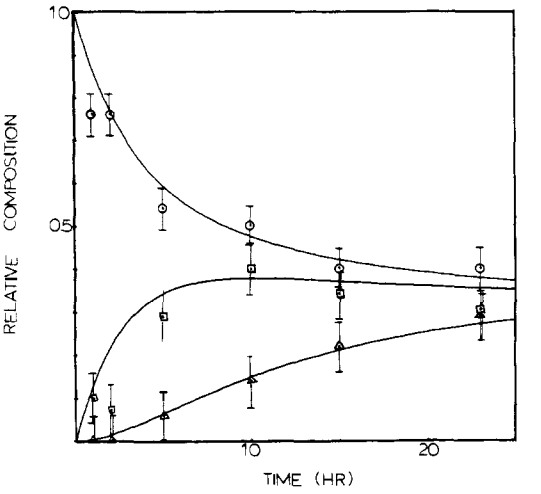
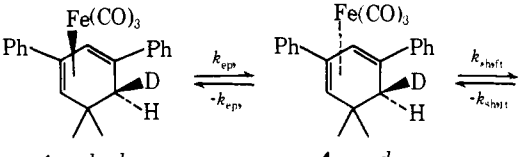


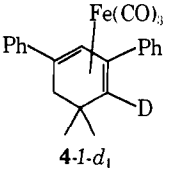
Figure 1. Plot of composition vs. time for the system 4-*endo*-d_1 (○) ⇌ 4-*exo*-d_1 (□) ⇌ 4-*1*-d_1 (△). The points are experimental values; the curves were generated by computer[19] using the rate constants mentioned in the text.

In contrast, the diphenyl complex 4-*endo*-d_1, when subjected to similar thermolysis conditions, readily scrambled deuterium among three of the four positions on the ring (H_1, H_{5X}, and H_{5N}). The results obtained are shown in Table VII. Some decomposition (ca. 10% after 24 hr) of this complex took place, with liberation of the free diene ligand. That exo–endo exchange of deuterium is not caused by intermolecular reactions involving exchange with the diene is shown by the two 5-hr entries in Table VII. Within experimental error, the presence of 1 equiv (a much larger quantity than is liberated during the thermolysis) had no effect on the rate of the reaction. Further, complex recovered from this reaction showed no change in deuterium content. The data in Table VII were analyzed in terms of the consecutive first-order equilibria shown in Scheme VI. The rate

Scheme VI



4-*endo*-d_1 4-*exo*-d_1



4-*1*-d_1

equations corresponding to this scheme were solved analytically[18] and estimates of the two independent rate constants made by fitting the experimental points to curves generated by a computer program.[19] The fit shown in Figure 1 was obtained with the values $k_{epi} = 4.3 \times 10^{-5}$ sec^{-1} and $k_{shift} = 1.8 \times 10^{-5}$ sec^{-1}; errors in these values are estimated to be ±25%.

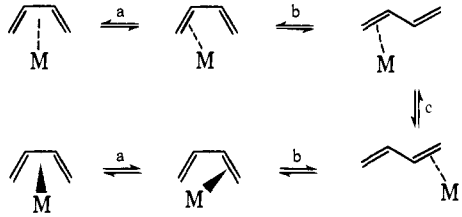
Discussion

The experiments described above demonstrate the exis-

tence of several thermal reactions of diene iron tricarbonyl complexes: cis-trans isomerization, metal epimerization, and hydrogen scrambling. All of these reactions can be explained as the result of the generation of a single coordinatively unsaturated olefin-$Fe(CO)_3$ complex in which only one of the two double bonds of the diene remains bound to iron. The properties of this intermediate will be of particular interest in this discussion.

The epimerization of diene complexes has been previously observed by Whitlock and co-workers,[20] who explained their results by means of the mechanism shown in Scheme VII. Three distinct reactions are involved in this process:

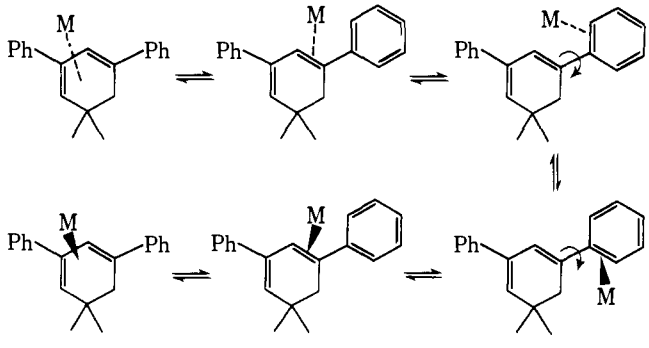
Scheme VII. Metal Epimerization Pathway[20] (here, and elsewhere, M = $Fe(CO)_3$)



dechelation (step a), bond rotation to the transoid diene (step b), and migration of the metal (step c). In order to obtain transfer of the metal from one face of the diene to the other, migration must occur in the transoid conformation, as shown; migration in the cisoid conformation is unproductive in this regard.

This reaction alone is sufficient to rationalize both the scrambling of deuterium in the acyclic complex *cis*-**3**-d_1 and the racemization of *cis*-**3***. As pointed out above, the absence of any measurable racemization other than that accounted for by the metal epimerization pathway rules out any substantial amount of 1,5-shift in this complex. In the cyclic compounds, it is difficult to rationalize the observed epimerization in, for example, **4**, without postulating that the aromatic rings may serve the same function as the freely rotating olefinic linkage in Scheme VII. Thus, in **4**, the metal may epimerize via the path shown in Scheme VIII.

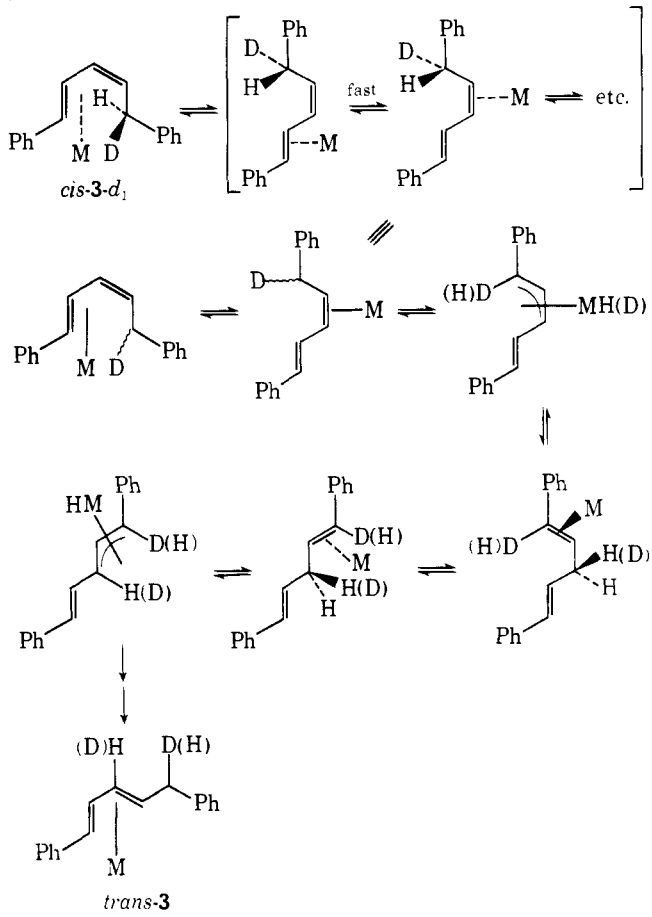
Scheme VIII



As might be expected, an aromatic ring is less effective than an isolated olefin at promoting epimerization. As explained below, the epimerization pathway in *cis*-**3** is much faster than hydrogen abstraction involving the same intermediate; in **4**, the rate of epimerization is comparable to abstraction (2.4 times faster). Strong support for the involvement of the aromatic rings is provided by comparison of the behavior of **4** with that of **5** and its deuterated analogues. Thus, **5**-*endo*-d_1 and **5**-*exo*-d_1 do not equilibrate ($k_{epi} \leq 2.3 \times 10^{-8}$ sec^{-1} at 145°)[21] under conditions where **4**-*endo*-d_1 and **4**-*exo*-d_1 equilibrate with a rate constant of 4.3×10^{-5} sec^{-1}; i.e., the presence of two phenyl rings increases the epimerization rate by at least 1800-fold.

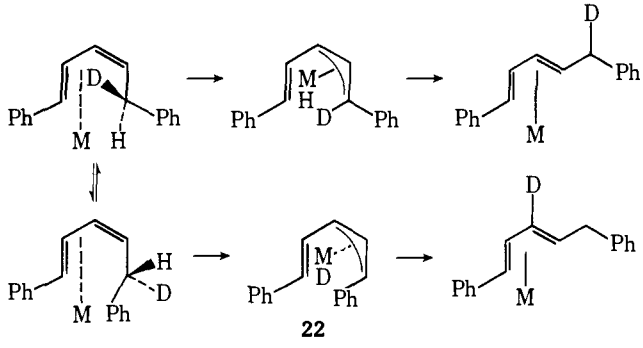
The cis-trans isomerization of **3** is coupled to hydrogen migration at least 40% of the time, as judged by the deuterium distribution in the product derived from *cis*-**3**-d_1. This observation, and the observations of Casey[7a] on the mechanisms of olefin isomerization catalyzed by iron carbonyls, suggests that a reasonable mechanism for cis-trans isomerization is as summarized in Scheme IX. The process is initiated as before by dechelation. Abstraction of hydrogen, to yield a (π-allyl) metal hydride (deuteride) and deposition of the hydride (deuteride) at position 3 leads to a species in which rotation about the C-3, C-4 bond is facile. Reabstraction of hydride and reversal of the above sequence lead to the trans complex.

Scheme IX. Cis-Trans Isomerization



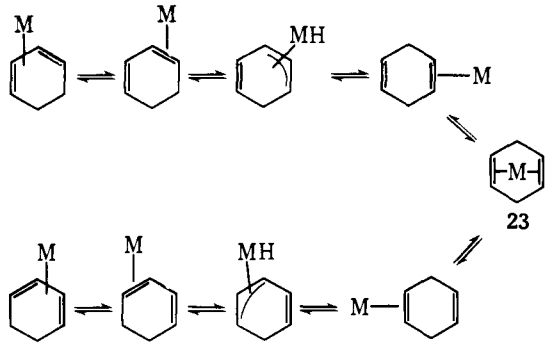
Assuming that this sequence adequately describes the mechanism, several interesting constraints on the relative rates of the reactions in Scheme IX can be adduced from our data. First, the epimerization process of Scheme VIII must be much faster than hydrogen abstraction to the (π-allyl) metal hydride. Otherwise, the deuterium distribution of the trans product would change during the course of the reaction. That is, the amount of hydrogen or deuterium migrating would depend on the stereoisomeric purity of the *cis*-**3**-d_1 from which the migrating intermediate is generated. Since the purity varies during the reaction as *cis*-**3**-d_1 epimerizes, so should the deuterium distribution of *trans*-**3**. In fact, as shown in Table II, the distribution of deuterium remains constant at least up to 70% reaction, at which time, *cis*-**3**-d_1 has essentially completely racemized (see the last entry in Table II). The unequal distribution of deuterium between positions 3 and 5 in *trans*-**3** is presumably the reflection of a small isotope effect on the abstraction; this observation also reinforces the conclusion that abstraction is slower than epimerization, since in order to observe an isotope effect, the metal must be able to select between H and D.

Scheme X



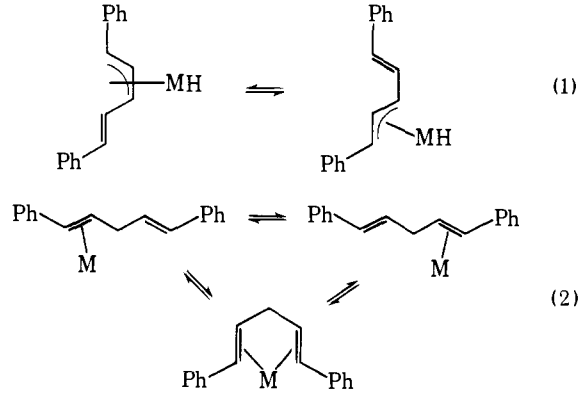
22

Scheme XI. Possible Mechanism for 1,5-Hydrogen Migration in Cyclic Compounds



The invariance with time also rules out a mechanism in which the only explanation for the partial shift of D to position 3 is one such as that in Scheme X, in which the isotope which moves is determined by the conformation of the methylene group at the time of abstraction. That an intermediate such as **22** is in fact not formed is likely to be the result of the substantial steric congestion associated with *two* large anti substituents on a π-allyl group. Further confirmation of these conclusions is found in the fact that *trans*-**3** derived from *cis*-**3*** is devoid of optical activity, since Scheme X predicts the formation of optically active product.

One other interesting constraint on the mechanism in Scheme IX is that at most only minor amounts of migration of the π-allyl metal hydride occurs before collapse, and that the 1,4-diene[$Fe(CO)_3$] complex formed by collapse remains unsymmetrical. That is, neither eq 1 nor eq 2 is important for **3** under our conditions.



If either of these reactions occurred to any great extent, the two ends of the pentadiene moiety would eventually become equivalent; experimentally, substantial amounts of deuterium would be incorporated at C-1. At most 5% of the deuterium (within experimental error of zero) is found in this position in *trans*-**3** and 7% (also zero within experimental error) in substantially scrambled *cis*-**3** (see Table II). It should be noted that one or both of these reactions must be occurring in the cyclic compounds, since overall 1,5-migration is found in these species. Of the two possibilities we prefer that summarized in eq 2, since there is no obvious reason why eq 1 could not operate in either series, while the cyclic nature of the ligand should make the chelated 1,4-diene complex **23** (Scheme XI) a relatively stable structure.[22] We therefore feel that probable mechanisms for the equilibration of **1** and **2** and the degenerate 1,5-migration of **4** and **5** involve two sequential 1,3-shifts as shown in Scheme XI rather than a 1,5-shift via an equilibrating π-allyl metal hydride.

Experimental Section

General. All reactions involving organometallics were routinely carried out under an atmosphere of dry nitrogen. Solvents were purified as follows: hexane (and other saturated hydrocarbons), stirring with concentrated H_2SO_4 and distillation from KOH pellets; benzene, distillation from a suspension of sodium benzophenone ketyl; THF and ether, distillation from a purple solution of sodium benzophenone dianion. The 270-MHz NMR spectra were performed on a Bruker WH270 instrument operating in FT mode with internal deuterium lock.

Reaction of *trans,trans*-1,5-Diphenyl-2,4-pentadienol (6) with $Fe_2(CO)_9$. A mixture of 5 g (21.2 mmol) of 1,5-diphenyl-2,4-pentadienol (**6**) and 14.5 g (40 mmol) of $Fe_2(CO)_9$ was refluxed in dry ether under nitrogen. After 2 hr, the dark mixture was filtered through alumina with ether and the solvent removed by rotary evaporation. The residue was subjected to column chromotography on alumina. Elution with hexane yielded 0.26 g (3.4%) of *trans,trans*-1,5-diphenyl-1,3-pentadieneiron tricarbonyl. Elution with benzene yielded 0.17 g (2.1%) of *trans,trans*-1,5-diphenyl-2,4-dieneoneiron tricarbonyl. Elution with ether gave 6.77 g (85%) of *trans,trans*-1,5-diphenyl-2,4-dienoliron tricarbonyl (**7**), obtained as a mixture of diastereomers: NMR (CS_2) δ 7.2 (10 H, m), 5.5 (1 H, dd, J = 5, 9 Hz), 5.2 (1 H, dd, J = 5, 8 Hz). 4.4 (1 H, d, J = 9 Hz), 2.2 (1 H, bs), 1.8 (1 H, d, J = 9 Hz), 1.4 (1 H, t, J = 8 Hz). This material was used without further purification for the preparation of the pentadienyl salt **8**.

Preparation of η^5-1,5-Diphenylpentadienyliron Tricarbonyl Tetrafluoborate (8). A solution of fluoboric acid and acetic acid was prepared by adding acetic anhydride (8.15 g, 80 mmol) dropwise to 2.4 g of 48% fluoboric acid (1.15 g, 13 mmol acid) at 0° under nitrogen. The acid solution was transferred dropwise at 0°C to 2.45 g (6.5 mmol) of *trans,trans*-2,4-dienoliron tricarbonyl, **7**, in 20 ml of acetic anhydride. The reaction was stirred for 10 min after addition. The solution was poured into 150 ml of dry ether and the resulting precipitate filtered and washed with ether yielding 3.7 g (75%) of η^5-1,5-diphenylpentadienyliron tricarbonyl tetrafluoborate as a yellow orange solid: NMR (CF_3CO_2H) δ 7.7 (10 H, m), 7.3 (1 H, t, J = 7 Hz), 6.7 (2 H, dd, J = 7, 12 Hz), 4.7 (2 H, d, J = 12 Hz); ir (KBr) 2104, 2060, 2050 cm^{-1}. Elemental analysis: C, H, Fe.

Reduction of Salt 8 with $NaBH_3CN$. A suspension of 1.0 g (2.2 mmol) of **8** in 100 ml of dry THF was cooled to −22°C under nitrogen by means of a CCl_4 slush bath. To this suspension was added 170 mg (2.2 mmol) of $NaBH_3CN$ and the reaction stirred for 20 min. The cold reaction mixture was poured into water and extracted with ether. The ether layer was washed with water and saturated NaCl and dried over $MgSO_4$. The solvent was removed by rotary evaporation and the residue subjected to column chromatography on silica gel. Two fractions were collected. Fraction 1 (eluted with hexane) yielded 0.30 g (38%) of *trans,cis*-1,5-diphenyl-1,3-pentadieneiron tricarbonyl (*cis*-**3**) as a yellow solid (mp 132–133.5° from EtOH): NMR (C_6D_6) δ 7.2 (10 H, m), 6.0 (1 H, dd, J = 5, 10 Hz), 5.2 (1 H, d, J = 5 Hz), 3.4 (1 H, d, J = 10 Hz), 2.4–3.0 (3 H, m); ir (CCl_4) 2046, 1980 cm^{-1}; mass spectrum 360 (M^+), 332, 304, 276 (base peak), 220, 129. Elemental analysis: Calcd for $C_{20}H_{16}FeO_3$: C, 66.69; H, 4.47; Fe, 15.51. Found: C, 66.73; H, 4.03; Fe, 15.47.

Fraction 2 (eluted with 50:50 hexane-benzene) yielded 0.32 g (40%) of **9** as an air sensitive, thermally unstable yellow oil: NMR

(C_6D_6) δ 7.1 (10 H, m), 4.6 (1 H, dd, J = 7, 12 Hz), 4.2 (1 H, d, J = 12 Hz), 3.6 (1 H, m), 2.7 (2 H, m), 1.1 (1 H, t, J = 9 Hz); ir (hexane) 2058, 1988, 1981 cm^{-1}.

Reaction of 8 with $NaBD_3CN$. The reaction was carried out as described above except that $NaBD_3CN$ was used as the reducing agent. Column chromatography again yielded two fractions. Fraction 1 (eluted with hexane) gave ***cis*-3-d_1** (86% d_1, 14% d_0 by mass spectral analysis): NMR (C_6D_6) δ 7.2 (10 H, m), 6.0 (1 H, dd, J = 5, 10 Hz), 5.2 (1 H, t, J = 5 Hz), 3.4 (1 H, d, J = 10 Hz), 2.6–3.0 (2 H, m).

Fraction 2 (eluted with 50:50 hexane–benzene) yielded **9-d_1**: NMR (CS_2) δ 7.2 (10 H, m), 5.2 (1 H, dd, J = 7, 12 Hz), 4.4 (1 H, d, J = 12 Hz), 4.1 (1 H, t, J = 6 Hz), 3.1 (1 H, bt, J = 8 Hz), 1.2 (1 H, d, J = 10 Hz).

Preparation of *trans,trans*-1,5-Diphenyl-1,3-pentadieneiron Tricarbonyl (*trans*-3). A solution of 40 mg (*cis*-**3**) in 2 ml of $CHCl_3$ was cooled to 0° under nitrogen. To this solution was added via syringe 1 ml of CF_3CO_2H and the reaction stirred for 15 min. The solvent was removed via rotary evaporation and the residue filtered through alumina yielding 32 mg (80%) of (*trans*-**3**): NMR (C_6D_6) δ 7.2 (10 H, m), 5.6 (1 H, dd, J = 5, 9 Hz), 5.2 (1 H, dd, J = 5, 8 Hz), 2.9 (2 H, d, J = 8 Hz), 1.9 (1 H, d, J = 9 Hz), 1.4 (1 H, q, J = 8 Hz); ir (CCl_4) 2046, 1981, 1970 cm^{-1}; mass spectrum 360 (M^+) 332, 304, 276 (base peak), 220, 129. High resolution mass spectrum, calcd for $C_{20}H_{16}FeO_3$: 360.0448. Found: 360.0445.

Preparation of Optically Active *cis*-3. To a solution of 20.2 mmol of $LiAlH_4$ (determined according the method of Felkin[24]) in 18 ml of dry ether was added 9.45 g (60.6 mmol) of *l*-menthol ($[\alpha]^{25}D$ −50) and the solution stirred under nitrogen for 10 min. The solution was cooled to −44° (CH_3CN–dry ice slush) and 3.0 g (6.7 mmol) of η^5-1,5-diphenylpentadienyliron tricarbonyl tetrafluoborate (**8**) was added in portions over a 20-min period. After 14 hr at −44°, the reaction was poured into water and extracted with ether. The ether layer was washed with saturated NaCl and dried over $MgSO_4$. The ether was removed by rotary evaporation and the menthol removed by sublimation (40°, 0.1 mm). Column chromatography of the residue yielded 228 mg (9.4%) of *cis*-**3*** $[\alpha]^{25}D$ 7.2 (*c* 2.42, xylene).

Thermolysis of Optically Active *cis*-3*. Aliquots of a solution of 154 mg of *cis*-**3*** ($[\alpha]^{25}D$ 7.2) in 40 ml of xylene were placed in three glass tubes equipped with ground glass joints. The solutions were degassed by three freeze–thaw cycles and sealed under vacuum. The tubes were heated in a constant temperature oil bath at 100° and removed periodically. The xylene was removed by vacuum distillation and the residue filtered through alumina with hexane. The hexane was removed by rotary evaporation and the composition of the mixture determined by NMR. The isomers were then separated by careful preparative TLC using 95:5 hexane–benzene as the eluent. The isolated complexes were dried under vacuum and the specific rotations measured.

Oxidation of 1–3,5-η^4-1,5-Diphenylpentadieneiron Tricarbonyl (9) with $Ce(NH_4)_2(NO_3)_2$. A solution of 310 mg (0.86 mmol) of **9** in 50 ml of MeOH was placed in a 100-ml round-bottom flask. To this solution was added solid $Ce(NH_4)_2(NO_3)_6$ with stirring until gas evolution ceased. The reaction mixture was poured into 200 ml of water and extracted three times with 100-ml portions of ether. The organic layers were washed with 100 ml of water and dried over $MgSO_4$. The solvent was removed and the residue subjected to column chromatography on silica gel. Elution with 90:10 benzene–hexane yielded several fractions. Fraction 1 (35 mg) and fraction 2 (23 mg) consisted of unidentified materials. Fraction 3 yielded 40 mg (17%) of *trans*-1,5-diphenyl-3,5-dimethoxy-1-pentene (**11**): NMR (CCl_4) δ 7.2 (10 H, s), 6.5 (1 H, d, J = 16 Hz), 5.9 (1 H, dd, J = 16, 8 Hz), 4.2 (1 H, m), 3.9 (1 H, m), 3.2 (3 H, s), 3.1 (3 H, s), 1.7 (2 H, m); ir (CCl_4) 3080, 3060, 3030, 2980, 2930, 2880, 2820, 1490, 1450, 1360, 1215, 1100(s), 965, 680(s) cm^{-1}. High resolution mass spectrum: calcd for $C_{19}H_{22}O_2$: 282.162. Found: 282.163. Fraction 4 yielded 39 mg (17%) of 1,5-diphenyl-1,5-dimethoxy-2-pentene (**12**): NMR (CCl_4) δ 7.2 (10 H, m), 5.5 (2 H, m), 4.4 (1 H, d, J = 7 Hz), 4.0 (1 H, t, J = 7.5 Hz), 3.2 (3 H, s), 3.1 (3 H, s), 2.4 (2 H, q, J = 7 Hz); ir (CCl_4) 3061, 3030, 2980, 2955, 2895, 2820, 1490, 1450, 1250(s), 1100(s), 965, 860(s), 690(s) cm^{-1}. High resolution mass spectrum: calcd for $C_{19}H_{22}O_2$: 282.162. Found: 282.161.

Preparation of Phenylcyclohexadiene. A suspension of 1-phenylcyclohex-2-en-1-ol (12.0 g, 66 mmol), prepared according to the method of Woods,[14] was refluxed for 16 hr in 400 ml of 0.5 *N* aqueous H_2SO_4. The reaction was neutralized with solid $NaHCO_3$ and extracted three times with 150-ml portions of ether. The organic layer was dried over $MgSO_4$ and the ether removed by rotary evaporation. Distillation of the crude oil yielded 3.2 g (30%) of a mixture (bp 62°, 0.05 mm) of phenylcyclohexadiene isomers as a clear oil which solidified in the receiver: NMR (CCl_4) δ 7.0–7.4 (5 H, m), 6.2 (1 H, m), 5.9 (2 H, m), 2.0–2.6 (4 H, m).

Preparation of 1-Phenyl-1,3-cyclohexadieneiron Tricarbonyl (1) and 2-Phenyl-1,3-cyclohexadieneiron Tricarbonyl (2). The phenylcyclohexadiene mixture (3.1 g, 19.8 mmol) and $Fe(CO)_5$ (4.9 g, 25 mmol) were dissolved in 90 ml of benzene in a cylindrical photolysis vessel equipped with a nitrogen inlet. The mixture was photolyzed for 2 hr and the solvent removed by rotary evaporation. The residue was filtered through alumina with hexane. The hexane was removed by rotary evaporation giving 4.12 g (70%) of orange-red oil. NMR analysis showed the oil to be a mixture of 27% **2** and 73% **1**.

The isomers were separated by careful chromatography on a 70 cm × 35 mm alumina column using hexane as the eluent. Fraction 1 was shown to be complex **2**, isolated as a yellow oil which resisted crystallization: NMR (C_6D_6) δ 7.0–4 (5 H, m), 5.3 (1 H, d, J = 6 Hz), 3.4 (1 H, dd, J = 2, 5 Hz), 2.7 (1 H, m), 1.1–1.8 (4 H, m); ir (hexane) 2050, 1980 cm^{-1}. High resolution mass spectrum: calcd for $C_{15}H_{12}O_3Fe$: 296.014. Found: 296.012.

Fraction 2 contained complex **1**, isolated as a yellow oil which solidified upon standing. Sublimation (40°, 0.05 mm) gave yellow crystals (mp 53–55°): NMR (C_6D_6) δ 7.2–7.3 (5 H, m), 5.3 (1 H, d, J = 4 Hz), 4.7 (1 H, dd, J = 4, 6.5 Hz), 2.8 (1 H, m), 1.2–2.4 (4 H, m); ir (hexane) 2050, 1980 cm^{-1}. Elemental analysis: C, H, Fe.

Preparation of 1-d_2 and 2-d_2. In a typical reaction, 2.5 g (8.5 mmol) of a mixture of 1 and **2** was stirred with 7.5 g (65.2 mmol) of CF_3CO_2D (99% d_1) under nitrogen at room temperature. After 1 hr, the solvent was removed by rotary evaporation and 7.5 g (65.2 mmol) of fresh acid added. After stirring an additional 45 min under nitrogen, the solvent was removed by rotary evaporation and the residue filtered through a short column of alumina yielding 2.24 g (89%) of orange red oil. NMR analysis showed it to be a mixture of 21 ± 1% **1**-d_2 and 79 ± 1% **2**-d_2. The isomers were separated by column chromatography as described above. Fraction 1 was shown to be **2**-d_2: NMR (C_6D_6) δ 7.0–7.4 (5 H, m), 5.4 (1 H, d, J = 6 Hz), 3.6 (1 H, bs), 2.9 (1 H, dd, J = 2, 6 Hz), 1.2–1.6 (2.3 H, m). Isotopic composition was (mass spectrometry) 2% d_0, 22% d_1, and 76% d_2.

Fraction 2 was shown to be **1**-d_2: NMR (C_6D_6) δ 7.0–7.4 (5 H, m), 5.2 (1 H, d, J = 4 Hz), 4.6 (1 H, dd, J = 4, 6.5 Hz), 2.7 (1 H, d, J = 7 Hz), 1.1 (2.2 H, bs). Isotopic composition was 2% d_0, 22% d_1, and 76% d_2.

Preparation of η^5-1-Phenylcyclohexadienyliron Tricarbonyl Fluoborate. A solution of 149 mg (0.50 mmol) of **1** in 5 ml of CH_2Cl_2 was stirred under nitrogen. A solution of 162 mg (0.49 mmol) of trityl fluoborate in 2 ml of CH_2Cl_2 was added. The solution gradually darkened and a yellow precipitate formed. After 1 hr, the solution was poured into 10 ml of ether. The precipitate was filtered, washed with ether, and dried under a stream of nitrogen yielding 31 mg (17%) of η^5-1-phenylcyclohexadienyliron tricarbonyl fluoborate (**13**-d_0). NMR (CF_3CO_2H) δ 7.4 (6 H, m, arom *H*, H_3), 5.8 (2 H, m, H_2, H_4), 4.2 (1 H, t, J = 6 Hz, H_5), 3.5 (1 H, dd, J = 6, 16 Hz, H_{6N}), 2.5 (1 H, d, J = 16 Hz, H_{6X}).

The reaction described above was performed under identical conditions using 1-d_2. NMR analysis of the recovered product showed it to be **13**: NMR (CF_3CO_2H) δ 7.4 (6 H, m), 5.8 (2 H, m), 2.6 (1 H, bs).

Reaction of 2 with Trityl Fluoborate. A solution of 207 mg (0.7 mmol) of **2** in 5 ml of CH_2Cl_2 was stirred under nitrogen. To this was added 220 mg (0.68 mmol) of trityl fluoborate in 2 ml of CH_2Cl_2. The reaction was carried out as described above, yielding 49 mg (19%) of yellow solid. NMR analysis showed it to be a 2:1 mixture of η^5-3-phenylcyclohexadienyliron tricarbonyl fluoborate (**14**-d_0) and η^5-2-phenylcyclohexadienyliron tricarbonyl fluoborate (**15**-d_0). The NMR for **14**-d_0 (CF_3CO_2H) showed absorbances at δ 7.2 (5 H, m, arom H), 6.4 (2 H, d, J = 7 Hz, H_2, H_4), 4.4 (2 H, t, J = 7 Hz, H_1H_5), 3.2 (1 H, m, H_{6N}), 2.4 (1 H, m, H_{6X}). The NMR for **15**-d_0 shows absorptions at δ 7.2 (6 H, m, arom H, H_3), 6.0 (1 H, m, H_4), 4.4 (2 H, m, H_1, H_5), 3.2 (1H, m, H_{6N}), 2.2

(1H, m, H_{6x}).

The above reaction was performed under identical conditions using **2**-d_2. The isolated product was shown to be a mixture of **14**-d_2 and **15**-d_2. The signals at δ 3.2 had disappeared, and those at 4.4 had been reduced in intensity to a total of one hydrogen.

Deuterium Isotope Effect on the Thermolysis of 1. A mixture of **1** and 1-d_2 was prepared by dissolving 84.5 mg of **1**-d_0 and 90.6 mg of **1**-d_2 in 2 ml of xylene. Mass spectral analysis of the resulting mixture showed the following intensities for the molecular ion cluster: 296 (100), 298 (90.1 ± 1.5). The xylene solution was sealed under vacuum in a Pyrex tube and heated at 145°C to 8.1 ± 2% conversion as determined by high pressure liquid chromatography. The mixture was separated by repeated preparative TLC on silica gel PF 240 using hexane as the eluent. After several separations, 10.5 mg of **2** was recovered, contaminated with 9.0% 1 as determined by high pressure liquid chromatography. Complex **1** was also recovered and shown to be free of isomer **2** by high pressure liquid chromatography.

m/e	1 start	1 recovered	2 recovered[a]
296	100	(100)	100
298	90.1 ± 1.5	92.5 ± 1.5	75.7 ± 1.2

[a] Contains 9% 1.

The relative amounts of d_0 and d_2 were calculated from the theoretical isotope cluster of the d_0 complex ($m - 2$ (6.3); $m - 1$ (1.2), m (100), $m + 1$ (18.8); $m + 2$ (0.4)), together with the values given above for the ratio of *m/e* 296 to *m/e* 298, from the equation:

$$R = \frac{m/e\ 296}{m/e\ 298} = \frac{0.063y + x}{y + 0.004x}$$

$$\frac{x}{y} = \frac{R - 0.063}{1 - 0.004R}$$

A correction was applied for the 9% contamination of recovered **2** by **1**. The results are summarized in Table VIII.

Thermolysis of 1 in the Presence of Triphenylphosphine. Two tubes were prepared, one containing a mixture of 0.43 g (1.4 mmol) of **1** and 2.95 g (11.2 mmol) of triphenylphosphine and the other containing 0.40 g of **1** and 2 ml of xylene. The tubes were simultaneously immersed in an oil bath at 145°. After 1.5 hr, the tubes were removed, cooled, and opened. The tube containing the triphenylphosphine was titurated with 10 ml of cold hexane causing formation of a yellow precipitate. The precipitate was washed with cold hexane yielding 685 mg (71%) of $Fe(CO)_3(PPh_3)_2$. The composition of the filtrate was analyzed by high pressure liquid chromatography and the area of the corresponding peaks was measured. The control experiment was analyzed in the same manner (vide infra).

	"1 + xylene"	"1 + PPh_3"
2-Ph[a]	36 ± 2	5.0 ± 0.7
1-Ph[b]	64 ± 2	95.0 ± 0.7

[a] 2 + 2-phenylcyclohexadiene. [b] 1 + 1-phenylcyclohexadiene.

Analysis of Reaction Mixtures by High Pressure Liquid Chromatography. Mixtures of 1 and **2** were analyzed by high pressure liquid chromatography using a Varian LC-4000 chromatograph equipped with a uv detector. The mixtures were separated on a 2 ft ($\frac{1}{8}$ in. o.d. × 0.093 in. i.d.) neutral alumina column using hexane as the eluent. A pressure of 250 psi was maintained on the resevoir to achieve maximum separation.

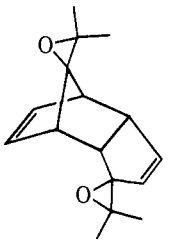
The response factor R was measured by coinjection of known amounts of **1** and **2** and measuring the area of the corresponding peaks with a planimeter. In this way R = **1**/**2** = 1.2.

Complexes **1** and **2** could not be separated from the corresponding free dienes **22** and **23**. Whenever such a mixture occurred, only the ratio of **1** + **22** to **2** + **23** could be obtained, and only by assuming that the response factor R for the free ligands was similar to R for the complexes. That this is a reasonable assumption was shown by the following experiment. A solution containing 13.7 mg (0.05 mmol) of a equilibrium mixture of **1** and **2** (**2**/**1** = 3.6 ± 0.1) and 124 mg (0.5 mmol) of triphenylphosphine in 2 ml of xylene was heated for 3 hr at 145°C. The tube was opened and the mixture of dienes plus complex analyzed by high pressure liquid chromatography. Measurement of the area of the corresponding peaks gave a ratio of **2**-phenyl species to **1**-phenyl of 3.6 ± 0.1. If the assumption is made that a minimal amount of isomerization accompanies decomplexation (see above) then the constancy of this ratio implies that the response factors for the complexes and free ligands are at least similar.

Table VIII. Ratio (d_0/d_2) of 1 and 2

	1 start	1 recovered	2 recovered
d_0/d_2	1.05 ± 0.03	1.02 ± 0.03	1.28 ± 0.4

Preparation of Epoxide Dimer 24. The epoxide dimer was prepared in 69% yield by hydrogen peroxide oxidation of dimethylfulvene according to the procedure of Alder et al.[15]



24

Preparation of 6,6-Dimethyl-2,4-cyclohexadienone (16). In a 50-ml round-bottom flask was placed 30 g (0.12 mmol) of epoxide dimer. The flask was attached to a 2 ft pyrolysis tube equipped with a vacuum side arm. The system was evacuated to 0.05 mm and the dimer distilled through the tube (400°, measured by an iron-constantan thermocouple). The distillate was collected in a dry ice trap and purified by distillation through a 10-cm Vigreaux column, yielding 5.3 g (18%) of **16**. This compound was identical with that described by Alder et al.,[15] prepared by a similar route.

Preparation of 6,6-Dimethyl-2,4-cyclohexadienoneiron Tricarbonyl 17. A solution of 4.2 g (34 mmol) of **16** and 22 g (60 mmol) of $Fe_2(CO)_9$ was refluxed in pentane under nitrogen for 3 hr. After this time, the reaction mixture was filtered through a sintered glass filter and the solvent removed by rotary evaporation. The residue was subjected to column chromatography on a 33 cm × 18 mm alumina column. Elution with benzene gave a single yellow band from which was obtained 5.5 g (62%) of the desired complex **17** as an orange oil: NMR (CS_2) δ 5.9 (1 H, m, C_3H), 5.6 (1 H, t, J = 5 Hz, C_4H), 3.1 (2 H, m, C_2H), 1.2 (3 H, s, $-CH_3$), 0.8 (3 H, s, $-CH_3$); ir (hexane) 2050, 1995, 1680 cm^{-1}.

Preparation of Alcohol Complex 18. To a solution of 1.7 g (6.5 mmol) of dienone complex **17** in 10 ml of methanol was added 250 mg (6.5 mmol) of $NaBH_4$ and the reaction stirred under nitrogen. The reaction was monitored by the disappearance of the ir band at 1680 cm^{-1} and the appearance of new bands at 2049 and 1965 cm^{-1}. When the band at 1680 cm^{-1} had disappeared the methanol was removed by rotary evaporation. The residue was titurated in hexane and filtered through a sintered glass filter. The hexane was removed by rotary evaporation yielding 0.95 g (55%) of alcohol complex **18**: NMR (C_6D_6) δ 4.8 (2 H, m), 3.6 (1 H, m), 2.6 (2 H, m), 1.7 (1 H, m), 0.9 (3 H, s), 0.7 (3 H, s); ir (hexane) 2049, 1965 cm^{-1}. This material was used without purification for the next step.

Preparation of η^5-6,6-Dimethylcyclohexadienyliron Tricarbonyl Fluoborate 19. To a magnetically stirred solution of 127 mg (48 mmol) of **18** in 3 ml of CH_2Cl_2 was added 150 mg (46 mmol) of trityl fluoborate in 2 ml of CH_2Cl_2. The reaction was stirred for 30 min under nitrogen and the resulting yellow precipitate recovered by suction filtration. The solid was washed several times with ether yielding 120 mg (75%) of salt **19**: NMR (CF_3CO_2H) δ 7.1 (1 H, t, J = 6 Hz), 5.7 (2 H, t, J = 6 Hz), 4.3 (2 H, d, J = 6 Hz), 1.6 (3 H, s), 0.9 (3 H, s).

Preparation of 5,5-Dimethyl-1,3-cyclohexadieneiron Tricarbonyl (20). To a suspension of 100 mg (0.3 mmol) of **19** in 15 of ml dry pentane was added 11.5 mg (0.3 mmol) of $NaBH_3CN$ in 10 ml of H_2O. The reaction was stirred for 1 hr under nitrogen at which time the hexane layer was separated and dried over $MgSO_4$. The hexane was removed yielding 40 mg (53%) of **5** as a yellow oil: NMR (CS_2) δ 5.0 (2 H, m), 2.8 (1 H, m), 2.6 (1 H, m), 1.4 (2 H, m), 0.8 (3 H, s), 0.7 (3 H, s); NMR (C_6D_6) δ 4.7 (2 H, m), 2.6 (2 H, m), 1.5 (1 H, dd, J = 15, 2.5 Hz), 1.3 (1 H, dd, J = 15, 2.5

Hz), 0.9 (3 H, s), 0.8 (3 H, s). Elemental analysis: C, H, Fe. Mass spectrum: *m/e* 248 (m^+), 220, 192, 148, 108, 93 (base peak).

Preparation of 5,5-Dimethyl-1,3-cyclohexadiene-*6-exo-d*$_1$-iron Tricarbonyl (*5-exo-d*$_1$). The reaction was carried out under the same conditions described for the preparation of **5**, except that $NaBD_3CN$ in 20 ml of D_2O was used. Work-up yielded ***5-exo-d*$_1$**: NMR (C_6D_6) δ 4.7 (2 H, m), 2.6 (2 H, m), 1.5 (1.1 H, m), 0.9 (3 H, s), 0.8 (3 H, s); mass spectral analysis, 85.7 ± 0.5% d_1, 14.3 ± 0.5% d_0.

Preparation of 5,5-Dimethyl-1,3-cyclohexadiene-*6-endo-d*$_1$-iron Tricarbonyl (*5-endo-d*$_1$). To 297 mg (1.1 mmol) of **5** was added with stirring 5 ml (65 mmol) of CF_3CO_2D (99% d_1). The reaction was stirred under nitrogen for 15 min and the acid removed by rotary evaporation. The residue was purified by chromatography on a 25 cm × 12 mm alumina column using hexane as the eluent. In this manner, 229 mg (70%) of ***5-endo-d*$_1$** was obtained: NMR (C_6D_6) δ 4.7 (2 H, m), 2.7 (2 H, m), 1.3 (1.1 H, m), 0.9 (3 H, s), 0.7 (3 H, s); mass spectral analysis, 95% d_1, 5% d_0.

Thermolysis of *5-endo-d*$_1$. A solution of 137 mg of ***5-endo-d*$_1$** in 2 ml of xylene was placed in a Pyrex tube equipped with a ground glass joint. The solution was degassed by three freeze–thaw cycles and sealed under vacuum. The sample was placed in an oil bath at 145 ± 3° and heated for 40 hr. The xylene was removed by vacuum distillation and the residue filtered through alumina with hexane. The hexane was removed by rotary evaporation yielding 59 mg (44%) of yellow oil. The sample was analyzed by NMR spectroscopy. No visible change had occurred.

The recovered complex was stirred twice with 3-ml portions of CF_3CO_2H for 10 min under nitrogen. The acid was removed by rotary evaporation, yielding 55 mg of yellow oil. The deuterium content was found to be 1 ± 1% by mass spectrometry.

Preparation of 3-Ethoxy-5,5-dimethyl-2-cyclohexenone. A 2-l. three-neck flask equipped with a mechanical sitrrer and distillation head was charged with 80 g (0.57 mol) of dimedone, 3 g of TsOH·H_2O, and 1.2 l. of benzene. To this suspension was added 360 ml of absolute ethanol, and the mixture became homogeneous. The mixture was heated to reflux and the azeotrope (bp 64–65°) distilled at a rate of 100 ml/hr. When the temperature of the distillate reached 78°, the reaction was poured into 100 ml of 10% NaOH. The organic layer was washed three times with 100-ml portions of saturated NaCl, dried over $MgSO_4$, and the solvent removed by rotary evaporation. The product was distilled (bp 77–79°, 0.05 mm) yielding 90.3 g (90.4%) of the desired enol ether. This product was identical with that prepared by a similar procedure.[25]

Preparation of 3-Phenyl-5,5-dimethyl-2-cyclohexenone. 3-Phenyl-5,5-dimethyl-2-cyclohexenone was prepared in 43% yield by PhMgBr addition to the above enol ether, followed by acid work-up according to the method of Woods.[16]

Preparation of 1,3-Diphenyl-5,5-dimethyl-1,3-cyclohexadiene. 1,3-Diphenyl-5,5-dimethyl-1,3-cyclohexadiene (**20**) was prepared by PhMgBr addition to 3-phenyl-5,5-dimethylcyclohexenone followed by vacuum distillation according to the method of Woods.[16] A 69% yield was obtained.

Preparation of 1,3-Diphenyl-5,5-dimethyl-1,3-cyclohexadiene-iron Tricarbonyl (4). A suspension of diene **20** (3.0 g, 11.5 mmol) and $Fe_3(CO)_{12}$ (7.6 g, 15 mmol) was refluxed in benzene under nitrogen. After 24 hr, the mixture was filtered through alumina to remove the excess $Fe_3(CO)_{12}$ and other inorganic material. The solvent was removed by rotary evaporation yielding 3.5 g (76%) of complex **4** as a yellow solid (mp 114–115°): NMR (C_6D_6) δ 7.2–7.4 (10 H, m), 6.2 (1 H, bs), 3.4 (1 H, d, J = 1.5 Hz), 2.4 (1 H, d, J = 15 Hz), 1.6 (1 H, d, J = 15 Hz), 1.2 (3 H, s), 0.9 (3 H, s). High resolution mass spectrum, calcd for $C_{23}H_{20}FeO_3$: 400.076. Found: 400.073. Ir (CCl_4): ν_{CO} 2065, 1990 cm^{-1}.

Preparation of 1,3-Diphenyl-5,5-dimethyl-1,3-cyclohexadiene-*6-endo-d*$_1$ (*4-endo-d*$_1$). To a solution of 150 mg (0.38 mmol) of **4** in 1 ml of $CDCl_3$ under nitrogen was added via syringe 1.0 ml (13 mmol) of CF_3CO_2D (99% d_1). After stirring for 30 min, the solvent was removed by rotary evaporation. To the residue was added 1 ml of $CDCl_3$ and 1.0 ml of fresh CF_3CO_2D under nitrogen. The reaction was stirred for an additional 30 min at which time the solvents were removed and the residue chromatographed on alumina yielding 118 mg (79%) of ***4-endo-d*$_1$**: NMR (C_6D_6) δ 7.0–7.4 (19 H, m), 6.2 (1 H, bs), 3.4 (1 H, d, J = 1 Hz), 1.6 (1 H, s), 1.1 (3 H, s), 0.9 (3 H, s). Mass spectra analysis: 93.6 ± 0.5% d_1.

Thermolysis Studies. Thermolysis experiments were carried out in sealed tubes in benzene, benzene-d_6, or toluene solution, except as noted above. The samples were prepared on a vacuum line, and carefully degassed by at least three freeze–pump–thaw cycles. The tubes were then sealed under vacuum, and immersed in an oil bath at the appropriate temperature. For kinetic runs, a thermostated (±0.1°) bath was used. In some cases, it was possible to run the reactions directly in NMR tubes, whose contents were monitored directly. In others, slight decomposition to paramagnetic impurities necessitated isolation of the complexes, generally by filtering the solutions with a polar solvent (usually ether) through a short column of alumina prior to analysis. For the isomerization of *cis*-**3** to *trans*-**3**, and for the equilibration of **1** and **2**, after the extent of reaction had been measured by NMR or HPLC on the crude reaction mixture, the isomers were separated by preparative TLC, and the deuterium content of each isomer was examined separately.

Acknowledgment. We would like to thank the National Science Foundation (GP16358) and the Chevron Research Corporation for support of this work.

References and Notes

(1) See, for example, F. Asinger and O. Berg, *Chem. Ber.*, **88**, 445 (1955); M. Johnson, *J. Chem. Soc.*, 4859 (1963).
(2) D. W. Hart and J. Schwartz, *J. Am. Chem. Soc.*, **96**, 8115 (1974).
(3) F. D. Mango, *Adv. Catal.*, **20**, 290 (1968); F. D. Mango and J. H. Schachtschneider in "Transition Metals in Homogeneous Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971, pp 223–296.
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, pp 114–132.
(5) T. H. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **95**, 5816 (1973).
(6) T. H. Whitesides and J. Shelly, *J. Organomet. Chem.*, in press.
(7) (a) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2248 (1973); (b) F. G. Cowherd and J. L. von Rosenberg, *ibid.*, **91**, 2157 (1969).
(8) (a) W. R. Roth and W. Grimme, *Tetrahedron Lett.*, 2347 (1966); (b) M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *Chem. Commun.*, 843 (1970); M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J. Chem. Soc., Perkin Trans 2*, 1141 (1972).
(9) G. Hesse and P. Thieme, *Justus Liebigs Ann. Chem.*, **686**, 64 (1965).
(10) R. Pettit and G. F. Emerson, *Adv. Organomet. Chem.*, 1, 1 (1964).
(11) R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.*, **93**, 2897 (1971).
(12) T. H. Whitesides and R. W. Arhart, *J. Am. Chem. Soc.*, **93**, 5296 (1971), and references cited therein.
(13) Similar reductions have been reported by Aumann: R. Aumann, *Angew. Chem., Int. Ed. Engl.*, **12**, 574 (1973); *J. Organomet. Chem.*, **47**, C29 (1973).
(14) G. F. Woods, N. C. Bolgiano, and D. E. Duggin, *J. Am. Chem. Soc.*, **77**, 1802 (1955).
(15) K. Alder, F. H. Flock, and M. Lessevich, *Chem. Ber.*, **90**, 1709 (1957).
(16) G. F. Woods, *J. Am. Chem. Soc.*, **69**, 2549 (1947).
(17) T. H. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **97**, 907 (1975).
(18) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1953, pp 175–176.
(19) The program was written for a Wang Model 720C programmable calculator; we thank Professor Howard Whitlock for the use of this machine.
(20) H. W. Whitlock and R. L. Markezich, *J. Am. Chem. Soc.*, **93**, 5290, 5291 (1971); H. W. Whitlock, C. Reich, and W. P. Woessner, *ibid.*, **93**, 2483 (1971); H. W. Whitlock and Y. N. Chuah, *ibid.*, **87**, 3605 (1965).
(21) After 40 hr at 145°, no detectable epimerization (≤1%) had occurred; thus, if we write

$$\textbf{5-}exo\text{-}d_1 \underset{k_{epi}}{\overset{k_{epi}}{\rightleftharpoons}} \textbf{5-}endo\text{-}d_1$$

an upper bound on k_{epi} is 2.3×10^{-8} sec^{-1}.
(22) Norbornadieneiron tricarbonyl[23] is a stable molecule.
(23) R. Pettit, *J. Am. Chem. Soc.*, **67**, 1266 (1959).
(24) H. Felkin, *Bull. Soc. Chim. Fr.*, 347 (1951).
(25) A. W. Crossley and N. Renouf, *J. Chem. Soc.*, **93**, 640 (1908).