inefficient. The flask was shaken periodically, and the mixture was warmed slowly to room temperature over 2.5 h. The solution was then pale yellow with a cream precipitate.

The mixture was filtered. The yellow filtrate was concentrated and refrigerated after the addition of one volume of hexane. A pale yellow solid was obtained which was filtered off, washed with hexane, and dried. It was identified by ^{1}H NMR analysis by comparison with (in methylene chloride and benzene) an authentic sample, as Cp_2ZrCl_2 (0.1 g, 0.34 mmol, 67% based on Zr). ^{1}H NMR(methylene chloride) δ 6.46 (s, Cp).

The yellow filtrate was pumped down and analyzed by ^{1}H NMR. It contained only $PMePh_2$ and Cp_2ZrCl_2.

The cream precipitate (75 mg, 0.27 mmol, 53% based on Zr), formed in the reaction, had the following spectral properties: ^{1}H NMR(D_2O) δ 8.2–7.5 (m, 10, Ph), 2.7 (d, 3, PMe, $^2J_{PH}$ = 14 Hz), 2.0 (br s, 3). IR(Nujol mull) 1760 (s), 1720, 1590, 1210, 1155 (s), 1020, 920, 820, 750 (m), 725, 690 cm^{-1}. These data are consistent with that expected for [(acetyl)(methyl)(diphenyl)phosphonium]chloride.

Acknowledgment. We acknowledge generous support for this work by the National Science Foundation (Grant No. 79-00996). One of us (K.I.G) also acknowledges support from a University Travelling Scholarship from the Australian National University.

Detailed Mechanism of Thermal Hydrogen Migration in Cyclohexadieneiron Tricarbonyl

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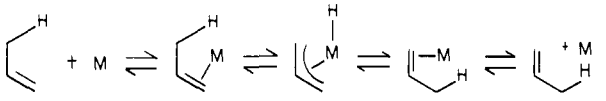
Abstract: The thermal isomerization of (cyclohexadiene-*5-exo-h-d*$_7$)iron tricarbonyl (**8**) was examined to obtain detailed information about the general mechanism of 1,5-hydrogen shifts in simple cyclic polyolefin iron tricarbonyl complexes. The isotopically labeled system, as opposed to substituent-labeled systems, was chosen to eliminate substituent effects on the relative rates of formation of intermediates and thus, ultimately, on the kinetically controlled product distributions. Thermolysis of **8** at 134 °C revealed identical initial rates of ^{1}H incorporation into the 1- and 2-positions of the cyclohexadiene ring ($\Delta G^{\ddagger}$ = 33.5 kcal/mol). This result is consistent only with a mechanism involving two simple sequential 1,3-shifts of deuterium endo to the metal. Results rule out several plausible alternative mechanisms, including one in which the intermediate 1,4-cyclohexadiene system is symmetrically bridged by iron.

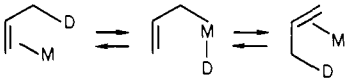
Metal-promoted hydrogen migration is a reaction that often occurs in both the iron carbonyl catalyzed isomerization of olefins and the thermal isomerization of polyolefin–iron tricarbonyl complexes. Because such reactions are of fundamental interest in organometallic chemistry, considerable effort has been made by several research groups to elucidate the detailed mechanisms of iron-catalyzed hydrogen migration in olefins.

Several possible mechanisms for iron carbonyl promoted hydrogen migrations have been suggested. The most common and generally accepted mechanism for metal-catalyzed isomerizations of olefins and stoichiometric isomerizations of diene iron carbonyl complexes involves sequential 1,3-hydrogen migrations which occur via formation of a π-allyliron hydride intermediate as illustrated in a general way below:



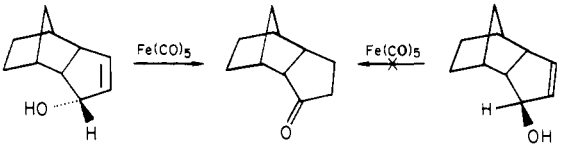
The elements of this mechanism were first proposed by Pettit[1] and Manuel[2] to account for the isomerizations by iron carbonyl compounds of both cyclic olefins (e.g., 1,4-cyclohexadiene and 1,5-cyclooctadiene) and acyclic olefins (e.g., 1-hexene and 2-methyl-1-pentene). More recently, Casey and Cyr[3] have convincingly demonstrated that such a mechanism can account for the $Fe_3(CO)_{12}$-catalyzed isomerization of 3-ethyl-1-pentene-*3-d*. Using a chiral complex as well as deuterium labeling, Whitesides and Neilan[4] have shown that such a mechanism, coupled with dechelation and bond rotation processes, accounts for isomerization of (*cis*-1,5-diphenyl-1,3-pentadiene)iron tricarbonyl to (*trans*-1,5-diphenyl-1,3-pentadiene)iron tricarbonyl.

Several variations of this mechanism have been advanced,[5,6] the most novel of which is a proposal by Green and Hughes that a σ-allyliron tricarbonyl hydride forms directly from an olefin–$Fe(CO)_3$ species (no π-allyl intermediate) and collapses in a different manner, as shown, to yield rearranged product.[7]



This mechanism was advanced to account for the thermal chemistry of [η^4-3-methylene-*endo*-4-vinyldihydrofuran-2(3*H*)-one]iron tricarbonyl.

Suprafacial 1,3-hydrogen shifts might also seem feasible in many systems, but attempts to observe metal-catalyzed suprafacial shifts have been unsuccessful. For example, Cowherd and von Rosenberg[8] found that in a mixture of isomeric alcohols **1** and



1 **3** **2**

2, $Fe(CO)_5$ smoothly catalyzed the conversion of **1** to the isomeric ketone **3**, whereas **2** was recovered unchanged.

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(4) T. Whitesides and J. P. Neilan, *J. Am. Chem. Soc.*, **98**, 63 (1976).
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(8) F. G. Cowherd and J. L. von Rosenberg, *J. Am. Chem. Soc.*, **91**, 2157 (1969).

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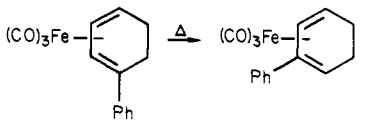
Several examples of *formal* 1,5-hydrogen shifts in cyclic diene systems have been reported including the isomerizations of (1-phenylcyclohexadiene)iron tricarbonyl (**4**),[4] (*exo*-methoxycyclo-



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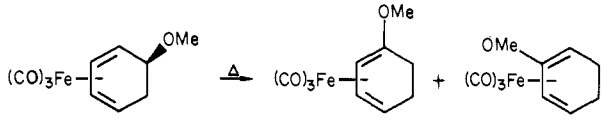
hexadiene)iron tricarbonyl (**5**),[9] deuterated derivatives of (2,5-



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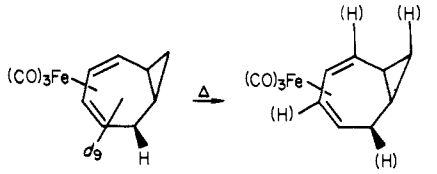
η^4-bicyclo[5.1.0]octa-2,4-diene)iron tricarbonyl (**6**),[10] and (5,5-



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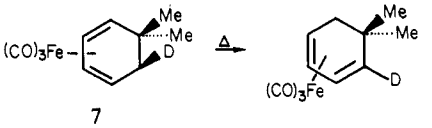
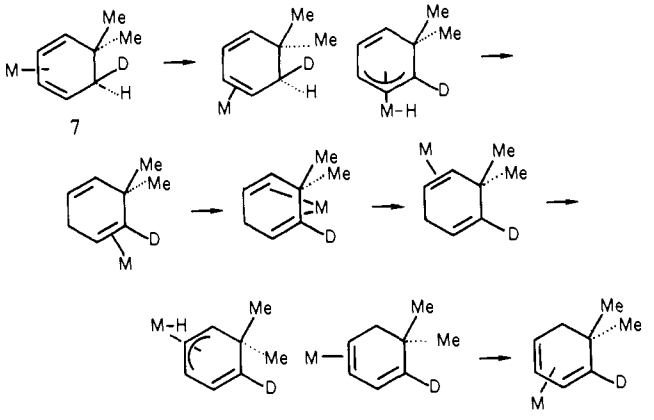
dimethylcyclohexadiene-*6-exo-d*)iron tricarbonyl (**7**).[4] Although



7

these studies clearly demonstrate that the isomerizations occur by an intramolecular shift of a hydrogen (or deuterium) endo to the metal, they fail to establish whether the mechanism of rearrangement involves a single-step 1,5-hydrogen shift or two sequential 1,3-shifts. Products from **4** and **5** can be rationalized by two simple sequential 1,3-hydrogen shifts; however, a different mechanism must apply to the isomerization of **6** and **7**, since in these systems, the second 1,3-shift is blocked by the presence of either a cyclopropane ring or a nonmigratory endo substituent. Because the isotope effect observed in the isomerization of **7** was small (k_H/k_D = 1.3), Whitesides and Neilan argued that a direct 1,5-hydrogen shift was not the major rearrangement pathway for **7**. Instead, they proposed a mechanism involving consecutive 1,3-hydrogen shifts and a symmetrically bridged 1,4-diene complex intermediate, as shown.



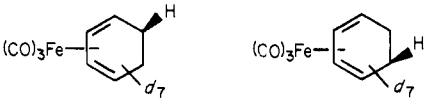
M = $Fe(CO)_3$

In these cyclic systems, detailed information cannot be obtained from systems containing nonisotopic substituents as "labels" (CH_3, PH, CH_3O, etc.) since substituent effects will alter the relative stabilities of intermediates and products and bias product distributions in an unpredictable way. Nor can further information be obtained from systems such as **6** and **7** for each of these complexes can rearrange to only one product regardless of which mechanism applies.

In order to resolve these mechanistic questions and gain insight into the fundamental mechanistic details of the formal 1,5-hydrogen shift in cyclic diene systems, we have chosen to examine rigorously the simplest system available, cyclohexadieneiron tricarbonyl. By determining the *initial* products in the thermal isomerization of suitably labeled isotopic derivatives of cyclohexadieneiron tricarbonyl, we have been able to discriminate among many possible mechanisms for isomerization. These results are discussed in detail below.

Results and Discussion

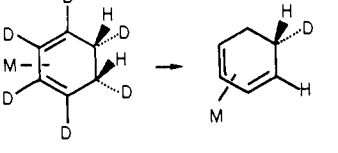
The system chosen for this study was the enantiomeric pair of monoprotio derivatives of cyclohexadieneiron tricarbonyl, **8** and



8 8′

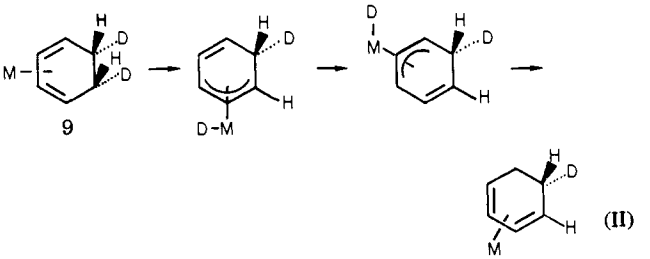
8′, subsequently referred to only as complex **8**. As explained in detail elsewhere,[11] this choice allows an accurate determination by ^1H NMR of the *initial* ratios of ^1H incorporation into the various ring sites, without biasing the data by substituent site preferences. Analysis of *initial ratios* (first 10–20% rearrangement) is critical to avoid biasing of ^1H site populations due to multiple shifts. After long times, all mechanisms predict randomization.

There are four plausible mechanisms which can be visualized for the degenerate isomerization of cyclohexadieneiron tricarbonyl. These mechanisms have been illustrated with the use of (cyclohexadiene-*5-exo,6-exo-*h_2-d_6)iron tricarbonyl, (**9**) to demonstrate in a compact form the results expected for monoprotio **8**. (Clearly the results will be identical for **8** and **9**; however, for **9**, with ^1H at both exo sites, only half as many reaction pathways need be drawn to illustrate the predicted scrambling results. All experiments were carried out with the use of monoprotio **8**.) The four mechanisms are as follows: (1) direct 1,5-hydrogen shift (mechanism I);[12] (2) 1,5-hydrogen shift involving a π-allyliron



9 (I)

hydride intermediate (mechanism II); (3) consecutive 1,3-hydrogen

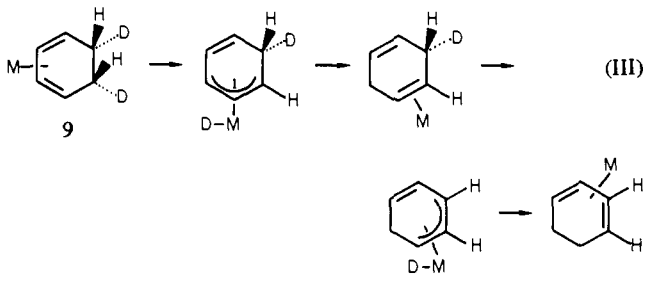


9 (II)

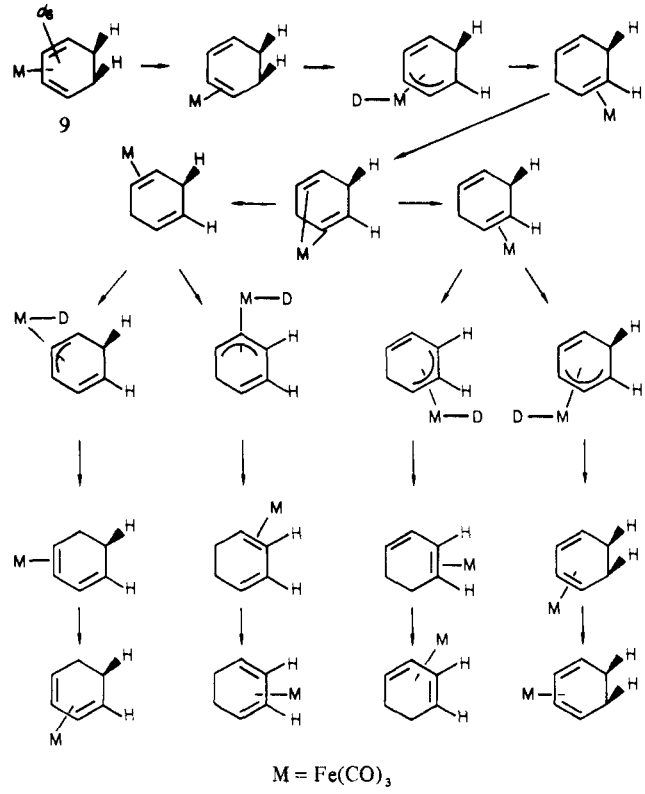
shifts in which the double bonds in the diene intermediate *do not*

(9) K. E. Hine, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1702 (1976).
(10) R. Aumann, *Chem. Ber.*, **109**, 168 (1976).
(11) W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, **102**, 3490 (1980).
(12) This mechanism is similar to one proposed by Pauson in which there is a metal-assisted migration of an endo hydrogen in the thermal rearrangement of cycloheptatriene complexes of chromium tricarbonyl. (See: M. I. Foreman, G. R. Knox, P. L. Pauson, K. H. Todd, and W. E. Watts, *J. Chem. Soc., Perkin II Trans. 2*, 1141 (1972).

become equivalent (mechanism III); (4) consecutive 1,3-hydrogen



shifts in which the double bonds in the 1,4-diene intermediate *do* become equivalent (mechanism IV).



The results predicted for the thermal isomerization of **9** (and thus **8**) are distinctly different for three of the above four mechanisms. The 1,5-hydrogen shift mechanisms (I and II) are experimentally indistinguishable and would result in *initial* incorporation of hydrogen into the 1-position only. The 1,3-hydrogen shift mechanism for which the double bonds of the diene intermediate *do not* become equivalent (mechanism III) predicts *initial* incorporation of hydrogen into the 1- and 2-positions in a 1:1 ratio. The second 1,3-hydrogen shift mechanism (IV) predicts initial incorporation of hydrogen into the 1- and 2-positions of the bound diene unit in a 2:3 ratio. Thus, by monitoring the early stages of the thermal isomerization of **8**, where multiple shifts do not yet contribute significantly to the observed rearrangement products, it should be possible to discriminate among three of the four mechanisms presented, as each of these three types of mechanism predict a different rate of initial incorporation of hydrogen into the 1- and 2-positions.

Deuterium Labeling and Thermal Isomerization. The monoprotio complex, (cyclohexadiene-*5-exo-h-d*$_7$)iron tricarbonyl (**8**), was prepared by reduction of the tetrafluoborate salt of $(C_6D_7Fe(CO)_3)^+$ with $NaBH_3CN$. Hydride attack is almost exclusively exo,[13] resulting in complexes with one exo ^{1}H NMR resonance at δ 1.37. Low-intensity signals were also observed at δ 2.96, 4.94 and 1.60, corresponding to products with residual ^{1}H in the 1-, 2-, and endo positions, respectively. The residual protio material (3–4% in each position) originates from the residual protons of incompletely deuterated cyclohexadiene used in the synthesis of $C_6D_8Fe(CO)_3$.

(13) The ratio of exo:endo hydride attack was found to be greater than 70:1 when $NaBH_3CN$ was used as the reducing agent. Somewhat less selectivity was obtained with $NaBH_4$ (exo:endo < 10:1).

Table I.[a] Thermolysis of Complex 8 at 134 °C. Distribution of $C_6HD_5Fe(CO)_3$ Isomers as a Function of Time

time,[b] h	8-*1-h*	8-*2-h*	8-*endo-h*	8-*exo-h*
0	6.0[c]	5.5[c]	6.6[c]	81.8
4	9.6	9.2	6.3	74.8
8	10.8	10.3	7.4	71.4
12.5	13.8	13.2	7.0	65.9
18.5	15.4	15.1	8.0	61.5

[a] Data obtained by integration of ^{1}H NMR spectra of thermolyzed sample of 8. [b] Hours at 134 °C. [c] Represents ca. 3% residual ^{1}H per carbon site.

Samples of the monoprotio cyclohexadieneiron tricarbonyl (**8**) in toluene-d_8 were prepared for thermal isomerization according to the procedures described in the Experimental Section. Thermal isomerizations were carried out in sealed 5-mm NMR tubes immersed in a thermostatically controlled oil bath. The progress of the reaction was monitored by periodic examination of the complex by ^{1}H NMR. Slight sample decomposition was visible after 4–6 h at 134 °C. So that any possible effects of the decomposition products on the course of isomerizations could be minimized, samples were redistilled (25 °C) and resealed several times in the course of the thermolysis experiments (see Experimental Section). ^{1}H NMR spectra recorded prior to and after resealing showed less than a 2% change in the ratio of the integrals for the four types of ring protons.

The data obtained for a typical thermolysis experiment is presented in Table I, where the integrals for the signals of the four types of ring protons have been normalized to: $H_1 + H_2 + H_{endo} + H_{exo} = 100$. Examination of this data reveals that the percentage of protio material in the endo-methylene position remains constant, implying that there is an insignificant amount of exo/endo exchange. This observation rules out the possibility that the isomerization mechanism involves dissociation and recombination of the complex. The first-order rate constant for the formation of (cyclohexadiene-*2-h-d*$_7$)iron tricarbonyl is $k = 7.7 \times 10^{-6}$ s^{-1} at 134 °C, corresponding to a free energy of activation of $\Delta G^{\ddagger} = 33.5$ kcal mol^{-1}.

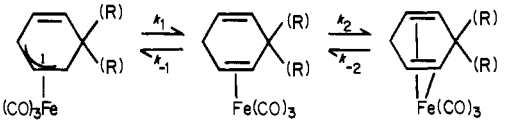
Most importantly, it can be seen from this data that H_{exo} isomerizes to the 1- and 2-positions *at equal rates*. This result is consistent only with that predicted by mechanism III; that is, iron migration by simple, consecutive 1,3-shifts involving an (η^2-1,4-cyclohexadiene)iron tricarbonyl intermediate in which the olefinic units *remain distinct*.

Analogous thermal isomerization experiments were performed with use of the corresponding monodeuterated complex, (cyclohexadiene-*exo-d*)iron tricarbonyl, which can be prepared with no detectable residual deuterium in positions H_1 and H_2. Monitoring by ^{2}H NMR the early stages (0–5% reaction) in the isomerization of this complex confirmed that the isotopic label is incorporated at the 1- and 2-positions at equal rates.

It is interesting to compare the results obtained for these isotopically labeled cyclohexadiene complexes with the results reported by Whitesides and Neilan for the dimethyl-substituted cyclohexadieneiron tricarbonyl complex, **7**. In spite of the marked similarity of the two systems, the detailed pathways for isomerization must obviously differ somewhat. Our results provide strong evidence that the unsubstituted cyclohexadiene complex rearranges via two simple, sequential 1,3-shifts (mechanism III). In contrast, the endo-methyl group of **7** precludes such as mechanism, and isomerization must follow a variant of this mechanism which includes a symmetrically-bridged 1,4-diene intermediate complex (mechanism IV) as suggested by Whitesides and Neilan.[4]

Given this situation it is interesting that the two compounds isomerize with very similar free energies of activation. If the

intermediates in the isomerization of **7** and **8** are assumed to have similar relative energies, some additional insights into the energetics of the isomerization process emerge. Consider the interconversion of the η^3-allyliron hydride with the η^2-1,4-dieneiron complex and the η^4-1,4-dieneiron complex. Since in the unsub-



η^3-allyliron hydride η^2-1,4-dieneiron η^4-1,4-dieneiron

stituted case (R = H or D) no symmetrical intermediate (η^4-1,4-dieneiron complex) intervenes, $k_{-1} > k_2$ and thus C–H insertion to form the allyliron hydride is more rapid than iron bridging. However, the fact that the activation energies for isomerization of **7** and **8** are similar suggests that the transition-state energy for conversion of the η^2-1,4-diene species to the η^4-1,4-diene species must not lie substantially above the transition-state energy for conversion of the ground-state η^4-1,3-diene complex to the η^2-1,4-diene complex.

A third 1,3-hydrogen shift mechanism discussed in the introduction is that proposed by Green and Hughes,[7] in which a σ-allyl metal hydride intermediate forms without the appearance of a π-allyl intermediate. Like mechanism IV, this mechanism predicts that the thermal isomerization of the isotopically labeled complex, **8**, would result in the initial incorporation of hydrogen into the 1- and 2-positions in a 2:3 ratio. This is not the observed ratio, and thus the σ-allyl metal hydride mechanism cannot be regarded as a general mechanism for the isomerization of the simple cyclohexadieneiron tricarbonyl complexes.

Experimental Section

General Procedures. All operations involving iron carbonyl compounds were carried out under an atmosphere of dry, oxygen-free nitrogen. ^{1}H and ^{2}H NMR samples of all iron tricarbonyl complexes were carefully degassed by several freeze–pump–thaw cycles and sealed under a vacuum. ^{1}H NMR spectra were recorded at 100 MHz with use of a Varian XL-100 FT-NMR spectrometer; ^{2}H NMR spectra were recorded at 15.35 MHz on the same instrument equipped with a multinuclear probe. NMR solvents were stored over 4 Å molecular sieves and distilled under vacuum prior to use. An insulated oil bath equipped with a direct-reading mercury thermoregulator provided constant temperatures for the thermal rearrangement studies (±0.1 °C).

1,4-Cyclohexanedione-d_8. 1,4-Cyclohexanedione was deuterium labeled following the procedure of Bailey and Lambert.[14] A solution of 1,4-cyclohexanedione (10 g), D_2O (20 mL), and PCl_5 (~0.5 g) was stirred and heated to 50 °C for 48–72 h. The cooled reaction mixture was extracted with CH_2Cl_2 (5 × 30 mL) and the combined extracts dried over $MgSO_4$. Following the removal of CH_2Cl_2 under reduced pressure, the exchange reaction was repeated. After four exchange sequences, the cyclohexanedione (9.9 g) contained 99.5% deuterium, as determined by ^{1}H NMR.

1,4-Cyclohexanediol-d_{10}. This compound was made in good yield from the lithium aluminum deuteride (LAD) reduction of 1,4-cyclohexanedione-d_8. 1,4-Cyclohexanedione-d_8 (12 g) was dissolved in anhydrous diethyl ether and added dropwise under nitrogen to a mechanically stirred slurry of LAD (3.5 g) and anhydrous diethyl ether (200 mL) in a 2-L three-necked flask. After addition of the dione, the mixture was stirred for 1 h and then quenched with 10% NaOH (6 mL) followed by 10 mL of water. Crude 1,4-cyclohexanediol-d_{10}, isolated from the ether layer and by ethanol extraction of the solid residue, was purified by Soxhlet extraction with the use of benzene (yield 12 g).

1,4-Cyclohexanediol-d_{12}. Cyclohexanediol-d_{10} was dissolved in D_2O (0.5 g D_2O/1 g diol) and allowed to stir at room temperature for 5 min. Water was then removed under a vacuum.

Cyclohexadiene-d_8. Although Zelinskii[15] reports that cyclohexanediol can be dehydrated by heating to 165–170 °C with either $MgSO_4$ or fused $KHSO_4$, we had little success with either method. The use of $KHSO_4$ alone gave mostly 3-cyclohexenol; unreacted diol sublimed out of the heated flask when $MgSO_4$ alone was used. However, when the diol was ground up with a 50:50 mixture of $MgSO_4$ and $KHSO_4$ and heated to 165–170 °C, cyclohexadiene was readily produced in a 55% yield. Comparison by ^{1}H NMR with a sample of C_6H_8 showed that the 3:2 mixture of 1,3- and 1,4-cyclohexadienes produced in this way contained 97–98% deuterium.

(Cyclohexadiene-*5-exo-h-d*$_7$)iron Tricarbonyl (8). (Cyclohexadiene-d_8)iron tricarbonyl was prepared by a procedure analogous to that described by Birch[16] for the preparation of $C_6H_8Fe(CO)_3$. Cyclohexadiene-d_8 was photolyzed with $Fe(CO)_5$ in degassed benzene for 12 h. After the solvent and excess $Fe(CO)_5$ were removed, the crude photolysis product was dissolved in CH_2Cl_2 and reacted with a slight excess of $Ph_3C^+BF_4^-$ in CH_2Cl_2. The addition of diethyl ether resulted in the precipitation of almost quantitative yields of $[C_6D_8\ Fe(CO)_3]^+BF_4^-$ (90–95% based on $C_6D_6Fe(CO)_3$). Treatment of this salt with 1 equiv of $NaBH_3CN$ gave predominantly (cyclohexadiene-*5-exo-h-d*$_7$)iron tricarbonyl, but small amounts of other isomers were formed as well. Residual protio material in the cyclohexadiene-d_8 gave rise to products also containing protons in the 1- and 2-positions of the cyclohexadiene ring (3.9% and 3.5%, respectively). Slightly larger amounts of the 5-endo isomer (4.2%) were formed due to the combined effects of the residual protio material in the cyclohexadiene-d_8 and a small amount of endo hydride attack.

Thermal Isomerization of (Cyclohexadiene-*5-exo-h-d*$_7$)iron Tricarbonyl. (Cyclohexadiene-*5-exo-h-d*$_7$)iron tricarbonyl was prepared for thermal isomerization by distilling (25 °C) the complex (~50 mg) into a Teflon stopcock adapted 5-mm NMR tube containing (t-Bu)$_6$Cr(acac)$_3$ (1–2 mg).[17] Solvent (toluene-d_8, 0.3 mL) was then distilled in (25 °C), the sample degassed by several freeze–pump–thaw cycles, and the NMR tube sealed in vacuo. Samples prepared in this manner were wrapped in aluminum foil (to eliminate any possible photochemical reactions) and heated at 134.2 ± 0.2 °C for periods of 3–6 h. ^{1}H NMR spectra were recorded periodically to monitor the progress of the isomerization. If sample decomposition was evident either by visual inspection of the sample or as a marked increase in line width in the ^{1}H NMR spectra, the sample (including solvent) was distilled (25 °C) into another NMR tube and thoroughly degassed before resealing.

(Cyclohexadiene-*5-exo-d*)iron Tricarbonyl. This complex was prepared in a manner analogous to that described above for the monoprotio complex **8**. Reduction of the salt $(C_6H_7Fe(CO)_3)^+BF_4^-$ to the desired product was accomplished by the use of $NaBD_4$. The ratio of exo:endo complexes as determined by ^{2}H NMR was 10:1; no other isomers were present.

Samples of this monodeuterio complex were prepared for thermal isomerization in a manner analogous to that described above for the monoprotio complexes, except that larger amounts of sample were used (0.2 g).

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(17) (t-Bu)$_6$Cr(acac)$_3$ was added to thermolysis samples to shorten and level T_1 values of all protons to a constant value and insure the FT NMR results gave accurate integrations.