

## THERMAL AND PHOTOCHEMICAL INTERCONVERSIONS OF ISOMERIC MONOCARBONYL $\eta^5$ -CYCLOPENTADIENYL( $\eta^3$ -ALLYL)IRON COMPLEXES

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(Received July 30th, 1975)

### Summary

The photolysis of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>- $\eta^1$ -C<sub>3</sub>H<sub>5</sub>Fe(CO)<sub>2</sub> at 10°C gives two stereoisomers of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>- $\eta^3$ -C<sub>3</sub>H<sub>5</sub>Fe(CO). The less stable isomer (*endo*) thermally isomerizes to the more stable (*exo*) isomer with a moderate rate at ambient temperatures. Similarly the *endo*- $\eta^3$ -methallyliron complex isomerizes completely to the *exo* isomer with  $\Delta G^\ddagger = 24.1$  kcal/mol. Photolyses of *cis*- and *trans*-1-substituted- $\eta^1$ -allyliron compounds yield the *syn*- and *anti*- $\eta^3$ -allyliron isomers stereospecifically as a mixture of *endo* and *exo* stereoisomers. In all the cases examined the *exo*,*syn* stereoisomers are the thermodynamically most stable while the *endo*, *anti* are the least stable isomers. Approximate rates for the thermal interconversion of the different stereoisomers have been determined. *Anti* to *syn* conversion occurs at a rate comparable to *endo* to *exo* isomerization and implies a similar mechanism involving a  $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$  transformation. Theoretical arguments are presented to explain the apparent change in mechanism for *endo* and *exo* interconversion of Group VI and VIII  $\eta^3$ -allyl complexes.

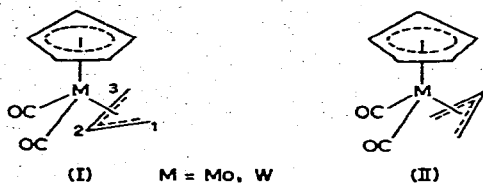
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### Introduction

Among the several forms of dynamic behavior which have been observed in organometallic complexes, the interconversion of stereoisomeric  $\eta^3$ -allylmetal complexes is well characterized for a number of these substances\*. For dicarbonyl  $\eta^5$ -cyclopentadienyl- $\eta^3$ -allyl-molybdenum and -tungsten complexes in particular, the existence of stereoisomers (I and II) has been amply demonstrated [2] and the thermodynamic parameters and activation energies associated with their interconversion have been determined [2d].

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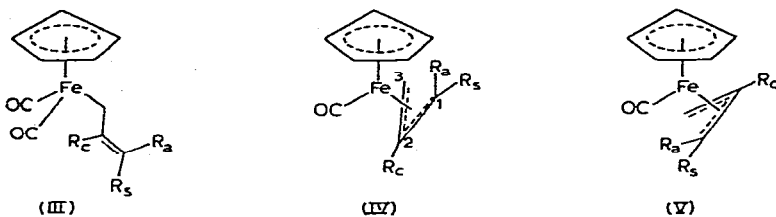
\* For a recent review of  $\eta^3$ -allylmetal compounds see ref. 1.



The chemistry of the closely related  $\eta^3$ -allyliron and -ruthenium complexes is, by contrast, poorly delineated. Green and Nagy [3] reported the preparation of monocarbonyl  $\eta^5$ -cyclopentadienyl- $\eta^3$ -allyl and - $\eta^3$ -butenyl complexes by photolysis of the corresponding  $\eta^1$ -allyliron complexes (IIIa, IIIb), but only one stereoisomer was isolated and its structure (IV or V) was not considered. Later, King and Ishaq [4] reported the photolysis of the corresponding  $\eta^1$ -allyl-ruthenium complex (IIIa, Ru instead of Fe) and provided spectral evidence for the formation of two stereoisomers.

In a more recent study, Faller, Johnson and Dryja [5] reported that only one stereoisomeric form of  $\eta^3$ -allyl-iron or -ruthenium complexes was formed in these photolysis reactions\*. These were assigned structures corresponding to V, based on magnetic anisotropies and shielding of protons calculated [2d] and observed for the analogous indenyl complexes ( $\eta^5$ -C<sub>9</sub>H<sub>7</sub>M(CO)<sub>x</sub>- $\eta^3$ -allyl; M = Mo, W, x = 2; M = Fe, Ru; x = 1).

These findings prompt us now to report the results of a more extensive examination of this system in which the characterization and chemistry of both stereoisomeric  $\eta^3$ -allyliron complexes are described. For simplicity these isomers are designated hereafter as "endo" (IV) and "exo" (V). We consider the factors affecting their relative stabilities, the mechanisms of their photochemical formation and thermal isomerization, and the intimate relationship between patterns of  $\eta^3$ -allyl substitutions and the rates of  $exo \rightleftharpoons endo$  interconversion.



	R <sub>a</sub>	R <sub>b</sub>	R <sub>c</sub>
a.	H	H	H
b.	H	H	Me
c.	OMe	H	H
d.	H	OMe	H
e.	Cl	H	H
f.	H	Cl	H
g.	OPh	H	H
h.	H	OPh	H

\* The possibility that both isomers were formed, but that one decomposed or interconverted during isolation was considered by these authors.

## Results and discussion

### Structural assignments

When photolysis of the  $\eta^1$ -allyl- or  $\eta^1$ -methallyl-iron complexes (IIIa or IIIb) is carried out in petroleum ether solutions at 10°C employing 350 nm light, a mixture of *endo* and *exo*  $\eta^3$ -allyliron complexes (IV and V) is formed\*.

The PMR and IR spectral data for these and other  $\eta^3$ -allyliron complexes, which form the basis for the structural assignments are given in Table 1.

The PMR spectral characteristics for  $\eta^3$ -allyliron isomers (IV and V) conform closely to those adduced by Faller [2] from a study of the related  $\eta^3$ -allylmolybdenum and -tungsten complexes (I and II). Chief among these are a significantly greater shielding of *anti* protons ( $H_a$ ) and a larger geminal coupling of *syn* and *anti* protons ( $J_{as}$ ) in the "exo" isomers (II and V). A comparison of the data for the iron, tungsten and molybdenum complexes, presented in Table 1, illustrate the close correlation in these parameters for these substances. The chemical shift differences for *anti* protons in the *exo* and *endo* isomers (I and II) have been largely associated with anisotropy of the cyclopentadienyl ring [2d], and it may be anticipated that the same factor plays an important role in the relative shielding of protons in IV and V\*\*.

By contrast, the relative infrared absorption frequencies of carbonyl groups in the *endo* and *exo* isomers (IV and Va, b, d) are reversed in the structurally related stereoisomers (I and II). For the latter, low frequency carbonyl absorption was found to be associated with the *exo* isomer (II), while it is the *endo* isomer (IV) in the iron complexes for which this relationship holds. It is perhaps worth noting that in each series it is that stereoisomer in which the carbonyl group or groups are eclipsed by a CH or CH<sub>2</sub> group of the allyl ligand which exhibits low frequency carbonyl absorption. However, in the absence of more precise structural information, the degree to which such physical proximity may be related to the IR data must remain speculative. Furthermore, it is clear that bonding interactions between allyl and metal orbitals may differ significantly for each of the stereoisomers and so lead to differing interactions with the remaining ligands\*\*\*. The effect of more subtle structural factors on carbonyl absorptions is to be seen in the further regularity within the *exo* isomers (Vc, d; Ve, f and Vg, h), in which lower frequency absorption correlates with the *syn* isomer of each pair.

### Photochemical kinetic products and stationary states

Photolyses were carried out at 350, 300 and 253.7 nm in petroleum ether solution. Both the  $\eta^1$ -allyl- and  $\eta^3$ -allyl-iron complexes exhibit absorption throughout this region, with the former showing a moderately intense peak at

\* The failure of earlier workers [3,5] to detect these is probably to be attributed to their method of isolation, which involved distillation (40°C) or sublimation. Under these conditions, the complete conversion of the *endo* to the more stable *exo* isomer, is rapid (vide infra).

\*\* Local anisotropy, associated with the carbonyl group may however make a contribution, especially to the shielding of  $H_c$  in the *endo* stereoisomers (IV), since these groups are very near to one another in this stereoisomer.

\*\*\* For a recent discussion of bonding in  $\eta^3$ -allylmetal complexes see ref. 6.

TABLE 1  
PMR AND IR DATA FOR  $\eta^3$ -ALLYLIRON COMPLEXES

Complex	Chemical shifts ( $\delta$ , ppm) <sup>a</sup>										Coupling Constants, J(Hz)							$\nu(\text{CO})$ ( $\text{cm}^{-1}$ )
	R <sub>C</sub>	R <sub>B</sub>	R <sub>A</sub>	$\eta^5\text{-Cp}$	R <sub>C</sub>	R <sub>B</sub>	R <sub>A</sub>	H <sub>B</sub>	H <sub>A</sub>	H <sub>B</sub>	R <sub>B</sub> R <sub>C</sub>	R <sub>A</sub> R <sub>C</sub>	H <sub>A</sub> H <sub>B</sub> <sup>c</sup>	H <sub>A</sub> R <sub>C</sub>	H <sub>B</sub> R <sub>C</sub>	H <sub>A</sub> R <sub>C</sub>		
IVa (endo)	H	H	H	H	4.55	3.67	2.87	1.46	2.87	1.45	7	12	<1	7	12	12	1039 <sup>d</sup> 1940 <sup>h</sup>	
Va (exo)	H	H	H	H	4.42	4.33	2.72	0.47	2.72	0.47	7	11	2.5	7	11	11	1060 <sup>d</sup> 1962 <sup>h</sup>	
IVb (endo)	Me	H	H	H	4.48	(4.35 1.67)	(2.71 2.77)	(0.49) <sup>b</sup> 1.60	2.77	1.60	(6.9)	11.1	(2.4) <sup>b</sup> <1				1953 <sup>b, e</sup> 1921 <sup>c</sup> 1937 <sup>h</sup> 1947 <sup>e</sup>	
Vb (exo)	Me	H	H	H	4.30	1.97	2.62	0.47	2.62	0.47			2.3				1958 <sup>h</sup> 1948 <sup>b, e</sup>	
I <sup>b</sup> (endo-Mo)	H	H	H	H	5.10	(1.98)	2.63	(0.47) <sup>b</sup> 1.76	2.72	1.76	6.4	10.5	<0.6	6.4	10.5	10.5	1970, 1903	
II <sup>b</sup> (exo-Mo)	H	H	H	H	5.10	3.92	2.78	0.98	2.78	0.88	7.3	10.8	2.4	7.3	10.8	10.8	1963, 1869	
I <sup>b</sup> (endo-W)	H	H	H	H	5.22	3.67	2.70	1.64	2.70	1.64	5.6	9.5	<0.6	5.6	9.5	9.5	1961, 1896	
II <sup>b</sup> (exo-W)	H	H	H	H	5.25	3.54	2.73	1.07	2.73	1.07	6.9	10.4	2.8	6.9	10.4	10.4	1953, 1876	
IVc (endo,anti)	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	4.48	2.93	6.30	3.28	3.12	2.16	4.5	7.0	<1.0	7.0	11.8	11.8	1960 <sup>h</sup>	
Vc (exo,anti)	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	4.35	3.50	6.17	3.08	3.12	1.44	4.7		1.3	7.2	11.3			
Vc <sup>g</sup>	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	4.07	3.40	6.08	3.16	3.15	1.83								
Vc <sup>f</sup>	H	H	OCH <sub>3</sub>	OCH <sub>3</sub>	4.49	3.67	6.32	3.22	3.22	1.58								
IVd (endo,syn)	H	OCH <sub>3</sub>	H	H	4.51	3.65	3.40	4.94	2.51	0.92	8.0	8.0	1.0	8.0	11.0	11.0	1940 <sup>h</sup>	
Vd (exo,syn)	H	OCH <sub>3</sub>	H	H	4.37	4.35	3.37	3.53	2.33	0.03	7.5	7.5	2.4	7.7	11.3	11.3	1940 <sup>c</sup> 1950 <sup>h</sup>	
Vd <sup>g</sup>	H	OCH <sub>3</sub>	H	H	4.16	4.37	3.15	3.63	2.33	0.20	4.2	4.2	<1.0	6.8	12.4	12.4	1987 <sup>h</sup>	
IVe (endo,anti)	H	H	Cl	Cl	4.58	3.75	5.39		3.32	2.46	5.0	5.0	1.5	7.0	11.0	11.0		
Ve (exo,anti)	H	H	Cl	Cl	4.48	4.20	5.40		3.16	1.50								
Ve <sup>g</sup>	H	Cl	H	H	3.83	3.73	6.32		2.90	1.75								
VI (exo,syn)	H	Cl	H	H	4.46	4.65		2.86	2.58	0.42	7.8	7.8	2.4	7.5	11.0	11.0	1971 <sup>h</sup>	
VI <sup>g</sup>	H	H	H	H	4.02	4.42		2.95	2.23	6.30	4.8	4.8	1.6	7.4	11.5	11.5	1977 <sup>h</sup> 1936 <sup>d</sup>	
Vg (exo,anti)	H	H	OPh	OPh	4.48	3.90	6.42	7.0	3.21	1.60								
Vg <sup>f</sup>	H	H	OPh	OPh	4.61	4.05	6.60	7.2	3.30	1.73								
Vg <sup>g</sup>	H	H	OPh	OPh	3.99	3.57	6.31	7.0	3.06	1.90								
Vh (exo,syn)	H	OPh	H	H	4.36	4.72	7.1	3.80	2.55	0.35	7.0	7.0	2.0	7.5	11.0	11.0	1953 <sup>h</sup>	
Vh <sup>g</sup>	H	OPh	H	H	4.07	4.62	7.0	3.92	2.36	0.38							1931 <sup>d</sup>	

<sup>a</sup> In ppm downfield from TMS at 60 and 90 MHz in CS<sub>2</sub> solution unless otherwise noted. <sup>b</sup> Ref. 6. <sup>c</sup> The parameter  $N = |J_{AB} + J_{AC}|$  is given for the AA'SS' set, corresponding to the separation of outer lines of the apparent triplet. <sup>d</sup> In KBr. <sup>e</sup> In CS<sub>2</sub>. <sup>f</sup> In CCl<sub>4</sub>. <sup>g</sup> In C<sub>6</sub>D<sub>6</sub>. <sup>h</sup> In petroleum ether or heptane.

TABLE 2  
STEREOISOMER PRODUCT RATIO FROM PHOTOLYSIS OF  $\eta^1$ - AND  $\eta^3$ -ALLYLIRON COMPLEXES

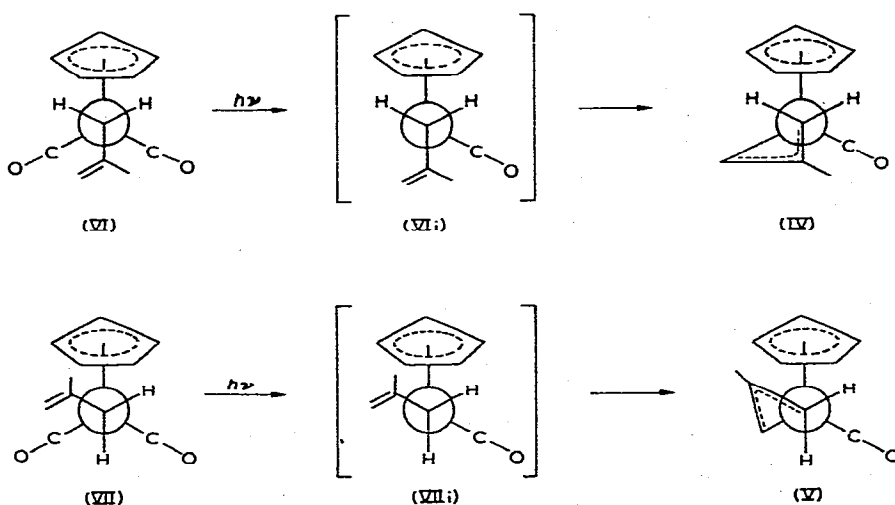
Complex	Light source $\lambda$ (nm)	Irradiation <sup>a</sup> time (h)	Percent conversion	Product ratio (endo/exo)
IIIa	350	1.25	25	45/55
		4.0	>95	45/55
IIIb	350	0.5	25	70/30
	350	2.5	>95	56/44
IVb/Vb (26/74) <sup>b</sup>	350	5.0		45/55 <sup>c</sup>
IIIb	300	1.5	20	71/29
IVb/Vb (45/55) <sup>b</sup>	300	5.75		59/41 <sup>c</sup>
IIIb	254	5.5	84	67/33
IVb/Vb (36/64) <sup>b</sup>	254	6.5		61/39 <sup>c</sup>

<sup>a</sup> All photolyses were carried out at 10°C. <sup>b</sup> Initial ratio of isomers (endo/exo). <sup>c</sup> Apparent equilibrium ratio.

320 nm and the latter a shoulder on the end absorption, near 270 nm. Spectral data for a number of  $\eta^1$ -allyl- and  $\eta^3$ -allyl-iron complexes are given in the experimental section (Table 5).

Since the  $\eta^3$ -allyl- and  $\eta^3$ -2-methallyl-iron *endo* and *exo* stereoisomers (IV and Va, b) isomerize thermally at a relatively slow rate compared with their rates of photochemical formation from IIIa, b), these processes can be independently examined. Photochemical isomerization of product does, however, occur competitive with its rate of formation. This is evident from a study of initial, and steady state proportions of isomers formed in the photolysis of these complexes. These data are summarized in Table 2. The distribution of stereoisomers formed in the photolysis of IIIa at 350 nm does not change between 25 percent conversion and complete conversion. However, this is not true for the methallyl

SCHEME 1



complex (IIIb), for which the initial ratio of isomers formed by photolysis at 350 or 300 nm is significantly different from the ratio observed either near completion or by carrying a mixture of *exo* and *endo* isomers to photochemical equilibrium. The larger initial rate of formation of the *endo* isomer (IVb), may reflect conformational populations in the  $\eta^1$ -allyl complex (IIIb). An examination of models suggests that conformation VI should be favored over VII, since substantial interactions may be expected between the  $\eta^1$ -methallyl ligand and ring protons in the latter conformation. If the photochemical process involves initial dissociation of carbon monoxide from III [7], followed by collapse of the coordinatively unsaturated intermediates (VII and VIII), the initial product ratio may be expected to reflect conformational preferences, provided collapse of the intermediate is rapid compared with rotations about Fe—C and C—C bonds (Scheme 1).

### Thermochemical equilibria

The thermochemical equilibria for a number of dicarbonyl  $\eta^5$ -cyclopentadienyl- $\eta^3$ -allyl-molybdenum and tungsten complexes have been reported [2d]. While the *exo* isomer (II) was found to be moderately favored for the parent complexes, substitution at C(2) was found to destabilize this isomer markedly owing apparently to steric interactions between the substituent and the cyclopentadienyl ring\*.

The situation is very different for the analogous  $\eta^3$ -allyliron complexes. For all of those which have been examined, including the 2-methallyl complex, the *exo* isomer (V) is by far the predominant isomer at equilibrium. On the basis of NMR spectral determinations less than 2% of the *endo* isomer exists in equilibrium with the *exo* isomer.

We believe that the differences in equilibria for the Group VI metal complexes and for the iron complexes can be attributed largely to a smaller dihedral angle between the ring and  $\eta^3$ -allyl planes in the *exo* configuration of the latter complexes.

When this work was begun, no crystallographic data existed for these allyliron complexes. However, a good approximation of their molecular parameters may be made using crystallographic data derived from a number of closely related  $\eta^3$ -allyliron complexes [8,9]. Following the approach of Faller [2d], and based on crystallographic data for a variety of  $\eta^3$ -allylmetal complexes [9], the allyl ligand is taken as occupying two coordination sites ( $s_1, s_2$ ), located 4/5 of the distance from the central carbon atom to each of the termini. Bond angles defined by these points, the metal atom and the carbonyl C atom are all taken to be  $90^\circ$ , in conformity with crystallographic data for a number of closely related dicarbonyl ( $\eta^5$ -cyclopentadienyl)-alkyl- and -vinyl-iron complexes [10]. These parameters, together with average values for the internal angle of the allyl ligand, Fe—C and C—C bond distances [8], fix the dihedral angle ( $\gamma$ ) between the cyclopentadienyl ring and the allyl plane, shown in Fig. 1. This is calculated to be  $14^\circ$  for the *exo* isomer and may be compared with an angle of  $44^\circ$  for the

\*  $K_{2/1}^{25}$  is 3.48 and 2.21 for the parent molybdenum and tungsten complexes respectively in  $\text{CHCl}_3$  solution, but is 0.128 for the 2-methallylmolybdenum complex.

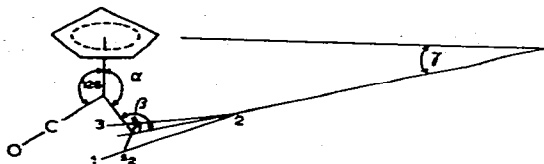


Fig. 1. Calculated dihedral angles in the *exo,anti*-1-phenoxyallyliron complex Vg:  $\alpha = 144.3^\circ$ ,  $\beta = 111.5^\circ$  and  $\gamma = 14.3^\circ$ .

analogous molybdenum complex II [2d]. Since bond parameters of these complexes are comparable, steric interactions between the allyl ligand, and especially between C(2) substituents on this ligand, and the cyclopentadienyl ring should be significantly smaller for the *exo* isomer V than for II. Furthermore, interactions between carbonyl groups and the  $\eta^3$ -allyl ligand, which are maximal in II are smallest in V, since C(1) and C(3) of the allyl ligand flank the lone carbonyl in the latter complex, while C(2) eclipses it in the *endo* isomer (IV). These interactions are reversed for the corresponding *endo* and *exo* isomers (I and II). Lastly, while interactions between the allyl group and the ring are minimized in V due to the small dihedral angle ( $\gamma$ ) for this configuration, this angle is considerably larger ( $58^\circ$ ) for the *endo* isomer. Consequently some destabilization of *endo* stereoisomers, in particular those having an *anti* substituent at C(1), may be anticipated. We will return to this point later.

A preliminary X-ray structure determination of the *exo, anti*-1-phenoxyallyliron complex (Vg) has now been carried out [11], which largely confirms the calculated molecular model and shows the dihedral angle ( $\gamma$ ) to be  $16^\circ$ .

#### Rates of thermal isomerization

The rates of stereochemical isomerization were conveniently followed by measuring the change in cyclopentadienyl proton resonances for each of the stereoisomers. Since  $H_c$  in Va overlaps the ring proton resonances of both isomers (IVa and Va), rate measurements could not be accurately made with the parent complex and kinetic studies were therefore carried out with the methallyl complex, which is free of this complication. These data are summarized in Table 3 and are the average of rates determined by following the increase in product and decrease in reactant cyclopentadienyl ring resonances. These differed in general by less than 3%. Thermodynamic parameters derived from these rates are given at the bottom of the table.

The most striking feature of these results is the very great difference in activation energy for isomerization of IVb and the related molybdenum and tungsten complexes, for which activation free energies for stereochemical change of 14-17 kcal/mol were observed [2d]. It is unlikely that such a large difference is related to steric factors, since the effective coordination number of the iron complexes is smaller by one than that of the Group VI metal complexes.

We were therefore led to consider the possibility that isomerization proceeds differently for the Groups VIII and VI complexes. Faller had earlier suggested this possibility on the basis of spectra provided him of the ruthenium complexes by King, but the absence of a second isomeric iron complex in his experiments, precluded his pursuing this point [5]. The Group VI substances,

TABLE 3  
RATES OF THERMAL ISOMERIZATION OF COMPLEX IVb

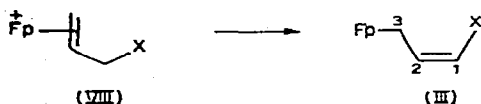
Temp. (°C)	$k \times 10^3$ (min <sup>-1</sup> ) <sup>a</sup>
29.5	1.68 ± 0.05
38.4	4.63 ± 0.08
43.1	11.4 ± 0.4
50.1	27.6 ± 2.2

$\Delta G^\ddagger = 24.1 \pm 1.2$  kcal/mol  
 $\Delta H^\ddagger = 26.2 \pm 1.4$  kcal/mol  
 $\Delta S^\ddagger = 7.0 \pm 2.4$  e.u.

<sup>a</sup> Determined in deuteriochloroform.

like bis- $\eta^3$ -allyl-nickel [12], -palladium [12] and -platinum [12] as well as tris- $\eta^3$ -allylrhodium [13] complexes have been shown to undergo stereochemical exchange by pseudorotation about the metal-allyl bond axis [2]. Such a process is characterized by the absence of concurrent *syn*⇌*anti* exchange of protons at C(1) and C(3) in the allyl ligand. By contrast a number of complexes, among them  $\eta^3$ -(C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>Zr [12a] and  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>PdCl complexes [14], undergo stereochemical exchange coupled with *syn*⇌*anti* interconversion. These reactions have been shown to proceed through a  $\eta^1$ -allyl intermediate.

We therefore chose to examine  $\eta^3$ -allyliron complexes substituted at C(1) in order to determine under what conditions *syn*⇌*anti* exchange would occur and if this process was coupled with *exo*⇌*endo* isomerization. The requisite  $\eta^1$ -allyliron complexes (IIIc, IIIe and IIIg) were obtained by deprotonation of the corresponding olefin complexes (VIII). We have previously shown [15] that deprotonation of VIII (X = OMe or Br, Fp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>) with triethylamine leads exclusively to the *cis*-1-substituted- $\eta^1$ -allyliron complexes (IIIc and IIIe). The same has now been determined to be the outcome when VIII (X = Cl or OPh) is deprotonated. The PMR spectra of the resulting products show them to be exclusively the *cis* isomers (IIIe, IIIg) ( $J_{1,2} = 5.5$  Hz).



c: X = OMe, e: X = Cl, g: X = OPh

Photolysis of IIIc, IIIe and IIIg at 10° yielded, in each case, a single isomer. The PMR spectra of these confirm the retention of stereochemistry in the products, showing them to be the 1-*anti*-substituted  $\eta^3$ -allyliron complexes by characteristic PMR coupling constants (Table 1,  $J_{s,c} = 4.2$ -4.8 Hz). Since only one isomer was obtained in these reactions, assignment of *exo* or *endo* configurations to the products was not possible. However, when photolysis of IIIc or IIIe was carried out at -45°C, both *endo* and *exo*, *anti* isomers (IVc, Vc and IVe, Ve) were observed in the low temperature (-35°C) PMR spectra of the crude products. A comparison of the PMR data for these stereoisomers with the *endo* and *exo* isomers (IVa, Va and IVb, Vb) shows that the unstable stereoisomer



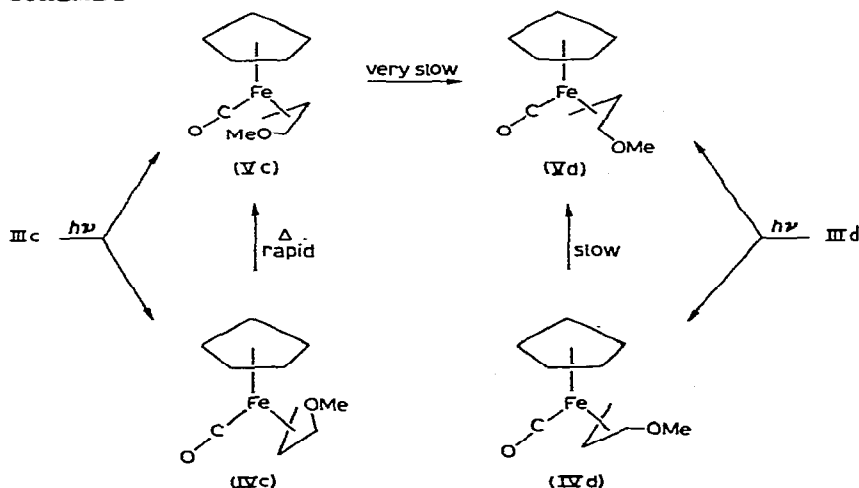
is *endo* (IVc and IVe). Above 0°C these isomerize rapidly to the *exo* isomers (Vc and Ve). Final confirmation of these assignments has now been obtained through an X-ray determination of the structure of the stable  $\eta^3$ -allyliron complex derived by photolysis of IIIg, which shows it to have the *exo,anti* structure (Vg) [11].

When the *exo,anti* isomers Vc, Ve and Vg were heated in benzene solution each was transformed cleanly to a single new substance, identified by its PMR spectrum (Table 1) as the *exo,syn* isomer (Vd, Vf and Vh).

In order to complete the series, the *endo,syn*-1-methoxyallyliron complex (IVd) was prepared. This isomer was obtained by metallation of *trans*-3-chloro-1-methoxy-1-propene with  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Na [15] and photolysis of the resulting  $\eta^1$ -allyl complex (III d) at 10°C. Isomerization of IVd to Vd proceeded at a moderate rate at room temperature.

A summary of the processes described here for the isomeric methoxy complexes along with half-lives for isomerization of all complexes examined is given in Scheme 2 and Table 4.

SCHEME 2



The results reflect the profound effect which substitution has upon the rates of *endo*→*exo* and *anti*→*syn* exchange. This is particularly evident for *endo*→*exo* exchange for the *anti*- and *syn*-methoxy derivatives (IVc and IVd) and for *anti*→*syn* exchange for the *exo*-methoxy and chloro derivatives (Vc and Ve). The latter rate difference corresponds to a difference in activation energies of roughly 3 kcal/mole. Processes which result in *anti*→*syn* exchange must proceed by a  $\eta^3 \rightleftharpoons \eta^1$  change, and for the reactions Ve→Vf and Vc→Vd each must involve the thermodynamically less stable 3-substituted  $\eta^1$ -allyl complex (IX)\*. For the present we must leave open the question whether these trans-

\* The comparative stabilities of 1° and 2° Fe—C bonds in  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>( $\eta^1$ -allyl) complexes is reflected in the reaction of the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>(2-butene) cation. On deprotonation, the only product obtained is a mixture of the *cis*- and *trans*- $\eta^1$ -2-butenyl complex. The isomeric methallyl complex, which is undoubtedly the initial product of the reaction is not observed [17]. This reaction finds a close parallel in the behaviour of allyl Grignard reagents [18] and the Group IV allyl derivatives [19].

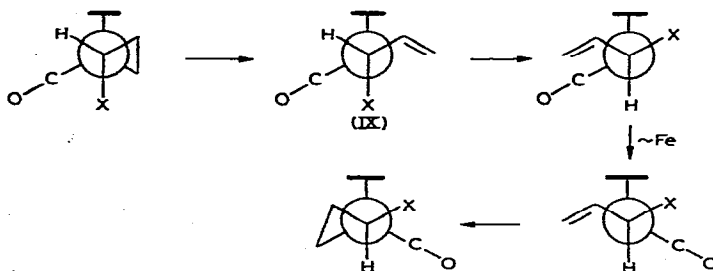
TABLE 4  
SUMMARY OF  $\eta^3$ -ALLYLIRON ISOMERIZATIONS

Reaction	Process	$t_{1/2}$ (min)	Temp. ( $^{\circ}$ C)
Ib $\rightarrow$ IIb	<i>endo</i> $\rightarrow$ <i>exo</i>	$1.17 \times 10^{-3}$	25
IVc $\rightarrow$ Vc	<i>endo</i> $\rightarrow$ <i>exo</i> ; <i>anti</i> $\rightarrow$ <i>anti</i>	<30	-10
IVe $\rightarrow$ Ve	<i>endo</i> $\rightarrow$ <i>exo</i> ; <i>anti</i> $\rightarrow$ <i>anti</i>	<30	-10
IVd $\rightarrow$ Vd	<i>endo</i> $\rightarrow$ <i>exo</i> ; <i>syn</i> $\rightarrow$ <i>syn</i>	33	36
IVa $\rightarrow$ Va	<i>endo</i> $\rightarrow$ <i>exo</i>	108	36
IVb $\rightarrow$ Vb	<i>endo</i> $\rightarrow$ <i>exo</i>	25	50
Ve $\rightarrow$ Vf	<i>exo</i> $\rightarrow$ <i>exo</i> ; <i>anti</i> $\rightarrow$ <i>syn</i>	40	62
Vc $\rightarrow$ Vd	<i>exo</i> $\rightarrow$ <i>exo</i> ; <i>anti</i> $\rightarrow$ <i>syn</i>	360	94

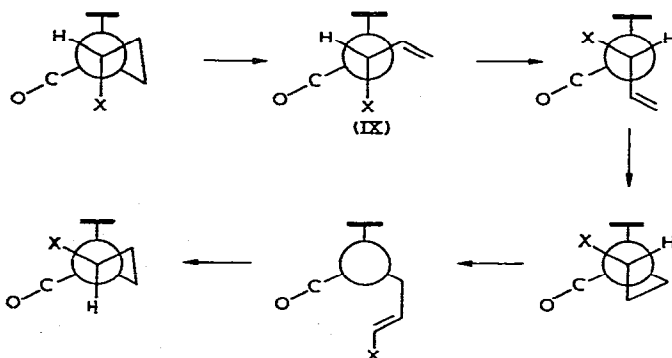
formations proceed with or without inversion at the metal atom (paths A or B, Scheme 3).

SCHEME 3. *Exo, anti*  $\rightarrow$  *exo, syn* exchange.

Path A

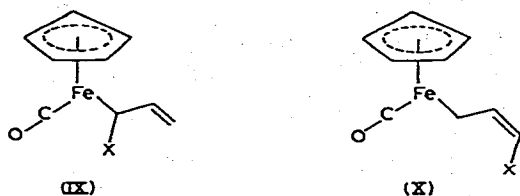


Path B



The absence of *anti*  $\rightarrow$  *syn* exchange in the isomerization of the *endo* complexes (IVc, IVe) to *exo* complexes (Vc, Ve) is to be anticipated, since the reaction would be expected to proceed through the preferred, 1-substituted  $\eta^1$ -allyl complex (X) which leaves the configuration at the substituted carbon center unchanged.

The high rate of these reactions is readily attributed to steric acceleration, since models clearly show that interactions between the *anti*-substituent and the



ring in the *endo*-stereoisomer are significant. When these factors are absent, as in the 1-methoxy *endo,syn* complex (IVd), isomerization proceeds at a rate comparable to that of the parent complex (IVa) or the 2-methallyl derivative (IVb).

#### Mechanism-theoretical analysis

We consider now the factors responsible for the change in mechanism for *endo*→*exo* interconversion in the  $\eta^3$ -allyliron and Group VI metal complexes. These factors may be exposed by examining the interactions between fragment orbitals associated with the cyclopentadienyl metal residue (CpM) and the remaining ligands in the complexes\*.

The orbitals associated with the CpM fragment can be derived most simply by making use of the extensive analyses of metallocene complexes ( $\text{Cp}_2\text{M}$ ) [20]. Virtually all of these are in accord with a level ordering  $e_{2g} < a_{1g} < e_{1g}$ \* for the highest bonding and lowest antibonding orbitals, all of which are principally metal-3d in character. For a CpM fragment in which the z-axis is taken to be coincident with the  $C_5$  symmetry axis, the splitting of 3d metal orbitals results in a similar low lying set of three nonbonding orbitals ( $d_{x^2-y^2}$ ,  $d_{xy}$ ,  $d_z^2$ ) and a higher set of two ( $d_{xz}$ ,  $d_{yz}$ ), antibonding within the CpM fragment. In addition a third antibonding hybrid metal orbital ( $s + p_z$ ) lies above the latter two. These latter three orbitals point away from the ring, suitable for bonding with additional ligands as indicated in Figure 2.

A set of symmetry orbitals may now be constructed from  $\pi_1$  and  $\pi_2$  allyl molecular orbitals and carbonyl  $\sigma$  orbitals. In these the allyl ligand is formalized in terms of a two center fragment, since the primary bonding interactions involve  $\pi_1$  and  $\pi_2$  of the allyl group [6]. For the Group VI and iron complexes, the interactions of these symmetry orbitals with CpM fragment orbitals are shown at the left of Figs. 3 and 4.

As with the metallocenes, we may anticipate appreciable interactions between the three low lying ligand orbitals ( $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ ) and metal  $d_{xz}$ ,  $d_{yz}$  and

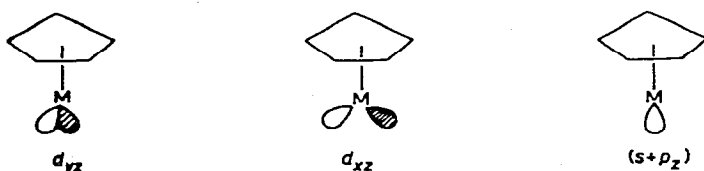


Fig. 2. Schematic representation of the orbitals associated with the CpM fragment.

\* A very similar analysis based on a formal replacement of the  $\text{CpM}(\text{CO})_x$  fragments by  $\text{M}(\text{CO})_{x+3}$  fragments has been made by Professor R. Hoffman. We are indebted to him for communicating this to us.

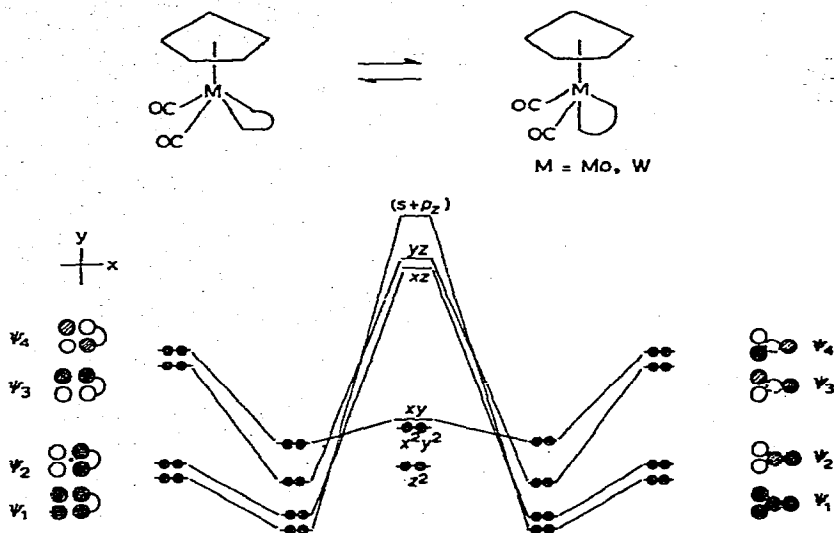


Fig. 3. Interactions of  $\pi_1$  and  $\pi_2$  allyl molecular orbitals and carbonyl  $\sigma$  orbitals in the Group VI metal complexes.

$(s + p_z)$  orbitals. A smaller bonding interaction may also subsist between  $\psi_4$  and  $d_{xy}$  for the Group VI metal complexes.

Rotation of the allyl ligand about the formal metal—allyl bond axis, for the Group VI metal complexes converts the local  $C_{4v}$  symmetry to  $C_{3v}$ , but as shown schematically at the right of Fig. 3, the ligand orbitals remain symmetry paired with a CpM fragment orbital. This is not true for the iron complex, since the interaction between  $\psi_3$  and  $d_{yz}$  in the ground state molecular configuration

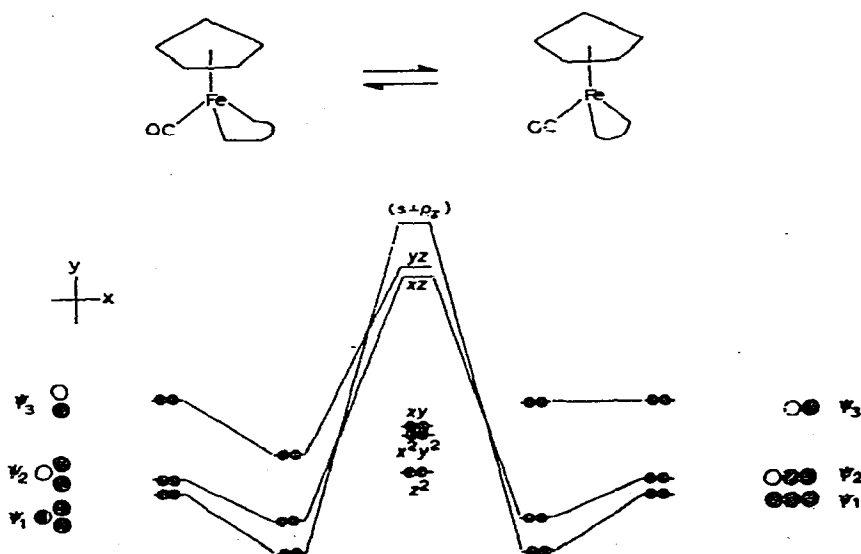


Fig. 4. Interactions of  $\pi_1$  and  $\pi_2$  allyl molecular orbitals and carbonyl  $\sigma$  orbitals in the iron complexes.

is lost in carrying out such a rotation. Thus, pseudorotation for the  $\eta^3$ -allyl complexes of the Group VI metals is symmetry allowed, while a similar rotation for the  $\eta^3$ -allyliron complexes requires a specific decrease in metal-allyl bonding since, for these complexes,  $\psi_3$  is entirely an allyl ligand orbital. Pseudorotation through  $90^\circ$  results then, in an energy state which must be close if not indistinguishable from that corresponding to a  $\eta^3 \rightarrow \eta^1$  change\*. The experimental results show that *endo*→*exo* exchange is best described in terms of this latter process.

## Experimental

All operations were carried out in a nitrogen atmosphere. Solvents were dried, degassed and stored under nitrogen and over molecular sieves. IR spectra were recorded on a Perkin-Elmer Model 567 spectrophotometer. UV-visible spectra were recorded on a Perkin-Elmer Model 323 spectrophotometer. PMR spectra were determined on a Varian A-60 or Perkin-Elmer R-32 (90 MHz) spectrometer with the latter being used for variable temperature and kinetic work. Melting points were determined in sealed capillaries and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

### Preparation of $\eta^1$ -allyliron complexes

**Complex IIIa.** Following a procedure similar to that described by Green and Nagy [3],  $[\text{CpFe}(\text{CO})_2]_2$  (18.0 g, 51 mmol) was reduced in 200 ml of THF with 1% Na(Hg) (4.5 g Na, 195 mmol). After one hour at room temperature, excess amalgam was removed and the solution was cooled to  $0^\circ\text{C}$ . Allyl chloride (9.4 g, 122 mmol) was added dropwise, and reaction was allowed to continue at  $0^\circ\text{C}$  for 45 min, then warmed to room temperature. Solvent was removed under reduced pressure and the residue filtered rapidly through 60 g of alumina (neutral, act III, prepared in ether). The product was eluted with Skelly B (17.8 g, 77%).

**Complex IIIb.** A similar procedure gave IIIb in 85% yield.

**Complex IIIc.** [15]. This substance was prepared in two steps involving the initial treatment of 1,2-epoxy-3-methoxypropane with  $\text{NaCpFe}(\text{CO})_2$ , followed by reaction with 48%  $\text{HBF}_4$ . The resulting cationic olefin was treated with triethylamine to give IIIc.

**Complex III d.** *trans*-3-Chloro-1-methoxy-1-propene was prepared according to the method of Hoff and Brandsma [22]. A THF solution of this substance was treated with  $\text{NaCpFe}(\text{CO})_2$  in THF producing a mixture of IIIc and III d which was separated by chromatography on alumina [15].

**Complex III e.** To a 500 ml flask containing  $\text{NaCpFe}(\text{CO})_2$  (52 mmol) in 130 ml of THF at  $0^\circ\text{C}$  was added neat epichlorohydrin (5.5 g, 60 mmol). This was left at  $0^\circ\text{C}$  for one hour then added to 300 ml of ether containing 17 ml of  $\text{HBF}_4$  (48%) at  $0^\circ\text{C}$ . Collection of the solid and reprecipitation from acetone with ether followed by further reprecipitation from nitromethane and then acetone gave the salt (VIII, X = Cl) as its tetrafluoroborate (9.5 g, 54%); IR (KBr) 2076, 2040  $\text{cm}^{-1}$ ; NMR ( $\text{CD}_3\text{NO}_2$ , 90 MHz)  $\delta$  5.76 (s, 5, Cp), 5.20 (m, 1,

\* The preferred geometries and rotational barriers for a number of olefin and  $\eta^3$ -allylmetal complexes has recently been the subject of a detailed theoretical treatment [21].

CH), 4.42 (dd, 1,  $J = 3$ , 11 Hz, CH<sub>2</sub>Cl), 4.15 (d, 1,  $J = 9$  Hz, *cis*-CH<sub>2</sub>) 3.87 (dd, 1,  $J = 7$ , 11 Hz, CH<sub>2</sub>Cl), 3.70 (d, 1,  $J = 15$ , *trans*-CH<sub>2</sub>).

The chloropropene salt (VIII, X = Cl) (1.43 g, 4.2 mmol) was taken up in 5 ml of nitromethane and the solution was cooled to 0°C. Diisopropylethylamine (0.61 g, 4.7 mmol) was added and after 10 min at 0°C, solvent was removed and the red oil was washed several times with ether/petroleum ether (1/1) to give IIIe, 0.86 g (81%); IR (CS<sub>2</sub>) 2015, 1948 cm<sup>-1</sup>; IR (petr. ether) 2020, 1967 cm<sup>-1</sup>; NMR (CS<sub>2</sub>, 90 MHz)  $\delta$  5.90 (dt, 1,  $J = 7$ , 9 Hz CCH), 5.58 (dt, 1,  $J = 7$ , 1 Hz, ClCH), 4.73 (s, 5, Cp), 2.05 (dd, 2,  $J = 9$ , 1 Hz, CH<sub>2</sub>).

**Complex IIIg.** To a solution of NaCpFe(CO)<sub>2</sub> (90 mmol) in 180 ml THF at 0°C was added 1,2-epoxy-3-phenoxypropane neat. The reaction was allowed to proceed for 1 h at 0°C and then added slowly to 30 ml of HBF<sub>4</sub> (48% in H<sub>2</sub>O) in 500 ml ether. The solid was collected and reprecipitated twice, first with acetone/ether and then nitromethane/ether to give a yellow solid (20.5 g, 51.5 mmol, 57%); IR (KBr): 2045, 2020 cm<sup>-1</sup>; NMR (CD<sub>3</sub>NO<sub>2</sub>, 90 MHz):  $\delta$  7.25 (m, 2, Ph), 1.98 (m, 3, Ph), 5.71 (s, 5, Cp), 5.35 (m, 1, CH), 4.72 (dd, 1,  $J = 14.3$ , CH<sub>2</sub>OPh), 4.51 (dd, 1,  $J = 14.4$ , CH<sub>2</sub>OPh), 4.17 (d, 1,  $J = 8.5$ , *cis*-CH<sub>2</sub>), 3.80 (d, 1,  $J = 14$ , *trans*-CH<sub>2</sub>). Analysis: Found: C, 48.59; H, 3.96. C<sub>16</sub>H<sub>15</sub>O<sub>2</sub>BF<sub>4</sub>Fe calcd.: C, 48.29; H, 3.80%.

The 3-phenoxypropene salt (VIII, X = OPh) (4.28 g, 10.7 mmol) was deprotonated with triethylamine (1.18 g, 11.7 mmol) in 20 ml nitromethane at 0°C. Evaporation of the solvent, extraction with ether, and chromatography on alumina gave IIIg as a red oil (2.40 g, 7.75 mmol, 72%); IR (Skelly B): 2015, 1960, 1597; NMR (CS<sub>2</sub>, 90 MHz):  $\delta$  7.10 (m, 2, Ph), 6.87 (m, 3, Ph), 6.07 (d, 1,  $J = 5.5$ , CHOPh), 5.03 (dt, 1,  $J = 5.5$ , 9.1, CHCH<sub>2</sub>), 4.67 (s, 5, Cp), 2.12 (d, 2,  $J = 9.1$ , CH<sub>2</sub>).

#### *Photolysis of $\eta^1$ -allyliron complexes. General procedure*

Photolyses were carried out in a Srinivasan type photochemical reactor employing either 350 (36 GE F8T5), 300 (16 RPR 3000 A), or 235.7 nm (36 Sylvania G8T5) lamps. Reaction vessels were either pyrex or quartz jacketed tubes through which cold water or methanol was circulated to maintain the desired temperature.

**Photolysis of IIIb.** The complex (0.816 g, 3.5 mmol) was dissolved in 25 ml of degassed petroleum ether in a centrifuge tube. The solution was centrifuged and then transferred to a nitrogen filled pyrex reaction vessel, which was placed in the photoreactor. Photolysis was carried out with the 350 nm lamps at 10°C. Reaction progress was monitored by removing a sample and recording its IR spectrum, which showed starting material bands at 2015 and 1960 cm<sup>-1</sup> being replaced by those of the product at 1958 and 1937 cm<sup>-1</sup>. After 2.5 h photolysis was stopped, solvent was removed on a rotary evaporator at 0°C and an NMR spectrum was taken in CS<sub>2</sub> at 0°C. The ratio of the two isomers (IVb/Vb) was 56/44 by integration of the *syn*-proton at  $\delta$  2.75 and 2.62 for each isomer. Less than 5% of starting material remained.

The product was chromatographed on a jacketed column maintained at 0°C, using neutral alumina (activity III), with degassed petroleum ether as eluting solvent.

**Photolysis of IIIb. Initial isomer ratio and wavelength dependence.** Photo-

lysis of 1.4 g (6 mmol) of IIIb at 10°C with 350 nm light for 35 min was carried out as above and solvent was removed at 0°C. The ratio of IVb/Vb determined by examination of the NMR spectrum of the product was 70/30 (25% conversion).

Similar photolysis in petroleum ether solution at 10°C was carried out in a quartz vessel with 300 nm light. Conversion, followed by IR, was slow and after 90 min workup at 0°C led to a product which had a ratio of IVb/Vb of 71/29 (20% conversion).

When photolysis of 1.95 g (8.4 mmol) of IIIb was carried out at 10°C with 253.7 nm light in a quartz vessel, an NMR spectrum of the crude material, taken after 5.5 h and at 0°C indicated a ratio of IVb/Vb of 67/33. Workup, as before, gave 1.28 g of product (75%) in three fractions from chromatography. The last fraction crystallized to a yellow solid, m.p. 31-33°C, and was identified as IVb.

*Photolysis of IIIa.* Photolysis of this complex at 10°C for 4 h employing 350 nm light gave a ratio of IVa/Va of 45/55.

Photolysis under the same conditions but for 1.25 h gave a ratio of IVa/Va of 45/55 at 25% conversion.

*Photochemical isomerization of  $\eta^3$ -methallyliron complexes (IVb, Vb).*

Mixtures of complexes IVb and Vb were photolyzed at 350, 300 and 253.7 nm and the ratio of products was determined periodically by withdrawing aliquots and recording their IR spectra until equilibrium had been reached (~5 h).

*Photolysis of IIIc. Preparation of Vc.* Photolysis of IIIc (0.44 g, 1.75 mmol) was carried out for 90 min at 10°C with 350 nm light, as with IIIa and IIIb. At the end of this period the carbonyl absorption bands characteristic of IIIc had disappeared. Solvent was removed at 0°C and an NMR spectrum showed essentially one compound. Chromatography of the product on 20 g of neutral alumina (activity III) and eluting with petroleum ether yielded a single band which afforded 0.29 g (75%) of Vc. Analysis: Found: C, 54.77; H, 5.50.  $C_{10}H_{12}O_2Fe$  calcd.: C, 54.55; H, 5.49%.

*Photolysis of IIIc. Formation of IVc and Vc.* Photolysis of IIIc (45 mg) in 10 ml petroleum ether at -45 to -50°C using 350 nm lamps was carried out for 3.5 h until no starting material could be observed in the IR spectrum. The solvent was removed at -35°C and a PMR spectrum obtained at -33°C showing IVc and Vc in a ratio of 60/40 respectively.

*Photolysis of IIIc. Formation of IVd and Vd.* Photolysis of IIIc at 350 nm and 10°C for 2 h resulted in complete consumption of starting material. Solvent was removed at 0°C and an NMR spectrum taken at 0°C showed the presence of IVd and Vd in a ratio of 3/4. A smaller amount of IVc in relative proportion of 1 was also present.

*Photolysis of IIIe. Preparation of Ve.* The chloropropene salt (VIII, X = Cl) (1.1 g, 3.1 mmol) was deprotonated as previously described and the product was extracted into 30 ml of petroleum ether. This was placed in the photolysis vessel and irradiated at 10°C with 350 nm light. After 2.5 h no further change was evident in the IR spectrum and the reaction was stopped. Solvent was removed at 0°C, and a PMR spectrum of the crude product showed only starting material and a single product. This was chromatographed on 15 g of neutral alumina (activating III) using petroleum ether as eluent, to give Ve.

*Photolysis of IIIe. Formation of IVe and Ve.* The IIIe complex was prepared

as above and dissolved in 10 ml of petroleum ether and transferred to a 15 ml centrifuge tube. Photolysis was done at  $-45$  to  $-50^{\circ}\text{C}$  using 350 nm light and after 7 h the solvent was removed at  $-35^{\circ}\text{C}$ . The residue was partially dissolved in  $\text{CS}_2$  at  $-78^{\circ}\text{C}$  and a PMR spectrum was obtained at  $-35^{\circ}\text{C}$  showing three Cp resonances assigned to the starting IIIe, and the products IVe and Ve in a relative ratio of 5/4/1 respectively.

*Photolysis of IIIg. Preparation of Vg.* Photolysis of IIIg was carried out in petroleum ether at  $10^{\circ}\text{C}$  using 350 nm lamps. After 3 h no starting material could be observed by IR and the solvent was removed from the solid which had formed. Recrystallization from ether/petroleum ether gave yellow crystals of Vg, m.p.  $125-135^{\circ}\text{C}$  (dec.). Analysis: Found: C, 63.91; H, 4.98.  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{Fe}$  calcd.: C, 63.86; H, 5.00%.

#### *Thermal isomerizations of $\eta^3$ -allyliron complexes*

*Complex IVb. Kinetic runs.* NMR samples of IVb were prepared in  $\text{CDCl}_3$  in a nitrogen atmosphere at  $0^{\circ}\text{C}$  and then placed in the NMR probe held at the desired temperature (determined using ethylene glycol). The integrals for cyclopentadienyl protons resonances for IVb and Vb were recorded at appropriate intervals. These were normalized and rates were calculated from the change in concentrations of IVb and Vb by a weighted least squares program on a Hewlett Packard Model 9820 A calculator. Results are given in Table 3.

On standing in  $\text{CDCl}_3$ , the compounds slowly decomposed, as evidenced by darkening of the solutions and formation of a solid residue. However, during the time used for kinetic runs no decomposition products were observed in the NMR spectrum, and no loss of resolution due to paramagnetic broadening occurred.

In one experiment complex Vb was heated in an NMR tube up to  $180^{\circ}\text{C}$  without appreciable decomposition.

*Complex IVa.* A single run in  $\text{CDCl}_3$  at  $36.3^{\circ}\text{C}$  for 1.2 half lives yielded a rate constant of  $6.4 \pm 0.4 \times 10^{-3} \text{ min}^{-1}$  ( $\rho = 0.973$ ).

On prolonged heating both IVa and Vb are transformed to the corresponding *exo* isomers. At equilibrium less than 2% of the *endo* isomers are present by NMR spectral determinations.

*Complex Vc.* The complex (136 mg) was placed in an NMR tube in benzene- $d_6$ , degassed and sealed in vacuo. The tube was then placed in a constant temperature bath maintained at  $94 \pm 0.5^{\circ}\text{C}$  and the reaction was followed by removing the tube from the bath and recording the NMR spectrum. The half life of the reaction was determined to be 6 h at  $94^{\circ}\text{C}$ . No appreciable decomposition was observed throughout the reaction. After 47 h, the reaction was stopped and spectral measurement gave a ratio of Vd/Vc of 97/3.

*Complex IVd.* The mixture of IVd and Vd obtained in the photolysis of IIId (see above) was taken up in  $\text{CS}_2$  and its equilibration was followed at  $36^{\circ}\text{C}$  in the NMR spectrometer. The rate constant calculated from the change in integration of  $\text{H}_s$  protons in IVd and Vd gave  $k = 2.1 \times 10^{-2} \text{ min}^{-1}$ .

*Complex Ve.* The complex was dissolved in benzene- $d_6$  and sealed in vacuo in an NMR tube. The sample was heated at  $62^{\circ}\text{C}$ , with considerable decomposition occurring, as evidenced by solid formation in the tube. However, good spectra could be obtained by centrifugation and by maintaining the NMR probe



TABLE 5  
UV SPECTRAL DATA

Complex	$\lambda_{\max}$	$\epsilon$
IIIa	311	5400
IIIb	317	6200
IIIc	337	7100
Vc	270	5500
Va	260	3700
Vb	265	6050
Vd	274	5000

at 10°C. The half-life for isomerization was estimated to be 40 min. After several hours at 62°C less than 3% of Ve remained at equilibrium with Vf.

*Complex Vg.* The phenoxyallyl complex was dissolved in benzene- $d_6$  and sealed in vacuo in an NMR tube. The tube was heated to 85-90°C with the reaction being followed periodically by PMR. The half-life of isomerization of Vg to Vh was estimated to be 10-12 h with <5% of Vg present after 67 h.

#### UV spectral data.

Spectral data recorded in heptane solution for  $\eta^1$ -allyl and  $\eta^3$ -allyliron complexes are tabulated in Table 5.

#### Acknowledgement

This research was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (GP-27991).

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