Organometallic Conformational Equilibria. XX. Preferred Orientations and Rotational Barriers of π-Olefins in Chiral Tin–Iron Compounds. The Isolation of Diastereoisomers in Prochiral Olefin Derivatives

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Abstract: The synthesis and spectral analysis of a series of η^5-cyclopentadienyl- and η^5-indenyliron–tin–olefin complexes have allowed the elucidation of the orientational preferences and dynamic properties of the olefin ligand. The olefins rotate about the metal–olefin bond with the barrier to rotation varying from 11 to 14 kcal, therefore permitting observation of both nonaveraged and averaged spectra. Evidence of restricted rotation about the tin–carbon bond was seen in low temperature spectra of the triphenyltin derivatives. Chemical shift differences resulting from the substitution of an indenyl ligand for a cyclopentadienyl ligand allow determination of the preferred orientations in the propene complexes. Angles of −10 and −15° from an orientation in which the C═C bond is parallel to the plane of the cyclopentadienyl ring are estimated for the trimethyltin and triphenyltin derivatives, respectively. The substitution of propene on a chiral iron produces diastereoisomers which form in equal quantities in the cyclopentadienyl complexes. In each instance one of the diastereoisomers is substantially less stable than the other. In the triphenyltin species a half-life of 5×10^3 sec is found for the less stable isomer at 20°. Decomposition proceeds with the release of free propene and addition of triphenylphosphine does not alter the rate. In the indene compounds only one diastereoisomer is observed.

We have recently reported the orientational preferences and dynamic properties of the olefin ligand in a series of $[\eta^5\text{-}C_5H_5Fe(CO)_2(\text{olefin})]BF_4$ complexes.[1] Substitution of a tertiary tin ligand for one of the carbonyls produces a series of neutral complexes having a chiral metal center. Since chiral centers are produced upon the binding of substituted olefins to metals,[2,3] the substitution of a prochiral olefin such as propene in this system produces diastereoisomers. Characterization of the diastereoisomers is important because of the possible use of the chiral olefin complex in studies of stereoselective reactions on coordinated olefins and asymmetric induction by chiral metal centers.

The rotational barriers in these complexes are sufficiently higher than the cationic complexes so that the complete dynamic processes, including the nonrotating orientations, can be observed on the NMR. This also facilitates calculation of the thermodynamically preferred orientations of the olefins, based on changes in chemical shifts resulting from ring current effects.[1]

We have therefore synthesized a number of cyclopentadienyl and indenyl derivatives of the propene and ethylene complexes. For each derivative, trimethyltin and triphenyltin were used as the tertiary tin substituent.

Results

Infrared spectra of the complexes in the carbonyl stretching region are summarized in Table I. The substitution of ethylene for a carbonyl ligand results in a single stretching frequency which is 5-10 cm^{-1} less than the lowest band of the analogous dicarbonyl compound. The substitution of propene leads to a further decrease of about 5 cm^{-1}.

Only one symmetrical carbonyl band was seen for each of the olefin complexes, including those for which NMR results indicated the presence of two diastereoisomers. Half-widths of carbonyl bands in triphenyltin-olefin compounds were 11-13 cm^{-1} while those of dicarbonyl or trimethyltin olefin complexes were 6-8 cm^{-1}.

Repetitive scans of the spectra of the propene complexes showed a decrease in the intensity of the carbonyl band of the olefin complex and a corresponding increase in the intensity of the two bands of its dicarbonyl precursor.

Proton NMR spectra are summarized in Table II. All of the complexes exhibited temperature-dependent spectra in the olefin region, with sharp signals generally observed at about −60 °C, followed by broadening as the temperature increased, and finally by sharp time-averaged spectra at or slightly above room temperature. Significant broadening of cyclopentadienyl or indenyl resonances was not observed. At temperatures of −70° or below further broadening of the olefin signals was seen in complexes containing triphenyltin. This effect was also observed in the aromatic pattern of the triphenyltin group.

Two sets of resonances of equal intensity were found for propene complexes containing the cyclopentadienyl ligand. At 20° in toluene-d_8 one set of resonances decreased in intensity with a half-life of approximately 5.0×10^3 sec, while the intensity of the other set remained constant. Addition of triphenylphosphine did not change the rate of decomposition, although the emergence of a new cyclopentadienyl signal, coupled by 1.7 Hz to phosphorus was noted and was presumed to be $\eta^5\text{-}C_5H_5Fe(CO)(SnPh_3)(PPh_3)$. Decomposition of the propene complexes resulted in the formation of free propene, detected at 1.67 and 1.72 ppm. No increase in intensity of the starting compound, $\eta^5\text{-}C_5H_5Fe(CO)_2(SnPh_3)$, was observed in the presence of PPh_3.

The indenyl propene compounds had only one set of olefin resonances. Decomposition was rapid at 20° for both triphenyltin and trimethyltin derivatives and was also accompanied by the formation of free propene.

Splittings of olefin resonances were ≃8 Hz for cis protons and 11-12 Hz for trans protons. An additional coupling of ≃0.9 Hz was detected between geminal protons in the propene complexes.

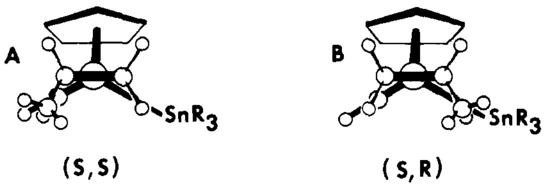
Both ^{119}Sn and ^{117}Sn satellites were observed for the trimethyltin signal with the $^{119}Sn\text{-}^1H$ coupling constants all in the range of 40-45 Hz. The triphenyltin multiplet was too complex to detect the tin satellites. Tin coupling to the remaining protons was very small, with the largest instance being the 1, 2, and 3 protons of the indenyl ring, where a coupling of 5 Hz was observed.

Carbon-13 spectra are summarized in Table III. The olefin signals exhibited temperature dependence though the effect was slight for propene resonances. In $\eta^5\text{-}C_5H_5Fe(C\text{-}$

Table I. Infrared Data

Compound	ν(CO) (cm^{-1})^a	$\nu_{1/2}$ (cm^{-1})
η^5-$C_5H_5Fe(CO)_2(SnMe_3)$	1943 1994	5.8
η^5-$C_5H_5Fe(CO)_2(SnPh_3)$	1954 2000	6.9
η^5-$C_9H_7Fe(CO)_2(SnMe_3)$	1940 1990	5.5
η^5-$C_9H_7Fe(CO)_2(SnPh_3)$	1950 1999	7.5
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_2H_4)$	1938	6.2
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_2H_4)$	1945	11.8
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_2H_4)$	1933	7.8
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_2H_4)$	1940	12.8
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_3H_6)$	1933	6.6
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_3H_6)$	1938	11.7
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_3H_6)$	1928	7.5
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_3H_6)$	1935	11.0

^{a} Spectra were recorded in cyclohexane solutions.



(S,S) (S,R)

Figure 1. Diastereoisomers in chiral iron propene complexes.

O)(SnPh$_3$)(C$_2$H$_4$), η^5-$C_9H_7Fe(CO)(SnMe_3)(C_2H_4)$, and η^5-$C_9H_7Fe(CO)(SnPh_3)(C_2H_4)$, two separate resonances were observed for the ethylene carbons at low temperatures and coalescence to a single resonance occurred upon raising the temperature. In η^5-$C_5H_5Fe(CO)(SnMe_3)(C_2H_4)$, the low temperature ethylene signals are virtually coincident, with a maximum separation of 1 Hz at 67.88 MHz.

Two patterns of olefin resonances were observed for cyclopentadienylpropene compounds. Indenyl analogues had only one set of olefin resonances. Identification of propene resonances was made by running undecoupled spectra and observing the characteristic ^1H-^{13}C coupling pattern of the three carbon atoms.

Significant coupling of carbon nuclei to ^{119}Sn and ^{117}Sn was observed for triphenyltin, trimethyltin, and carbonyl groups, but was unresolved for olefin, cyclopentadienyl, and indenyl groups.

Discussion

An initial comparison of the olefin compounds containing a tertiary tin ligand with those of the cationic dicarbonyl series reveals a number of interesting differences resulting from the change in electron density and the creation of a chiral center at the iron atom.

As a result of the chirality at iron, the ethylene nuclei in the limiting low temperature spectra become magnetically nonequivalent, as observed in ^{13}C and ^1H NMR spectra. The presence of a second chiral center on the molecule results in two pairs of diastereoisomers, as occurs upon substitution of propene. The chirality of the metal center and the olefin center can be designated by the (*R*) and (*S*) nomenclature of Prelog and Ingold;[4,5] hence, two pairs of diastereoisomers (*R*,*R*)-(*S*,*S*) and (*S*,*R*)-(*R*,*S*) are formed, as illustrated in Figure 1. When irradiation of a toluene solution of either of the cyclopentadienyl dicarbonyl derivatives is carried out in the presence of propene at −23°, the ^1H and ^{13}C NMR spectra of the products indicate formation of nearly equal quantities of both pairs of diastereoisomers (see Figure 2). Thus there is little, if any, stereoselectivity in the initial formation of the olefin complex in either case. Separation of a pure diastereoisomer, however, is straightforward because in each case one of the isomers is substantially less stable than the other and appears to decompose with the loss of propene, leaving solely the more stable enantiomeric pair. The most stable configuration appears to be the (*S*,*S*)-(*R*,*R*) pair, based on steric requirements. (Attempts to assign the configurations by the use of the nuclear Overhauser effect were unsuccessful.)

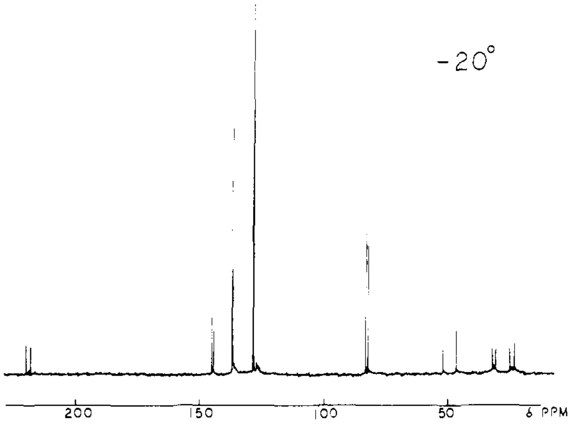


Figure 2. Carbon-13 spectrum of η^5-$C_5H_5Fe(CO)(SnPh_3)(C_3H_6)$ showing resonances of each diastereoisomer. (For assignments, see Table III.)

Replacement of the cyclopentadienyl ligand with the larger indenyl group apparently destabilizes the system in both trimethyltin and triphenyltin cases. The same reaction procedure produced only one observable enantiomeric pair in each derivative. Unlike the cyclopentadienyl compounds, the more stable indenyl pair of enantiomers decomposes rapidly in solution. Presumably the (*R*,*S*-*S*,*R*) configuration is too unstable to have more than a transient existence before decomposition resulting in the loss of propene occurs.

Evidence for isomerism resulting from a third type of chirality is seen in each of the triphenyltin-olefin compounds. Broadening of olefin and phenyl resonances in low-temperature ^1H spectra can be attributed to inversion of helicity in the triphenyltin moiety and hindered rotation about the tin-carbon bond, similar to that observed in analogous triphenylphosphine iron compounds.[6] This effect, producing diastereoisomers in all complexes having a chiral iron and a triphenyltin group, may account for the increase in half-width of carbonyl bands in these compounds.

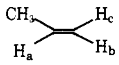
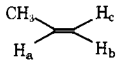
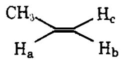
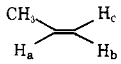
The temperature dependence of the olefin resonances in the cationic dicarbonyl compounds was determined to be the result of restricted rotation of the olefin about the iron-olefin axis. A similar rotation is anticipated for the tin derivatives and free energy barriers to such rotation can be readily calculated from rate constants resulting from line broadening measurements. Since limiting low temperature spectra are observed in each complex, the rate constant for the rearrangement can be estimated from the slow-exchange limit equation, where

$$k = \pi(\nu_{1/2} - \nu'_{1/2})$$

and k represents the rate constant for leaving a given site, as determined by the increase in its half-width.

Limiting low temperature spectra of the ethylene compounds indicate a single orientation in which, by analogy to the dicarbonyl cation, the C=C axis is assumed to be parallel to the plane of the cyclopentadienyl ring, as shown in Figure 3. The two configurations in Figure 3 would of course have identical populations with rotation about the metal-olefin axis averaging trans protons as indicated. Rate

Table II. Proton Nuclear Magnetic Resonance Data

Compound	Assignment[a]	δ[b]	Multiplicity[c]	Intensity
η^5-$C_5H_5Fe(CO)_2(SnMe_3)$	C_5H_5	4.70	s	5
	$SnMe_3$	0.30	s	9
η^5-$C_5H_5Fe(CO)_2(SnPh_3)$	$SnPh_3$	7.37	m	15
	$SnPh_3$	7.18	m	
	C_5H_5	4.66	s	5
η^5-$C_9H_7Fe(CO)_2(SnMe_3)$	C_9H_7	7.31	m	4
	C_9H_7	4.95	t (2.7)	1
	C_9H_7	4.79	d (2.7)	2
	$SnMe_3$	0.28	s	9
η^5-$C_9H_7Fe(CO)_2(SnPh_3)$	$SnPh_3$ C_9H_7	7.42	m	19
	$SnPh_3$ C_9H_7	7.21	m	
	C_9H_7	4.97	t (2.7)	1
	C_9H_7	4.80	d (2.7)	2
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_2H_4)$	C_5H_5	4.28	s	5
	C_2H_4	1.90	m	4
	C_2H_4	1.51	m	
	$SnMe_3$	0.29	s	9
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_2H_4)$	$SnPh_3$	7.37	m	15
	$SnPh_3$	7.16	m	
	C_5H_5	4.46	s	5
	C_2H_4	2.40	m	4
	C_2H_4	1.79	m	
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_2H_4)$	C_9H_7	7.40	m	4
	C_9H_7	5.37	m	1
	C_9H_7	4.77	m	2
	C_2H_4	0.90	m	4
	$SnMe_3$	0.27	s	9
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_2H_4)$	$SnPh_3$ C_9H_7	7.40	m	19
	$SnPh_3$ C_9H_7	7.20	m	
	C_9H_7	5.26	t (2.7)	1
	C_9H_7	4.94	d (2.7)	1
	C_9H_7	4.82	d (2.7)	1
	C_2H_4	1.32	m	4
	C_2H_4	1.01	m	
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_3H_6)$	C_5H_5 (A)	4.28	s	5
	C_5H_5 (B)	4.26	s	5
	H_a (A)	3.57	m	1
	H_a (B)	2.14	m	1
	CH_3 (B)	1.64	d (6.0)	3
	H_b (A)	1.57	d (8.0)	1
	H_c (B)	1.40	d (12.1)	1
	CH_3 (A)	1.29	d (6.3)	3
	H_b (B)	1.10	d (8.0)	1
	H_c (A)	0.73	d (11.3)	1
	$SnMe_3$ (A)	0.27	s	9
	$SnMe_3$ (B)	0.20	s	9
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_3H_6)$	$SnPh_3$ (A) (B)	7.30	m	30
	C_5H_5 (A) (B)	4.33	s	10
	H_a (A)	3.82	m	1
	H_a (B)	2.35	m	1
	H_b (A)	1.97	d (8.0)	1
	H_b (B)	1.92	d (8.0)	1
	H_c (B)	1.84	d (12.8)	1
	CH_3 (B)	. 1.76	d (5.5)	3
	H_c (A)	1.51	d (11.3)	1
	CH_3 (A)	1.33	d (5.6)	3
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_3H_6)$	C_9H_7	7.38	m	4
	C_9H_7	5.27	m	1
	C_9H_7	4.57	m	2
	H_a	1.71	m	1
	CH_3	1.05	d (5.8)	3
	H_c	0.78	d (11.6)	1
	H_b	0.61	d (8.4)	1
	$SnMe_3$	0.37	s	9
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_3H_6)$	$SnPh_3$ C_9H_7	7.38	m	19
	$SnPh_3$ C_9H_7	7.22	m	
	C_9H_7	5.17	t (2.7)	1
	C_9H_7	4.86	d (2.7)	1
	C_9H_7	4.75	d (2.7)	1
	H_a	1.63	m	1
	H_c	1.50	d (12.1)	1
	H_b	1.20	d (8.0)	1
	CH_3	0.88	d (5.9)	1

[a] (A) and (B) refer to the diastereoisomers in Figure 1. [b] Chemical shifts are relative to TMS in CS_2 solutions and represent time-averaged spectra at or near room temperature. [c] Splittings are given in Hz as s, singlet; d, doublet; t, triplet; m, multiplet.

Table III. Carbon-13 Nuclear Magnetic Resonance Data

Compound	Assignment[a]	δ[b]	$J(^{119}Sn-^{13}C)$[c]
η^5-$C_5H_5Fe(CO)_2(SnMe_3)$	CO	215.80	133.0
	C_5H_5	81.18	n.r.
	$SnMe_3$	−5.03	233.6
η^5-$C_5H_5Fe(CO)_2(SnPh_3)$	CO	214.15	146.3
	C_1	(phenyl) 143.89	353.5
	C_2,C_6	(phenyl) 136.32	35.7
	C_3,C_5	(phenyl) 127.97	42.7
	C_4	(phenyl) 127.87	10.6
	C_5H_5	81.97	n.r.
η^5-$C_9H_7Fe(CO)_2(SnMe_3)$	CO	214.18	126.9
	C_4,C_7	(indene) 126.21	n.r.
	C_5,C_6	124.02	n.r.
	C_8,C_9	(indene) 103.19	n.r.
	C_2	(indene) 86.61	n.r.
	C_1,C_3	(indene) 70.00	n.r.
	$SnMe_3$	−4.92	224.6
η^5-$C_9H_7Fe(CO)_2(SnPh_3)$	CO	213.79	145.5
	C_1	(phenyl) 143.04	342.4
	C_2,C_6	(phenyl) 136.21	n.r.
	C_3,C_5,C_4	(phenyl) 128.01	n.r.
	C_4,C_7	(indene) 127.36	n.r.
	C_5,C_6	124.30	n.r.
	C_8,C_9	(indene) 103.23	n.r.
	C_2	(indene) 86.65	n.r.
	C_1,C_3	(indene) 70.93	n.r.
η^5-$C_5H_5Fe(CO)(SnMe_3)$-(C_2H_4)	CO	216.94	166.9
	C_5H_5	82.64	n.r.
	C_2H_4	27.24	n.r.
	$SnMe_3$	−4.43	233.3
η^5-$C_5H_5Fe(CO)(SnPh_3)$-(C_2H_4)	CO	217.35	183.4
	C_1	(phenyl) 144.62	340.3
	C_2,C_6	(phenyl) 136.42	33.6
	C_3,C_5	(phenyl) 127.86	39.2
	C_4	(phenyl) 127.72	10.2
	C_5H_5	82.54	n.r.
	C_2H_4	28.28	n.r.
η^5-$C_9H_7Fe(CO)(SnMe_3)$-(C_2H_4)	CO	218.36	159.4
	C_4	126.82	n.r.
	C_5	(indene) 125.60	n.r.
	C_6	125.24	n.r.
	C_7	122.00	n.r.
	C_8	(indene) 101.36	n.r.
	C_9	100.82	n.r.
	C_2	(indene) 81.04	n.r.
	C_1	(indene) 74.49	n.r.
	C_3	70.75	n.r.
	C_2H_4	37.66	n.r.
	$SnMe_3$	−5.10	235.9
η^5-$C_9H_7Fe(CO)(SnPh_3)$-(C_2H_4)	CO	219.33	184.6
	C_1	(phenyl) 144.41	320.1
	C_2,C_6	(phenyl) 136.46	n.r.
	C_3,C_5	(phenyl) 127.46	n.r.
	C_4	(phenyl) 127.83	n.r.
	C_4	128.15	n.r.
	C_5	(indene) 126.39	n.r.
	C_6	125.96	n.r.
	C_7	121.43	n.r.
	C_8	(indene) 103.16	n.r.
	C_9	100.26	n.r.
	C_2	(indene) 81.50	n.r.
	C_1	(indene) 75.17	n.r.
	C_3	70.43	n.r.
	C_2H_4	39.25	n.r.
η^5-$C_5H_5Fe(CO)(SnMe_3)$-(C_3H_6)	CO (A) (B)	216.33	170.9
	C_5H_5 (A) (B)	82.07	n.r.
	=CH (B)	47.60	n.r.
	=CH (A)	43.41	n.r.
	$=CH_2$ (A)	32.03	n.r.
	$=CH_2$ (B)	31.34	n.r.
	$-CH_3$ (B)	25.23	n.r.
	$-CH_3$ (A)	24.02	n.r.
	$SnMe_3$ (A) (B)	−4.86	229.5
η^5-$C_5H_5Fe(CO)(SnPh_3)$-(C_3H_6)	CO (B)	218.51	198.0
	CO (A)	216.92	198.0
	C_1 (A)	(phenyl) 144.95	325.6
	C_1 (B)	(phenyl) 144.52	322.3
	C_2,C_6 (A)	(phenyl) 136.57	31.7
	C_2,C_6 (B)	(phenyl) 136.46	31.7
	C_3,C_5 (A) (B)	(phenyl) 127.83	39.1
	C_4 (A) (B)	(phenyl) 127.65	n.r.
	C_5H_5 (A)	82.62	n.r.
	C_5H_5 (B)	82.55	n.r.
	=CH (B)	52.62	n.r.
	=CH (A)	46.79	n.r.
	$=CH_2$ (A)	32.34	n.r.
	$=CH_2$ (B)	31.58	n.r.
	$-CH_3$ (B)	25.00	n.r.
	$-CH_3$ (A)	23.42	n.r.
η^5-$C_9H_7Fe(CO)(SnMe_3)$-(C_3H_6)	CO	217.96	167.6
	C_4	127.97	n.r.
	C_5	(indene) 126.53	n.r.
	C_6	125.78	n.r.
	C_7	120.60	n.r.
	C_8	(indene) 102.08	n.r.
	C_9	101.50	n.r.
	C_2	(indene) 81.36	n.r.
	C_1	(indene) 74.02	n.r.
	C_3	71.07	n.r.
	=CH	56.18	n.r.
	$=CH_2$	38.70	n.r.
	$-CH_3$	22.84	n.r.
	$SnMe_3$	−4.85	219.8
η^5-$C_9H_7Fe(CO)(SnPh_3)$-(C_3H_6)	CO	218.90	188.0
	C_1	(phenyl) 144.60	322.2
	C_2,C_6	(phenyl) 136.57	34.2
	C_3,C_5	(phenyl) 127.83	41.0
	C_4	(phenyl) 127.68	n.r.
	C_4	128.26	n.r.
	C_5	(indene) 126.43	n.r.
	C_6	125.63	n.r.
	C_7	121.97	n.r.
	C_8	(indene) 103.48	n.r.
	C_9	101.14	n.r.
	C_2	(indene) 81.29	n.r.
	C_1	(indene) 74.89	n.r.
	C_3	70.36	n.r.
	=CH	60.86	n.r.
	$=CH_2$	39.17	n.r.
	$-CH_3$	21.69	n.r.

[a] (A) and (B) refer to the diastereoisomers in Figure 1. [b] Chemical shifts are relative to TMS in $CDCl_3$ solutions with 0.5 *M* $Cr(acac)_3$ used as a relaxation agent. The shifts represent time-averaged spectra at or near room temperature. [c] Splittings are given in Hz unless not resolved (n.r.).

constants and rotational free energy barriers for these compounds are summarized in Table IV. Free energies are calculated from the equation:

$$\Delta G = 2.3RT(10.3 + \log T - \log k)$$

The temperature dependence of the olefin region of the propene compounds results from the exchange of configurations having unequal populations (Figure 4), with the degree of broadening dependent on the populations of the configurations. It was possible to measure rate constants from signal broadening in several of the propene complexes and the resultant free energy barriers are also included in Table IV.

In view of the estimated rotational barriers of 8 kcal/mol

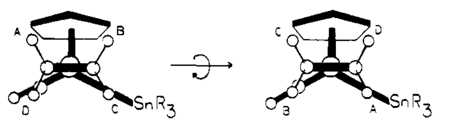


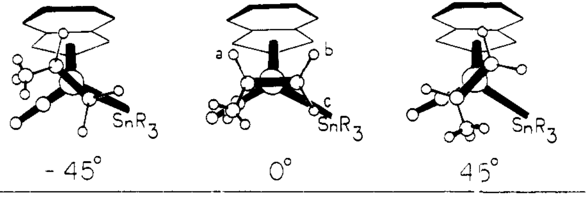
Figure 3. The effect of rotation about the metal–olefin bond on ethylene protons.

Table IV. Approximate Rate Constants and Energy Parameters

Compound	T (°C)	k (sec^{-1})	ΔG^* (kcal/mol)
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_2H_4)$	−50	1.57	12.8
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_2H_4)$	−40	5.34	12.8
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_2H_4)$	−50	5.97	12.2
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_2H_4)$	−60	0.94	12.4
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_3H_6)$ (A)	−30	1.57	14.0
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_3H_6)$ (B)	−70	3.14	11.3
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_3H_6)$	−50	1.41	12.8

Figure 4. 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.

Table V. Ring Current Effects from the η^5-Indenyl Ligand[a]



Angle (deg)	H_a	H_b	H_c	$H_a/H_b/H_c$
45	0.90	7.08	1.27	1.00/7.87/1.41
15	1.55	4.22	0.79	1.00/2.72/0.51
0	2.49	2.49	0.68	1.00/1.00/0.27
−10	3.57	1.74	0.65	1.00/0.49/0.18
−15	4.22	1.55	0.58	1.00/0.37/0.14
−30	5.77	1.16	0.61	1.00/0.20/0.11
−45	7.08	0.90	0.58	1.00/0.13/0.08
$SnMe_3$ (obsd)	1.94	1.04	−0.08	1.00/0.54/−0.04
$SnPh_3$ (obsd)	2.48	0.91	−0.13	1.00/0.37/−0.05

[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.

reported for the cationic olefin complexes, it is apparent from Table IV that there is a significant increase in the rotational barrier for the neutral olefin complexes. This effect would be expected from the increase in the π-back-bonding component of the metal–olefin bond which results from greater electron density at the metal.

The magnitude of the barrier does not seem to be sensitive to the nature of the tin group, although a change from cyclopentadiene to indene lowers the barrier slightly. An interesting difference in rotational barriers is seen for the propene diastereoisomers, where the more stable isomer has a barrier nearly 3 kcal higher than that of the less stable isomer, with the ethylene analogue having an intermediate value. The barrier of the only stable indenyl propene isomer is also somewhat larger than the analogous indenyl ethylene compound.

Taking into account errors in temperature and broadening measurements, the maximum uncertainty in ΔG^* would be ±0.3 kcal/mol.

The limiting low-temperature spectra of the propene complexes indicate the presence of only one set of resonances for each of the diastereoisomers shown in Figure 1. Although some broadening of signals results upon raising the temperature, the time-averaged spectra of both cyclopentadienyl and indenyl compounds have chemical shifts very close to those of the unaveraged case, which suggests that one orientation of the olefin predominates at low temperatures. Comparison with analogous allylmolybdenum systems[7] suggests that significant 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.

Calculation of the effect of the magnetic anisotropy of the indenyl ligand based on methods previously described for indenylmolybdenum systems[7] has been used to estimate the preferred orientations of the cationic iron propene complexes.[1] The calculated effects also provide an estimate of the orientational preference in the neutral propene complexes. Assuming that the single isomer in both of the indenyl complexes corresponds to that of the more stable cyclopentadienyl isomer (A in Figure 1), the differences in chemical shifts for the low temperature resonances have been measured and are listed in Table V.

In comparing the shifts of propene protons of the cyclopentadienyl and indenyliron 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. Comparison of the ratios of observed values with those of angles of −10 and −15° are quite favorable for the trimethyltin and triphenyltin derivatives, respectively. Considering the lack of correlation with other conformations, we believe that these angles adequately describe the lowest energy configuration of the olefin. The negative angle defines a tilt away from a 0° orientation, in which H_a is closer to the indenyl ring than H_b. As shown in the cationic species, the preferred orientation is one in which the C=C axis is nearly parallel to the ring, although the tilt is in the opposite direction in the tin compounds. A molecular model indicates that a tilt of this type may minimize the steric interaction of the tin ligand, particularly triphenyltin, with the methyl group of the propene. Alternatively, interactions with the tin substituents could favor a preferred orientation of the indene, in which the ring is not directly over the center of the olefin. Calculations assuming a 10° rotation away from the tin and no tilt of the olefin also correlate well with the observed shifts.

The magnitudes given in Table V assume a fixed orientation of the indenyl ligand over the olefin. Since free rotation of the indenyl has been demonstrated in the molybdenum analogues 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. (The effect of a potential well and integration over all angles has been treated elsewhere.[7]) This fraction is between 55 and 60% and appears to be quite constant in both cationic and neutral propene complexes.

The observation of broadening and differences in high and low temperature chemical shifts suggests the presence of some conformations significantly different from C (Figure 4). Failure to observe signals for these conformations at low temperatures indicates that their populations are extremely small, and certainly less than 5%. The data therefore clearly indicate that over a given time interval the

Table VI. Physical Properties of Dicarbonyl Compounds

Compound	Color	Mp (°C)	Calcd % C	Calcd % H	Found % C	Found % H
η^5-$C_5H_5Fe(CO)_2(SnMe_3)$	Amber	Liquid	see ref 9			
η^5-$C_5H_5Fe(CO)_2(SnPh_3)$	Light yellow	135	see ref 8			
η^5-$C_9H_7Fe(CO)_2(SnMe_3)$	Amber	Liquid	43.03	4.13	41.87	4.15
η^5-$C_9H_7Fe(CO)_2(SnPh_3)$	Yellow	171	60.36	3.84	60.61	3.74

Table VII. Physical Properties of Olefin Complexes

Compound	Color	Mp (°C)	Calcd % C	Calcd % H	Found % C	Found % H
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_2H_4)$	Amber	Liquid	38.77	5.32	39.04	5.41
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_2H_4)$	Yellow	141–143 dec	see ref 10			
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_2H_4)$	Orange	Liquid	46.09	5.16	46.34	5.21
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_2H_4)$	Red-orange	110 dec	62.44	4.54	62.81	4.41
η^5-$C_5H_5Fe(CO)(SnMe_3)(C_3H_6)$	Orange	Liquid	40.62	5.68	40.30	5.54
η^5-$C_5H_5Fe(CO)(SnPh_3)(C_3H_6)$	Orange	130–133 dec	59.94	4.84	59.66	4.85
η^5-$C_9H_7Fe(CO)(SnMe_3)(C_3H_6)$	Orange	36 dec	[a]			
η^5-$C_9H_7Fe(CO)(SnPh_3)(C_3H_6)$	Red	90 dec	[a]			

[a] Indenylpropene complexes decomposed rapidly and were not analyzed.

methyl group is usually oriented away from the ring and that a configuration similar to D (Figure 4) is thermodynamically unfavorable.

Experimental Section

Chromatographic separations utilized low activity alumina (Fisher A-540). NMR spectra were obtained at 67.88 MHz for carbon-13 and at 270-MHz for protons, using a Bruker HX 270 spectrometer equipped with a variable temperature apparatus. Chemical analyses were performed by the Baron Consulting Analytical Laboratory, Milford, Conn.

All of the olefin complexes were prepared by ultraviolet irradiation of a particular dicarbonyl compound in the presence of an excess of olefin. The starting dicarbonyl compounds were prepared by the method of Gorsich.[8] The anionic metal complex, either η^5-$C_5H_5Fe(CO)_2^-$ or η^5-$C_9H_7Fe(CO)_2^-$, was added to tetrahydrofuran solutions of trimethyltin or triphenyltin chloride at 0° and allowed to reach room temperature. Evaporation of the solvent and chromatography on alumina produced yields of approximately 80% for each of the dicarbonyl compounds. Crystallization of the triphenyltin derivatives was with benzene-hexane. The trimethyltin derivatives were liquids at room temperature. The physical properties of the dicarbonyl compounds are summarized in Table VI.

Following a procedure described by Kolobova et al.[10] the ethylene complexes were prepared by bubbling a stream of ethylene through a benzene solution of the desired dicarbonyl compound while irradiating the solution with an ultraviolet sunlamp placed at a distance of about 10 cm. The reactions were carried out in a jacketed Pyrex reaction vessel through which cold water was circulated. In a typical reaction η^5-$C_5H_5Fe(CO)_2(SnPh_3)$ (3.0 g) was dissolved in 400 ml of benzene and irradiated for a period of 4 hr, resulting in a 90% conversion to η^5-$C_5H_5Fe(CO)(SnPh_3)(C_2H_4)$. The solvent was evaporated and the product was recrystallized with benzene-hexane. A total of 2.4 g of the ethylene product was recovered for an overall yield of 80%.

The propene complexes were synthesized in a similar manner except that toluene was used as the solvent and the temperature was maintained at −23°C by circulating CCl_4 from a CO_2-CCl_4 bath through the jacketed reaction vessel. Following the irradiation, the reaction solution was centrifuged and decanted and the toluene removed at 0° by a vacuum pump. Irradiation times and overall yields were similar to the ethylene reactions. The residues were kept cold and low-temperature ^1H and ^{13}C spectra were taken immediately upon completion of the reaction. Properties of the olefin complexes are summarized in Table VII.

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