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XVIII. PREFERRED ORIENTATIONS AND ROTATIONAL BARRIERS OF π-OLEFINS IN CYCLOPENTADIENYL AND INDENYL COMPLEXES OF IRON AND RUTHENIUM

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Summary

The synthesis and spectral analysis of a series of some η^5-cyclopentadienyl- and η^5-indenyl-iron—olefin complexes have allowed the elucidation of the orientational preferences and dynamic properties of the olefin ligand. The olefins rotate rapidly about the metal—olefin bond with the barrier to rotation on the order of 8 kcal as determined by the observation of signal broadening in several of the ethylene complexes. Dissociation of the olefin and rotation about the carbon double bond are excluded as possible mechanisms on the basis of spectral evidence. The mode of rotation is consistent with the behavior of the olefin ligands in η^5-$C_5H_5Rh(C_2H_4)_2$ first noted by R. Cramer [J. Amer. Chem. Soc., 86 (1964) 217].

The thermodynamically preferred orientations were determined for each of the olefin complexes. Chemical shift differences resulting from the substitution of an indenyl ligand for a cyclopentadienyl ligand allow determination of the preferred orientations in the ethylene and propylene complexes. For ethylene, the orientation in which the C=C bond is parallel to the plane of the cyclopentadienyl ring is preferred. Methyl substitution of the olefin produces a deviation of preferred orientation. A dihedral angle of about 10° is estimated for the propylene complex.

Introduction

Although [η^5-$C_5H_5Fe(CO)_2$(olefin)]X complexes have been synthesized [1-5], knowledge of the orientation or possible rotation of the olefin ligand is limited. Green and Nagy [3] proposed two orientations for the ethylene group relative to the metal (Fig. 1), and predicted, on the basis of a molecular orbital description, the greater stability of configuration A. The proton NMR spectrum of

Fig. 1. Possible orientations of ethylene in [η^5-$C_5H_5Fe(CO)_2$(olefin)]X.

this complex consists of two singlets, one of which was assigned to the averaged cyclopentadienyl protons, the result of free rotation about the metal—ring axis. The remaining resonance was attributed to all four of the olefin protons. Cramer [6], being unable to differentiate these protons, commented that the shielding difference was either too small for detection or the rotational barrier was so low that the protons equilibrated too rapidly for observation.

The equilibration of the protons could conceivably occur by a number of mechanisms. Rapid rotation of coordinated ethylene about either the C=C bond or the metal—olefin bond as an axis could lead to a single proton signal. Furthermore, dissociative mechanisms would allow either side of the planar olefin moiety to face the iron atom and average the environments.

In addition to the indenyliron and cyclopentadienylruthenium analogs of the ethylene complex, a number of substituted olefin complexes have been prepared for the purpose of determining the orientation of the olefin and the mechanism of averaging of the olefinic protons.

Results and discussion

Room temperature PMR spectra of [η^5-$C_5H_5Fe(CO)_2(C_2H_4)$]BF_4, [η^5-C_9H_7-$Fe(CO)_2(C_2H_4)$]BF_4, and [η^5-$C_5H_5Ru(CO)_2(C_2H_4)$]BF_4 display a single resonance for the olefinic protons. At lower temperatures these resonances begin to broaden, in contrast to the proton signals arising from the cyclopentadienyl or indenyl rings. This is particularly evident in the indenyl case, where the olefin signal has a half-width of 16 Hz at −90°C. It was impractical to record spectra below −100°C due to the poor solubility of the salts in suitable low-temperature solvents.

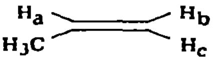
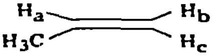
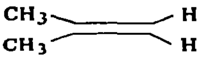
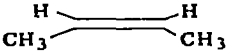
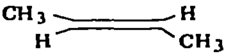
The rate constant for the rearrangement can be estimated from the fast-exchange limit equation for two equally-populated sites [7] (eqn. 1).

$$k = \pi(\delta\,\nu)^2/2(\Delta\nu'_{\frac{1}{2}} - \Delta\nu_{\frac{1}{2}}) \qquad (1)$$

The parameter $\delta\nu$ denotes the chemical shift difference between the two sites and the quantity ($\Delta\nu'_{1/2} - \Delta\nu_{1/2}$) is the increase in half-width of the signal due to averaging. The valid use of this expression requires that only two environments be present in significant concentration; hence, it is assumed that only one of the conformations shown in Fig. 1 is present and if the mechanism is dissociative, significant amounts of free olefin are not formed. The free energy of activation can be obtained from the results of eqn. 1, if the chemical shift difference, $\delta\nu$, is known. However, ΔG^* is not a sensitive function of $\delta\nu$ and a crude estimate of chemical shift separation will suffice for a reasonably accurate value of ΔG^*. An estimate for the $\delta\nu$ value may be obtained by comparison with the spectra of the propene (C_3H_6) complexes, [η^5-$C_5H_5Fe(CO)_2(C_3H_6)$]BF_4 and

TABLE 1

PROTON NUCLEAR MAGNETIC RESONANCE DATA

Compound	Assignment	δ^a	Multiplicity^b	Intensity
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_2H_4)]BF_4$	C_5H_5	5.61	s	5
	C_2H_4	3.75	s	4
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_2H_4)]BF_4$	C_9H_7	7.69	m	4
	C_9H_7	6.53	d(3.0)	2
	C_9H_7	6.03	t(3.0)	1
	C_2H_4	2.88	s	4
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_6)]BF_4$	C_5H_5	5.57	s	5
	H_a	5.08	m	1
	H_b	3.84	d(8.3)	1
	H_c	3.43	d(14.7)	1
	CH_3	1.79	d(6.3)	3
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$	C_9H_7	7.74	m	4
	C_9H_7	6.63	d(3.0)	1
	C_9H_7	6.34	d(3.0)	1
	C_9H_7	5.98	t(3.0)	1
	H_a	4.14	m	1
	H_c	3.18	d(14.4)	1
	H_b	1.90	d(8.0)	1
	CH_3	1.65	d(6.0)	3
$[\eta^5\text{-}C_5H_5Ru(CO)_2(C_2H_4)]BF_4$	C_5H_5	5.97	s	5
	C_2H_4	3.89	s	4
$[\eta^5\text{-}C_5H_5Fe(CO)_2(1\text{-}C_4H_8)]BF_4$	C_5H_5	5.70	s	5
	H_a	5.16	m	1
	H_b	3.88	d(8.5)	1
	H_c	3.47	d(15.0)	1
	CH_2	2.40	m	1
	CH_2	1.60	m	1
	CH_3	1.16	t(7 0)	3
$[\eta^5\text{-}C_5H_5Fe(CO)_2(i\text{-}C_4H_8)]BF_4$	C_5H_5	5.52	s	5
	H	3.81	s	2
	CH_3	1.84	s	6
	C_9H_7	7.68	m	4
	C_9H_7	6.35	d(4.0)	2
	C_9H_7	5.98	t(4.0)	1
	H	3.82	s	2
	CH_3	1.40	s	6
$[\eta^5\text{-}C_5H_5Fe(CO)_2(cis\text{-}2\text{-}C_4H_8)]BF_4$	C_5H_5	5.77	s	5
	H	5.28	m	2
	CH_3	1.78	m	6
$[\eta^5\text{-}C_5H_5Fe(CO)_2(trans\text{-}2\text{-}C_4H_8)]BF_4$	C_5H_5	5.77	s	5
	H	4.88	m	2
	CH_3	1.86	m	6

[a] Relative to $Si(CH_3)_4$ as internal standard in acetonitrile-d_3. [b] Splittings are given in Hz as s, singlet; d, doublet; t, triplet; m, multiplet.

$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$ (Table 1) which, as will be shown in detail subsequently, provide models for the two types of protons for a coordinated ethylene in configuration B. At 100 MHz the chemical shift difference between the geminal protons, H_b and H_c, in the cyclopentadienyl complex is +39 Hz. The methyl group in free propene [7] causes a greater upfield shift in the *trans*-geminal pro-

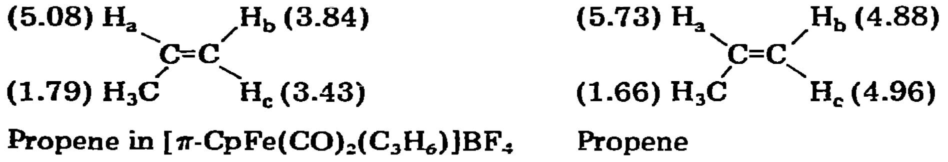


Fig. 2. The chemical shifts of free and coordinated propene.

ton (H_b) than in the *cis*-proton (H_c) producing a difference of −8 Hz. Although comparison of complexed with free propene (Fig. 2) indicates an upfield shift of the geminal protons on coordination, the influence of the methyl group would be expected to be similar. Therefore, the estimate of ~47 rather than 39 Hz for the geminal proton difference in the ethylene complex would be more appropriate *. A similar comparison results in an estimated separation of +136 Hz for the indenyl complex. The ^{13}C NMR spectra (Table 2) will be discussed below.

Using these values for $\delta\nu$, rate constants were obtained from observed line broadenings and eqn. 1. Free energies obtained from eqn. 2 are tabulated in Table

$$\Delta G^* = 2.3\,RT(10.3 + \log T - \log k) \qquad (2)$$

3. Comparison indicates that the values of ΔG^* are virtually the same for all three complexes. Taking account of errors in temperature measurement, approximation of chemical shift differences, and broadening measurements, the maximum uncertainty in ΔG^* would be ±0.5 kcal/mol*. No increase in the barrier to rotation occurs in substituting an indenyl ligand for a cyclopentadienyl ligand. Similarly, the rotation seems to be unaffected by a change in the metal from iron to ruthenium.

Preferred orientations of monosubstituted ethylenes

The absence of significant low-temperature (−80°) broadening and the characteristic chemical shifts in the propene complexes [η^5-$C_5H_5Fe(CO)_2(C_3H_6)$]BF_4 and [η^5-$C_9H_7Fe(CO)_2(C_3H_6)$]BF_4 suggest a great preference for one olefin orientation. Comparison with analogous allylmolybdenum systems [8] suggest that significant chemical shift differences would be expected for various orientations of the olefin. In particular, protons in close proximity to the indenyl ligand should exhibit large upfield shifts due to the magnetic anisotropy of the six-membered ring. Since various orientations would produce large deviations in chemical shift, reference to eqn. 1 indicates that extensive broadening would be observed if there were substantial populations of more than one configuration.

In comparing the shifts of propene protons of the cyclopentadienyl- and indenyl-iron complexes, the upfield shifts of H_a and H_b suggest a significantly closer average distance to the ring than either H_c or the methyl group. This suggests a preferred orientation of the olefin in which the C=C axis is approximately parallel to the five-membered-ring plane, as in configuration B, but with a methyl group directed away from the ring. The relative shifts of H_a and H_b differ

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* A crude approximation is usually sufficient. For example, with a broadening of 10 Hz at −90°, a separation of 39 and 47 Hz gives values of ΔG^* of 8.00 and 7.90 kcal/mol respectively.

TABLE 2

CARBON-13 NUCLEAR MAGNETIC RESONANCE DATA

Compound	δ(CO)[a]	δ(Cp)[a]	δ(Indene)[a]		δ(Olefin)[a]	
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_2H_4)]BF_4$	209.43	89.83			56.86	
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_2H_4)]BF_4$	208.32		134.01	C(4),C(7)	63.48	
			124.27	C(5),C(6)		
			105.33	C(8),C(9)		
			87.92	C(2)		
			77.14	C(1),C(3)		
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_6)]BF_4$	209.09	87.90			83.92	$=CH$
	207.18				53.89	$=CH_2$
					19.87	$-CH_3$
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$	209.17		133.82	C(4)	89.68	$=CH$
	207.89		132.67	C(5)	61.30	$=CH_2$
			124.78	C(6)	19.68	$-CH_3$
			122.47	C(7)		
			107.39	C(8)		
			103.50	C(9)		
			87.57	C(2)		
			76.68	C(1)		
			74.86	C(3)		
$[\eta^5\text{-}C_5H_5Fe(CO)_2(1\text{-}C_4H_8)]BF_4$	209.12	88.13			89.32	$=CH$
	207.13				52.35	$=CH_2$
					28.36	$-CH_2-$
					15.15	$-CH_3$
$[\eta^5\text{-}C_5H_5Fe(CO)_2(\textit{trans}\text{-}2\text{-}C_4H_8)]BF_4$	204.88	87.99			89.17	$=CH$
	201.29				21.24	$-CH_3$
$[\eta^5\text{-}C_5H_5Fe(CO)_2(i\text{-}C_4H_8)]BF_4$	208.81	87.57			118.84	$=CMe_2$
					51.22	$=CH_2$
					26.45	$-CH_3$
$[\eta^5\text{-}C_9H_7Fe(CO)_2(i\text{-}C_4H_8)]BF_4$	209.26		132.83	C(4),C(7)	118.55	$=CMe_2$
			124.05	C(5),C(6)	59.01	$=CH_2$
			106.98	C(8),C(9)	24.08	$-CH_3$
			88.42	C(2)		
			74.39	C(1),C(3)		

[a] Chemical shifts are measured in ppm downfield from TMS. All spectra were obtained from solutions in acetonitrile-d_3 with 0.5 *M* Cr(acac)$_3$ used as a relaxation reagent.

TABLE 3

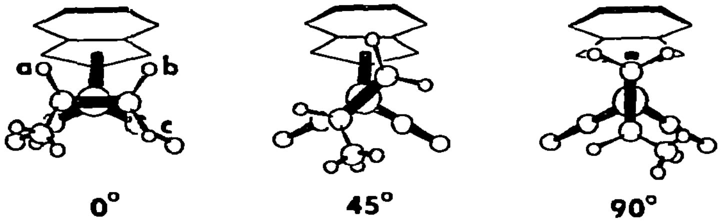
APPROXIMATE RATE CONSTANTS AND ENERGY PARAMETERS

Compound	T (°C)	W[a] (Hz)	$10^{-3}k$ (sec^{-1})	ΔG^* (kcal/mol)
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_2H_4)]BF_4$	−80	0.5	7.0	7.8
	−90	2.0	1.7	7.9
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_2H_4)]BF_4$	−62	0.5	58	7.6
	−80	4.0	7.3	7.7
	−90	14.0	2.1	7.8
$[\eta^5\text{-}C_5H_5Ru(CO)_2(C_2H_4)]BF_4$	−80	0.3	11.6	7.6
	−95	1.0	3.5	7.5

[a] W is the difference between the full width at half-height and the width at room temperature.

TABLE 4

RING CURRENT EFFECTS FROM THE η^5-INDENYL LIGAND[a]



Angle(°)	H_a	H_b	H_c	$H_a/H_b/H_c$
90	0.63	4.57	4.57	1.0/7.3/7.3
45	0.90	7.08	1.27	1.0/7.9/1.4
30	1.16	5.77	0.97	1.0/5.0/0.84
15	1.55	4.22	0.79	1.0/2.7/0.53
10	1.74	3.57	0.75	1.0/2.1/0.43
0	2.49	2.49	0.68	1.0/1.0/0.27
Observed	0.94	1.92	0.25	1.0/2.0/0.27

[a] The difference in chemical shifts (ppm) between the cyclopentadienyl and indenyl complex. Calculated values are given for various orientations of the olefin and all represent upfield shifts on replacement of cyclopentadienyl by indenyl.

considerably in magnitude, however, which indicates that the olefin may be tilted at an angle. A quantitative estimate of the shifts may be computed by methods previously described for indenylmolybdenum systems [8]. A geometric model was developed based on bond lengths and angles in similar compounds and the six-membered ring of the indenyl ligand was oriented directly over the olefin. The effect of the magnetic anisotropy of the indenyl ligand was then calculated using standard formulae and coordinates based on the model*. These estimated shifts are summarized in Table 4.

The magnitudes given in Table 4 assume a fixed orientation of the indenyl ligand over the olefin. Since free rotation of the indenyl has been demonstrated in the molybdenum analogs and a similar situation would be expected here, lower values of shift can be expected than are calculated. The observed shifts are averages of all of the orientations of the indenyl ligand. When the six-membered ring is oriented away from the olefin no effect of the ring is expected; hence as a first approximation, one would expect the observed shifts to each be a fraction of calculated values**. Comparison of the ratios of observed values with those of an angle of 10° are quite favorable. Considering the lack of correlation with other conformations, we believe that the lowest energy configuration is adequately demonstrated as that in which the olefin is nearly parallel to the ring (Fig. 3C).

The broadening observed in the ethylene complexes is attributed to proton exchange between two equally-populated non-equivalent sites in the lowest en-

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* The assumptions involved did not warrant an extensive investigation of various models. Numerical values of the shifts were taken from a tabulation of calculated shielding effects produced by ring currents [7].

** The effect of a potential well and integration over all angles has been treated elsewhere [8].

Fig. 3. Two possible conformations of propene complexes. Structure D represents a 180° rotation of the olefin from that in C; however, it is unlikely to represent a local minimum in energy.

ergy conformation. Substitution of the ethylene in the low energy conformation produces configurations which would not be expected to have identical populations (Fig. 3). Generally a smaller degree of broadening would be expected with unequal populations in fast exchange spectra. In the indenyl—propene complex broadening of 0.8 Hz was observed for H_c at −85° in contrast to a value of 9 Hz in the ethylene complex. This broadening suggests that conformations significantly different from C (Fig. 3) are present to an extent of less than ten percent*. A complete analysis of the potential curve associated with the rotation is impractical; nevertheless, it is unrealistic to consider only the two extreme conformations, since several propene conformations with small angular deviations from 10° (Table 4) may also represent minima. Regardless, the data clearly indicate that over a given time interval the methyl group is usually oriented away from the ring and that a configuration similar to D (Fig. 3) is thermodynamically unfavorable.

Further proof in predicting the preferred orientation of ethylene in $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_2H_4)]BF_4$ and $[\eta^5\text{-}C_9H_7Fe(CO)_2(C_2H_4)]BF_4$ arises from the predicted shifts for the two orientations A and B (Fig. 2). Configuration A would predict a 2.60 ppm shift of the averaged olefin signal in the indene compound whereas B should result in a 1.59 ppm shift. The observed shift is 0.87 ppm, about 55% of that predicted for B, which is the same fraction found in the propene complexes. This reduced value of the shift arises from the preferred orientation of the indenyl ligand (vida supra) and the similarity suggests that B is the more probable orientation.

The mechanism of conformational interconversion

The most plausible intramolecular mechanism of conformational interconversion would appear to be rotation of the olefin about an axis between the metal and the centroid of the olefin. An analogous mechanism has been discussed by Cramer [9] and extended by Johnson [10] for some rhodium complexes. Rotation about the C=C axis or intramolecular exchange are also possibilities which should be considered; however, dissociative mechanisms can be conclusively eliminated by consideration of the NMR spectra of the less-symmetrical propene and 1-butene compounds. The $[\eta^5\text{-}C_5H_5Fe(CO)_2(1\text{-}C_4H_8)]BF_4$ complex closely resembles its propene analog in its physical and spectral properties, and in addition, displays two separate proton multiplets for the methylene protons

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* This percentage is based on a crude two-site approximation outlined in the experimental section. The observed broadening is consistent only with a certain range of chemical shifts, populations and rates. When these rate and shift parameters are restricted to reasonable values, only a limited variation in calculated population occurs.

(see Table 1). Complete dissociation of the olefin cannot occur because the diastereotopic methylene protons would become equivalent. That is, the 1-butene is prochiral and binding to the metal produces a chiral center which causes the methylene protons to appear non-equivalent. If dissociation occurred, a pathway would be provided for the chirality to be inverted and the methylene protons would appear equivalent in the NMR.

The formation of the chiral center on binding of the olefin produces two enantiomers, as shown for the indenyl—propene complex in Fig. 4. The nonequivalence of the diastereotopic 1- and 3-protons and 1- and 3-carbon atoms of the indenyl ligand is a consequence of this chiral center. Since dissociation would provide a path for rapid racemization, nuclei at the 1- and 3-positions would become equivalent if it occurred. However, ^{13}C and ^{1}H NMR spectra of $[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$ show nonequivalence of nuclei in the 1- and 3-positions of the indene. A similar argument would predict equivalence of carbonyl carbons in propene and 1-butene complexes, assuming a dissociative process. In all such compounds prepared, two carbonyl carbon resonances are observed (Table 2); hence a dissociative process is not responsible for the observed broadening.

Interconversion of configurations could occur by rotation about the carbon—carbon double bond axis. A rotation of this type would rupture the coordination bond and the expected energy requirements would be greater than the 8 kcal/mol observed [6]. This type of conversion however would still allow the nonequivalence of the methylene protons, indenyl protons, and carbonyl carbons observed in the NMR spectrum of 1-butene and propene complexes. Clear evidence that rotation about the carbon—carbon double bond axis does not occur is illustrated by the ^{13}C NMR spectrum of the *trans*-2-butene derivative (Table 2). Upon coordination of the *trans*-2-butene two enantiomers are formed; hence, the two diastereotopic carbonyl groups are nonequivalent in the NMR spectrum. Rotation about the C=C bond interconverts enantiomers, whereas rotation about the metal—olefin bond does not. Therefore, the mode of interconversion must be rotation about the metal—olefin bond.

Interconversion of conformations does not require a full 360° rotation of the olefin. An oscillatory process in which the angle (Table 4) varies between approximately 10 and 160° would appear to be the lowest energy path. This motion would not require the methyl group to pass near the ring, a process which one might anticipate to be a higher energy pathway. Nevertheless, a complete rotation of the olefin should be possible and the barrier for passing 270° should not be excessive; vida infra, the rotation of *trans*-2-butene.

Although the rate of rotation was evaluated for the ethylene complexes, extension of the rates to substituted ethylenes in computations would appear to

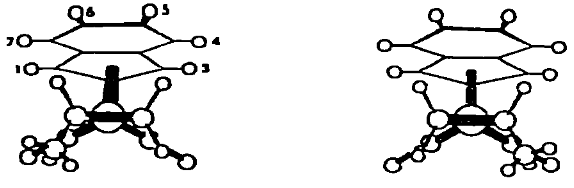

Fig. 4. Enantiomers of $[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$.

be justified. Faster rates in substituted olefins would tend to invalidate some of the previous conclusions; however, slower interconversions are anticipated. Steric effects tend to dominate rotational barriers in other systems and substituting alkyl groups for olefinic hydrogens atoms would tend to increase the barrier to rotation. Conversely, alkyl substitution should make the olefin less π-acidic, weaken the π-bonding in the metal—olefin bond, and lower the barrier to rotation. Although several studies of steric and electronic factors on olefin bond strength have been made [11-14], their relationship to rotational barriers in the systems under investigation here are best compared to the observations of Lewis et al. [15,16]. These workers noted a slight increase in ΔG^* upon replacement of ethylene with propene, *cis*-2-butene, or *trans*-2-butene in four-coordinate Pt(acac)Cl(olefin) complexes. Electronic effects appeared to play a secondary role in those complexes and a similar situation would be expected in the cyclopentadienyl- and indenyl-iron complexes. Furthermore, electronic factors would be expected to be even less important, since the back-bonding interactions from the metal would be minimized in cationic complexes. Consideration of molecular models suggests that alkyl substitution would not produce substantial increases in steric interactions. Consequently, steric interactions tend to compensate for changes in bond strengths and large deviations in rotational barriers are not anticipated for the olefin complexes studied here.

Preferred orientations of di-substituted ethylenes

As with the propene complex (vida supra) it appears that there is a thermodynamic preference for methyl group orientation away from the cyclopendienyl ring. The *cis*-2-butene complex shows only one methyl proton signal and one vinyl proton signal, neither of which broaden at low temperature. This suggests the stable symmetrical configuration shown in Fig. 5; however, the data would also be consistent with rapid averaging between two configurations tilted at the same angle but in opposite directions of the configuration shown in Fig. 5. A large tilt angle (~ 10°) would be unlikely unless the ΔG^* for rotation were severely reduced because chemical shift differences would be introduced which should produce significant broadening*.

The *trans*-2-butene complex exhibits a single resonance for the methyl and vinyl protons at room temperature but both broaden considerably at lower temperatures (—60°). This suggests an interconversion between two equally probable configurations. Two extreme conformations are shown in Fig. 6. The data do

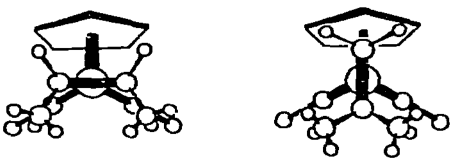

Fig. 5. Symmetrical orientation of ligands in *cis*-2-butene and isobutene complexes.

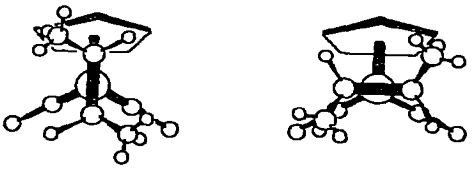

Fig. 6. Possible orientations of the *trans*-butene complex.

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* Indenyl complexes of *cis*- and *trans*-2-butene appear to be too unstable to permit synthesis from the epoxide.

not allow an assignment of preferred configuration, but comparison with previous results suggests that interaction with the ring predominates and interaction with the carbonyls is secondary. Hence, an intermediate configuration between those shown in Fig. 6 is probably appropriate (~—10°, Table 4).

Both isobutene complexes show single resonances for the methyl and vinyl protons but no broadening is observed at $-80°C$. As with the *cis*-2-butene, this could be attributed to a symmetrical configuration (Fig. 5) or to an equilibrium between two equally probable orientations with the olefin tilted at some angle to the configuration shown. We believe the latter to be more likely; however, a large deviation from the vertical orientation (A) would produce a significant broadening at low temperatures if the barrier to rotation were not lower. Further study will be required to establish the preferred conformation of this particular complex*. The absence of significant upfield shifts upon substitution of the indenyl ligand suggests that the six-membered ring prefers an orientation away from the olefin. unlike that observed in the propene compounds. A splitting (0.08 ppm) of the equivalency of the 4, 5, 6, and 7 indenyl protons, not observed in the ethylene or propene compounds, is, by comparison with allyl analogues [8,18], further evidence of a loss of preferred orientation over the olefin.

Experimental

Preparations, reactions, and purifications were carried out under a nitrogen atmosphere. Chromatographic separations utilized low activity alumina (Fisher A-540). NMR spectra were obtained using Varian HA-100 and CFT-20 spectrometers. Infrared spectra were obtained using a Perkin—Elmer 421 spectrometer calibrated with DCl.

Syntheses

All of the neutral starting alkyls and allyls were prepared by standard methods [1] using care to add the anionic metal complex (e.g. η^5-$C_5H_5Fe(CO)_2^-$) to tetrahydrofuran solutions of the halide or epoxide at $-78°C$. Three methods of preparation were used for obtaining the cationic olefin complexes, the properties of which are summarized in Table 5.

Method I. Hydride abstraction from the σ-ethyl complex by trityl tetrafluoroborate was effective for the ethylene complexes [3]. The σ-complexes were identified by infrared spectra in the region of carbonyl stretching frequencies: η^5-$C_5H_5Fe(CO)_2C_2H_5$, ν(CO) 2009, 1950 cm^{-1} in C_6H_{12} (lit. [19] 2010, 1950 cm^{-1} in CCl_4); η^5-$C_5H_5Ru(CO)_2C_2H_5$, ν(CO) 2011, 1942 cm^{-1} in $CHCl_3$ (lit. [20] 2029, 1960 cm^{-1} in CS_2). The new complex, η^5-$C_9H_7Fe(CO)_2C_2H_5$ had CO absorptions at 2004 and 1948 cm^{-1} in C_6H_{12}. Cationic ethylene complexes also showed characteristic carbonyl stretching frequencies: η^5-$C_5H_5Fe(CO)_2$-$(C_2H_4)^+$, ν(CO) 2080, 2044 cm^{-1} in CH_3CN (lit. [1] 2083, 2049 cm^{-1}); η^5-C_5H_5-$Ru(CO)_2(C_2H_4)^+$, ν(CO) 2089, 2047 cm^{-1} in CH_3CN (lit. [21] 2090, 2048 cm^{-1}). For the new complex η^5-$C_9H_7Fe(CO)_2(C_2H_4)^+$, ν(CO) 2074, 2036 cm^{-1} in CH_3CN.

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* Prof. M. Rosenblum has conducted a carbon-13 NMR study of some of these olefin complexes and has reached a similar conclusion regarding the stability of the B conformation in most derivatives [17].

TABLE 5

SUMMARY OF SYNTHETIC PROCEDURES

Compound	Method of preparation[a]	Yield (%)		ν(CO) (cm^{-1}) (acetonitrile)	
		Precursor	Overall		
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_2H_4)]BF_4$	I	57	45	2044	2080
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_2H_4)]BF_4$	I	30	29	2036	2074
$[\eta^5\text{-}C_5H_5Ru(CO)_2(C_2H_4)]BF_4$	I	28	25	2047	2089
$[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_6)]BF_4$	II	95	90	2036	2074
$[\eta^5\text{-}C_9H_7Fe(CO)_2(C_3H_6)]BF_4$	II		25	2030	2070
$[\eta^5\text{-}C_5H_5Fe(CO)_2(1\text{-}C_4H_8)]BF_4$	II		35	2037	2074
$[\eta^5\text{-}C_5H_5Fe(CO)_2(i\text{-}C_4H_8)]BF_4$	II		70	2029	2067
$[\eta^5\text{-}C_9H_7Fe(CO)_2(i\text{-}C_4H_8)]BF_4$	II		15	2021	2064
$[\eta^5\text{-}C_5H_5Fe(CO)_2(\textit{cis}\text{-}2\text{-}C_4H_8)]BF_4$	III		30	2031	2069
$[\eta^5\text{-}C_5H_5Fe(CO)_2(\textit{trans}\text{-}2\text{-}C_4H_8)]BF_4$	III		30	2031	2071

[a] I, hydride abstraction from σ-alkyl; II, protonation of σ-allyl; III, protonation of alkoxide.

The ethylene complexes were all air-stable solids. The cyclopentadienyl- and indenyl-iron compounds were yellow and orange respectively, and the ruthenium complex was colorless.

Method II. Several of the substituted olefin complexes were prepared by protonation of the σ-allyl complex with HBF_4 [2]. The allyl complexes were identified by their infrared spectra: η^5-$C_5H_5Fe(CO)_2C_3H_5$, ν(CO) 2010, 1950 cm^{-1} in cyclohexane (lit. [2] 2010, 1948 cm^{-1} neat); η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$, ν(CO) 2009, 1951 cm^{-1} in cyclohexane (lit. [2] 2016, 1950 cm^{-1} neat); η^5-C_5H_5-$Fe(CO)_2CH_2C(CH_3){=}CH_2$ [22], ν(CO) 2010, 1950 cm^{-1} in C_6H_{12}.

Two new indenyl compounds were synthesized: η^5-$C_9H_7Fe(CO)_2C_3H_5$, ν(CO) 2008, 1952 cm^{-1} in C_6H_{12} and η^5-$C_9H_7Fe(CO)_2CH_2C(CH_3){=}CH_2$, ν(CO) 2004, 1950 cm^{-1} in C_6H_{12}. Cationic complexes identified by their IR spectra included: η^5-$C_5H_5Fe(CO)_2(C_3H_6)^+$, ν(CO) 2074, 2036 cm^{-1} in CH_3CN (lit. [2] 2082, 2053 cm^{-1} in Nujol mull); η^5-$C_5H_5Fe(CO)_2(1\text{-}C_4H_8)^+$, ν(CO) 2074, 2037 cm^{-1} in CH_3CN (lit. [2] 2088, 2055 cm^{-1} in Nujol mull); η^5-$C_5H_5Fe(CO)_2(i\text{-}C_4H_8)^+$ [22], ν(CO) 2067, 2029 cm^{-1} in CH_3CN. Two new cationic indenyl complexes were prepared: η^5-$C_9H_7Fe(CO)_2(C_3H_6)^+$, ν(CO) 2070, 2030 cm^{-1} in CH_3CN and η^5-$C_9H_7Fe(CO)_2(i\text{-}C_4H_8)^+$, ν(CO) 2064, 2021 cm^{-1} in CH_3CN. Precipitation of the cationic species of the cyclopentadienyl complexes occurred readily upon protonation at room temperature. Synthesis of the indenyl compounds was greatly facilitated by cooling the solution of the allyl complex to —78° before protonation with HBF_4. The indenyl complex of isobutene was the most difficult to prepare and required operations at —78° to isolate and crystallize the dark red-orange product. All of the other complexes were air-stable solids ranging in color from yellow to orange.

Method III. The *cis*- and *trans*-butene complexes were most conveniently prepared by protonation of the alkoxide formed by reaction of η^5-$C_5H_5Fe(CO)_2^-$ with the corresponding epoxide [5]: η^5-$C_5H_5Fe(CO)_2(\textit{cis}\text{-}2\text{-}C_4H_8)^+$, ν(CO) 2069, 2031 cm^{-1} in CH_3CN (lit. [23] 2065, 2025 cm^{-1} in CH_3NO_2); η^5-$C_5H_5Fe(CO)_2$-$(\textit{trans}\text{-}2\text{-}C_4H_8)^+$, ν(CO) 2071, 2031 cm^{-1} in CH_3CN (lit. [23] 2065, 2025 cm^{-1} in CH_3NO_2). If low temperatures were not maintained during the preparation of the *cis*- and *trans*-butene complexes, decreased yields of olefin complex and large quantities of the tricarbonyl cation, η^5-$C_5H_5Fe(CO)_3^+$ were obtained. It did not appear that tricarbonyl cation formation was directly linked to olefin complex decomposition.

All of the BF_4 salts were purified by crystallization from acetonitrile and diethyl ether. Decomposition occurred at temperatures greater than 150°, but definitive melting points were not observed below 300°. A reaction occurs slowly between acetonitrile and the isobutylene complexes; hence, NMR spectra were recorded at −25°.

Chemical shift calculations

The determination of ring current effects followed the methodology used previously [8] and utilized the tabulated values of Bovey [7]. A "piano-stool" geometry was assumed for a model with angles formed by the iron—carbonyl bonds and the iron—olefin—centroid vector taken as 90° (e.g. η^5-$C_5H_5Mn(CO)_3$ with C—Mn—C = 92°) [13]. The Fe—$C(C_5H_5)$ distances were taken to be 2.10 Å and Fe—C(olefin) distance to be 2.00 Å as estimated from a series of metal—olefin complexes [25-27]. An increase in olefin bond length upon coordination was assumed and the following bond lengths and angles used in the calculation: C—C = 1.42 Å; C—H 1.05 Å; H—C—H = 111°; H—C—C = 117°.

Estimation of populations necessary to produce observed broadening

For two sites of unequal population, the line broadening due to exchange is given by [7]:

$$(\nu'_{1/2} - \nu_{1/2}) = p_A^2 p_B^2 [2\pi(\nu_A - \nu_B)]^2 (\tau_A + \tau_B)$$

where $(\nu'_{1/2} - \nu_{1/2})$ denotes the excess broadening of the half-width of the averaged signal and $(\nu_A - \nu_B)$ the chemical shift difference (Hz) of the unaveraged signals. The residence times in each site are designated τ_A and τ_B and the fractional populations of the A and B sites are given as p_A and p_B.

The total lifetime, $\tau = 1/(1/\tau_A + 1/\tau_B)$ was estimated as $(2k)^{-1}$ of the value for equally populated sites. This corresponds to $(4200)^{-1}$ sec at −85° based on a ΔG^* of 7.8 kcal/mol. Using the estimated separation of 70 Hz, one obtains a population of the less favorable conformation of 6%. It should be recognized that two conformations are insufficient to accurately describe the system and all orientations of the olefin and the probability of assuming a given orientation should be considered. This gross approximation however, provides some insight into the effect of barrier height, population difference and chemical shift separation.

Assuming a 70 Hz separation and ΔG^* of 7.3, 7.8, and 8.3 kcal/mol, populations of 97/3, 94/6, and 85/15 are obtained. For the same values of ΔG^* with a 50 Hz separation and 90 Hz separation, values of 95/5, 89/11, 68/32 and 98/2, 97/3 and 92/8 are found respectively. It is clear that for separations of nearly 100 Hz, errors in the approximations do not significantly affect the results. We are currently studying these materials at 270 MHz in order to further justify these approximations.

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