2.0–3.3 (m, 4 H, CH$_2$), 3.75–4.5 (m, 1 H, methine); ^{19}F nmr 14.9 ppm (s, isomer 1, area 170, COF), 13.5 ppm (s, isomer 2, area 106, COF), 111 ppm (m, isomer 1, area 170, CF), 94 ppm (m, isomer 2, area 106, CF). Glpc analysis also suggests the presence of both cis and trans isomers.

3-Chlorocyclobutanone (9). 1-Fluoro-3-*tert*-butoxycyclobutyl fluoroformate (200 g, 0.96 mol) was quickly added to 350 g (1.68 mol) of phosphorus pentachloride. The temperature of the mixture reached 57°, and additional heat was applied until the mixture began to reflux (85°). During the heating period, two 2.5-ml portions of boron trifluoride ethereate were added, and during the reflux period (1 hr), four 0.5-ml portions were added. Starting material had been consumed at this point (glpc), and the mixture was cooled and poured onto ice. When the temperature of the hydrolysis mixture reached 15°, bubbles of carbon dioxide were evolved. The water was extracted with ether, which was then washed with water. Removal of solvent and distillation gave 12.5 g of **9** of about 80% purity, and 28 g of **9** of about 95% purity (∼35% yield): bp 66° (47 mm); n^{25}D 1.4626; ir (neat) 3.32, 3.38, 5.54 μ; nmr (neat) δ 4.50–4.92 (m, 1 H, methine), 3.0–4.0 (m, 4 H, CH$_2$); mass spectrum *m/e* 104 (5.5% relative intensity) [M]$^+$, 76 (21% relative intensity) [CH$_2$CHClCH$_2$]$^+$, 62 (8.5% relative intensity) [CH$_2$CHCl]$^+$, 42 (base peak) [CH$_2$CO]$^+$, 39 (48% relative intensity) [cyclopropenium ion].

Cyclobutenone (5) from 3-Chlorocyclobutanone (9). To 40 ml (0.17 mol) of tri-*n*-butylamine at 25° was added 12.3 g (0.12 mol) of **9** over 25 min. After 10 additional min volatile material was removed into a cold trap (−78°) at 0.2 mm. The material in the trap was then pumped into a second cold trap at 15 mm, allowing the first trap to come to 25°. This gave 5 ml (∼5 g, 0.07 mol, 62%) of **5**.

Cyclobutenone (5) from 3-Bromocyclobutanone (4). To a solution of 14.9 g (0.1 mol) of **4** in 100 ml of diethyl Carbitol was added at 0° over 1 hr a solution of 23 ml (0.097 mol) of tri-*n*-butylamine in 80 ml of diethyl Carbitol. The mixture was stirred at 0° for 0.5 hr and then warmed to 25° over 1 hr. The volatile material was pumped into a cold trap (−78°) for 2 hr at 0.3 mm. The materal in the trap was then pumped into a second cold trap at 15 mm, allowing the first trap to come to 25°. The **5** in the second trap weighed 4.0 g (0.058 mol, 58%).

Synthesis and Interconversion of Some Shift Isomeric Polyene–*Tetrahapto*iron Tricarbonyl Complexes

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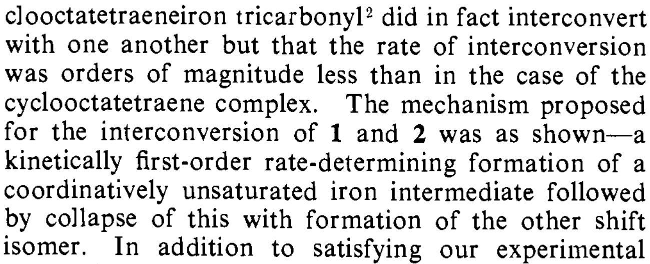
Abstract: A series of *tetrahapto*iron tricarbonyl complexes of 1,6-disubstituted hexatrienes and 1,8-disubstituted octatetraenes has been synthesized. The mechanism of interconversion of shift isomers of these complexes has been studied. Electronic effects on equilibria are small. Electronic effects on rates are somewhat larger. The interconversion of the three shift isomers of 1-phenyl-8-tolyloctatetraeneiron tricarbonyl was studied.

Several years ago we[1] reported a study of the interconversion of the two shift isomers **1** and **2** of 1-phenyl-6-tolyl-1,3,5-hexatrieneiron tricarbonyl (eq 1). It was found that these two open-chain analogs of cyclooctatetraeneiron tricarbonyl[2] did in fact interconvert with one another but that the rate of interconversion was orders of magnitude less than in the case of the cyclooctatetraene complex. The mechanism proposed for the interconversion of **1** and **2** was as shown—a kinetically first-order rate-determining formation of a coordinatively unsaturated iron intermediate followed by collapse of this with formation of the other shift isomer. In addition to satisfying our experimental data, this picture is consistent with the great difference in rate between the cyclic and acyclic cases. The cyclic complexes possess the possibility of the metals' moving in concert with valence tautomerism of the ligand, thus leading to reestablishment of the original bonding picture with minimal intermediate structural changes (a "single jump"). The acyclic cases on the other hand lack the ability for valence tautomerization and must pass the iron a greater distance (a "double jump") along the chain before the original type of structure is reestablished.



The aim of the work now reported was to test the principal prediction of the above stepwise mechanism, that movement of an iron tricarbonyl residue from one end of a complexed octatetraene to the other *via* double jumps must of necessity proceed *via* the intermediate complex with the iron in the middle of the octatetraene (eq 2). In the course of testing this prediction we have prepared a number of shift isomers[3] of polyene–iron tricarbonyl complexes and have been able to examine the effect of the electronic nature of the terminal substituents on both the position and their rate of attainment of equilibrium. Our conclusions, as discussed below, are that (1) there is a relatively small effect of the electronic nature of the terminal substituents on the position of equilibrium, (2) substituents exhibit a somewhat greater effect on the rate of interconversion of

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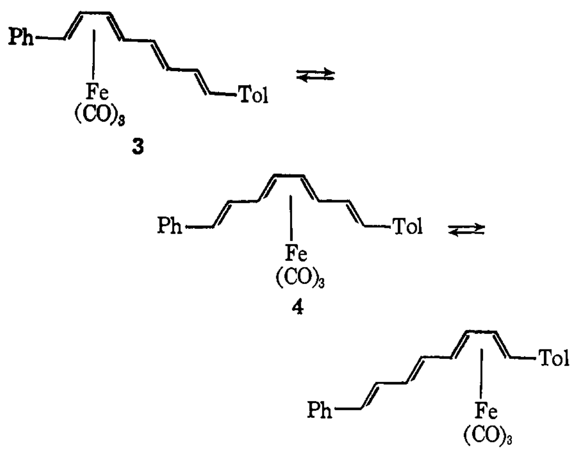
[1] H. W. Whitlock and Y. N. Chuah, *J. Amer. Chem. Soc.*, **87**, 3606 (1965).

[2] A large variety of fluxional organometallic complexes has been reviewed recently by F.A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

[3] "Shift" isomers as used here are polyene–iron tricarbonyl complexes that differ by virtue of the site of attachment of the iron tricarbonyl group to the polyene (*e.g.*, **1** and **2**; **3**, **4**, and **5**).



3

4

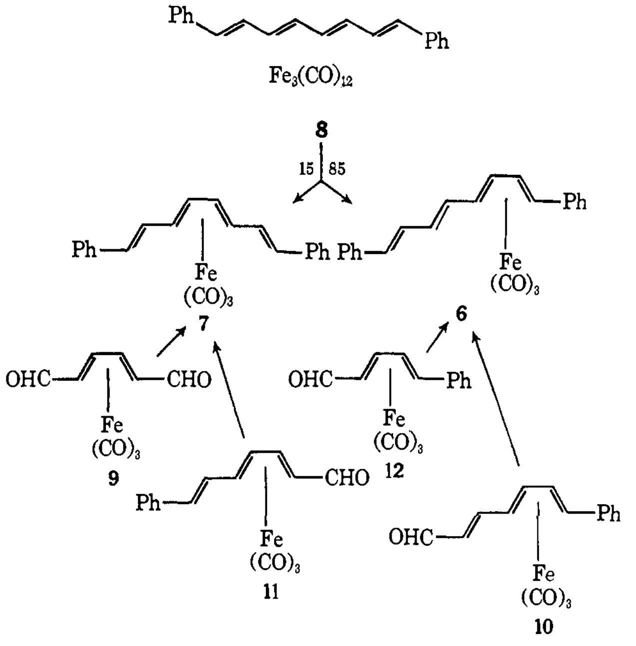
5

shift isomers, and (3) that contrary to the prediction above movement of the iron residue from one end to the other in **3**, **4**, and **5** can occur *without* the obligatory intermediacy of the middle isomer **4**.

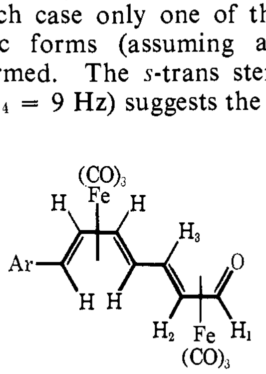
Synthesis of Complexes. There are effectively two methods for the preparation of polyene–iron tricarbonyl complexes. The classical procedure, and the one that is attractive when the starting polyene is readily available, is the reaction between the potential ligand and an iron carbonyl in an appropriate inert solvent.[4,5] This method suffers from several drawbacks, however. When there is any question concerning the site of attachment of the iron tricarbonyl residue one may reasonably expect that a mixture of shift isomers may result on reaction between the metal carbonyl and olefin (*e.g.*, the three *tetrahapto*[6] complexes **3**, **4**, and **5** derived from 1-phenyl-8-*p*-tolyl-1,3,5,7-octatetraene). This can create problems as to both identification and separation of the isomers produced. A second difficulty appears when one considers the possibility of complexation of more than one iron tricarbonyl moiety by the polyene, although this can be minimized by adjusting the ratios of reagents.

The other method, and the one of choice in the present work, is construction of the desired complex by means of a Wittig reaction of a preformed aldehyde–iron tricarbonyl complex and the appropriate phosphine ylide. As 1,4-disubstituted butadiene–iron tricarbonyl complexes may normally be prepared in a stereochemically pure manner[4] and the Wittig condensation affords trans olefins stereoselectively,[7,8] this method is attractive in that it avoids the objections voiced above. Preparation of the two shift isomers **6** and **7** of 1,8-diphenyl-1,3,5,7-octatetraene (**8**) illustrates the two methods. Reaction of **8** with triiron dodecacarbonyl in warm benzene affords in good yield an inseparable 85:15 mixture of the terminal (**6**) and internal (**7**) complexes (Scheme I). The mixture is the equilibrium one and in fact the conditions of the reaction (benzene, triiron dodecacarbonyl, 65°) effect isomerization of the pure isomers. The mechanism of this is, however, unclear. In contrast with the direct method both isomers **6** and **7** can be prepared in an isomerically pure form by Wittig condensations involving **9** or **11** and **10** or **12**, respectively. In all four cases the Wittig condensation proceeded with completely stereoselective formation of a single isomer. Synthesis of complexes from more than one precursor as in Scheme I and the straightforward analysis of the nmr spectra of many of these complexes (see Experimental Section) leave little doubt as to the trans stereochemistry of the double bond introduced in the Wittig reaction and the all-trans stereochemistry of the complexes themselves. With the exception of one case (1-anisyl-6-(4′-pyridyl)-1-3,5-hexatriene) all Wittig condensations examined to date have yielded only one stereo- or shift isomer. The complexes prepared are listed in Table I.

Scheme I



The two double complexes **13** and **14** isolated from the reactions of the corresponding heptatrienals and triiron dodecacarbonyl in benzene are novel structures.[9,10] In each case only one of the two possible diastereoisomeric forms (assuming all-trans double bonds) were formed. The *s*-trans stereochemistry of the 3–4 bond (J_{34} = 9 Hz) suggests the stereochemistry shown.



13, Ar = C_6H_5

14, Ar = p-$CH_3C_6H_4$

Interconversion of the Shift Isomers. Heating any one of a set of shift isomers leads to formation of an equilibrium mixture of all members of the set. The

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[4] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, 1 (1964).

[5] D. Seyferth and R. B. King, "Annual Reviews in Organometallic Chemistry," Vol. 1 *et seq.*, Elsevier, Amsterdam, 1964.

[6] F. A. Cotton, *J. Amer. Chem. Soc.*, 90, 6231 (1968).

[7] R. N. McDonald and T. W. Campbell, *Org. Syn.*, 40, 36 (1960).

[8] L. D. Bergelson and M. M. Shemyakin, *Tetrahedron*, 19, 149 (1963).

[9] The spectral properties of these two complexes, in particular disappearance of the carbonyl stretching frequency of the aldehyde carbonyl, are similar to those of cinnamaldehyde-*O*,1,2,3-*tetrahapto*-iron tricarbonyl.[10]

[10] K. Stark, J. E. Lancaster, H. O. Murdoch, and E. Weiss, *Z. Naturforsch.*, 13, 284 (1964).

Table I. 1(*R*),4(*R*^{1})-Disubstituted Butadiene–Iron Tricarbonyl Complexes

R	R^1	No.	Yield,[f] %	Method of synthesis
CHO	CHO	9	5	A[a]
C_6H_5	CHO	12	72[g]	A
C_6H_5	CH=CHCHO	10	15	A
C_6H_5CH=CH	CHO	11	55	A
Tol[b]	CHO	27	69	A
Tol[b]	CH=CHCHO	28	12	A
TolCH=CH	CHO	29	22	A
H	CHO	30	25	A
An[c]	CHO	31	52	A
DCP[d]	CHO	32	55	A
Tol	CH=CH_2	19	55	B,[e] **27**
TolCH=CH	H	20	96	B, **30**
C_6H_5CH=CH	HC=CHC_6H_5	7	25, 64	B, **9**, **11**
C_6H_5(CH=CH)$_2$	C_6H_5	6	50	B, **10**
TolCH=CH	CH=CHTol	24	49	B, **29**
Tol(CH=CH)$_2$	Tol	23	67	B, **27**
C_6H_5	CH=CHCHO · Fe(CO)$_3$	13	1	A
Tol	CH=CHCHO · Fe(CO)$_3$	14	3	A
TolCH=CH	CH=CHC_6H_5	4	44	B, **11**
Tol (CH=CH)$_2$	C_6H_5	3	85	B, **12**
Tol	(CH=CH)$_2C_6H_5$	5	63	B, **27**
An	CH=CHDCP	17	70	B, **31**
AnCH=CH	DCP	18	54	B, **32**
C_6H_5	CH=CHAn	16	74	B, **12**
C_6H_5CH=CH	An	15	64	B, **31**

[a] Method A, formation of the complex by reaction of the corresponding ligand with an iron carbonyl. [b] Tol = *p*-tolyl. [c] An = *p*-methoxyphenyl. [d] DCP = 3,4-dichlorophenyl. [e] Method B, reaction of the numbered complex shown with the appropriate phosphorous ylide. [f] The yields quoted are of isolated material. [g] Reference 1.

same equilibrium mixture can be formed from all members of the set. Decomposition to the free ligand and iron carbonyls and cis–trans isomerization of the uncomplexed double bonds were not observed under conditions of interconversion of shift isomers. The complexes could, however, be split into the polyene ligand and bis(triphenylphosphine)iron tricarbonyl on extended heating with triphenylphosphine in benzene. Simple first-order kinetics and the lack of effect of added triphenylphosphine on the rate of interconversion of the shift isomers were observed. Determination of the rates of interconversion of the shift isomers was carried out using infrared or nuclear magnetic resonance (see Experimental Section). The equilibrium constants and rates obtained are shown in Table II. A typical kinetic plot is presented in Figure 1.

The isomerization of **7** was carried out in the presence of a 5- and 20-fold excess of triphenylphosphine. In both cases, treatment of the rate data in terms of a reversible first-order process gave first-order kinetics through 80% isomerization (Figure 2). Since insignificant incorporation of triphenylphosphine or polar solvent such as diglyme occurs during the course of isomerization, we consider an intermolecular ligand exchange process to be a very unlikely mechanism for these isomerizations.

In general the behavior of the interconverting isomers, first-order kinetics and intramolecularity, fits the general picture of the mechanism of interconversion of shift isomers (eq 1). Comparison of the rate of isomerization of the complexes **6** and **7** in toluene and diglyme suggests that there is little effect of solvent polarity on the rate of isomerization.[11] The position of equilibrium is relatively uneffected by the nature of the terminal substituents as is seen by comparison of K_{eq} for interconversion of the two phenyltolylhexatriene isomers[1] **1** and **2** (K_{eq} = 1) with those of the isomeric anisylphenylhexatriene complexes **15** and **16** (K_{eq} = 1.21 favoring the phenyl end) and the isomeric anisyl-3,4-dichlorophenylhexatriene complexes **17** and **18** (K_{eq} = 1.26 favoring the dichlorophenyl end). Isomers **10** and **11**, with a greater disparity in the electronegativity of the terminal substituents, still show a K_{eq} of only 2.88.

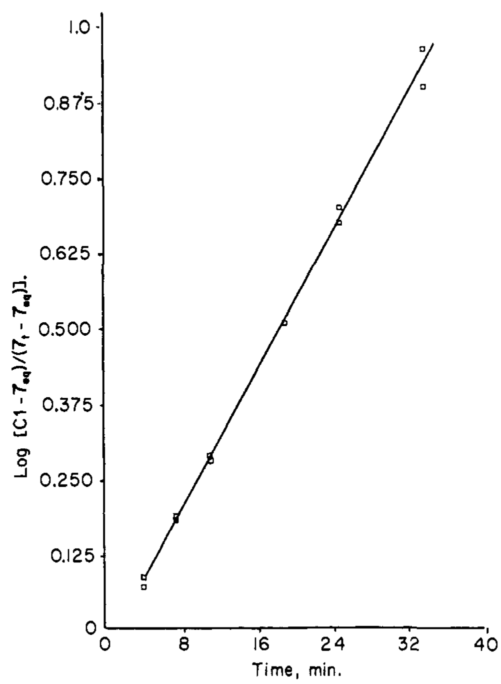

Figure 1. Least-squares fit of data from the isomerization of **7** in toluene at 119.4° based on reversible first-order kinetics.

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(11) It should be pointed out, however, that solubility problems have prohibited verification of this in all (particularly 10 ⇆ 11) cases.

Table II. Interconversion of Shift Isomeric Complexes

Reaction	T, °C	K	Solvent	10^3k, min^{-1}	10^3k,[d] min^{-1}	Method
$\mathbf{10} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{11}$	64.9	2.88	Diglyme[a]	1.20 ± 0.06	0.42 ± 0.03	Nmr
$\mathbf{19} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{20}$	119	14.2	Toluene	5.32 ± 0.32	0.374 ± 0.04	Ir
$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$	78.45	2.96	Toluene	0.21 ± 0.01	0.071 ± 0.004	Ir
$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$	99.4	2.96	Toluene	2.75 ± 0.18	0.93 ± 0.06	Ir
$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$	119.4	2.94	Toluene[c]	27.3 ± 0.7	9.3 ± 0.2	Ir
$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$	99.4	3.3	Diglyme	2.92 ± 0.12	0.88 ± 0.04	Ir
$\mathbf{24} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{23}$	99.4	3.2	Toluene	3.68 ± 0.14	1.15 ± 0.05	Ir
$\mathbf{17} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{18}$	100.1	1.26	THF[b]	4.4 ± 0.3	3.62 ± 0.4	Nmr
$\mathbf{4} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{3} + \mathbf{5}$	99.4	3.10	Toluene	3.38 ± 0.24	1.09 ± 0.08	Nmr
$\mathbf{4} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{3} + \mathbf{5}$	99.4	3.11	Toluene	3.76 ± 0.24	1.21 ± 0.2	Nmr
$\mathbf{15} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{16}$	99.4	1.21	THF	1.36 ± 0.60	1.12 ± 0.05	Nmr

[a] Diethylene glycol dimethyl ether. [b] Tetrahydrofuran. [c] E_a = 32 ± 1.8 kcal/mol. $\Delta S^{\ddagger}$ = +15.8 ± 0.7 eV (99.4°). For $\mathbf{1} \rightleftharpoons \mathbf{2}$, E_a = 33 kcal/mol, $\Delta S^{\ddagger}$ = +16 eV (99.6°). [d] The spectral bands and absorption maxima used for the analyses are presented in the Experimental Section. The equilibrium constants are corrected for the symmetrical nature of **6** and **7**, and **23** and **24**.

Unlike the position of equilibrium, the rate of equilibration of the shift isomers is relatively dependent on the nature of the substituents. This is most dramatically seen in comparing the interconversion of the aldehyde complexes **10** and **11** with the three diaryl complexes. It is apparent that the rate of interconversion of the isomers does not depend in any simple manner on the electron-donating or -attracting power of the para substituents. Although one can calculate a ρ of approximately -0.6 for migration of the iron tricarbonyl group toward the more electronegative (phenyl) end of the phenyl anisyl complexes **15** and **16**, adding two chlorines to the phenyl end to give the 3,4-dichlorophenyl-*p*-anisyl complexes **17** and **18** results not in a rate decrease as one would suppose, but a further rate increase. The rate increase is about that expected if the *difference* in ρ values of the two sets of para substituents is the governing factor.

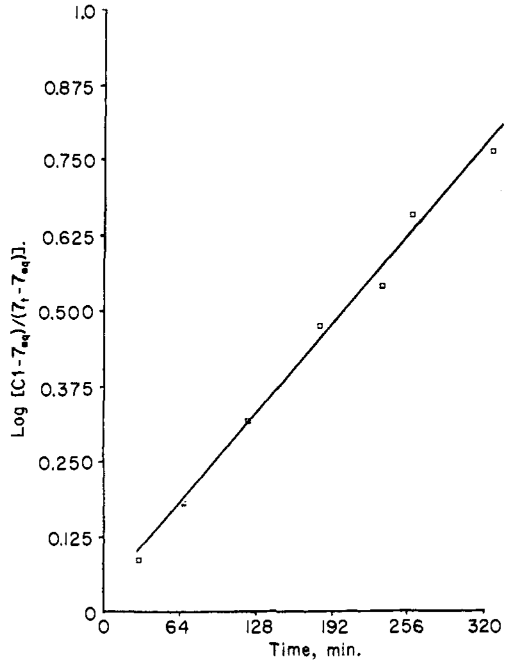
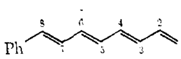
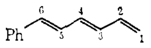
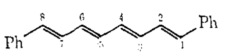


Figure 2. Least-squares fit of data from the isomerization of **7** in toluene at 99.4° in the presence of a fivefold excess of triphenylphosphine, based on reversible first-order kinetics.

Steric effects on both rates and equilibrium constants are interesting in this series of compounds in that there do not appear to be any consistent ones. In the diaryloctatetraene complexes the iron tricarbonyl group shows a modest but surprising tendency to lie next to the more bulky (and more electronegative) aryl terminals. On the other hand the iron tricarbonyl group tends to move away from the tolyl group toward the vinyl substituent in the pair of complexes **19** and **20**. The complex and somewhat contradictory nature of the steric and electronic effects of the substituents is seen again in comparing the tolyl hexatriene complex, wherein the iron prefers to lie away from the tolyl (K_{eq} = 14.2) with its formyl derivatives **10** and **11** (K_{eq} = 3), which suggests that introduction of a formyl substituent entails mutually antagonistic steric and electronic effects.

Our present interpretation of these results is as follows. It seems unlikely that classical steric effects are operating in this system. It is also unlikely that the interconversions proceed through either a polar intermediate or a very polar transition state leading to the intermediate pictured in eq 1. This is supported by the absence of either detectable solvent effects on the rates or a consistent dependence of the rate on either electron-attracting or -donating substituents. We suggest that the polar substituent effect on the rate of isomerization

Table III. Changes in Delocalization Energies (L_B, in Terms of β) on Complexation of Diene Units of the Complexes by Metal[a]

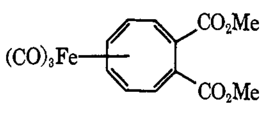
π system	Atoms complexed	L_B	ΔL_B	K_{EQ}
	5678	2.6403	0.0089	2.88
	3456	2.6314		
	4567	2.9546		
	3456	2.6605	0.079	14.2
	1234	2.5815		
	1234	2.6509	0.0005	2.95
	3456	2.6514		

[a] The calculations here are after A. Streitwieser ["Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 335]. The parameters used are those of Nicholson;[12] the resonance integral between carbons both of which are in a complexed butadiene was set at 0.5, that between carbons one of which is in a complexed and one of which is not in a complexed butadiene being 0.7. L_B is defined by Streitwieser as the decrease in delocalization energy on formation of the complex.

may represent a destabilization of the ground state of the complexes. This is reasonable if one considers that the balance between forebonding and backbonding between the iron tricarbonyl moiety and the ligand will be disturbed on introduction of either electron-attracting or -donating substituents onto the ligand. This argument assumes that unsymmetrical introduction of electronically different substituents should not cancel out the effect of each. In the Hückel approximation, introduction of strongly electron-donating and -attracting substituents at the two ends of a hexatriene builds up a marked alternation of charge along the chain. A destabilization of the complex resulting from an interaction of this type that is more or less evenly spread along the chain is in agreement with the observation that the equilibrium is disturbed to a lesser degree than the rate of attainment of equilibrium.

A somewhat related explanation for the seemingly unpredictable behavior of the iron tricarbonyl group in migrating up and down the polyene chain lies in the argument of Nicholson[12] in a related context that the important factor in determining the preferred site of binding of a low-valent metal to a polyene is changes in the localization energies associated with the effective removal of the complexed diene from electronic interaction with the remainder of the polyene. In fact Hückel calculations bear this out. In all cases calculated the isomer suffering the smallest loss in delocalization energy from partial tying up of its complexed diene is that isomer favored experimentally (Table III). The proposal that there is localization of the π system involved in interaction with the metal is strengthened by the observation that there is a decrease in conjugation between substituents separated by a complexed butadiene relative to the same substituents separated by an uncomplexed diene.[13] It is interesting to note that this localization must not be accompanied by any great degree of rehybridization of the terminal carbons of the complexed diene.

Our results in the acyclic series are not in qualitative agreement with the observations of Rubbs, *et al.*,[14] on the cyclooctatetraene complexes **21** and **22**. These workers observed that the effect of introduction of the indicated substituents was to freeze out the equilibrium to favor the complexes shown.



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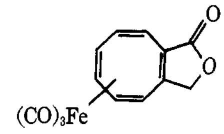

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Isomerization of Diaryloctatetraene Complexes. Quantitatively, the three sets of diaryloctatetraene–iron tricarbonyl complexes resemble the various hexatriene complexes studied above. Thus the position and rate of attainment of equilibrium of the two sets of compounds are similar to each other and the hexatriene complexes (Table IV). Comparison of the behavior of 1,8-diphenyloctatetraene complexes **6** and **7** with the 1,8-di(*p*-tolyl)octatetraene complex pair **23** and **24** shows the expected lack of change in rate or equilibrium on introduction of two *p*-methyl substituents. The equilibrium constant (terminal–internal complex) is 2.95 ± 0.25 in the former cases and 3.20 ± 0.23 in the latter case (for equilibration of the internal and *one* of the terminal isomers). The rates of equilibration are essentially the same in both cases. Comparison of the position of equilibrium in the unsymmetrical case, 1-phenyl-8-*p*-tolyl-1,3,5,7-octatetraene, with those of the

Table IV. Comparison of the Rate Constants for Interconversion of Internal (**7**, **24**, and **4**) and Terminal (**3**, **5**, **6**, and **24**) Isomers of the Diaryloctatetraeneiron Tricarbonyl Complexes

Complexes	Solvent	T, °C	$k \times 10^{-3}$	$k' \times 10^{-3}$
$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$	Toluene	99.39 ± 0.02	2.75 ± 0.18	0.93 ± 0.06
$\mathbf{23} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{24}$	Toluene	99.40 ± 0.01	3.68 ± 0.14	1.15 ± 0.04
$\mathbf{4} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{5}^{a,b}$	Toluene	99.41 ± 0.02	3.38 ± 0.24	1.09 ± 0.08
$\mathbf{4} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{3}^{a,c}$	Toluene	99.42 ± 0.02	3.77 ± 0.63	1.21 ± 0.30

[a] One-half of the rate constant for the reaction: $\mathbf{3} + \mathbf{5} \rightleftharpoons \mathbf{4}$. [b] From **5**. [c] From **3**.

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(12) B. J. Nicholson, *J. Amer. Chem. Soc.*, **88**, 5156 (1966).

(13) *E.g.*, failure of i to enolize at the 6 position under basic conditions (C. Reich, unreported).

$CH_3CH{=}CHCH{=}CHCHO{:}Fe(CO)_3$

i

(14) R. G. Rubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Amer. Chem. Soc.*, **89**, 6864 (1967).

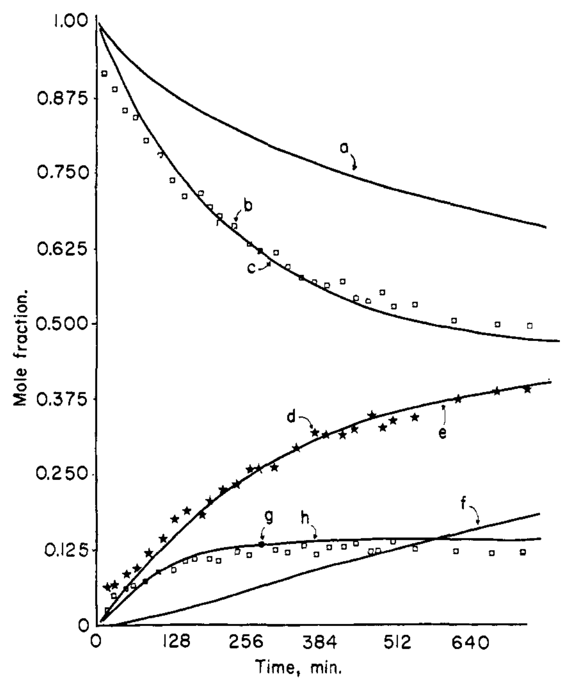
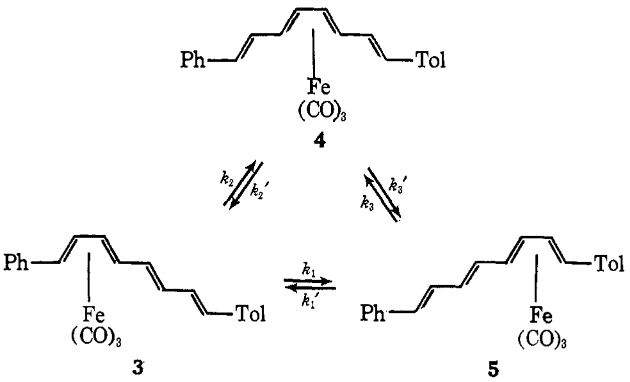


Figure 3. Experimental and calculated time–concentration plots for equilibration of **3**, **4**, and **5** starting from **5**: (a) calculated [**5**] for linear interconversion scheme using rate constants (Table IV) for the symmetrical complexes; (b) experimentally determined [**5**]; (c) calculated best fit [**5**] for cyclic scheme (Table IV); (d) experimental [**3**]; (e) "best fit" calculated [**3**] for cyclic scheme; (f) calculated [**3**] using rate constants for symmetrical complexes (Table IV) and assuming linear scheme; (g) experimental [**4**]; (h) calculated [**4**] for both linear and cyclic scheme. For further discussion of the calculations see the Experimental Section.

two symmetrical cases shows it to be in good quantitative agreement with them (**3**/**4** = 2.8 ± 0.4, **5**/**4** = 3.1 ± 0.5, **3**/**5** = 1.1 ± 0.2 at equilibrium starting from **3** and 3.2 ± 0.5, 3.5 ± 0.5, and 1.1 ± 0.2, respectively, starting from **5**). The experimental and several calculated time–concentration plots for interconversion of

Scheme II



the three shift isomers **3**, **4**, and **5** are presented in Figure 3. It is apparent that the reaction course calculated on the basis of a linear relationship between the three isomers, and using rate constants derived from the symmetrical complexes, does not satisfactorily reproduce the experimental observations. The calculated lag period for formation of **5** from **3** associated with the linear scheme could only be eliminated by increasing all rate constants by a factor of 4. We consider that this is an unreasonable set of values in view of the demonstrated similarity between this set of three shift isomers and the two symmetrical cases. The physical interpretation of the lack of a lag period associated with the formation of **3** from **5** (and *vice versa*) is that there is a pathway between these two terminal complexes that does not involve **4** as an intermediate. The cyclic scheme (Scheme II) satisfies this criterion and in fact the experimental observations can be reproduced in a satisfactory manner by using the rate constants based on the two symmetrical models. The set of rate constants associated with a best fit of the experimental data are, at 99.41° (Scheme II), $k_1 = k_1' = 1.3 \times 10^{-3}$ min^{-1}, $k_2 = k_3 = 1.04 \times 10^{-3}$ min^{-1}, and $k_2' = k_3' = 3.22 \times 10^{-3}$ min^{-1}. It is seen that **3** is formed from **5** at about the same rate as is **4**. There are a number of possible explanations for this peculiar behavior, but a partial representation of what appears to be the simplest is pictured in Scheme III. The accompanying argument is that migration of the iron tricarbonyl group along the polyene chain is competitive with (1) sequential rotation about the σ bond to regenerate the *s*-cis stereochemistry followed by (2) collapse to the pentacoordinate iron complex. This argument implies that there be a low activation energy for migration of the iron tricarbonyl group along the polyene chain. Although in the Hückel approximation the bond order between adjacent nondoubly bonded carbons increases with the length of the polyene chain,[15] it seems intuitively unreasonable that migration should be so fast as to compete with the two above processes. The superficial similarity between the migration of an iron tricarbonyl group along a polyene chain and around a cyclooctatetraene ring is just that. The open-chain counterpart of the process that (presumably) facilitates the migration in the cycloolefin case, coupled migration and valence tautomerization, would be interconversion of the two bonding situations **25** and **26**. Whether or not this is reasonable is difficult to say at present.

Experimental Section[16]

Analysis of Mixtures. Two-Component System. The isomerization of a two-component system, *e.g.*, **6** and **7**, was analyzed as follows. The infrared analysis was carried out using the formula

$$\frac{\mathbf{7}}{\mathbf{6}} = (D_{\mathrm{m}}^{\nu_1} D_6^{\nu_2} - D_{\mathrm{m}}^{\nu_2} D_6^{\nu_1})/(D_{\mathrm{m}}^{\nu_2} D_7^{\nu_1} - D_{\mathrm{m}}^{\nu_1} D_7^{\nu_2})$$

wherein D_{m}, D_6, and D_7 are optical densities of the mixture and compounds **6** and **7**, respectively; ν_1 and ν_2 refer to frequencies 987 and 965 cm^{-1}, respectively. In all cases a series of known mixtures was analyzed and compared with the values calculated as above. Calculated and experimental ratios were within 5% in all cases. A plot of log $(\mathbf{1} - \mathbf{7}_{\mathrm{eq}})/(\mathbf{7}_t - \mathbf{7}_{\mathrm{eq}})$ *vs.* time was constructed, where $\mathbf{7}_{\mathrm{eq}}$ and $\mathbf{7}_t$ refer to the mole fraction of **7** at equilibrium and time *t*, respectively. The least-squares slope of the plot was $(2k + k_1)2.303$ where k and k_1 refer to the forward and reverse rates for

$$\mathbf{7} \underset{k_1}{\overset{k}{\rightleftharpoons}} \mathbf{6}$$

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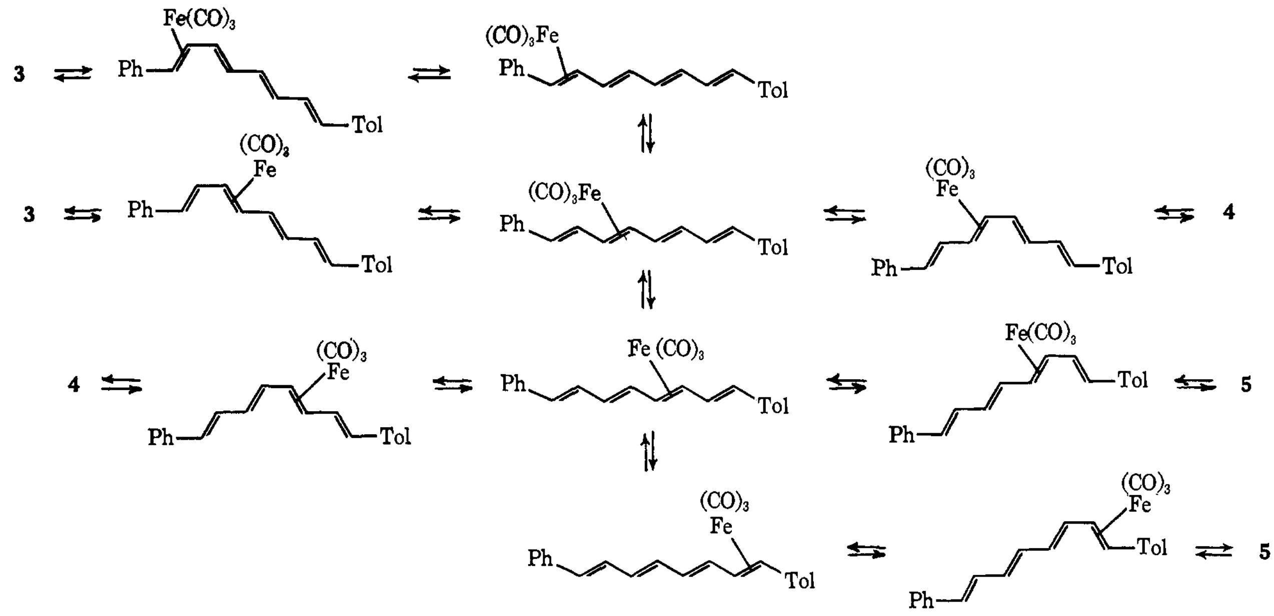
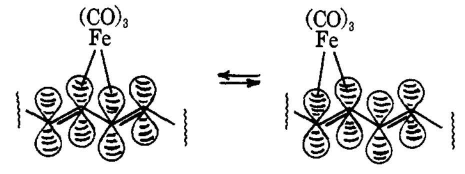
[15] E. Heilbronner, "Huckel Molecular Orbitals," Springer Verlag, New York, N. Y., 1966.

[16] "Work-up" entails partitioning of the reaction mixture between water and ether, washing the ether layer with water and saturated salt solution, drying over anhydrous sodium sulfate, and evaporation. Nmr spectra were determined at 60 MHz unless noted otherwise. Mass spectra were determined on a CEC-103C mass spectrometer at 70 eV nominal.

Scheme III. Proposed "Cyclic" Interconversion of **3**, **4**, and **5**





25 **26**

The 2*k* arises from the two ways of forming **6**. A plot from the interconversion of **7** and **6** at 119.4° in toluene is presented in Figure 1.

Three-Component Systems. The isomerization of **3**, **4**, and **5** was analyzed by infrared analysis according to the formulas

$$\frac{\mathbf{3}}{\mathbf{4}} = (D_{\mathrm{m}}^{\nu_1}(D_5^{\nu_2}D_4^{\nu_3} - D_4^{\nu_2}D_5^{\nu_3}) - D_{\mathrm{m}}^{\nu_2}(D_5^{\nu_1}D_4^{\nu_3} - D_4^{\nu_1}D_5^{\nu_3}) + D_{\mathrm{m}}^{\nu_3}(D_5^{\nu_1}D_4^{\nu_2} - D_4^{\nu_1}D_5^{\nu_2})/D_{\mathrm{m}}^{\nu_1}(D_3^{\nu_2}D_5^{\nu_3} - D_5^{\nu_2}D_3^{\nu_3}) - D_{\mathrm{m}}^{\nu_2}(D_3^{\nu_1}D_5^{\nu_3} - D_5^{\nu_1}D_3^{\nu_3}) + D_{\mathrm{m}}^{\nu_3}(D_3^{\nu_1}D_5^{\nu_2} - D_5^{\nu_1}D_3^{\nu_2}))$$

$$\frac{\mathbf{5}}{\mathbf{4}} = D_{\mathrm{m}}^{\nu_1}(D_3^{\nu_2}D_4^{\nu_3} - D_4^{\nu_2}D_3^{\nu_3} - D_{\mathrm{m}}^{\nu_2}(D_3^{\nu_1}D_4^{\nu_3} - D_4^{\nu_1}D_3^{\nu_3}) + D_{\mathrm{m}}^{\nu_3}(D_3^{\nu_1}D_4^{\nu_2} - D_4^{\nu_1}D_3^{\nu_2}))/D_{\mathrm{m}}^{\nu_2}(D_3^{\nu_1}D_5^{\nu_3} - D_5^{\nu_1}D_3^{\nu_3}) - D_{\mathrm{m}}^{\nu_2}(D_3^{\nu_1}D_5^{\nu_3} - D_5^{\nu_1}D_3^{\nu_3}) + D_{\mathrm{m}}^{\nu_3}(D_3^{\nu_1}D_5^{\nu_2} - D_5^{\nu_1}D_3^{\nu_2}))$$

wherein D_{m}, D_3, and D_5 are optical densities for the mixture **3**, **4**, and **5**, respectively; ν_1, ν_2, and ν_3 refer to frequencies 962, 810, and 754 cm^{-1}, respectively. A series of known mixtures was prepared and analyzed over the entire range of pertinent ratios. A Beers law relationship was found to be valid. The results of isomerization are given in Table V and plotted in Figure 3. The integrated rate expressions for a system of three components, all in equilibrium with one another, have been reported.[17] The rate constants used for initial calculation of the time–concentration plot of the interconversion of **4** with **3** and **5** are taken from the experimental values for the symmetrical systems **7** and **6** and **23** and **24**. The rate constants for the interconversion of **3** and **5** were set equal to each other and were set equal to zero for a linear mechanism or systemically varied to a graphical fit for a cyclic mechanism. The results of these calculations are plotted along with the experimental values in Figure 3.

Table V. Mole Fractions of **3**, **4**, and **5**, Formed on Heating **5** in Degassed Toluene Solution at 99.41 ± 0.02°[a]

3	**4**	**5**	Time, min
5.7	2.7	91.6	16
6.3	4.5	89.2	32
8.1	5.8	86.1	49
9.5	6.2	84.3	66
11.7	7.5	80.8	87
13.3	8.7	78.0	108
16.8	9.1	74.1	131
18.3	10.4	71.3	153
18.0	10.7	71.3	174
20.0	10.6	69.4	195
21.5	10.5	68.0	212
22.5	10.5	66.0	238
25.0	11.8	63.2	260
25.3	12.8	61.9	281
25.9	12.2	61.9	304
28.5	12.2	59.3	326
29.3	12.9	57.8	348
31.5	11.9	56.6	370
31.0	12.7	56.3	392
30.8	12.9	56.3	417
32.2	13.4	54.1	441
33.9	12.5	53.6	463
32.5	12.5	55.0	484
33.4	13.5	53.1	503
34.5	12.6	52.9	540
36.8	12.6	50.6	607
37.9	12.2	49.9	676
38.5	12.4	49.1	729
40.0	12.2	47.8	783
40.3	12.0	47.7	845

[a] Infrared analysis as in the text. The data are plotted in Figure 1.

***trans,trans,trans*-7-*p*-Tolyl-2,4,6-heptatrienal.** The general procedure of Marshall and Whiting[18] was used. To a stirred solution of ethylmagnesium bromide in tetrahydrofuran, from 4.85 g (0.2 g-atom) of magnesium and 31.8 g (0.2 mol) of ethyl bromide in 100 ml of tetrahydrofuran, was added 16.4 g (0.2 mol) of 1-methoxy-1-buten-3-yne in 30 ml of tetrahydrofuran. After stirring at 25°

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(17) W. O. Haag and H. Pines, *J. Amer. Chem. Soc.*, **82**, 387 (1960).

(18) D. Marshall and M. C. Whiting, *J. Chem. Soc.*, 4082 (1956).

for 1 hr, a solution of 26.4 g (0.18 mol) of *p*-methylcinnamaldehyde in 50 ml of tetrahydrofuran was added dropwise with cooling over 1 hr. The reaction mixture was stirred for 4 hr, cooled to 5°, and 10 ml of ethanol was added. After 45 min at room temperature the reaction mixture was again cooled to 5° and 6.9 g (0.18 mol) of lithium aluminum hydride was added over 1 hr. After stirring at room temperature for 12 hr the reaction mixture was treated with 200 ml of 5 *N* sulfuric acid and worked up to afford on recrystallization (benzene–hexane) 13 g (38% yield of *trans,trans,-trans*-7-*p*-tolyl-2,4,6-heptatrienal as yellow needles, mp 108–110° (benzene–hexane); mp 108–110°; $\lambda_{max}^{CHCl_3}$ 3.55 μ, 3.65, 6.0; δ (CDCl$_3$) 9.52 (1 H, C*H*O, doublet, $J_{12} = 8$ Hz).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.82; H, 7.12. Found: C, 84.70; H, 7.23.

trans,trans-**2,4-Pentadienal** was prepared by the above procedure from formaldehyde in 32% yield, bp 46° (30 mm) (lit.[19] bp 36–37° (32 mm)); δ (CDCl$_3$) 9.57 (1 H, C*H*O), doublet, $J_{12} = 8.0$ Hz).

trans,trans,trans-**7-Phenyl-2,4,6-heptatrienal** was prepared from cinnamaldehyde by the above procedure in 32% yield as yellow diamonds: mp 115–116.0° (benzene) (lit.[20] mp 116°); δ (CDCl$_3$) 9.53 (1 H, C*H*O, doublet, $J_{12} = 7.5$ Hz).

trans,trans-**2,3-Hexanedienedial** was prepared from 2,4-hexadienediol[21] by the general procedure of Attenburrow, *et al.*,[22] in 43% yield, mp 108–113° (lit.[23] mp 112°); δ (CDCl$_3$) 9.77 (2 H, C*H*O, doublet, $J_{12} = 8$ Hz); $\lambda_{max}^{CHCl_3}$ 3.53 μ, 3.64 5.95, 6.30.

trans,trans-5-(3,4-Dichlorophenyl)-2,4-pentadienal was prepared by the above procedure from 3,4-dichlorobenzaldehyde in 34% yield as light yellow plates, mp 124.0–125.0°.

Anal. Calcd for $C_5H_8Cl_2O$: C, 58.18; H, 3.56; Cl, 31.22. Found: C, 58.12; H, 3.59; Cl, 31.31.

2,4-Hexadienedial-2,3,4,5-*tetrahapto*iron Tricarbonyl (9). A mixture of 7.0 g of 2,4-hexadienedial, 160 ml of iron pentacarbonyl, and 25 ml of benzene was heated under reflux with stirring under nitrogen for 114 hr. The reaction mixture was diluted with hexane and filtered, and the filtrate was evaporated. The residue was recrystallized from benzene to afford 0.75 g (5% yield) of the title complex as orange plates, mp 97–98°.

Anal. Calcd for $C_9H_6O_5Fe$: C, 43.24; H, 2.42; Fe, 22.34. Found: C, 43.11; H, 2.37; Fe, 22.58.

2,4-Pentadienal-2,3,4,5-*tetrahapto*iron Tricarbonyl (30). A mixture of 3.0 g of 2,4-pentadienal and 15.3 g of triiron dodecacarbonyl in 50 ml of benzene was heated under reflux under nitrogen for 5 hr. The reaction was followed by observing the decrease in the 6.2-μ ir band of the free ligand and was stopped when this band disappeared. The reaction mixture was cooled and filtered, and adsorbed on a column of silica gel. Elution with ethyl acetate–benzene (5:95) and distillation of the eluate, 50° (0.01 μ), afforded 2.0 g (25% yield) of **30** as an orange viscous oil: δ (CDCl$_3$) 9.32 (1 H, C*H*O, doublet, $J_{12} = 4.1$ Hz).

Anal. Calcd for $C_8H_6O_4Fe$: C, 43.28; H, 2.73; Fe, 25.16

5-(3,4-Dichlorophenyl)-2,4-pentadienal-2,3,4,5-*tetrahapto*iron Tricarbonyl (32). Reaction of the aldehyde with triiron dodecacarbonyl in benzene as above afforded **32** in 55% yield as orange prisms, mp 186.5–187.5°.

Anal. Calcd for $C_{14}H_8O_4Cl_2Fe$: C, 45.82; H, 2.20; Fe, 15.22. Found: C, 46.04; H, 2.15; Fe, 15.27.

trans,trans-p-**Methoxyphenyl-2,4-pentadienal-2,3,4,5-*tetrahapto*iron Tricarbonyl (31).** Reaction of the corresponding aldehyde with triiron dodecacarbonyl in benzene as above afforded **31** in 52% yield as orange prisms, mp 119.5–120°

Anal. Calcd for $C_{15}H_{22}O_5Fe$: C, 54.91; H, 3.69; Fe, 17.02. Found: C, 55.01; H, 3.81; Fe, 16.90.

5-*p*-Tolyl-2,4-pentadienal-2,3,4,5-*tetrahapto*iron Tricarbonyl (27). (The following is a distinctly better preparation of this compound than that from iron pentacarbonyl.[1]) A mixture of 11.0 g (64 mmol) of 5-*p*-tolyl-2,4-pentadienal and 26.5 g (53 mmol) of triiron dodecarbonyl[24] in 50 ml of benzene was heated under nitrogen with stirring at 60° for 115 min. The reaction was monitored periodically by withdrawing small samples and following the disappearance of the 6.15-μ (C=C) absorption band due to uncomplexed ligand in the sample. Continued reaction after disappearance of this band rapidly led to complete decomposition of the complex. The cooled reaction mixture was filtered and evaporated and the residue was adsorbed on a column of 500 g of silica gel. Elution first with benzene and then with benzene–ethyl acetate (20:1) afforded 13.8 g (69% yield) of **27**, mp 139.5–142.5° after recrystallization from ethyl acetate: $\lambda_{max}^{CHCl_3}$ 4.92 μ, 5.06 (FeC=O), 6.0 (HC=O).

Anal. Calcd for $C_{15}H_{12}O_4Fe$: C, 57.72; H, 3.88; Fe, 17.89. Found: C, 57.68; H, 3.90; Fe, 18.00.

1,8-Diphenyl-1,3,5,7-octatetraene-1,2,3,4-*tetrahapto*- (6) and -3,4,-5,6-*tetrahapto*iron Tricarbonyl (7). Reaction of 1.00 g of 1,8-diphenyl-1,3,5,7-octatetraene with 1.95 g of triiron dodecacarbonyl in 40 ml of refluxing benzene for 3.5 hr afforded on filtration 2.2 g of a mixture of starting tetraene and triiron dodecacarbonyl. Chromatography of the filtrate afforded 325 mg of an 85:15 mixture (by ir) of **6** and 7. When a mixture of 11 mg of diphenyloctatetraene, 80 mg of **7**, and 22 mg of triiron dodecacarbonyl was treated under the above reaction conditions, there was recovered by filtration 23 mg of a mixture of ligand and iron carbonyl and by chromatography of the filtrate 74 mg of 58:42 mixture of terminal–internal complex.

7-*p*-Tolyl-2,4,6-heptatrienal-2,3,4,5-*tetrahapto*- (29) and -4,5,6,7-*tetrahapto*iron Tricarbonyl (28) and -*O*,1,2,3,4,5,6,7-bis*tetrahapto*diiron Hexacarbonyl (14). With infrared monitoring of the 6.2-μ (C=C) infrared band of aliquots, a mixture of 6.84 g (34.5 mmol) of 7-*p*-tolyl-2,4,6-heptatrienal and 17.4 g (34.5 mmol) of triiron dodecacarbonyl in 50 ml of benzene was heated at 75° with stirring under nitrogen for 3 hr. The reaction mixture was cooled, filtered, concentrated, and adsorbed on a column of 500 g of silica gel. Elution with benzene removed residual triiron dodecacarbonyl that was discarded. Elution with benzene–ethyl acetate (9:1) afforded 7.6 g of a yellow solid. This was readsorbed on a column of 1 kg of silica gel. Elution with benzene–ethyl acetate (99:1) afforded the following materials.

A faster moving red band was found that afforded 2.5 g of an orange solid. Trituration of this with benzene afforded the benzene-insoluble *0*,1,2,3,4,5,6,7-bis*tetrahapto*diiron hexacarbonyl complex **14** [400 mg; mp 123° dec; $\lambda_{max}^{CHCl_3}$ 4.80 μ, 4.90, 5.0 (broad, Fe$_2$-(CO)$_3$), no 6 μ or 3.6 μ maxima; δ_{CDCl_3} 7.42 (1 H, C*H*O, singlet), 7.05 (4 H, Ar*H*, broadened singlet), 5.47–5.87 (3 H, *H*2, *H*5, *H*6, multiplet), 2.27 (3 H, ArC*H*$_3$, singlet), 2.42 (1 H, *H*4, triplet, $J_{43} = J_{45} = 9$ Hz), 2.20 (1 H, *H*7, doublet, $J_{67} = 8$ Hz), 1.25 (1 H, *H*3, double doublet, $J_{23} = 8$ Hz, $J_{34} = 9$ Hz) (*Anal.* Calcd for $C_{20}H_{14}O_7Fe_2$: C, 50.26; H, 2.95; Fe, 23.37. Found: C, 50.39; H, 2.86; Fe, 23.04)] and benzene-soluble 7-*p*-tolyl-2,4,6-heptatrienal-2,3,4,5-*tetrahapto*iron tricarbonyl complex **29** [1.7 g; mp 115–117° after one recrystallization from benzene–hexane; δ_{CDCl_3} 9.30 (1 H, C*H*O, doublet, $J_{12} = 4.5$ Hz), 7.17 (4 H, Ar*H*, multiplet), 6.47 (2 H, *H*6, *H*7, AB part of a first-order ABX pattern, $J_{67} = 15.5$ Hz, $J_{56} = 9.0$ Hz), 5.63 (2 H, *H*3, *H*4, multiplet), 2.30 (3 H, ArC*H*$_3$, singlet), 1.55 (1 H, *H*2, double doublet, $J_{23} = 8$ Hz, $J_{12} = 4.5$ Hz) (*Anal.* Calcd for $C_{17}H_{14}O_4Fe$: C, 60.40; H, 4.17; Fe, 16.52. Found: C, 60.11; H, 4.20; Fe, 17.57)].

A slower moving orange band was found, 1.4 g, mp 171–174° after recrystallization from benzene, identified as the 7-*p*-tolyl-2,4,6-heptatrienal-4,5,6,7-*tetrahapto*iron tricarbonyl complex **28**: δ_{CDCl_3} 9.45 (1 H, C*H*O, doublet, $J_{12} = 7.5$ Hz), 7.12 (4 H, Ar*H*, singlet), 6.43 (2 H, *H*2, *H*3, AB part of an ABXY pattern), 5.73 (2 H, *H*5, *H*6, AB part of an ABXY pattern), 2.62 (1 H, *H*7, doublet, $J_{67} = 9$ Hz), 2.28 (3 H, ARC*H*$_3$, singlet), 2.00 (1 H, *H*4, triplet, $J_{34} = J_{45} = 9$ Hz). Spin decoupling confirmed the following first-order coupling constants: $J_{23} = 15$ Hz, $J_{34} = 9$ Hz, $J_{45} = 9$ Hz, $J_{56} = 5$ Hz, $J_{67} = 9$ Hz (*Anal.* Calcd for $C_{17}H_{14}O_4Fe$: C, 60.40; H, 4.17; Fe, 16.52. Found: C, 60.69; H, 4.22; Fe, 16.62).

Reaction of 7-Phenyl-2,4,6-heptatrienal with Triiron Dodecacarbonyl. 7-Phenyl-2,4,6-heptatrienal-2,3,4,5- (11) and -4,5,6,7-*tetrahapto*iron Tricarbonyl (10) and 7-Phenyl-2,4,6-heptatrienal-*O*,1,2,3,4,5,6,7-bis*tetrahapto*diiron Hexacarbonyl (13). A mixture of 5.66 g of *trans,trans,trans*-7-phenyl-2,4,6-heptatrienal and 15.7 g of triiron dodecacarbonyl in 50 ml of benzene was heated at 70° under nitrogen for 4.75 hr. As the reaction proceeded, the ir band at 6.2 μ due to uncomplexed ligand decreased in intensity to a small but constant value. The reaction mixture was cooled and filtered, and the filtrate was adsorbed onto a column of 500 g of silica gel. Elution with ethyl acetate-benzene (1:9) followed by rechromatography and recrystallization of the eluate afforded, in order of elution, (1) 7-phenyl-2,4,6-heptatrienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**11**) [5.58 g (55% yield), orange stars, mp 110.5–112.0° (benzene–ethyl acetate); δ_{CDCl_3} 9.30 (1 H, C*H*O, doublet, J_{12} =

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(19) G. F. Woods and H. Sanders, *J. Amer. Chem. Soc.*, **68**, 2483 (1946).

(20) J. Schmitt, *Justus Liebigs Ann. Chem.*, **547**, 270 (1941).

(21) A modification of the procedure of F. B. Bates, E. R. H. Jones, and M. C. Whiting [*ibid.*, 1854 (1954)] was used.

(22) A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and J. Attenburrow, *J. Chem. Soc.*, 1094 (1952).

(23) S. M. Makin and N. I. Telegina, *Zh. Obshch. Khim.*, **32**, 1104 (1962).

(24) R. B. King in "Organometallic Syntheses," Vol. I, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N. Y., 1965, p 95.

4.0 Hz), 2.57 (1 H, *H*5, triplet $J_{56} = J_{45} = 9.0$ Hz), 1.57 (1 H, *H*2, double doublet, $J_{12} = 4.0$ Hz, $J_{23} = 8.0$ Hz) (*Anal.* Calcd for $C_{16}H_{12}O_4Fe$: C, 59.27; H, 3.73; Fe, 17.24. Found: C, 59.12; H, 3.75, Fe, 17.06)]; (2) 7-phenyl-2,4,6-heptatrienal-4,5,6,7-*tetrahapto*iron tricarbonyl (**10**) [1.53 g (15% yield) red prisms, mp 169.5–171.0° (ethyl acetate); $\delta_{\mathrm{CDCl_3}}$ 9.52 (1 H, doublet C*H*O, $J_{12} = 8.0$ Hz), 2.61 (1 H, doublet, *H*7, $J_{67} = 9.5$ Hz), 2.02 (1 H, triplet, *H*4, $J_{34} = J_{45} = 8.5$ Hz) (*Anal.* Calcd for $C_{16}H_{12}O_4Fe$: C, 59.27; H, 3.73; Fe, 17.24. Found: C, 59.40; H, 3.76; Fe. 16.95)]; (3) 7-phenyl-2,4,6-heptatrienal-*0*,1,2,3,4,5,6,7-bis*tetrahapto*diiron hexacarbonyl (**13**) [orange plates, dec 135°, *ca.* 1% yield; $\delta_{\mathrm{CDCl_3}}$ 7.42 (1 H, C*H*O, singlet), 2.78 (Ar*H*, broad singlet, 5 H), 5.5–5.9 (3 H, multiplet, *H*2, *H*5, *H*6), 2.59 (1 H, *H*7, doublet, $J_{67} = 9$ Hz), 7.75 (1 H, *H*4, triplet, $J_{45} = J_{34} = 8.5$ Hz), 8.70 (1 H, *H*3, $J_{23} = 11$ Hz, $J_{34} = 8$ Hz) *Anal.* Calcd for $C_{19}H_{12}O_7Fe_2$: C, 49.18; H, 2.61; Fe, 24.07. Found: C, 49.35; H, 2.57; Fe, 24.20)].

Polyene–*Tetrahapto*iron Tricarbonyl Complexes *via* the Wittig Condensation. The general procedure is illustrated by the preparation of 1,8-diphenyl-1,3,5,7-octatetraene-3,4,5,6-*tetrahapto*iron tricarbonyl (**7**).

(a) To a stirred solution of benzylidenetriphenylphosphorane, from 2.21 g (5.70 mmol) of benzyltriphenylphosphonium chloride and 1.73 ml of 2.20 *M* butyllithium in hexane in 100 ml of tetrahydrofuran, was added a solution of 1.0 g (3.08 mmol) of 7-phenyl-2,4,6-heptatrienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**11**) in 20 ml of tetrahydrofuran. The reaction mixture was stirred at 0° under nitrogen for 2 hr and worked up. The crude product, 2.13 g, was adsorbed on a column of 100 g of silica gel. Elution with benzene and recrystallization (benzene) gave 790 mg (64% yield) of **7** as red needles: mp 157–159°; $\delta_{\mathrm{CDCl_3}}$ 2.27 (2 H, *H*3, *H*6, double doublet, $J_{23} = J_{67} = 8.7$ Hz, $J_{34} = J_{56} = 8.7$ Hz), 5.30 (2 H, *H*4, *H*5, doublet, $J_{34} = J_{56} = 7.5$ Hz); the AB part of an ABX pattern centered at δ 6.47, area 4 H, a broad singlet at δ 7.27, ArH. Spin decoupling confirmed the above coupling constants.

Anal. Calcd for $C_{23}H_{18}O_3Fe$: C, 69.39; H, 4.54; Fe, 14.02. Found: C, 69.21; H, 4.21; Fe, 14.14.

(b) From benzylidenetriphenylphosphorane and 2,4-hexadienedial-2,3,4,5-*tetrahapto*iron tricarbonyl (**9**) under the above conditions in 25% yield. Use of a 1:1 ratio of ylide–**9** did not allow the isolation of **11**; only the octatetraene complex was isolated.

1,8-Diphenyl-1,3,5,7-octatetraene-1,2,3,4-*tetrahapto*iron Tricarbonyl (6). Reaction between benzylidenetriphenylphosphorane and 1-phenyl-2,4,6-heptatrienal-4,5,6,7-*tetrahapto*iron tricarbonyl (**10**), same scale and conditions as above, afforded on work-up 1.16 g of crude product Chromatography of this as above afforded 337 mg (50% yield) of **6**, mp 161–162° Salient features of its nmr spectrum were $\delta_{\mathrm{CDCl_3}}$ 2.30 (1 H, *H*1, doublet, $J_{12} = 9.3$ Hz) and 2.25 (1 H, *H*4, triplet, $J_{34} = J_{45} = 9.3$ Hz).

Anal. Calcd for $C_{23}H_{18}O_3Fe$: C, 69.39, H, 4.54; Fe, 14.02. Found: C, 69.27; H, 4.25; Fe, 14.20.

1,8-Ditolyl-1,3,5,7-octatetraene-1,2,3,4-*tetrahapto*iron tricarbonyl (23) was prepared as above from 5-*p*-tolyl-2,4-pentadienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**27**) and *p*-methylcinnamylidenetriphenylphosphorane in 67% yield, orange-yellow needles: mp 159.0–160.0° (benzene–hexane), $\delta_{\mathrm{CDCl_3}}$ 2.25 (8 H, ArC*H*$_3$, *H*1, *H*4, broadened singlet).

Anal. Calcd for $C_{25}H_{22}O_3Fe$: C, 70.44; H, 5.20; Fe, 13.10. Found: C, 70.72; H, 5.16; Fe, 13.34.

1,8-Ditolyl-1,3,5,6-octatetraene-3,4,5,6-*tetrahapto*iron tricarbonyl (24) was prepared as above from 7-*p*-tolyl-2,4,6-heptatrienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**29**) and *p*-methylbenzylidenetriphenylphosphorane in 49% yield as orange-yellow needles: mp 160.0–161.0° (benzene–hexane); $\delta_{\mathrm{CDCl_3}}$ 2.28 (8 H, ArC*H*$_3$, *H*3, *H*6, broadened singlet).

Anal. Calcd for $C_{25}H_{22}O_3Fe$: C, 70.44; H, 5.20; Fe, 13.10. Found: C, 70.72; H, 5.16; Fe, 13.34. A mixture melting point of **23** and **24** was 152–159°.

1-Phenyl-8-*p*-tolyl-1,3,5,7-octatetraene-5,6,7,8-*tetrahpato*iron tricarbonyl (5) was prepared as above from cinnamylidenetriphenylphosphorane and 5-*p*-tolyl-2,4-pentadienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**27**) in 63% yield: mp 164.5–166.0°; yellow-orange plates (benzene–hexane); $\delta_{\mathrm{CDCl_3}}$ 2.27 (5 H, ArC*H*$_3$, *H*1, *H*4, singlet.

Anal. Calcd for $C_{24}H_{20}Fe$: C, 69.92; H, 4.89. Found: C, 70.17; H, 5.02; Fe, 13.48.

1-Phenyl-8-*p*-tolyl-1,3,5,7-octatetraene-3,4,5,6-*tetrahapto*iron tricarbonyl (4) was prepared as above from *p*-methylbenzylidene triphenylphosphorane and **11** in 44% yield: mp 134.5–136° (benzene–hexane); orange-yellow needles, $\delta_{\mathrm{CDCl_3}}$ 2.28 (5 H, ArC*H*$_3$, *H*3, *H*6, singlet).

Anal. Calcd for $C_{24}H_{20}O_3Fe$: C, 69.92; H, 4.89; Fe, 13.55. Found: C, 69.73; H, 4.78; Fe, 13.80.

1-Phenyl-8-*p*-tolyl-1,3,5,7-octatetraene-1,2,3,4-*tetrahapto*iron carbonyl (3) was prepared as above from *p*-methylcinnamylidenetriphenylphosphorane and **12** in 65% yield: mp 144.5–146° (benzene–hexane); fine orange needles, $\delta_{\mathrm{CDCl_3}}$ 2.31 (5 H, ArC*H*$_3$, *H*1, *H*4, broadened singlet).

Anal. Calcd for $C_{24}H_{20}O_3Fe$: C, 69.92; H, 4.89; Fe, 13.55. Found: C, 69.99; H, 4.86; Fe, 13.79.

1-*p*-Tolyl-1,3,5-hexatriene-1,2,3,4-*tetrahapto*iron tricarbonyl (19) was prepared as above from **27** and methylenetriphenylphosphorane in tetrahydrofuran: yellow plates, mp 69.5–72.0°, 55% yield: $\delta_{\mathrm{CDCl_3}}$ 2.27 (3 H, ArC*H*$_3$, singlet), 2.27 (1 H, *H*1, doublet, $J_{12} = 9.5$ Hz), 2.05 (1 H, *H*4, triplet, $J_{34} = J_{45} = 9.0$ Hz); $\nu_{\mathrm{max}}^{\mathrm{CS_2}}$ 990 cm^{-1}, 900 cm^{-1} (vinyl).

Anal. Calcd for $C_{16}H_{14}O_3Fe$: C, 61.97; H, 4.55; Fe, 18.01. Found: C, 62.38; H, 4.80; Fe, 17.74.

1-*p*-Tolyl-1,3,5-hexatriene-3,4,5,6-*tetrahapto*iron tricarbonyl (20) was prepared as above from 2,4-pentadienal-2,3,4,5-*tetrahapto*iron tricarbonyl (**30**) and *p*-methylbenzylidenetriphenylphosphorane in 86% yield: mp 72.0–73.0°, orange rhombs; $\delta_{\mathrm{CDCl_3}}$ 2.28 (3 H, ArC*H*$_3$, singlet), 1.93 (triplet, 1 *H*, *H*3, $J_{43} = J_{23} = 8.7$ Hz), 1.77 (multiplet, 1 H, *H*6 (*anti*)), 9.48 (1 H, double doublet, *H*6 (syn)), $J_{6s6a} = 2.6$ Hz, $J_{6s5} = 8.5$ Hz); $\nu_{\mathrm{max}}^{\mathrm{CS_2}}$ 963 cm^{-1} (trans CH═CH).

Anal. Calcd for $C_{16}H_{14}O_3Fe$: C, 61.97; H, 4.55; Fe, 18.01. Found: C, 62.23; H, 4.70; Fe, 17.90.

1-*p*-Methoxyphenyl-6-(3,4-dichlorophenyl)-1,3,5-hexatriene-1,2,-3,4-*tetrahapto*iron tricarbonyl (17) was prepared as above from 3,4-dichlorobenzylidenetriphenylphosphorane and **31** in 70% yield, mp 170–171.5°

Anal. Calcd for $C_{22}H_{16}O_3Cl_2Fe$: C, 56.08; H, 3.31; Fe, 11.85. Found: C, 56.05; H, 3.47; Fe, 12.23.

1-*p*-Methoxyphenyl-6-(3,4-dichlorophenyl)-1,3,5-hexatriene-3,4,-5,6-*tetrahapto*iron tricarbonyl (18) was prepared as above from *p*-methoxybenzylidenetriphenylphosphorane and **32** in 54% yield, mp 152–153°.

Anal. Calcd for $C_{22}H_{16}O_3Cl_2Fe$: C, 56.08; H, 3.31; Fe, 11.85. Found: C, 56.25; H, 3.52; Fe, 12.09.

1-Phenyl-6-(*p*-methoxyphenyl)-1,3,5-hexatriene-1,2,3,4-*tetrahapto*iron tricarbonyl (16) was prepared as above from *p*-methoxybenzylidenetriphenylphosphorane and **12** in 74% yield, mp 141–142°.

Anal. Calcd for $C_{22}H_{18}O_4Fe$: C, 65.69; H, 4.62; Fe, 13.89. Found: C, 65.74; H, 4.62; Fe, 14.18.

1-Phenyl-6-(*p*-methoxyphenyl)-1,3,5-hexatriene-3,4,5,6-*tetrahapto*iron tricarbonyl (15) was prepared as above from benzylidenetriphenylphosphorane and **31** in 64% yield, mp 161–163°.

Anal. Calcd for $C_{22}H_{18}O_4Fe$: C, 65.79; H, 4.62; Fe, 13.89. Found: C, 65.74; H, 4.61; Fe, 14.19.

Interconversion of 10 and 11. A degassed (10^{-5} mm) 0.094 *M* solution of **11** in diethylene glycol dimethyl ether in a sealed nmr tube was heated at 64.93 ± 0.01°. At intervals the nmr tube was removed from the bath and quenched in an ice bath, and the spectrum was determined. The progress of the reaction was followed by observing the change in the aldehyde hydrogens' signals (δ 9.31, $J_{12} = 4.0$ Hz for the 2,3,4,5-*tetrahapto* complex **11** and δ 9.54, $J_{12} = 8.0$ Hz for the 4,5,6,7-*tetrahapto* complex **10**. At the end of 70 hr the ratio **11**:**10** was 2.88. A least-squares plot of log ((1 − [**11**]$_t$/[**11**]$_t$ − [**11**]$_{\mathrm{eq}}$) *vs.* time afforded the rate constant $k_{11\rightarrow10} = 1.20 \pm 0.06 \times 10^{-3}$ min^{-1} at 64.93°. The equilibrium mixture of the two complexes was separated by chromatography and the components were identified by comparison with authentic samples.

Interconversion of 6 and 7. Interconversions were carried out in dilute degassed toluene solutions in sealed tubes in the dark. For analysis a tube was opened, solvent was removed, and the residue was dissolved in carbon disulfide and subjected to infrared analysis.[17] (The 987-cm^{-1} band of **6** and the 965-cm^{-1} band of **7** were used.) Samples consisted of 4.5 ± 0.5 mg in 0.04 ml of carbon disulfide. Least-squares analysis of the data as above afforded $k_{7\rightarrow6} = 2.10 \pm 0.13 \times 10^{-4}$ min^{-1} at 78.45°. Equilibrium constants, K_{eq} = [**6**]/[**7**] = 2.95 ± 0.25 (toluene) or 3.30 ± 0.28 (diglyme), were obtained on heating either isomer in the appropriate solvent of 99° for 35 hr.

Interconversion of 23 and 24. The 986-cm^{-1} ir band of **23** and the 966-cm^{-1} band of **24** were used to monitor mixtures of the two complexes. Analysis of the data as above afforded $k_{24\rightarrow23} = 3.68 \pm 0.14 \times 10^{-3}$ min^{-1} at 99.40° and K_{eq} = [**23**]/[**24**] = 3.20 ± 0.23 in degassed toluene solution.

Interconversion of 19 and 20. Infrared analysis, using the 963-cm^{-1} ir band of **19** and the 900-cm^{-1} band of **20**, was employed to analyze mixtures of the two complexes. Equilibrium, K_{eq} = [**20**]/[**19**] = 14.2 ± 0.2, was approached from both complexes. Least-squares analysis as above afforded $k_{19\rightarrow20}$ = 5.32 ± 0.32 × 10^{-3} min^{-1} at 119.55 ± 0.05° in degassed toluene solution. The complexes could not be separated by chromatography.

Interconversion of the Isomeric 1-*p*-Methoxyphenyl-6-(3,4-dichlorophenyl)-1,3,5-hexatriene*tetrahapto*iron Tricarbonyl Complexes (17) and (18). The isomerization was approached from both directions, using **17**-*4*-d_1 and **18**-*3*-d_1.[25] In the nmr spectra of each of these deuterated complexes, the ratio of the upfield olefinic hydrogen peaks to the methoxy hydrogen peak is 1:3, while in the spectra of their shift isomers **16**-*4*-d_1 and **12**-*3*-d_1, respectively, the ratio is 2:3. Therefore the ratio varies over the interval 0.333–0.667 on equilibrating **17**-*4*-d_1 and **18**-*4*-d_1, and **18**-*3*-d_1 and **17**-*3*-d_1. Integration of the two areas (20 integrals) after heating dilute degassed tetrahydrofuran solutions of the two complexes at 110° for 19 half-lives and isolation of the mixture of complexes by chromatography afforded K_{eq} = (**18**)/(**17**) = 55/45 = 1.26 ± 0.02. Analysis of the first-order equilibration rate at 100.08 ± 0.02° afforded $k_{17\rightarrow18}$ = 4.4 ± 0.3 × 10^{-3} min^{-1}.

Interconversion of the Two Isomers of 1-Phenyl-7-anisyl-1,3,5-hexatriene*tetrahapto*iron Tricarbonyl. The ratio of **16** and **15** was determined by taking advantage of the small separation of the methoxy resonances in the nmr spectra of the two complexes. The peaks are separated by 1.3 Hz, in $CDCl_3$, that of **16** being at the lower field. Heating each of the isomers at 110° for *ca.* 20 half-lives and isolating the mixture by chromatography afforded K_{eq} = **16**/**15** = 1.21 ± 0.02. The kinetics of the interconversion of the two isomers was investigated using the same analytical techniques on the deuterated derivatives of **15** and **16** as was used above for the dichlorophenyl–anisyl complexes.

For interconversion of **15** and **16** $k_{15\rightarrow16}$ = 1.36 ± 0.6 × 10^{-3} min^{-1} at 99.37° in degassed tetrahydrofuran solution.

Isomerization of 3, 4, and 5. Infrared absorbances employed to analyze mixtures of these three complexes were the 962-cm^{-1} band of **4**, the 810-cm^{-1} band of **5**, and the 754-cm^{-1} band of **3**.

Kinetic runs were performed in dilute freeze–thaw degassed (10^5 mm) toluene solutions in the dark. For analysis, a tube was opened, solvent was removed by evaporation *in vacuo*, and the residue was dissolved in carbon disulfide and subjected to infrared analysis.[17] Samples consisted of 5.0 ± 0.5 mg in 0.04 ml of carbon disulfide. Two spectra were determined of each sample. A typical result of analysis of unknown mixtures of the three complexes, arising from 1-phenyl-8-tolyloctatetraene-5,6,7,8-*tetrahapto*iron tricarbonyl, is shown in Table V. Time–concentration plots are presented in Figure 1.

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[25] These deuterated complexes were prepared by the base-catalyzed hydrogen–deuterium exchange of the deuterium-free complex with ethanol-d_1 (C. Reich and R. Markezich, to be reported).

Stereospecific Syntheses of Uleine and Epiuleine

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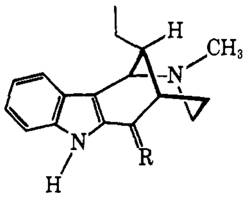
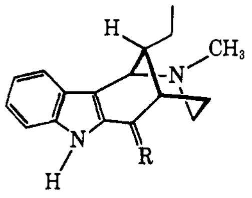
Abstract: 1-Aminohexan-3-one (**12**) prepared from the known 1-chlorohexan-3-one (**5**) *via* the phthalimide **11** on Mannich condensation with 3-formylindole gave the trans-disubstituted piperidone **13**. The stereochemistry of the corresponding formamide **15**, which exists preferentially as a diaxially substituted piperidone, was established by nuclear magnetic resonance spectroscopy. Condensation of the ketone **15** with acetylene to the carbinol **21** was followed by treatment with mercuric acetate furnishing the acetoxy ketone **23**. Reduction of the latter with lithium in liquid ammonia, cyclization of the resulting *trans,trans*-methyl ketone **24**, and reduction of the formamide **29** with lithium aluminum hydride completed the stereospecific synthesis of epiuleine (**3**). The tetrasubstituted α,β-unsaturated ketone **31**, available by pyrolysis of the acetate **23** on catalytic reduction, afforded mostly the *cis,cis*-methyl ketone **35** in addition to minor portions of the *cis,trans*-methyl ketone **37**. Cyclization of the former with boron trifluoride followed by hydride reduction gave uleine (**1**). A reversal of the usual conformational stability relationship was encountered in several of the intermediates and attributed to the vicinal alkyl amide effect.

Uleine, a secondary plant metabolite of *Aspidosperma ulei* Mgf., belongs to a small group of indole alkaloids whose structures lack the tryptamine unit. Work on the two-dimensional constitution of uleine was complete in 1959[2] but the configuration of the ethyl group remained to be established. The first evidence concerning this point was provided by the reaction of the alkaloid with methyl iodide. The high rate of quaternization observed suggested that the ethyl group is situated equatorially away from the basic nitrogen atom.[3] An examination of *Aspidosperma subincanum* carried out in the same year led to the isolation of a new alkaloid which proved to be epiuleine.[4] The C-methyl



1, R = CH_2
2, R = O



3, R = CH_2
4, R = O

triplet in the nuclear magnetic resonance spectrum of epiuleine appears at δ 1.08 while it is shifted upfield to 0.88 in uleine. This difference was attributed to long-range shielding from the indole ring and uleine and epiuleine were assigned the configurations **1** and **3**, respectively.[4]

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