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PERMANENT ADDRESS:

74 Broomfield Rise.....
Abbots Langley........
Herts U.K.......

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THE UNIVERSITY OF ALBERTA

π-CYCLOPENTADIENYL COMPOUNDS OF TITANIUM AND ZIRCONIUM CONTAINING CHELATING 2,4-DIKETONES

BY

JOHN GERALD EVANS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF

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EDMONTON, ALBERTA

FALL, 1971

UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

π-CYCLOPENTADIENYL COMPOUNDS OF TITANIUM AND ZIRCONIUM
CONTAINING CHELATING 2,4-DIKETONES

submitted by JOHN GERALD EVANS in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

....
Supervisor

..........Bennett..........

..........Rabenstein..........

....

....

P. Legzdins
....
External Examiner

Date...June 9, 1971...

ABSTRACT

The preparation and properties of the compounds (π-system)Ti(hfac)$_2$Cl are reported. π-system = π-C_5H_5, π-$CH_3C_5H_4$, π-$C_5(CH_3)_5$; hfac = $CF_3COCHCOCF_3$. These compounds were studied by the nmr technique and found to exist in solution as a mixture of two isomers. Rapid intramolecular exchange of chelate substituent environments was detected over the temperature range studied ($-30^0$to $+80^0$). The exchange rate was retarded by bulky substituents of the π-system. The existence of two isomers was rationalized on the basis of dodecahedral coordination for the Ti(IV) atom.

The compounds π-C_5H_5Zr(chelate)$_2$Cl (where chelate = tfac $CF_3COCHCOCH_3$, bztfac $CF_3COCHCOC_6H_5$ and ttfac $CF_3COCHCOC_4H_3S$) were prepared and subsequently studied by nmr. A preference for certain orientations of the chelate rings, reflected in the observation of forms of widely varying abundance, was noted. This preference was also noted for mixed chelate compounds such as π-C_5H_5Zr(chelate)(chelate')Cl (where chelate = hfac,tfac,bztfac and ttfac; chelate' = acac $CH_3COCHCOCH_3$ and dpm $C_4H_9COCHCOC_4H_9$) which were prepared _in situ_ by intermolecular exchange. The preference was found to be almost independent of chelate substituents other than the CF_3 group.

The nmr study of such compounds as π-C_5H_5Zr(hfac)$_3$ indicated that the exchange of chelate substituent environments of only two of the chelated ligands took place rapidly below 90^0, while at temperatures above 100^0, exchange became rapid and general among all three chelated groups. The difference between these selective and non-selective exchanges could be rationalized in terms of the known

bond lengths in the approximately pentagonal bipyramidal structure. The rates of selective exchange at 260^{0}K were in the order:- π-$C_5H_5Hf(hfac)_3$ > π-$C_5H_5Zr(hfac)_3$ > π-$CH_3C_5H_4Zr(hfac)_3$.

Tris chelate compounds containing asymmetric chelates e.g. (π-system)Zr(chelate")$_3$ (where π-system = π-C_5H_5 and π-$CH_3C_5H_4$; chelate" = tfac and bztfac) were used in studies of possible rearrangement pathways. The selective exchange was either operative via a dissociation of an equatorial Zr-O bond or via twisting of an equatorial chelate. These compounds were of particular importance in the attempted assignments and correlations of ^{1}H and ^{19}F nmr spectra.

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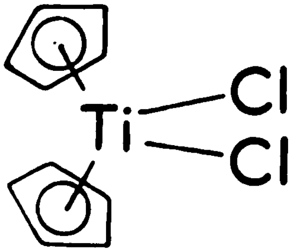
CHAPTER I.

Introduction.

Titanium, zirconium and hafnium generally exist in the +IV oxidation state when chemically combined. The energy for removal of four electrons is so high that existence of Ti(4+), Zr(4+) and Hf(4+) is not favoured and Ti(IV), Zr(IV) and Hf(IV) are generally covalent in nature.

A. Organometallic Chemistry of Ti, Zr, Hf.

The organometallic chemistry of these elements has been largely concerned with π-cyclopentadienyl (π-C_5H_5) derivatives, such as $(\pi\text{-}C_5H_5)_2TiCl_2$ (I) prepared by Wilkinson and Birmingham (1) and shown by Alekseev and Ronova (2) to have a 'canted ring sandwich' structure.

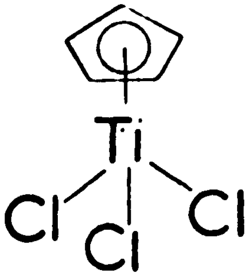


(I)

More recent work (3) has definitively investigated the syntheses and properties of the compounds $(\pi\text{-}C_5H_5)_2MX_2$ where M = Ti, Zr, Hf and X = F, Cl, Br, I.

Bis π-C_5H_5 compounds of the above metals and 'half sandwich' or mono π-C_5H_5 compounds such as π-$C_5H_5TiX_3$ (II), where X = Cl, Br, I.(4)., have been widely used as starting materials in preparative routes to many novel compounds containing either of the apparently stabilizing

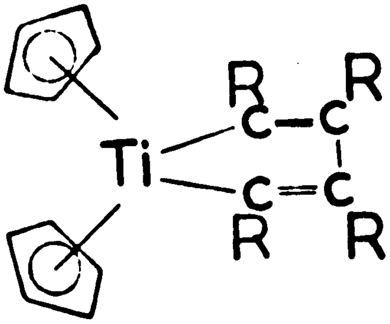
$(\pi\text{-}C_5H_5)_2M$ or $\pi\text{-}C_5H_5M$ moieties (M = Ti, Zr, Hf.)



(II)

The preparation and properties of $(\pi\text{-}C_5H_5)_2M_AM_B(C_6H_5)_3Cl$ where M_A = Ti, Zr. M_B = Si, Sn., and of $(\pi\text{-}C_5H_5)_2Ti(Sn(C_6H_5)_3)_2$ have been reported (5),(6), and a structural study of $\{(\pi\text{-}C_5H_5)_2TiAl(C_2H_5)_2\}_2$ has been carried out (7), but in general few compounds containing metal-metal bonds involving Ti,Zr, or Hf have been reported and investigated.

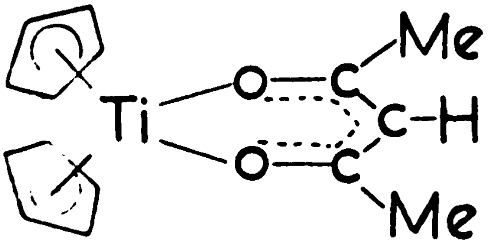
Certain aspects of the chemistry of the titanium group have much in common but it may be emphasized that while zirconium and hafnium are very similar in reactivity and compound formation, titanium does provide some interesting differences. Thus, the only known carbonyl of titanium, $(\pi\text{-}C_5H_5)_2Ti(CO)_2$, has been prepared as a very reactive solid.(8). This carbonyl has been used in reactions with alkynes forming compounds such as $(\pi\text{-}C_5H_5)_2Ti(\text{alkyne})_2$ (9) in which the alkyne molecules were thought to be condensed into a five-membered ring with the titanium atom. (III).



(III)

The rapid expansion of the organometallic chemistry of π-C_5H_5 derivatives of the titanium group metals has also focussed interest on substituent effects in the π-C_5 ring (10) and on the investigation of structural characteristics by techniques such as nuclear magnetic resonance (nmr) (3), (11), infra-red spectroscopy (12), (13), and mass spectrometry (14), (15), or a combination of the above techniques.

The reactions of β-diketones with π-C_5H_5 compounds of Ti, Zr and Hf had been investigated, at the commencement of this work, by two groups. The preparation of π-$C_5H_5Zr(CH_3COCHCOCH_3)_2Cl$ had been reported by Brainina et al. (16),(17) and the preparation of the $\{(\pi$-$C_5H_5)_2Ti(CH_3COCHCOCH_3)\}(+)$ ion by Doyle and Tobias. (18).(IV).



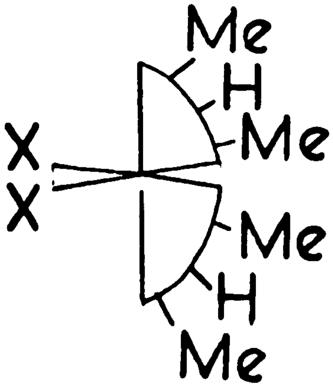
(IV)

B. Compounds of Ti, Zr and Hf with β-diketones.

Reactions of metal tetrahalides with β-diketones have been investigated by Cox, Lewis and Nyholm (19), producing a variety of chelate compounds such as $M(acac)_2Cl_2$ and $M(acac)_3Cl$, where M = Zr, Hf and acac = $CH_3COCHCOCH_3$. In addition $Ti(acac)_2Cl_2$ and an ionic product $Ti(acac)_3(+)Cl(-)$ were also prepared. The compound $Zr(acac)_4$, studied extensively by Brainina (20), (21), has been the object of an X-ray crystallographic analysis by Silverton and Hoard (22) who found the structure to be based on a square antiprismatic array of oxygen atoms surrounding a central zirconium atom.

One of the most interesting facets of the chelate chemistry of the titanium group was the ability of a given metal to form compounds with coordination numbers of six (presumably octahedral), seven (of unknown stereochemistry), and eight (square antiprismatic). Further studies on these compounds, in the hope of structure elucidation by the nmr technique, provided evidence of rapid intramolecular chelate exchange in the $Zr(chelate)_4$ system, where the chelate was acac, tfac ($CF_3COCHCOCH_3$) or hfac ($CF_3COCHCOCF_3$). (23), (24), (25).

The studies of Fay et al. involving the octahedral $Ti(chelate)_2X_2$ system, where chelate = acac (V), bzac ($CH_3COCHCOC_6H_5$), and bzbzac ($C_6H_5COCHCOC_6H_5$), X = F, Cl, Br, indicated that these compounds existed, in solution, as the cis isomer and were undergoing rapid intramolecular chelate exchange. (26), (27).



(V)

The exchange process was not observable for the similar zirconium system but could be analysed for $Ti(acac)_2X_2$ (where X = F, Cl, Br.) (28). Certain speculation on the actual mechanism by which chelate exchange occurs in these systems has been made (26), (27),(29).

C. Fluxional Molecules.

By far the largest amount of research in this field has been concerned with metal carbonyl derivatives. In general, the terminology evolved by Cotton (30) will be followed. The following points should be noted.

The structure seen by the short time scale techniques, X-ray, I.R. etc. is termed the instantaneous structure.

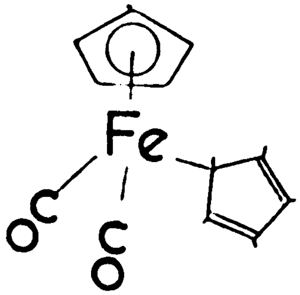
The rearrangement of nuclei as the molecular configuration changes from one instantaneous structure to another with a different permutation of nuclei is called the rearrangement pathway.

The rearrangement of nuclei between sites or the site exchange process has been found in many cases to be on a suitable time scale for study by the nuclear magnetic resonance technique. Both shape and width of nmr signals are affected by time dependent processes when the lifetime τ of each species under observation is in the order of $1/\delta\nu$ (where $\delta\nu$ is the chemical shift between exchanging groups). Many reference texts on the nmr technique which cover both the basic theory and practice and this particular aspect are available. (31), (32), (33), (34).

There are several classes of fluxional molecules and several examples need to be cited to illustrate the use and drawbacks of the nmr method

The first organometallic σ-cyclopentadienyl carbonyl which exhibited fluxional character was synthesized by Piper and Wilkinson

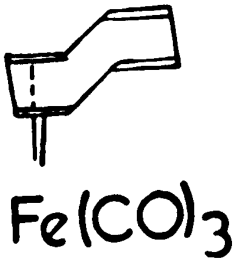
(35) who categorized the compound as π-$C_5H_5Fe(CO)_2\sigma$-C_5H_5(VI) based on evidence such as its infra-red spectrum and chemical reactivity.



(VI)

The nmr spectrum of this compound at 40° consisted of two singlet C_5H_5 resonances. The original formulation was confirmed by an X-ray crystal structure (36) and the low temperature (-80°) nmr spectrum was compatible with the X-ray structure. The rearrangement pathway was deduced from the spectral changes and was postulated in this and in the isoelectronic molecule π-$C_5H_5Cr(NO)_2\sigma$-C_5H_5 to occur by 1, 2 shifts of the σ-bound C_5H_5 ring (37). The authors pointed out that a definitive assignment of the limiting low temperature spectrum was required before the 1, 2 shift mechanism could be regarded as proven. A reversal of assignment would discount the 1,2 shift mechanism and favour a 1,3 shift.

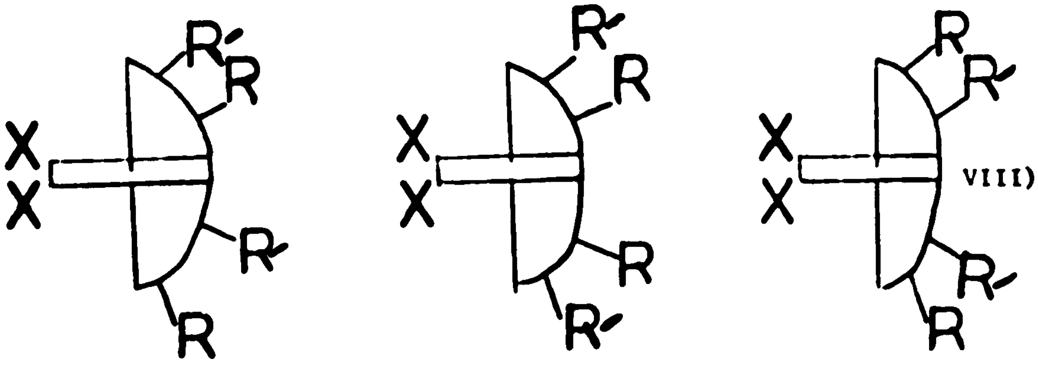
Much controversy arose from the study of the $C_8H_8Fe(CO)_3$ molecule (VII) , three groups interpreting the same poorly-resolved low temperature spectra in three different ways.(38),(39),(40).



(VII)

A more likely interpretation has been possible using the better-resolved spectra of the ruthenium analogue by comparison of actual spectra with computer-simulated spectra for possible rearrangement pathways. In this case a 1,2 shift mechanism was inferred as the primary rearrangement pathway.(41),(42). Recent studies of the osmium analogue, which shows well-resolved , presumably limiting, low-temperature spectra, have also been made.(43). These studies have indicated the importance of obtaining limiting low-temperature nmr spectra for fluxional systems.

A field more closely allied to the present study was the investigation of the Ti(IV) and Zr(IV) chelate compounds described previously.(26),(27),(28). The nmr spectra (40^0) of $Ti(acac)_2Cl_2$ and $Ti(bzac)_2Cl_2$ (bzac = $CH_3COCHCOC_6H_5$) in the methyl region consisted of a single sharp resonance. The low temperature spectrum of $Ti(acac)_2Cl_2$ consisted of a doublet in this region due to the two sets of non-equivalent methyl groups which occur only in the *cis*-isomer. The distribution of CH_3 resonances in the low temperature spectra of $Ti(bzac)_2Cl_2$ and $Ti(bzac)_2F_2$, coupled with the ^{19}F nmr spectrum of $Ti(bzac)_2F_2$, indicated that a mixture of the three possible *cis*-isomers was present.(VIII).



VIII)

The behaviour of the intermediate spectra gave limited evidence of the rearrangement pathway, no differentation between unselective chelate exchange via bond rupture or via chelate twisting being possible.

From the limited number of examples chosen, it appears that certain criteria must preferably be met if the intricacies of the rearrangement pathway are to be understood. The following are required. 1.) The interpretation and assignment of the nmr spectra. 2.) A true limiting low-temperature spectrum. 3.) An X-ray structure which is compatible with the limiting low-temperature spectrum. However, in certain circumstances, these conditions are not sufficient and although knowledge of the process exists, the rearrangement pathway may not be inferred.(26),(27),(28).

The Treatment of Exchange Rates by the Nmr Technique.

The treatment follows that in a standard text.(35).

a) Slow exchange. For two environments A and B, there exist two Larmor frequencies ω_A and ω_B.(units radians sec^{-1}). The chemical shift between these environments is $\omega_A - \omega_B$ radians sec^{-1}. It is assumed that while a nucleus is in an A site, there is a constant probability τ_A^{-1} per unit time of its making a jump to a B site, via a chemical reaction. τ_A is then the mean lifetime for a stay on A sites. A corresponding lifetime τ_B may also be defined. The fractional populations of A and B sites p_A and p_B ($p_A + p_B = 1$) are related to τ_A and τ_B by:- $p_A = \tau_A / \tau_A + \tau_B$, $p_B = \tau_B / \tau_A + \tau_B$

For slow exchange, a broadened signal centred on ω_A with width given by $T_{2A}'^{-1} = T_{2A}^{-1} + \tau_A^{-1}$ is observed.

where $T_{2A}'^{-1}$ = transverse relaxation time with exchange,

T_{2A} = transverse relaxation time in absence of exchange.

The relaxation times are related to the peak width at half-height ($\nu_{1/2}$) by the equation $\nu_{1/2} = 2/T_2$ (where $\nu_{1/2}$ is measured in radians $\sec^{-1}$). A similar broadened signal centred on ω_B is also observed. The broadening provides a means of measuring both τ_A and τ_B provided appreciable overlap of the signals does not occur.

b) Rapid exchange. In the limit of rapid exchange τ_A and τ_B are small and a single resonance is observed centred on a mean frequency ω_m.

$$\omega_m = p_A\omega_A + p_B\omega_B$$

If the exchange is not rapid enough to give complete collapse to a single sharp line then the following relation holds

$$T_2^{-1} = p_A/T_{2A} + p_B/T_{2B} + p_A^2 p_B^2 (\omega_A - \omega_B)^2 (\tau_A + \tau_B)$$

c) Intermediate exchange rates.

It has been shown (<u>44</u>) that for moderate exchange rates <u>i</u>.<u>e</u>. in the transition region from two to one resonance, the following equation is applicable for small, equal relaxation times T_{2A} and T_{2B} and equal populations.

$$\frac{\text{Separation of resonances}}{\text{Separation of resonances for large } \tau} = \left[1 - \frac{1}{2\pi^2\tau^2(\nu_A - \nu_B)^2} \right]^{1/2}$$

where $\nu_A - \nu_B$ is in cycles per sec.(cps) and $2\tau = \tau_A = \tau_B$.

The rate constant for an exchange (k) is related to the site populations and lifetimes and may be determined from the nmr spectrum at a particular temperature. The rate constant may be measured at other temperatures from the appropriate nmr spectra and activation energies and entropies determined. This type of study has been carried out for many classes of compounds. (<u>45</u>),(<u>46</u>),(<u>47</u>),(<u>26</u>).

CHAPTER II.

Experimental.

A. Techniques.

Nuclear magnetic resonance (nmr).

Three instruments were available; these were a Varian A60 used for ^1H nmr spectra, measured at 60.0 megacycles sec.$^{-1}$(Mcs), a Varian HA 100 (^1H nmr at 100.0 Mcs) and a Varian A56/60A (^1H nmr at 60.0 Mcs and ^{19}F nmr at 56.4 Mcs).

Sample preparation of solids was carried out by solution in an appropriate solvent and then filtration into the nmr tube. Due to difficulties encountered with solubility, overlapping resonances and freezing or boiling points, a wide selection of solvents was employed. In general, solvents suitable over the entire temperature range required were difficult to find, and a solvent change at about 40^0 was usually necessary. Solvents used at ambient temperatures (40^0 instrument probe temperature) were:- deuteriochloroform $CDCl_3$, chloroform $CHCl_3$, acetone, acetone-d^6, benzene. Solvents used for high temperature investigations were:- dibromomethane, bromobenzene and methylcyclohexane. Solvents used for low temperature investigations were generally those used at ambient temperatures with the omission of benzene and the inclusion of dichloromethane. Extreme low temperature work (-70^0 and below) could only be carried out with acetone, acetone-d^6, dichloromethane and to a lesser extent, carbon disulphide (CS_2).

All positions of resonance lines for ^1H nmr spectra will be reported on the τ scale using the internal reference tetramethylsilane (TMS) $\tau = 10.00$. For the ^{19}F spectra it was inconvenient to use the internal standard $CFCl_3$ because of its distant position from the ^{19}F resonances under investigation. Many spectra will be reported using the free β-diketone as an internal standard. It has been found that ^{19}F resonances may be shifted by such factors as solvent, dilution and temperature. However, in the present study, ^{19}F shifts were small (up to 10 cps) on change of solvent using free β-diketone as reference. The addition of β-diketone was advantageous due to the proximity of the singlet CF_3 resonance to the resonances under investigation. The possibility of exchange between the chelating agent and the chelate compound could also be investigated (on the nmr time scale).

^{19}F nmr spectra are followed, as are ^{1}H spectra, by an integration value for each resonance. Further values of peak width at half-height follow for the ^{19}F nmr data. Where integrations or peak widths are unmeasurable due to overlapping resonances, this situation has been denoted by (x) in Tables III-V.

Sample temperatures were monitored on the Varian A 56/60 A by a Varian V-6040 temperature controller. The temperatures indicated were accurate to ± 4^0 , not unreasonable when compared with a stated error of ± 2^0 and a reproducibility of ± 3^0(48). More accurate temperatures were obtained for the attempted calculations of activation energies using a methanol-filled capillary tube situated within the spinning nmr sample tube. The chemical shift between the methyl and hydroxyl proton resonances provided the means of temperature measurement (48). The temperature was found to stabilize in about 10-15 minutes and its stability over the period required to record the nmr spectrum was very good, the maximum temperature variation over this period being ± 1^0.

The instrumental set-up was carried out as recommended by the manufacturer and the nmr spectrum recorded using the most favourable combination of filter bandwidth, radio-frequency field, spectrum amplitude and sweep time in order to have the best possible signals which were maximized by operation of the fine-tuning Y-axis control. Spectra recorded on the A 60 and H A 100 instruments were run by the technical staff of the Department of Chemistry. Spectra recorded on the A 56/60 A instrument and variable-temperature experiments using this instrument were carried out by the author.

Mass Spectrometry.

The mass spectral characteristics of the compounds prepared were recorded using a high resolution, double-focussing A.E.I. MS9 instrument. For sample introduction of solids, a direct probe was used, with heating if required to achieve sufficient sample volatility. The use of mass spectrometry in the present work was mainly concerned with compound identification, either from breakdown patterns or from the identification of a parent molecular ion. Several texts and reviews of the mass spectrometric technique and its applications are available. (49),(50),(51),(52).

Infra-red Spectroscopy.

This technique was used for comparison and identification of compounds. The instruments employed in the present study were a Perkin-Elmer 337 (range 4000-400 cm^{-1}) associated with a Hewlett-Packard 7127 A strip chart recorder for expansion of spectra, a Perkin-Elmer 421 (range 4000-650 cm^{-1}) and a far infra-red instrument, a Beckmann I.R. 11 (range 800-33 cm^{-1}).

Sample preparation of solids involved the use of mulling agents, and several spectra were recorded using solutions in 0.5mm cells with KBr or KCl windows. Spectra were calibrated with polystyrene. Several standard texts on the technique and use of infra-red spectroscopy are available. (53),(54),(55).

Analyses and melting points.

Analyses for C,H and Cl were carried out by the Department of Chemistry technical staff. Fluorine analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, by a special technique for fluorine-containing materials which possess appreciable volatility. Melting points were determined on a Kofler hot-stage microscope and are uncorrected. In many cases the melting points were not sharp; this was noted particularly in the cases where other evidence indicated that the compound could consist of a mixture of isomers.

B. Preparation of Compounds.

Starting materials for several syntheses were available commercially. The compounds $(\pi\text{-}C_5H_5)_2TiCl_2$ (Arapahoe Chemicals), $(\pi\text{-}C_5H_5)_2ZrCl_2$ (Arapahoe Chemicals), $(\pi\text{-}C_5H_5)_2HfCl_2$ (Alfa Inorganics), were of particular interest. Metal tetrahalides $TiCl_4$ (Fisher Chemicals) and $ZrCl_4$ (Alfa Inorganics Inc.) and the compound $\pi\text{-}C_5H_5TiCl_3$ (Alfa Inorganics) were also used. The selection of β-diketones was as follows, with formulae, common names and abbreviations included.

1. 2,4-pentanedione; $CH_3COCH_2COCH_3$; acetylacetone ; Hacac; Keto-isomer (IX); Enol-isomer (X) .

2. 1-phenyl-1,3-butanedione; $C_6H_5COCH_2COCH_3$; 1-benzoylacetone; Hbzac.

3. 1,3-diphenyl-1,3-propanedione; $C_6H_5COCH_2COC_6H_5$; Hbzbzac.

4. 2,2,6,6-tetramethyl-3,5-heptanedione ; $(CH_3)_3CCOCH_2COC(CH_3)_3$ dipivaloylmethane ; Hdpm.

5. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione ; $CF_3COCH_2COCF_3$; hexafluoroacetylacetone ; Hhfac.

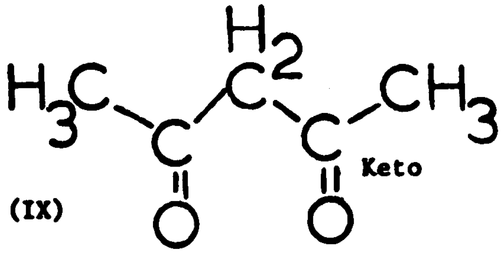
6. 1,1,1-trifluoro-2,4-pentanedione ; $CF_3COCH_2COCH_3$; trifluoroacetylacetone ; Htfac.

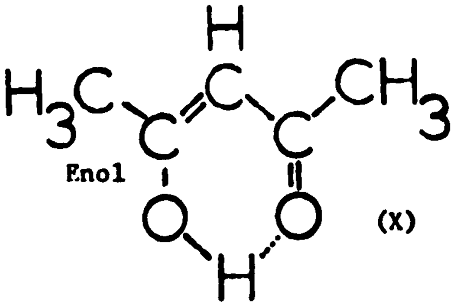
7. 1-phenyl-4,4,4-trifluoro-1,3-butanedione ; $C_6H_5COCH_2COCF_3$; benzoyltrifluoroacetone ; Hbztfac.

8. 1-(2-thenoyl)-4,4,4-trifluoro-1,3-butanedione ; $C_4H_3SCOCH_2COCF_3$; 2-thenoyltrifluoroacetone ; Httfac.

9. 1-(2-napthyl)-4,4,4-trifluoro-1,3-butanedione ; $C_{10}H_7COCH_2COCF_3$; Hnphtfac.

Compounds 1-3 were obtained from the Aldrich Chemical Co..Compounds 4-8 from the Pierce Chemical Co. and 9 from Eastman Organics. Many of the above β-diketones exist predominantly in the enol-form (56),(57). (IX), (X).


(IX) Keto


Enol (X)

Tetrahydrofuran was distilled from lithium aluminium hydride before use and Ansul ether 121 (monoglyme) was dried with molecular sieves. Other solvents were reagent grade and were used without special procedures. Reactions were carried out, for oxygen sensitive materials, under a slight positive pressure of nitrogen. In the preparation of moisture-sensitive compounds, drying tubes were also fitted to the apparatus. Analytical data for the compounds prepared may be found in Tables I and II.

TABLE I PHYSICAL PROPERTIES

COMPOUND	COLOUR	mp ^{0}C	ANAL. FOUND				ANAL. CALCD.			
			C	H	Cl	F	C	H	Cl	F
π-$C_5H_5Ti(hfac)_2Cl$	Red-black	50-55	32.15	1.35	6.07	41.73	32.03	1.25	6.30	40.53
π-$CH_3C_5H_4Ti(hfac)_2Cl$	Red-black	45-50	33.34	1.80	6.09	...	33.31	1.57	6.15	...
π-$C_5(CH_3)_5Ti(hfac)_2Cl$	Green-black	dec.60	37.00	2.84	...	...	37.97	2.28	...	...
π-$C_5H_5Zr(tfac)_2Cl$	White	235-240	36.52	2.76	7.16	22.41	36.18	2.63	7.12	22.89
π-$C_5H_5Zr(tfac)_3$	White	85-90	39.04	2.79	0.00	...	39.03	2.78	0.00	...
π-$C_5H_5Zr(bztfac)_2Cl$	Yellow	180-185	48.38	2.87	...	...	48.27	2.75	...	...
π-$C_5H_5Zr(ttfac)_2Cl$	Yellow	170-180	40.42	1.95	...	...	39.78	2.07	...	...
π-$C_5(CH_3)_5TiCl_3$	Red	197-200	41.53	4.78	36.72	...	41.49	5.22	36.74	...

TABLE II PHYSICAL PROPERTIES

COMPOUND	COLOUR	mp ^{0}C	ANAL. FOUND				ANAL. CALCD.			
			C	H	Cl	F	C	H	Cl	F
π-$C_5H_5Zr(hfac)_3$	Yellow	98-99	31.05	1.07	...	44.20	30.90	1.04	...	43.98
π-$CH_3C_5H_4Zr(hfac)_3$	Yellow	93-95	31.84	1.27	...	...	31.87	1.27	...	...
π-$C_5H_5Hf(hfac)_3$	Yellow	95-98	28.20	1.24	...	40.52	27.78	0.93	...	39.54
π-$CH_3C_5H_4Zr(tfac)_3$	White	80-85	40.37	3.17	...	...	40.06	3.04	...	...
π-$C_5H_5Zr(bztfac)_3$	Yellow	110-120	52.33	3.21	...	...	52.43	2.89	...	...
π-$CH_3C_5H_4Zr(bztfac)_3$	Yellow	105-112	52.95	3.25	...	...	53.00	3.10	...	...
π-$C_5H_5Ti(tfac)_2Cl$	Red	dec. 70	39.50	2.79	7.52	...	39.55	2.88	7.78	...
π-$C_5H_5Ti(bztfac)_2Cl$	Red	dec. 80	51.78	3.01	...	...	51.78	2.95	...	...
π-$C_5H_5Ti(ttfac)_2Cl$	Red	dec. 80	42.05	2.17	...	...	42.61	2.21	...	...

Preparation of Starting Materials.

Dichlorobis(methyl π-cyclopentadienyl)titanium(IV).

$(\pi\text{-}CH_3C_5H_4)_2TiCl_2$. This compound was prepared in a manner similar to that employed by Wilkinson and Birmingham (1). The dimer of methylcyclopentadiene was first thermally cracked to yield the monomer and this re-distilled to ensure minimum contamination by dimer. A sample of 39.5g (0.5 mole) of methylcyclopentadiene (purity checked by nmr) was added, under nitrogen, to an ice-cooled, magnetically stirred suspension of finely-divided sodium (12.5g - 0.5mole) in monoglyme or tetrahydrofuran. The mixture was rapidly stirred for several hours until evolution of hydrogen ceased.

$$2CH_3C_5H_5 + 2Na \rightarrow 2Na^+CH_3C_5H_4^- + H_2$$

The solution of sodium salt was then slowly added to an agitated, cooled, benzene solution of titanium tetrachloride (38g - 0.20mole).

$$2Na^+CH_3C_5H_4^- + TiCl_4 \rightarrow (\pi\text{-}CH_3C_5H_4)_2TiCl_2 + 2NaCl$$

The mixture was allowed to warm to room temperature and left to stir to complete the reaction. The combined solvents were evaporated under reduced pressure and the solid dried under vacuum for 12 hours. The solids were subjected to Soxhlet extraction with benzene giving a bright red solution, which was concentrated, filtered, and crystallized by addition of n-pentane . Approximately 20.5g. (36%) of product was isolated as golden-red flakes.

The nmr spectrum exhibited an asymmetric multiplet centred at

τ3.66 (Intensity 4) assigned to the πC_5H_4 system - an AA'BB' system (58) and a singlet at τ7.70 (Intensity 3) assigned to the methyl (CH_3) group. The unsymmetrical nature of the AA'BB' system was probably caused by weak coupling of the methyl protons to one half of the AA'BB' system. This assignment was supported by the appearance of the spectrum using acetone-d^6 as solvent, the AA' and BB' portions of the spectrum being well resolved in this instance. It was of interest to note the magnetic equivalence of the ring substituents of both rings, presumably due to free rotation about the metal-ring axes, even at -80° in the sterically hindered conformation with canted π-$CH_3C_5H_4$ moieties. Anal. calc. for $C_{12}H_{14}TiCl_2$, C 51.80; H 5.04; Cl 25.55: Anal. found, C 52.18; H 5.19; Cl 25.46:

Dichlorobis(methylπ-cyclopentadienyl)zirconium(IV). $(\pi\text{-}CH_3C_5H_4)_2ZrCl_2$.

This compound was prepared in a similar manner to that used for the titanium analogue, using zirconium tetrachloride. The final purification step in this case was sublimation at 200° and 0.1mm onto a water-cooled probe. The white solid (12% yield based on $ZrCl_4$) gave a similar nmr spectrum to that of the titanium analogue, τ 3.75 (4)-π-C_5H_4, and τ 7.73 (3)- singlet CH_3. Anal. calc. for $C_{12}H_{14}ZrCl_2$, C 44.95; H 4.36: Anal. found, C 44.80; H 4.52:

Trichloro(methylπ-cyclopentadienyl)titanium(IV). $\pi\text{-}CH_3C_5H_4TiCl_3$.

Originally, a reaction similar to that described by King (59) was used. This reaction involved the 'scrambling' of the metallocene and titanium tetrachloride in xylene.

$$(\pi\text{-}CH_3C_5H_4)_2TiCl_2 + TiCl_4 \rightarrow 2\ \pi\text{-}CH_3C_5H_4TiCl_3$$

This technique produced only low yields of desired product, possibly due to an incomplete scrambling reaction. Solutions of π-$CH_3C_5H_4TiCl_3$ were prepared by the chlorine cleavage of one of metal-π-system bonds of $(\pi\text{-}CH_3C_5H_4)_2TiCl_2$, followed by flushing with nitrogen in order to remove excess chlorine from solution. The solution was used without further treatment. (10).

Trichloro(pentamethylπ-cyclopentadienyl)titanium(IV). π-$C_5(CH_3)_5TiCl_3$.

The unusual method of Roehl (60) was employed in this case. A sample of $TiCl_4$ (10g.-0.05 mole) and 50 ml. of 1-pentene were placed in a 100 ml. capacity stainless steel rocking bomb and the bomb sealed. The bomb and contents were heated to $255^0 \pm 10^0$and rocked for 48 hours; the pressure at this stage was about 1000lbs/sq.in. After cooling to ambient temperature, excess gases were vented and the bomb opened cautiously. At this stage the product consisted of a large mass of carbon and a red solution. The solid material was extracted with acetone and as much of the combined liquids as possible was evaporated under reduced pressure at 100^0.

The liquid product (which was made up of $TiCl_4$ and product) was distilled under reduced pressure (1.0mm) through a Vigreux column to remove $TiCl_4$ and dissolved when cool in hexane. Filtration and cooling yielded 2.0g. of red crystals (20% based on $TiCl_4$). The purity of the sample was checked by nmr and analysis. A single sharp ^1H nmr signal was observed at τ 7.88 in $CDCl_3$ due to the five equivalent methyl groups.

Synthesis of π-cyclopentadienyl chelates containing β-diketones.

1. Unfluorinated β-diketones.

The reactions were carried out in a suitable solvent using a slight excess of β-diketone (chelating agent) according to the method of Braina et. al. (17).

Chlorobis(2,4-pentanedionato)π-cyclopentadienylzirconium(IV).

π-$C_5H_5Zr(acac)_2Cl$. A sample of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (2.9g. 0.01 mole) and 4.0g. of acetylacetone (0.04 mole) were mixed in 150ml. of chloroform and the mixture heated under reflux for 48 hours, or until evolution of hydrogen chloride ceased.

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 2\ Hacac \rightarrow \pi\text{-}C_5H_5Zr(acac)_2Cl + HCl + C_5H_6$$

The solvent was evaporated under reduced pressure and the remaining solid washed with several portions of hot hexane in order to remove as much unreacted Hacac and dicyclopentadiene as possible. The solid was dissolved in 50 ml. of dichloromethane, decolourised with activated charcoal and filtered. Slow crystallization, after the addition of 20 ml. pentane, gave 2.8g.of colourless plates (70%), m. p 184-186°; lit. 188-190°. This compound has recently been studied and characterised (61) and its structure determined by X-ray crystallography (62). Anal. calc. for $C_{15}H_{19}O_4ClZr$, C 46.20; H 4.91; Cl 9.09: Anal. found, C 46.51; H 4.88; Cl 8.89:

The nmr spectrum in $CDCl_3$ at 40° was recorded and interpreted as follows:- π-C_5H_5 3.64(5) , >CH 4.64 (resolved as a 1:1 doublet in benzene and bromobenzene) (2) and CH_3 7.98 (3), 8.03 (3), 8.12, 8.13 (6). The spectrum was also recorded in C_6H_5Br

for temperature investigations.

Chlorobis(1-phenyl-1,3-butanedionato)π-cyclopentadienylzirconium(IV). π-$C_5H_5Zr(bzac)_2Cl$. This compound was prepared in a similar manner to that used above. From 2.9g. (0.01 mole) of (π-$C_5H_5)_2ZrCl_2$ and 4.0g. (0.03 mole) of Hbzac, 3.1g.(60%) of pale-yellow crystals of π-$C_5H_5Zr(bzac)_2Cl$ were isolated. m.p. 173-178 . Anal. calc. for $C_{25}H_{23}O_4ClZr$, C 58.40; H 4.51; Cl 6.90: Anal. found, C 58.11; H 4.51; Cl 6.85:

The nmr spectrum in $CDCl_3$ indicated four major regions of absorption:- C_6H_5 1.9-3.0 (10) complex, π-C_5H_5 3.50, 3.52 (5), >CH 3.75, 3.82 (2) complex, CH_3 7.80, 7.82, 7.98, 8.06, 8.08 and 8.09 (6). Further examination using the HA 100 instrument indicated the existence of at least three π-C_5H_5 resonances, four methine resonances and eight methyl resonances. The compound was also subjected to variable temperature experiments in C_6H_5Br as solvent.

2. Fluorinated β-diketones.

The analytical values for the following compounds are presented in Tables I and II. The nmr spectra of these compounds are reported in Tables III and IV. The spectra will be discussed in detail at a later stage.

A. Hexafluoroacetylacetone. Hhfac.

Chlorobis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)π-cyclopentadienyl titanium(IV). $\pi\text{-}C_5H_5Ti(hfac)_2Cl$.

Hexafluoroacetylacetone (Hhfac) reacted with $\pi\text{-}C_5H_5TiCl_3$ in such solvents as chloroform, dichloromethane, benzene and cyclohexane to produce $\pi\text{-}C_5H_5Ti(hfac)_2Cl$ with evolution of hydrogen chloride.

$$\pi\text{-}C_5H_5TiCl_3 + 2\ Hhfac \rightarrow \pi\text{-}C_5H_5Ti(hfac)_2Cl + 2\ HCl$$

A sample of $\pi\text{-}C_5H_5TiCl_3$ (2.2g. 0.01 mole) was dissolved in 150 ml. of chloroform to give a yellow solution. On addition of 8.3g. (0.04 mole) of Hhfac the solution immediately turned purple and this colour intensified as the solution was heated under reflux to expel hydrogen chloride. The reaction was complete in 30 minutes. The solution was filtered, evaporated under reduced pressure and stored at -10⁰ to give 4.0g.(≈71%) of red-purple crystals which tenaciously retained traces of Hhfac. The compound gradually decomposed on heating (approx. m. p. 50-55⁰). The compound was a non-electrolyte in acetone. Solutions of $\pi\text{-}C_5H_5Ti(hfac)_2Cl$ were unstable at temperatures above 15⁰ in the absence of small amounts of Hhfac.

TABLE III . Nmr spectral data ($CDCl_3$ solvent) 40^0.

Compound	τ π-C_5H_5 or π-C_5H_4	τ C-H or C_6H_5	τ CH_3	^{19}F nmr resonances
π-$C_5H_5Ti(hfac)_2Cl$	3.16(5) Minor isomer not assigned	3.76(2)		Minor isomer(25%):-EFGH, -76.0(1)(1.2);-66.0(1)(1.4);-22.0(1)(2.0);-4.0(1)(2.4). Major isomer(75%):-ABCD, -72.0(3)(1.3);-57.0(3)(1.5);-31.0(3)(1.9);+21.0(3)(2.5).Recorded at -30^0.
π-$CH_3C_5H_4Ti(hfac)_2Cl$	3.0-3.6(4) Minor isomer not assigned	3.69(2)	7.56(2.25) 7.63(0.75)	Minor isomer(25%):-EFGH, -80.0(1)(1.2);-63.0(1)(x);-18.0(1)(1.5);0.0(x)(x). Major isomer (75%):-ABCD, -74.0(3)(1.4);-63.0(3)(x);-30.0(3)(1.9);+22.0(3)(2.3).Recorded at -10^0.
π-$C_5(CH_3)_5Ti(hfac)_2Cl$		Not assigned	7.96(6) 7.75(4)	Minor isomer(40%):-EFGH, -101.0(4)(1.1); -83.0(4)(1.3);-47.0(4)(1.5);+37.0(4)(1.8). Major isomer(60%):-ABCD, -105.0(6)(1.1); -80.0(6)(1.3);-47.0(6)(1.5);+38.0(6)(1.8). Recorded at-20^0.
π-$C_5H_5Zr(tfac)_2Cl$	3.49(5)	3.95(2)	7.70,7.85 7.89(total 6)complex	Form1(50%), -83.0(5)(0.9);-42.0(5)(1.2). Form2(35%), -87.0(3.5)(0.8);-84.0(3.5)(0.9). Form3(10%), -43.0(1)(1.8);-37.0(1)(2.0). Form4(5%), -76.0(0.5)(0.9);-34.0(0.5)(1.5).
π-$C_5H_5Zr(tfac)_3$	3.75(3) 3.79(2)	4.19,4.23 4.36(3)	7.87,7.92, 7.93,8.21. (9)	Form1(60%)AB,-61.0(2.0)(1.0);-34.0(4.0)(1.2). Form2(40%)XY,-36.0(2.6)(1.8);-25.0(1.3)(2.0). Recorded at ambient temperature.
π-$C_5H_5Zr(bztfac)_2Cl$	3.45 - 3.60 (7)	1.9-2.7(10)		Form1(50%),-82.0(1.0);-40.0(1.2):Form2(40%), -85.0(0.9);-81.0(1.0):Form3(7%),-42.0(2.0); -35.0(2.0): Form4 not identified.
π-$C_5H_5Zr(ttfac)_2Cl$	3.50(5)	C_4H_3S and C-H complex		Form1(55%),-37.0(1.0);-3.0(1.3):Form2(45%), -49.0(0.9);-41.0(1.0). Other forms not identified.

TABLE IV Nmr Spectral Data ($CDCl_3$ solvent) 40^0.

COMPOUND	τ π-C_5H_5 or π-C_5H_4	τ C-H or C_6H_5	τ CH_3	^{19}F nmr resonances
π-$C_5H_5Zr(hfac)_3$	3.57(5)	3.73(2) 3.87(1)		+3.2(1)(1.1);+14.8(4)(1.3);+32.0(1)(2.0).
π-$CH_3C_5H_4Zr(hfac)_3$	3.58 - 3.94(7)		7.78(3)	+5.4(1)(1.0);+10.2(4)(1.4);+26.7(1)(2.0).
π-$C_5H_5Hf(hfac)_3$	3.66(5)	3.72(2) 3.85(1)		+7.6(1)(1.0);+21.8(4)(1.3);+38.5(1)(2.0).
π-$CH_3C_5H_4Zr$ $(tfac)_3$	3.70 - 4.40(7)		7.87- 8.02(12)	Form 1 (56%). -63.0(56)(0.9); -44.0(112)(1.0) Form 2 (44%). -48.0(88)(1.2); -39.0(44)(1.8).
π-$C_5H_5Zr(bztfac)_3$	3.58 3.62(5)	3.40- 3.73(3) 1.90- 2.80(15)		-56.0(x)(1.2);-41.0(x)(2.4);-37.0(x)(2.0).
π-$CH_3C_5H_4Zr$ $(bztfac)_3$	3.52- 3.92(7)	1.90- 2.80	7.65 7.67	-53.0(x)(1.0);-47.0(x)(7.0).
π-$C_5H_5Ti(tfac)_2Cl$	3.28(5)	4.12(2)	7.67- 8.03(6)	Form 1 (50%). -103.0,-77.0; 2(30%).-109.0,-106.0. Other forms unassigned. (-20°).
π-$C_5H_5Ti(bztfac)_2$ Cl	3.20(5)	3.70(2) 1.80-2.80(10)		Form 1 (50%). -104.0,-71.0; 2(30%).-116.0,-97.0. Other forms unassigned.
π-$C_5H_5Ti(ttfac)_2$ Cl	3.17(5)	3.59(2) 2.0- 3.2(6)		Form 1. (50%). -55.0,-25.0; 2(35%). -77.0,-60.0. Other forms unassigned.

The compound π-$CH_3C_5H_4Ti(hfac)_2Cl$ was prepared in an analogous manner to the π-$C_5H_5Ti(hfac)_2Cl$ compound above using a solution of π-$CH_3C_5H_4TiCl_3$ prepared from $(\pi$-$CH_3C_5H_4)_2TiCl_2$ as described previously. The pentamethylcyclopentadienyl analogue was prepared in situ for nmr examination. This compound appeared to be unstable in the solid state, yet stable in solutions containing Hhfac. All the bis (hfac) - cyclopentadienyl compounds indicated the presence of two solution isomers as judged from the ^{19}F nmr spectra.

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)π-cyclopentadienyl zirconium(IV). π-$C_5H_5Zr(hfac)_3$.

A sample of $(\pi$-$C_5H_5)_2ZrCl_2$(2.9g. 0.01 mole) and 8.3g. (0.04mole) of Hhfac were added to 150ml. of dichloromethane and the mixture gently heated under reflux for 48 hours, giving a pale yellow solution after evolution of large amounts of hydrogen chloride.

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 3Hhfac \rightarrow \pi\text{-}C_5H_5Zr(hfac)_3 + 2HCl + C_5H_6.$$

The solvent and excess Hhfac were removed at reduced pressure and remaining solids extracted several times with hot hexane until the extracts were no longer yellow. The hexane extracts were filtered, concentrated and cooled to yield 7.0g. (90%) of pale yellow crystals of π-$C_5H_5Zr(hfac)_3$. Similar reactions were attempted using $(\pi$-$CH_3C_5H_4)_2ZrCl_2$ and $(\pi$-$C_5H_5)_2HfCl_2$ and produced π-$CH_3C_5H_4Zr(hfac)_3$ and π-$C_5H_5Hf(hfac)_3$ respectively.

Several unsuccessful attempts to isolate π-$C_5H_5Zr(hfac)_2Cl$ were made. In all cases, the only product containing hfac was π-$C_5H_5Zr(hfac)_3$. No information on intermediate compounds was available by following the course of the reaction by nmr. The reaction appeared in all cases to produce π-$C_5H_5Zr(hfac)_3$ independent of solvent, reaction temperature and mole ratio of reactants. The nmr spectra of this compound at variable temperatures have been reported (63), and the structure has been determined by X-ray crystallography using a sample prepared in this work (64).

B. Trifluoroacetylacetone. Htfac.

Initial investigations of the reaction of Htfac with $(\pi$-$C_5H_5)_2ZrCl_2$ led to isolation of π-$C_5H_5Zr(tfac)_3$. The reaction was followed by nmr sampling and under carefully controlled conditions gave indications of the presence of π-$C_5H_5Zr(tfac)_2Cl$ from the ^{19}F nmr spectra. The reaction products, in this case, were found to be dependent upon reaction conditions, notably temperature and mole ratio of reactants.

Tris(1,1,1-trifluoro-2,4-pentanedionato)π-cyclopentadienylzirconium(IV) π-$C_5H_5Zr(tfac)_3$ and chlorobis(1,1,1-trifluoro-2,4-pentanedionato) π-cyclopentadienylzirconium(IV). π-$C_5H_5Zr(tfac)_2Cl$.

Method 1.

A process similar to that employed for the preparation of π-$C_5H_5Zr(hfac)_3$ was carried out using chloroform as a solvent. Approximately 60% yield of π-$C_5H_5Zr(tfac)_3$ was isolated as colourless crystals.

Method 2.

A sample of $(\pi$-$C_5H_5)_2ZrCl_2$(2.9g. 0.01mole) and 4.7g. (0.03 mole) of Htfac were mixed in 50ml of dichloromethane and the mixture heated under reflux. The ^{19}F nmr spectrum of the solution was followed at intervals as the solution darkened and hydrogen chloride was evolved. After approximately 68 hours reflux, the spectrum was interpreted to indicate the presence of $\pi\text{-}C_5H_5Zr(tfac)_2Cl$ and Htfac together with small amounts of $\pi\text{-}C_5H_5Zr(tfac)_3$ and $(\pi\text{-}C_5H_5)_2ZrCl_2$ by inspection of the ^1H nmr spectrum.

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 2Htfac \rightarrow \pi\text{-}C_5H_5Zr(tfac)_2Cl + HCl + C_5H_6.$$

The dichloromethane solution was evaporated under reduced pressure and the remaining slurry extracted with ten 100 ml. portions of hot hexane.

The volume of the hexane extracts was reduced to 50 ml. and cooling produced a white powder - identified from the nmr spectrum as the observed intermediate, $\pi\text{-}C_5H_5Zr(tfac)_2Cl$.

The mother liquor and pentane washings of this solid were added to the extracted slurry, evaporated to dryness and dissolved in 50 ml. of chloroform. This chloroform solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$, $\pi\text{-}C_5H_5Zr(tfac)_3$ and unextracted $\pi\text{-}C_5H_5Zr(tfac)_2Cl$ was heated under reflux with a further 4.7g. (0.03 mole) of Htfac for 48 hours. $\pi\text{-}C_5H_5Zr(tfac)_3$ was isolated from this solution by the method outlined in A.

<u>Tris(1,1,1-trifluoro-2,4-pentanedionato)methylπ-cyclopentadienyl zirconium(IV)</u>. $\pi\text{-}CH_3C_5H_4Zr(tfac)_3$.

This preparation was carried out by a similar method to that employed in B above. In this case, the formation of the tris complex was greatly favoured over the bis complex at the reflux temperature of dichloromethane.

Chlorobis(1,1,1,trifluoro,2,4-pentadionato)π-cyclopentadienyltitanium(IV) π-$C_5H_5Ti(tfac)_2Cl$.

The compound was prepared by a similar method to that used for π-$C_5H_5Ti(hfac)_2Cl$.

C. Benzoyltrifluoroacetone Hbztfac and Thenoyltrifluoroacetone Httfac.

Preparation of π-$C_5H_5Zr(bztfac)_2Cl$ and π-$C_5H_5Zr(bztfac)_3$ followed the method outlined in B for π-$C_5H_5Zr(tfac)_2Cl$ and π-$C_5H_5Zr(tfac)_3$. π-$C_5H_5Ti(bztfac)_2Cl$ and π-$C_5H_5Ti(ttfac)_2Cl$ were prepared in a similar manner to π-$C_5H_5Ti(tfac)_2Cl$.

Chlorobis(1-(2-thenoyl)-4,4,4-trifluoro-1,3-butanedionato)π-cyclopentadienylzirconium(IV). π-$C_5H_5Zr(ttfac)_2Cl$.

This compound was prepared in a similar manner to that employed for π-$C_5H_5Zr(bztfac)_2Cl$. Isolation by solution in $CHCl_3$ and cooling yielded the bis chelate in ~ 40% yield, contaminated with small amounts of unreacted (π-$C_5H_5)_2ZrCl_2$. The attempted isolation of the tris-complex produced oils which resisted all attempts at crystallization.

Miscellaneous reactions.

The compounds $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$ were prepared by published methods (19), (28) for spectroscopic purposes.

Preparation of dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato) titanium(IV). $Ti(dpm)_2Cl_2$.

Samples of 1.9g. (0.01 mole) of $TiCl_4$ and 5.5g. (0.03 mole) of dipivaloylmethane (Hdpm) were mixed in 100ml of chloroform and the mixture heated under reflux for 24 hours. On crystallization, after addition of pentane, a red moisture-sensitive solid having the approximate formula Ti(dpm)Cl_3 was isolated. This compound was redissolved in chloroform and heated under reflux with a further 5.5g. (0.03 mole) of Hdpm for 72 hours.

The final orange solution was filtered, evaporated to a small volume and cooled to -40^0 to produce an orange oil. Repeated solution and cooling of this oil in a dichloromethane/hexane solvent yielded orange crystals of product (3.1g.- 64%), m. p. $97-98^0$. Anal.calc. for $C_{22}H_{38}O_4Cl_2Ti$, C 54.32; H 7.88; Cl 14.59: Anal. found, C 54.35; H 7.97; Cl 14.98:

The ambient temperature nmr spectrum of this compound in $CDCl_3$ indicated two resonances:- >CH 3.90(2) and $(CH_3)_3C$ 8.85(36). The singlet t-butyl resonance broadened considerably on cooling and eventually split into a well-resolved doublet at -50^0 . This behaviour paralleled that of the compounds $(acac)_2TiX_2$ (X = F, Cl, Br.) (<u>26</u>) . The limiting low temperature spectrum observed indicated that the 'instantaneous structure' in solution was the <u>cis</u>-form.

<u>Reaction of $(\pi-C_5H_5)_2ZrCl_2$ with Hdpm.</u>

This reaction was carried out in the hope of producing $\pi-C_5H_5Zr(dpm)_2Cl$. The starting materials were heated under reflux in benzene in a 1:3 mole ratio. The reaction was slow and a further equal quantity of Hdpm was added to the reaction mixture after 48 hours. After a total reflux time of 110 hours, the solution was worked up as for $\pi-C_5H_5Zr(acac)_2Cl$ producing colourless crystals of $Zr(dpm)_3Cl$ (55%). Anal. calc. for $C_{33}H_{57}O_6ClZr$, C 58.57; H 8.50; Cl 5.24: Anal.found, C 58.63; H 8.40; Cl 5.68:

The nmr spectrum in $CDCl_3$ showed two resonances:- >CH 3.97(3) and $(CH_3)_3C$ 8.83(54). The t-butyl resonance remained as a singlet even at -100^0 in acetone-d^6 , a similar situation to that observed for $Zr(acac)_3Cl$ (28).

1,1,1 Trifluoro 4-(2-thenoyl)4-mercaptobut-3-ene-2-one.

$CF_3COCHCSH(C_4H_3S)$. This compound was isolated using the technique reported by Chaston et. al. (65). This analogue of Httfac did not react with $(\pi\text{-}C_5H_5)_2ZrCl_2$ or displace Hacac from $\pi\text{-}C_5H_5Zr(acac)_2Cl$.

Preparation of bis-acetylacetone ethylenediimine.

$(CH_3COCH_2C(CH_3)NCH_2)_2$.

This compound and the trifluoroacetylacetone analogue were prepared by condensation of the 2,4-diketone and ethylene diamine ($H_2NCH_2CH_2NH_2$) (66) . Reaction with $\pi\text{-}C_5H_5Zr(acac)_2Cl$ and $\pi\text{-}C_5H_5$ $Zr(hfac)_3$ produced no product incorporating the β-ketimines as tetra-coordinated moieties. (67), (68). The nmr investigation of heated mixtures of $\pi\text{-}C_5H_5Zr(hfac)_3$ and bis-trifluoroacetylacetone ethylenediimine showed no exchange of the coordinated hfac chelates with β-ketimine at 110^0 over a period of 1 hour. Bromobenzene was used as solvent.

Reaction Mechanisms.

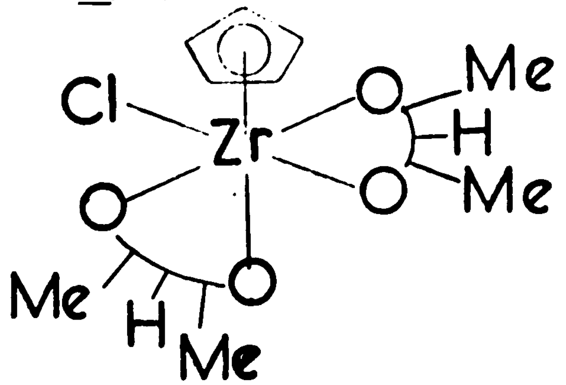
Some comments on possible reaction mechanisms of $(\pi\text{-}C_5H_5)_2$ $ZrCl_2$ are included on p.55. Evidence for possible reaction mechanisms was available from both the preparative studies and from nmr studies of mixed chelate compounds.

CHAPTER III.

Results and Discussion of the Bis-chelate Derivatives of Zr(IV).

π-$C_5H_5Zr(acac)_2Cl$.

The solid state structure of this complex has been shown to approximate dodecahedral coordination more closely than the alternative octahedral description.(62). (XI).

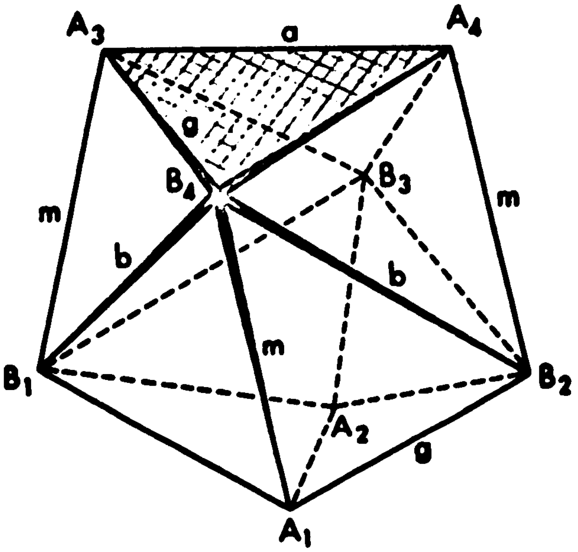


(XI)

The π-C_5H_5 ring may be envisaged as occupying an AAB triangular face comprising three coordination sites, the chlorine atom a characteristic B site and the two chelate rings bridging AB edges. Fig. 1. The marked lack of symmetry of this molecule was manifested in solution. The four methyl group substituents on the two chelate rings had different environments, demonstrated by the detection of four equal intensity methyl resonances in the nmr spectrum of the compound using $CDCl_3$, benzene or bromobenzene as solvent. Fig. 2. Two methine resonances were observed in benzene and bromobenzene at 40^0, further confirming the lack of symmetry in the system. These resonances were almost isochronous (69) in $CDCl_3$.

Chemical shifts of resonances were affected to different extents by different solvents in this case. For example, the methyl resonances

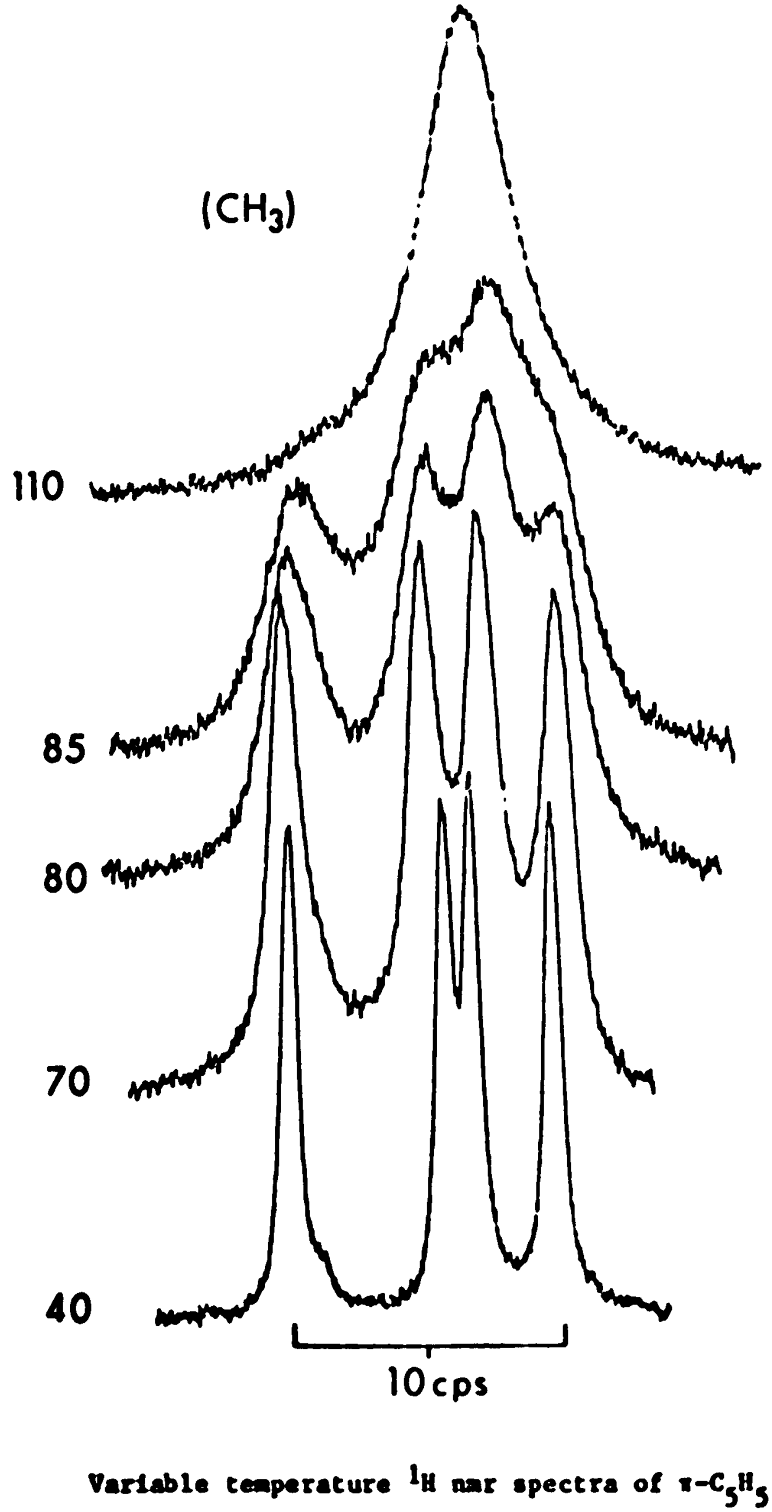
Figure 1.



DODECAHEDRON

The position of the π-C_5H_5 ring is indicated by the cross-hatched area.

Figure 2.



Variable temperature ^1H nmr spectra of π-C_5H_5 $Zr(acac)_2Cl$ (methyl region) in bromobenzene. Recorded at 100 Mcs.

were completely resolved using a solvent comprised of equal volumes of $CDCl_3$ and benzene. This effect of solvent has been noted and ascribed to a solvent-induced variation of local diamagnetic anisotropy (<u>70</u>).

The single π-C_5H_5 resonance was a common feature of a π-bonded group (<u>71</u>) and arose from a rapid rotation of the π-system about the metal-ring axis. The substitution of a π-C_5H_5 group for smaller ligands such as Cl in $(acac)_2ZrCl_2$ or an acac group in $Zr(acac)_3Cl$ appears to confer extra stereochemical rigidity on the chelate system. Thus Fay and Pinnavaia have reported rapid intramolecular chelate exchange for both $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$ even at temperatures of -120^0 (<u>28</u>) while for π-$C_5H_5Zr(acac)_2Cl$ such chelate exchange occurred at <u>ca</u>.+ 60^0 .

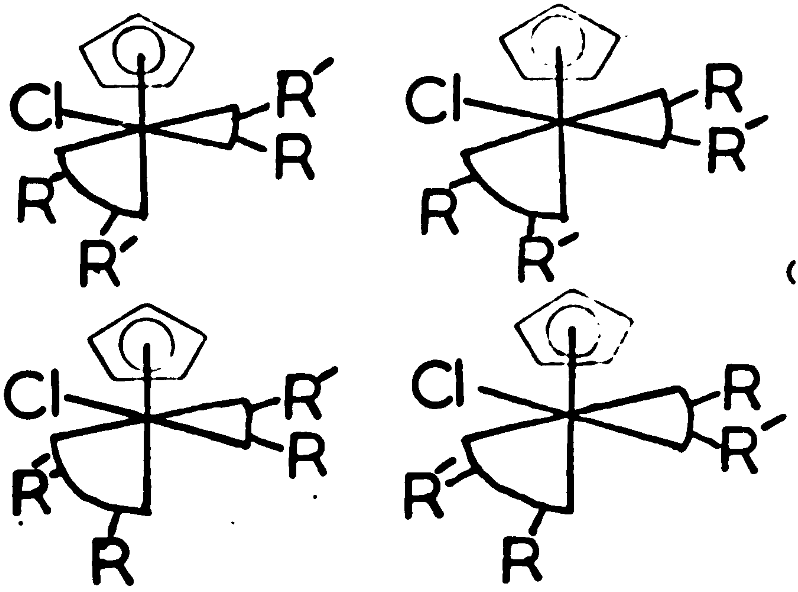
The behaviour of π-$C_5H_5Zr(acac)_2Cl$ in solution was investigated by temperature variation. Fig. 2. The environments of the four methyl groups were interconverted by a chelate exchange process which also interconverted the environments of the methine protons. The spectra were independent of concentration, indicating an intramolecular exchange process. They were also independent of the presence of free acetylacetone, the methyl resonance of the keto-isomer remaining sharp over the temperature range investigated (up to about 100^0).

Higher temperature spectra, recorded in bromobenzene, indicated the possibility of intramolecular exchange between the enol form of the β- diketone and π-$C_5H_5Zr(acac)_2Cl$ and / or further reaction to produce either π-$C_5H_5Zr(acac)_3$ or $Zr(acac)_3Cl$.

The foregoing results indicated that an intramolecular chelate exchange process was operative and was much faster than possible intermolecular processes involving chelate transfer or exchange with free chelating agent via a proton transfer process.

π-$C_5H_5Zr(bzac)_2Cl$.

Since one isomer of π-$C_5H_5Zr(acac)_2Cl$ was detected in solution, the treatment of more complex molecules using the octahedral description yields qualitatively the same results as the dodecahedral description. In order to avoid confusion, the following terminology is introduced. The term isomer is reserved for different arrangements of metal-ligand bonds in the coordination polyhedron while the term form is reserved for configurations arising from different orientations of (usually) asymmetric chelated ligands. Thus, the nmr spectrum of π-C_5H_5 $Zr(bzac)_2Cl$, which shows eight methyl resonances, (Fig.3) could be rationalized in terms of a four form mixture.(XII).



(XII)

The nmr spectra indicated that the abundance of each form was invariant over several preparations. The distribution presumably represents an equilibrium mixture. The existence of some factor, leading to favoured forms, was considered at this stage of the investigation, although the favouring in this case did not appear to be extreme.

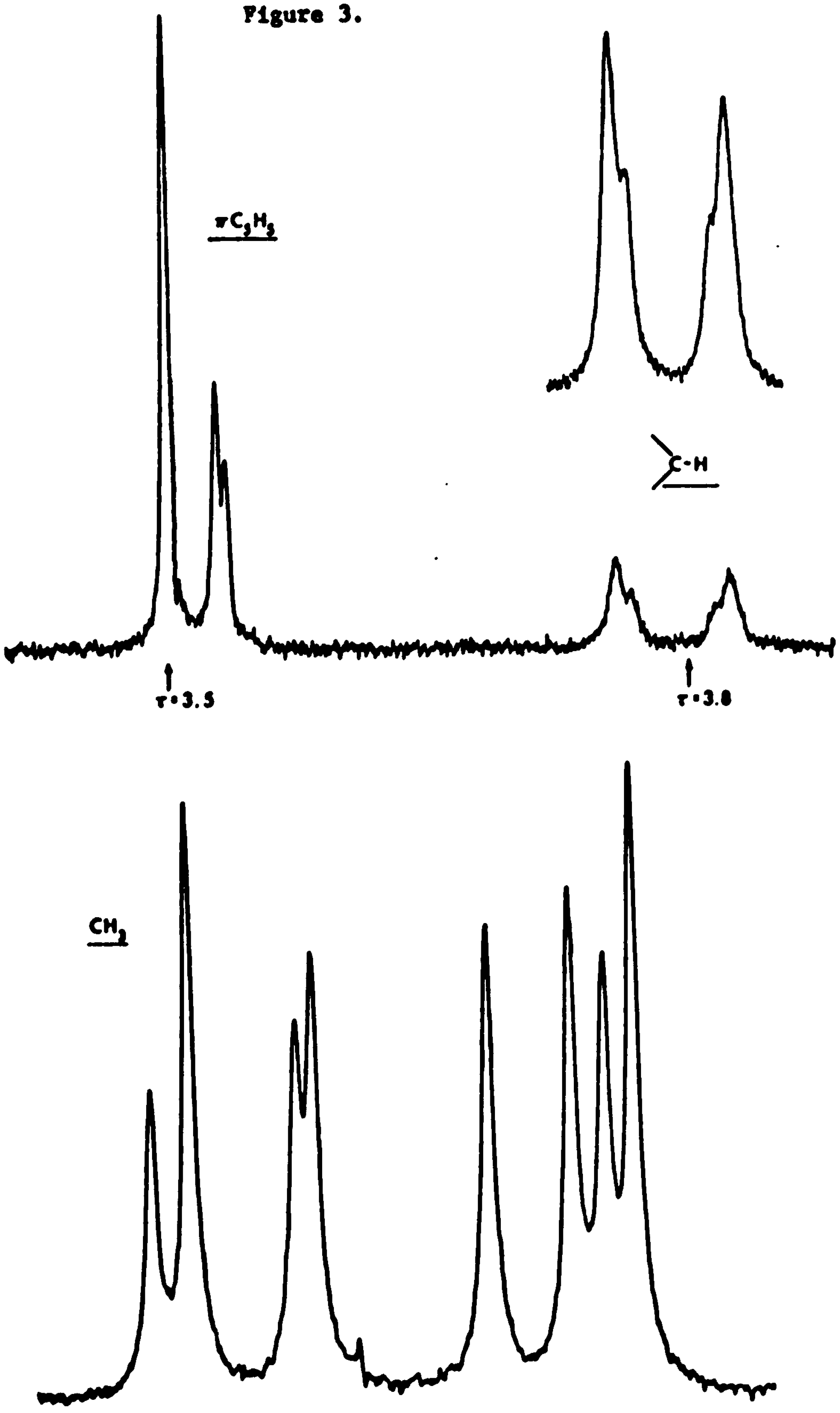
The behaviour of the nmr spectrum Fig.4. on raising the temperature indicated that the environments of all eight methyl groups were averaged. Simultaneous averaging of π-C_5H_5, methine and phenyl environments also occurred. The coalescence of resonances due to minor forms occurred at slightly lower temperatures than general coalescence and the intermediate stages (~90^0) were similar to certain stages in the coalescence of methyl resonances of $Ti(bzac)_2Cl_2$ (<u>27</u>) (<u>28</u>).

The spectra were independent of concentration and also of the presence of free chelating agent Hbzac, indicating that the rearrangement processes were intramolecular and further that these intramolecular rearrangements were much faster than any intermolecular mode of exchange.

<u>π-$C_5H_5Zr(tfac)_2Cl$</u>

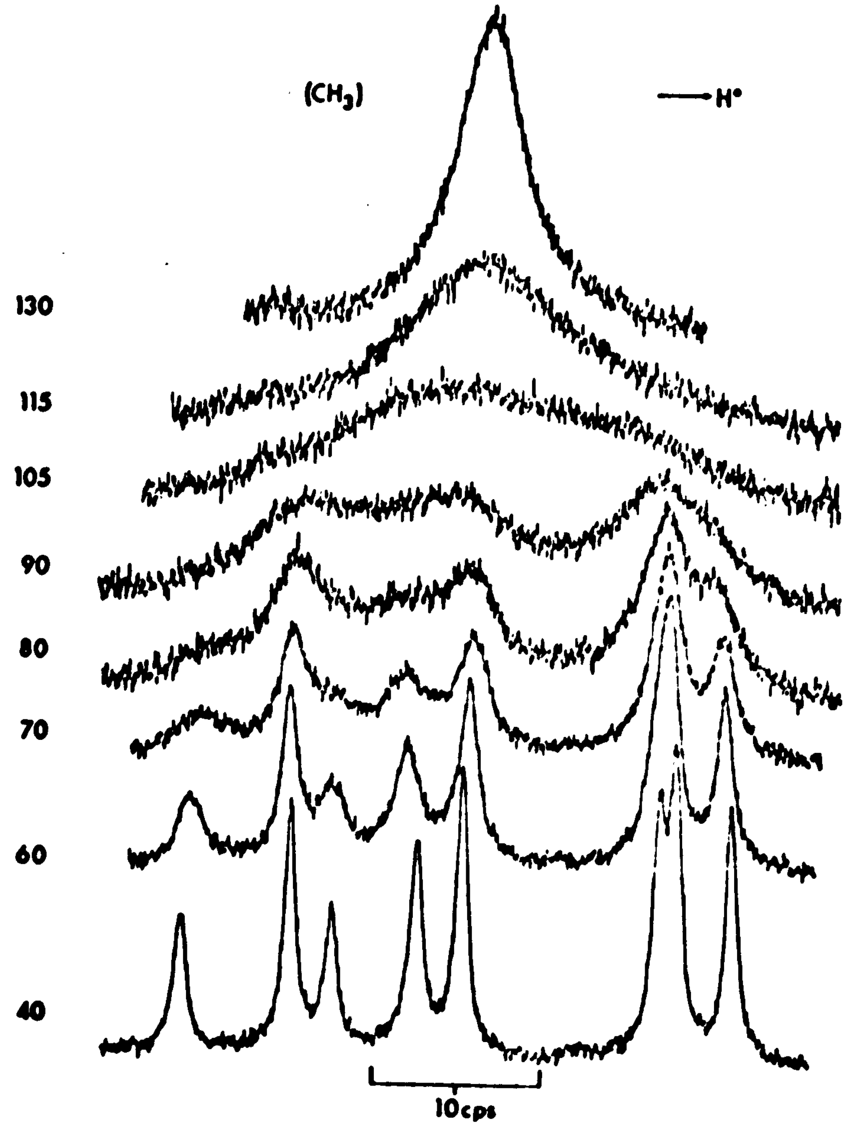
Initial examination of the CF_3 region showed two doublets of major intensity and several minor resonances. The minor resonances were always present in the ^{19}F nmr spectrum of π-$C_5H_5Zr(tfac)_2Cl$ and the entire spectrum could be rationalized on the basis of a mixture of

Figure 3.



Ambient temperature ^1H nmr spectrum of π-C_5H_5 Zr(bzac)$_2$Cl in $CDCl_3$. Recorded at 100 Mcs.

Figure 4.



Variable temperature nmr spectra of π-$C_5H_5Zr(bzac)_2Cl$ indicating an unselective exchange process at elevated temperatures. Recorded at 100 Mcs. in C_6H_5Br.

four forms in solution.(Fig.5).

The wide variation in form abundance measured from the ^{19}F nmr spectrum was also indicated, although less clearly, by the ^{1}H nmr spectrum in the methyl region. The distribution suggested that preferences for certain chelate ring orientations were more marked for this compound than in the case of π-$C_5H_5Zr(bzac)_2Cl$. The distribution of the four forms, measured in $CDCl_3$ (50%,35%,10%,5%), was independent of preparation and appeared to be an equilibrium mixture. The major CF_3 resonances occurred at low field.

Fast intramolecular exchange was indicated by a concentration independent nmr spectrum at 130^0 which consisted of singlet π-C_5H_5, methyl, methine and trifluoromethyl resonances.(Fig.6).

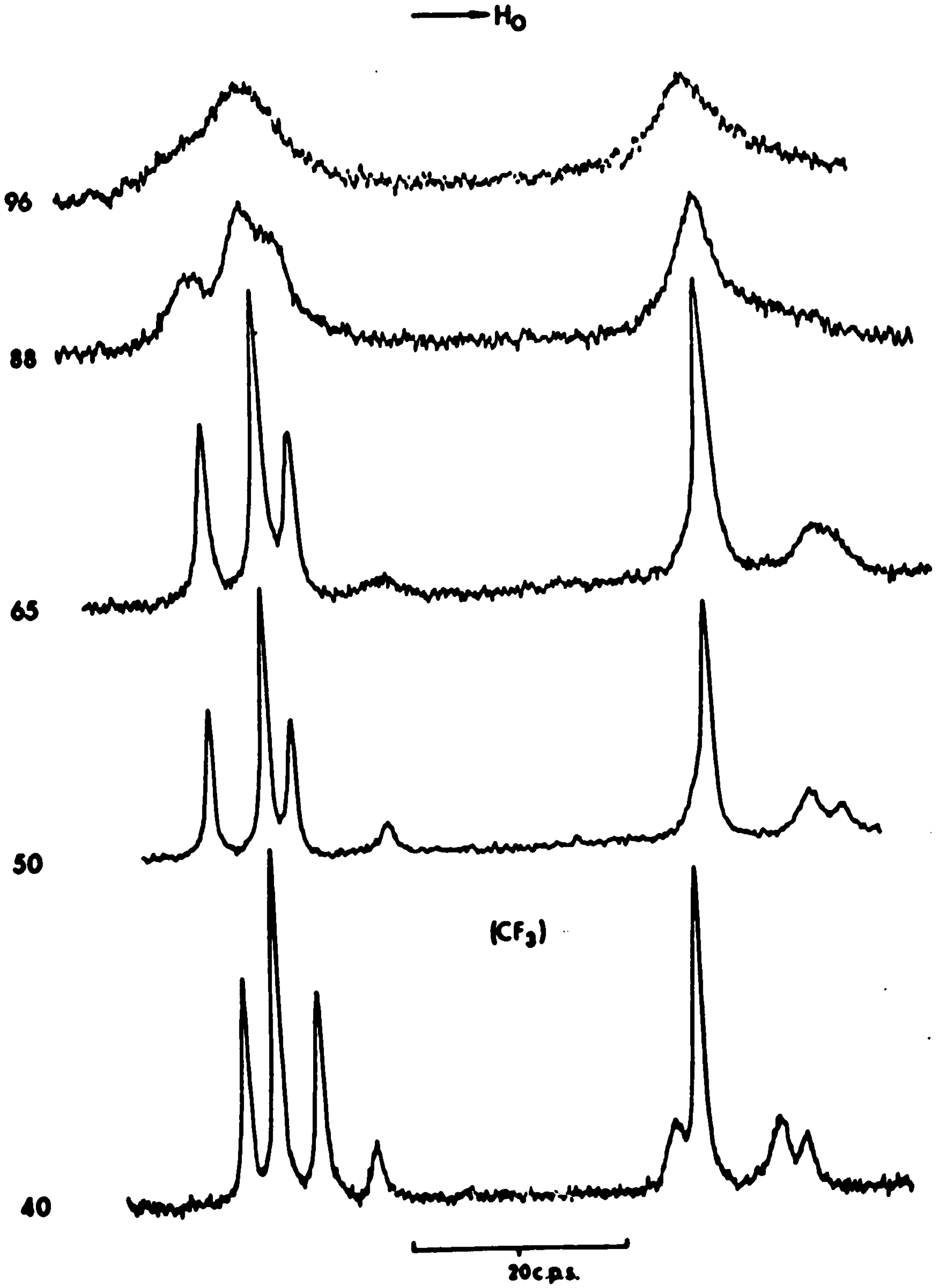
The most to least abundant forms were catalogued according to chemical shift (Δ) between the doublets concerned.

Form ($CDCl_3$)	%	$\Delta^{19}F$(cps)	$\Delta^{1}H$(cps)
A	50	41	19.0
B	35	3	4.2
C	10	6	4.0
D	5	42	Undetected.

π-$C_5H_5Zr(bztfac)_2Cl$ and π-$C_5H_5Zr(ttfac)_2Cl$.

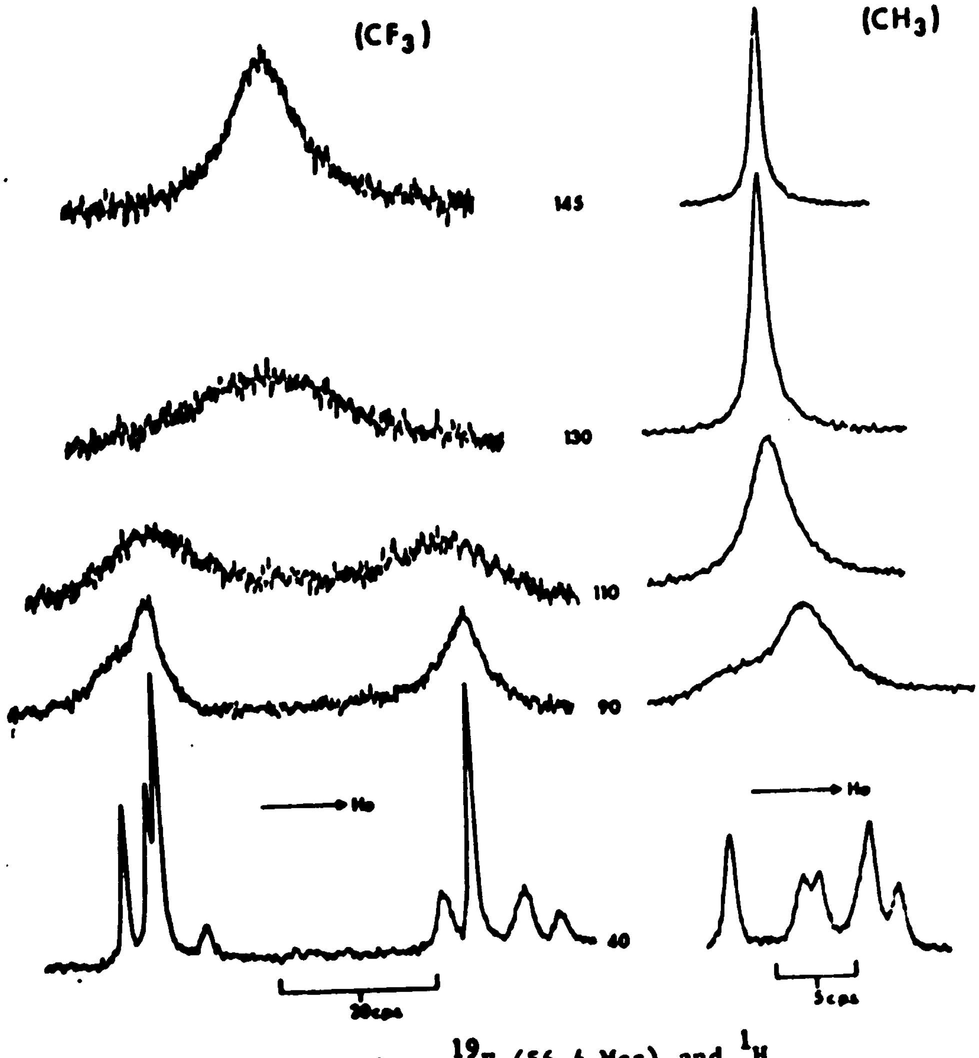
The four expected forms of this compound were observed at 40^0 as four sets of doublets in the trifluoromethyl region of the ^{19}F spectrum. The abundances and doublet separations were as follows:-

Figure 5.



Variable temperature ^{19}F nmr spectra of π-$C_5H_5Zr(tfac)_2Cl$ in CH_2Br_2. Recorded at 56.4 Mcs.

Figure 6.



Variable temperature ^{19}F (56.4 Mcs) and ^{1}H (60.0 Mcs) nmr spectra of the CF_3 and CH_3 regions of π-$C_5H_5Zr(tfac)_2Cl$. Bromobenzene solvent.

Form ($CDCl_3$)	%	$\Delta^{19}F$ (cps)
A	50	42
B	40	4
C	7	7
D (observed in C_6H_5Br)	3	43

An almost identical distribution of forms was observed for π-$C_5H_5Zr(ttfac)_2Cl$.

Form ($CDCl_3$)	%	$\Delta^{19}F$ (cps)
A	48	34
B	41	8
C	7	6
D	4	44

The three complexes containing fluorinated β-diketones as chelates all have remarkably similar ^{19}F spectra, both with respect to doublet separations and abundances. In effect, for these compounds, the doublet separations could be correlated with form abundance and vice-versa. This unusual state of affairs indicated that the stereochemistry of these complexes was determined largely by a preference of CF_3 groups for special environments. This preference would, of course, account for the spectral similarities observed.

The behaviour of the nmr spectra of the chelates on raising the temperature was very similar to that of π-$C_5H_5Zr(tfac)_2Cl$. Minor form environments were averaged first, followed closely by major form environments. The exchanges were intramolecular since the spectra recorded were independent both of concentration and the presence of free chelating agent (Hbztfac or Httfac).

The rapid intramolecular chelate exchange observed for these compounds indicated that perhaps other chelate compounds could be prepared which would provide information on both the exchange process and the stereochemical preference of the fluorinated chelates. Two other methods of preparation were investigated. These were intermolecular exchange with other chelate compounds and intermolecular exchange with free β-diketones.

Intermolecular Chelate Exchange.

In general, chelate exchanges to form mixed chelate compounds such as π-$C_5H_5Zr(tfac)(acac)Cl$ were carried out in situ in an nmr tube. Experiments using the readily available titanium chelates $Ti(acac)_2Cl_2$ and $Ti(dpm)_2Cl_2$ had indicated that these were indeed cis isomers and were undergoing some form of rapid chelate exchange at ambient temperature. Mixtures of these two compounds were prepared and nmr examination revealed resonances which could be attributed to neither of the starting materials, but could be assigned to the mixed chelate $Ti(acac)(dpm)Cl_2$. In this instance although intermolecular exchange was slow on the nmr time scale, this mode of exchange was rapid enough, for a mixture of chelates, to be essentially complete in the time taken to record a spectrum.

This phenomenon was next sought in the π-$C_5H_5Zr(chelate)_2Cl$ system, and it was found that the nmr spectrum of an equimolar mixture of π-$C_5H_5Zr(acac)_2Cl$ and π-$C_5H_5Zr(tfac)_2Cl$ showed some resonances in addition to those of the original components indicating that intermolecular exchange was sufficiently rapid at ambient temperature (40°) to be complete by the time the spectrum was recorded. A similar phenomenon has been reported for mixtures of $Zr(acac)_4$ and $Zr(tfac)_4$, in which all possible compounds $Zr(acac)_n(tfac)_{4-n}$ were observed. (23) (24).(n = 0,1,2,3,4.)

The nmr spectrum of the mixed chelate π-$C_5H_5Zr(acac)(tfac)Cl$ was expected to be very complex due to the presence of a possible four forms, giving a total of 4 π-C_5H_5, 8 methine, 12 methyl and 4 trifluoromethyl resonances. The complexity of all but the

^{19}F spectrum in the CF_3 region led to primary investigation of this region for the mixed chelates.

Preparation of π-$C_5H_5Zr(acac)(tfac)Cl$.

To a solution of π-$C_5H_5Zr(tfac)_2Cl$ in $CDCl_3$ were added small amounts of π-$C_5H_5Zr(acac)_2Cl$. The ^{19}F nmr spectrum eventually was constant and unaffected by further additions of π-$C_5H_5Zr(acac)_2Cl$. At this stage, π-$C_5H_5Zr(acac)_2Cl$ was in large excess and the ^{19}F spectrum consisted of three singlet resonances in the CF_3 region, with the possibility of a fourth, low intensity resonance almost isochronous with the low field, most intense, singlet. The equilibrium reaction may be expressed as:-

$$\pi\text{-}C_5H_5Zr(acac)_2Cl + \pi\text{-}C_5H_5Zr(tfac)_2Cl \rightleftharpoons 2\ \pi\text{-}C_5H_5Zr(acac)(tfac)Cl$$

$$\text{with } K = \frac{\{\pi\text{-}C_5H_5Zr(acac)(tfac)Cl\}^2}{\{\pi\text{-}C_5H_5Zr(acac)_2Cl\}\{\pi\text{-}C_5H_5Zr(tfac)_2Cl\}}$$

and for a purely statistical distribution K = 4.

In the present case, the concentration of π-$C_5H_5Zr(acac)_2Cl$ was high, the concentration of π-$C_5H_5Zr(tfac)_2Cl$ correspondingly low (if K does not differ much from four) and the major fluorine containing chelate in the system was π-$C_5H_5Zr(tfac)(acac)Cl$. The CF_3 spectrum corresponded to that of π-$C_5H_5Zr(acac)(tfac)Cl$ at this stage.

By a similar method to that outlined above, the ^{19}F nmr spectra of the following mixed chelates were recorded.

π-$C_5H_5Zr(acac)(bztfac)Cl$

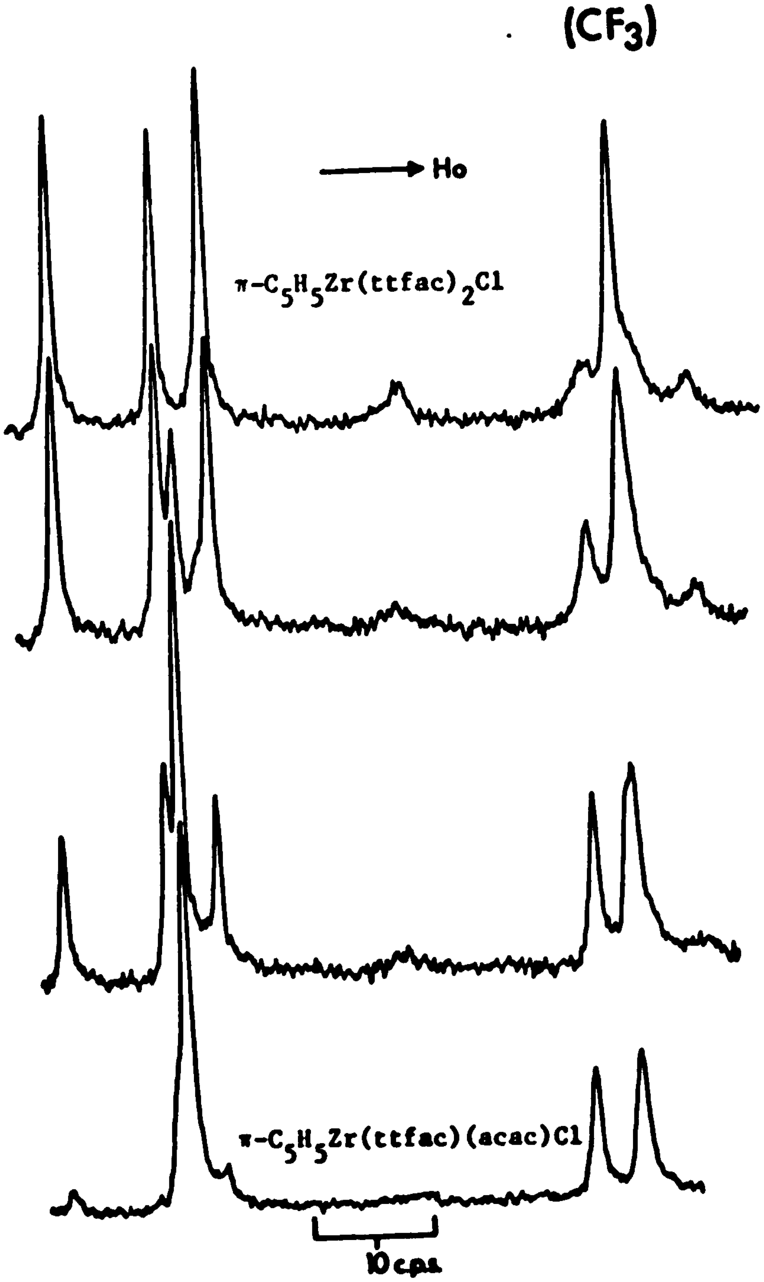
π-$C_5H_5Zr(acac)(ttfac)Cl$

Figure 7 indicates the spectral changes from π-$C_5H_5Zr(ttfac)_2Cl$ to π-$C_5H_5Zr(acac)(ttfac)Cl$ as π-$C_5H_5Zr(acac)_2Cl$ was added. The slightly different approach of adding π-$C_5H_5Zr(ttfac)_2Cl$ to π-$C_5H_5Zr(acac)_2Cl$ and observation of changes in the methyl region led to the methyl region spectrum of π-$C_5H_5Zr(acac)(ttfac)$ Cl Fig.8.

The ^{19}F spectra of these mixed complexes were very similar both from positional and intensity considerations.

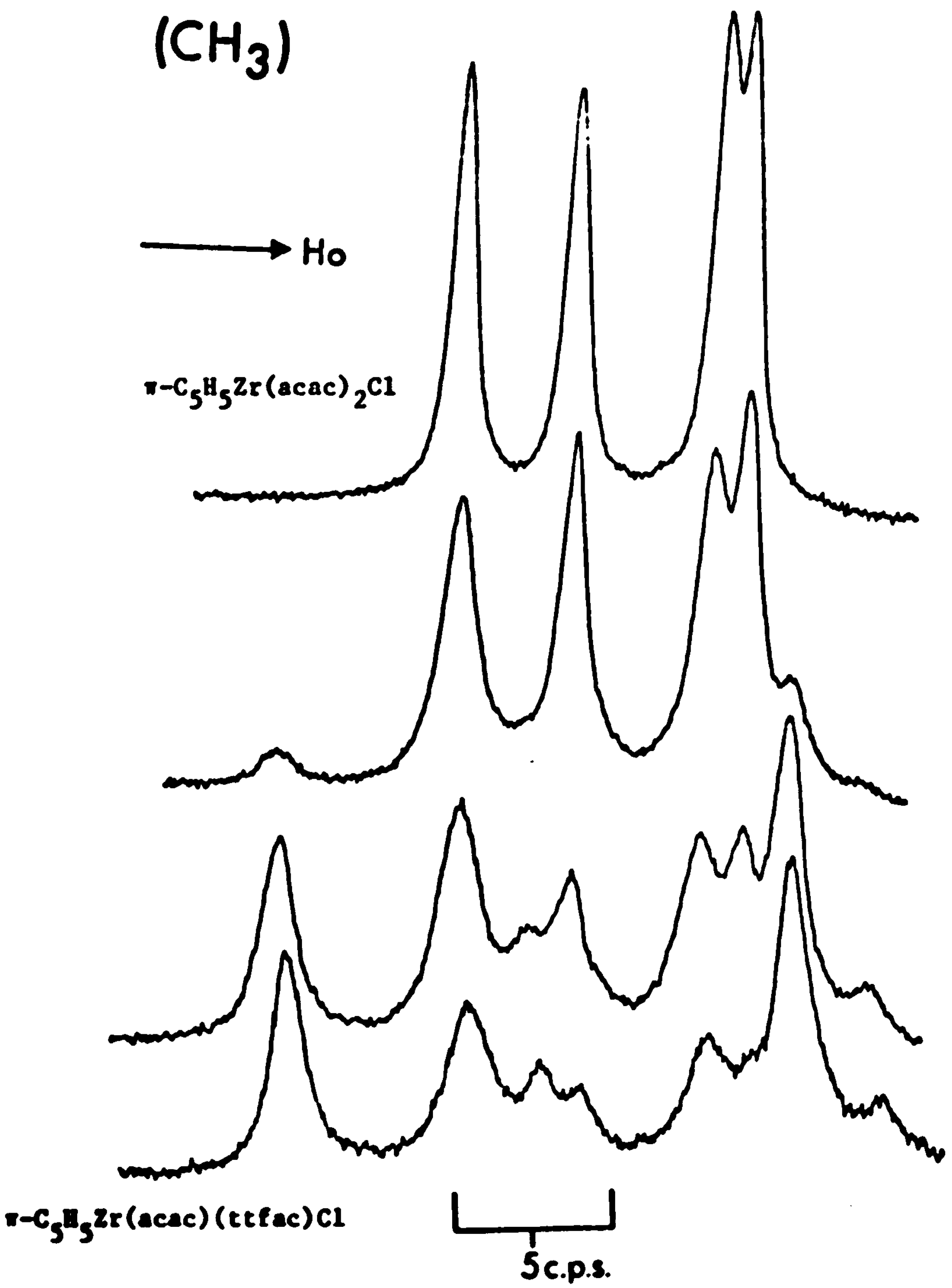
It seemed likely at this stage of investigation that the distribution of forms observed for compounds containing fluorinated β-diketones was primarily due to a selective site competition by trifluoromethyl groups for the four available environments. The effect appeared independent of the steric or electronic properties of chelate substituents other than the trifluoromethyl group.

Figure 7.



Production of the ^{19}F nmr spectrum of π-C$_5$H$_5$Zr(ttfac)(acac)Cl by addition of π-C$_5$H$_5$Zr(acac)$_2$Cl to a solution of π-C$_5$H$_5$Zr(ttfac)$_2$Cl in CDCl$_3$.

Figure 8.



Production of the CH_3 region spectrum of π-$C_5H_5Zr(ttfac)(acac)Cl$ by addition of π-$C_5H_5Zr(ttfac)_2Cl$ to a solution of π-$C_5H_5Zr(acac)_2Cl$ in $CDCl_3$. Recorded at 60.0 Mcs.

Intermolecular Exchange with β-diketones.

The ease of intermolecular chelate exchange in the preceding systems led to investigations of similar exchanges with free β-diketones.

The reaction of π-$C_5H_5Zr(acac)_2Cl$ with Htfac.

To a solution of π-$C_5H_5Zr(acac)_2Cl$ in $CDCl_3$ were added small amounts of Htfac and the nmr spectrum recorded in both ^{19}F and ^1H regions.

At 40^0 the following observations were made with increasing additions of Htfac.

a) Diminution of the ^1H nmr resonances of π-$C_5H_5Zr(acac)_2Cl$ with appearance of new methyl, methine and π-C_5H_5 resonances. In particular a resonance due to free acetylacetone and new CF_3 resonances corresponding to those of π-$C_5H_5Zr(acac)(tfac)Cl$ were observed.

b) Further reduction of the resonances of π-$C_5H_5Zr(acac)_2Cl$, increase of Hacac, considerable alteration in the π-C_5H_5 and CH regions and the appearance of new CF_3 resonances corresponding to those observed for π-$C_5H_5Zr(tfac)_2Cl$.

c) Complete disappearance of resonances due to π-$C_5H_5Zr(acac)_2Cl$ and π-$C_5H_5Zr(acac)(tfac)Cl$, constant resonances of π-$C_5H_5Zr(tfac)_2Cl$ and Hacac, together with increase of the resonances due to Htfac.

d) Slow production of the resonances of π-$C_5H_5Zr(tfac)_3$ with consequent reduction of those of π-$C_5H_5Zr(tfac)_2Cl$.

The foregoing observations were explained using the equilibria.

1. π-$C_5H_5Zr(acac)_2Cl$ + Htfac = π-$C_5H_5Zr(acac)(tfac)Cl$ + Hacac

2. π-$C_5H_5Zr(acac)(tfac)Cl$ + Htfac = π-$C_5H_5Zr(tfac)_2Cl$ + Hacac

This is then followed by the attack of Htfac in a slow step at 40°.

π-$C_5H_5Zr(tfac)_2Cl$ + Htfac → π-$C_5H_5Zr(tfac)_3$ + HCl

The equilibrium in equation 1. lay far to the right-hand side as judged by the absence of Htfac up to equimolar concentrations. The equilibrium in equation 2. also favoured the right-hand side although to a much lesser extent than in equilibrium 1.

The reaction of π-$C_5H_5Zr(tfac)_2Cl$ <u>in situ</u> with Hacac indicated the formation of the mixed chelate compound by a reversal of equilibrium 2. The ^{19}F spectra of π-$C_5H_5Zr(acac)(bztfac)Cl$ and π-$C_5H_5Zr(acac)(ttfac)Cl$ were duplicated by this technique. The ^{19}F spectra of a large number of mixed chelate compounds were thus available and selected examples were recorded. The possible chelate compounds available were:-

π-$C_5H_5Zr(L')(L'')Cl$

where L' = acac, bzbzac, dpm.

L" = tfac, bztfac, ttfac, npthtfac.

The ^{19}F spectra of all the mixed chelate compounds were very similar. Table V . The spectra were almost independent of L'- the unfluorinated chelate, and also independent of the substituent (other than CF_3) of L" <u>i.e.</u>, methyl, phenyl, 2-thenoyl or 2-napthyl. The observation of a wide variation in the abundance of the four forms

TABLE V ^{19}F NMR SPECTRA OF MIXED CHELATE COMPOUNDS

π-$C_5H_5ZrL'L''Cl$ in $CDCl_3$ at 40°C

L'	L"	^{19}F resonances
acac	tfac	-84.0(6.0)(0.8), -82.0(x)(x),-49.0(2.0)(1.1) -42.0(1.0)(1.2)
acac	bztfac	-81.0(5.0)(0.7), unobserved , -45.0(3.0)(1.0) -39.0(2.0)(x),
acac	ttfac	-40.0(5.0)(0.8), unobserved , -6.0(3.0)(1.0) -2.0(2.0) (x)
acac	hfac	(-10°C). Isomer 1(70%) -49.0(7.0)(1.0), +6.0(7.0)(1.2). Isomer 2.(30%): -41.0(3.0)(2.0), - 9.0(3)(2.2)
dpm	tfac	-75.0(6.1)(1.0), -75.0(x)(x) , -49.0(2.0)(1.2) -40.0(2.5)(1.3)

of the chelate compound was consistent with much of the argument concerning chelate selectivity.

The reaction of π-$C_5H_5Zr(acac)_2Cl$ with Hhfac.

This reaction was carefully studied in $CDCl_3$ at 40^0 using the procedure described. The initial product formed was π-C_5H_5Zr-(acac)(hfac)Cl which was identified by its expected ^{19}F spectrum consisting of two unequally intense doublets. The doublets arise from the possible existence of two forms of the chelate compound, each form having non-equivalent CF_3 environments. The formation of the mixed chelate compound paralleled an equilibrium similar to (1). p.51.

The reaction products, after more than an equimolar amount of Hhfac had been added, indicated only the presence of π-$C_5H_5Zr(hfac)_3$ with no detectable amount of the presumed intermediate π-C_5H_5Zr $(hfac)_2Cl$. The equilibrium corresponding to (2).p.51. is apparently displaced by a fast irreversible step to produce π-$C_5H_5Zr(hfac)_3$.

The study of the methyl region of π-C_5H_5Zr(acac)(hfac)Cl was carried out by addition of Hhfac to a solution of π-$C_5H_5Zr(acac)_2Cl$ until the resonances of the chelate compound had just disappeared. The spectrum at this stage consisted of one CH_3 doublet with extra resonances possibly arising from the minor form. The spectrum was complicated by the presence of a large Hacac resonance from Hacac liberated in the reaction.

The doublets were observed to sharpen considerably as the temperature was lowered; the exchange of the CF_3 environments occurred at about 60^0 using bromobenzene as solvent.

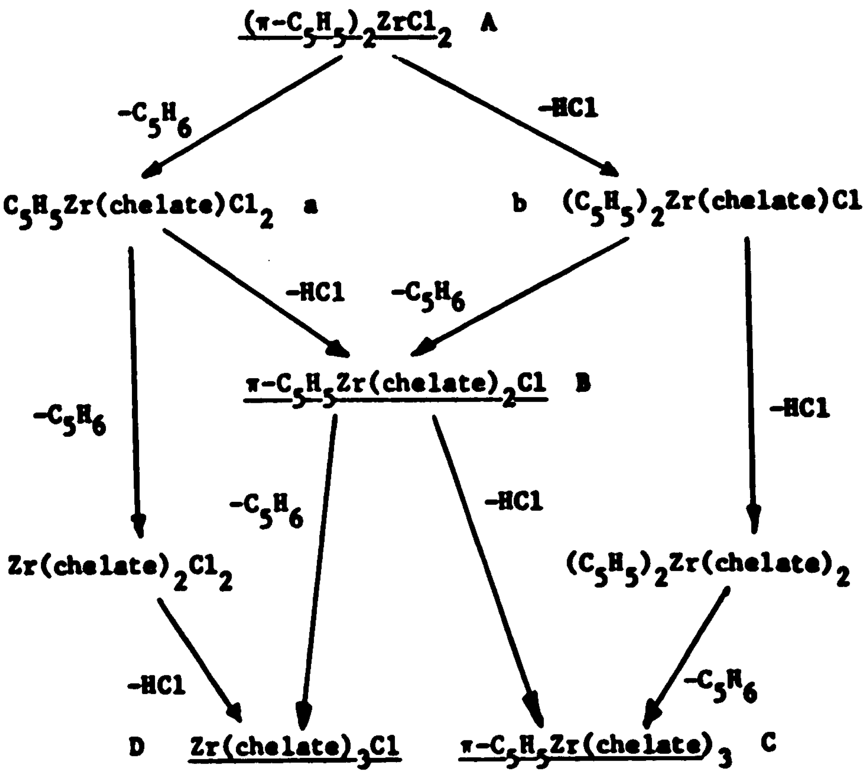
Some Comments on Possible Reaction Mechanisms of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with β-diketones.

The compound $(\pi\text{-}C_5H_5)_2ZrCl_2$ probably reacted with the enol-form of the β-diketone by two possible routes, either eliminating cyclopentadiene or hydrogen chloride. The intermediate compound $(C_5H_5)_2Zr(chelate)Cl$ or $(C_5H_5)Zr(chelate)Cl_2$ was not detected in any reaction mixture, indicating a rapid reaction with further β-diketone to form $\pi\text{-}C_5H_5Zr(chelate)_2Cl$. The further reaction of this compound with β-diketone has been shown to give $\pi\text{-}C_5H_5Zr(chelate)_3$ in certain instances. A possible reaction scheme is shown in Figure 9, with compounds isolated in this reaction underlined.

It was of special interest that $\pi\text{-}C_5H_5Zr(hfac)_2Cl$ could not be prepared by the reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with Hhfac or by a ligand exchange reaction of $\pi\text{-}C_5H_5Zr(acac)_2Cl$ with Hhfac, two observations which attest to the instability of $\pi\text{-}C_5H_5Zr(hfac)_2Cl$ in the presence of Hhfac.

The β-diketone was product-controlling under the reaction conditions *i.e.*, only $\pi\text{-}C_5H_5Zr(chelate)_2Cl$ was isolated using the unfluorinated β-diketones Hacac and Hbzac, only $\pi\text{-}C_5H_5Zr(hfac)_3$ with Hhfac and only $Zr(dpm)_3Cl$ with Hdpm.

Figure 9.



Reaction route is A → a → B and/or A → b → B

For B, chelate = acac, bzac, tfac, bztfac, ttfac.

Reaction route to produce C is B → C

For C, chelate = tfac, bztfac, hfac (fast)

Reaction route to produce D is not known.

CHAPTER IV.

Results and Discussion of Bis Chelate Compounds of Ti(IV).

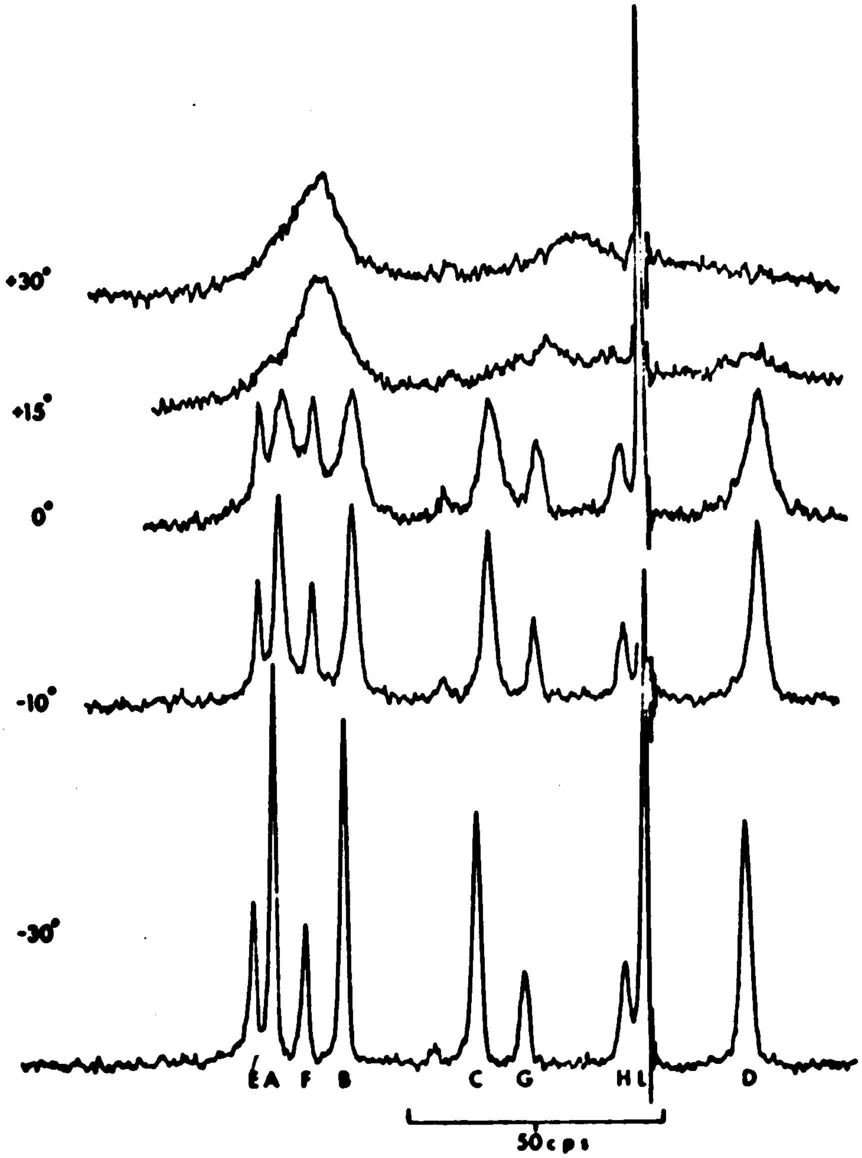
The Zr(IV) compound π-$C_5H_5Zr(acac)_2Cl$ has been shown (61) to exist in solution as a single solution isomer. The titanium compounds incorporating symmetric chelates appeared to give two solution isomers with similar nmr spectra. The octahedral description used for the Zr (IV) compounds is no longer adequate to describe these Ti(IV) compounds.

The discussion of the Ti(IV) compounds attempts to rationalize the presence of two isomers on the basis of dodecahedral coordination. This particular coordination polyhedron was preferred by the author, based on the occurrence of closely dodecahedral structures for related compounds such as π-$C_5H_5Zr(acac)_2Cl$ (62) and π-C_5H_5Ti-(quinoline)$_2$Cl (98). Stereochemical problems in dodecahedral coordination have been subject to careful analysis (72),(73), and the titanium compounds seemed to be more amenable to treatment on this basis than alternative coordination polyhedra such as the square antiprism or the hendecahedron. Even when X-ray studies are available, no definite evidence on the configuration of the coordination polyhedron in solution is available.

π-$C_5H_5Ti(hfac)_2Cl$.

The ^{19}F nmr spectrum of this compound at 40^0 indicated a degree of fluxional behaviour which was resolved by cooling to -20^0 using dichloromethane or $CDCl_3$ as solvent. At this temperature, the spectrum indicated that a mixture of two isomers, identified by two sets of four equal intensity resonances, was present.(Fig.10).

Figure 10.



Variable temperature ^{19}F nmr spectra of π-$C_5H_5Ti(hfac)_2Cl$, Recorded at 56.4 Mcs in $CDCl_3$. L = Hhfac.

The isomers were not of equal abundance, the major isomer (corresponding to resonances ABCD) totalling 75% and the minor isomer (corresponding to resonances EFGH) totalling 25%.(Fig.10). The resonance denoted by L was due to free ligand Hhfac.

The basic treatments of dodecahedral geometry indicated the following guidelines (72), (73).

1) Variation in the size of different ligands favours dodecahedral coordination over square antiprismatic coordination.

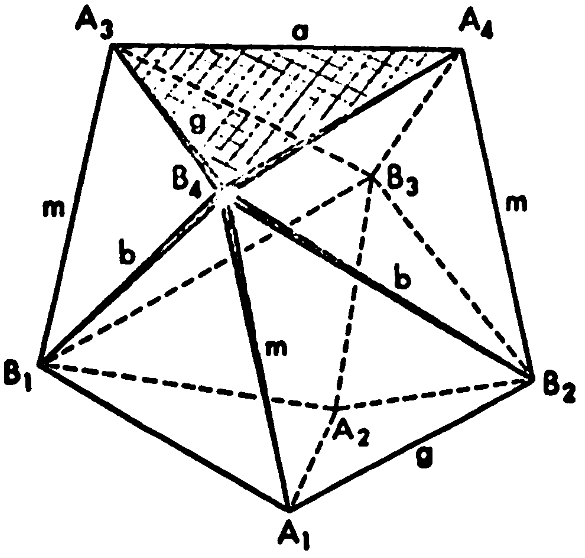
2) Most dodecahedral M(IV) compounds containing metal-oxygen bonds have M - O_B (metal-B site oxygen) bonds shorter and presumably stronger than M - O_A bonds.

3) Small ligands prefer A site coordination while large ligands prefer B site.

4) A general minimization of constraints calls for a dimensional matching of chelate ring span with appropriate polyhedron edges.

The treatment outlined appeared to be consistent with the dodecahedral description of the structure of π-$C_5H_5Zr(acac)_2Cl$.(62). Although the gross features of the structure were apparent, several inconstancies appeared in this paper.(62). A communication from Prof. H.A.Eick acknowledges the errors (Nov. 2. 1970) and enables the structure to be more rigidly defined. The π-C_5H_5 group was envisaged as occupying an AAB face of the dodecahedron (Fig.11) with the Cl atom placed in a B site (apparently the B_3 site in Fig.11). This arrangement left two A and two B sites vacant; these sites were filled by acac chelate rings bridging appropriate edges of the dodecahedron.

Figure 11.



DODECAHEDRON

The position of the π-C_5H_5 ring is indicated by the cross-hatched area.

Use of the empirical arguments outlined led to the placement of the Cl atom, in a π-$C_5H_5MO_4Cl$ system, at a B site, an occurrence already demonstrated for π-$C_5H_5Zr(acac)_2Cl$ (62), and $TiCl_4(diarsine)_2$ (74). The π-C_5H_5 ring, occupying three coordination sites and being a small ligand when averaged over these three sites, was expected to occupy one of the four equivalent AAB faces. There remain some possibilities in the siting of the chelate rings to bridge the available two A and two B sites. Table VI.

Inspection of possible isomers indicated that equivalent Cl sites B_1 and B_2 produce equivalent bridging structures i.e., the edges B_2A_1, B_1A_1, are equivalent as are B_3A_2, B_3A_2. A similar state of affairs was found for the edges B_1A_2, B_2A_2 and B_2A_1, B_1A_1, giving a single isomer for the chlorine atom in B_3. The structures designated as possible (Table VI) were related to give a possibility of two isomers, depending on the location of the chlorine atom in a B_1 or B_3 site. (Fig. 11.)

The coalescence of resonances A, B, C, and D together with the less readily observed behaviour of resonances E, F, G, H implied an averaging of the CF_3 environments by an exchange of hfac chelates Fig. 10. The methine resonance doublet observed at -20° also coalesced to a singlet over the temperature range studied, further supporting this conclusion. The spectra were independent of concentration and the resonance due to the free β-diketone Hhfac (L) remained sharp throughout the temperature range. Exchange was thus intramolecular.

TABLE VI STRUCTURAL ANALYSIS OF DODECAHEDRAL π-C_5H_5 M(diketone)$_2$Cl COMPOUNDS. (diketone = acac, hfac)

π -C_5H_5	$A_3A_4B_4$					
Cl	B_1		B_2		B_3	
Sites available	B_2, B_3	A_1, A_2	B_1, B_3,	A_1, A_2	B_1, B_2,	A_1, A_2
Chelate edges	B_2B_3	B_2A_1	B_1B_3	B_3A_2	B_1A_2	B_1A_1
	A_1A_2	B_3A_2	A_1A_2	B_1A_1	B_2A_1	B_2A_2
Edge class	b, a	m,g	b,a	m,g	g,g	g,g,
Edge ratio	~1.25	~1.0	~1.25	~1.0	~1.0	~1.0
Edges possible	X	✓	X	✓	✓	✓

An alternative arrangement of the π-C_5H_5 ligand occupying an ABB face also produced the result of two possible chelate arrangements.

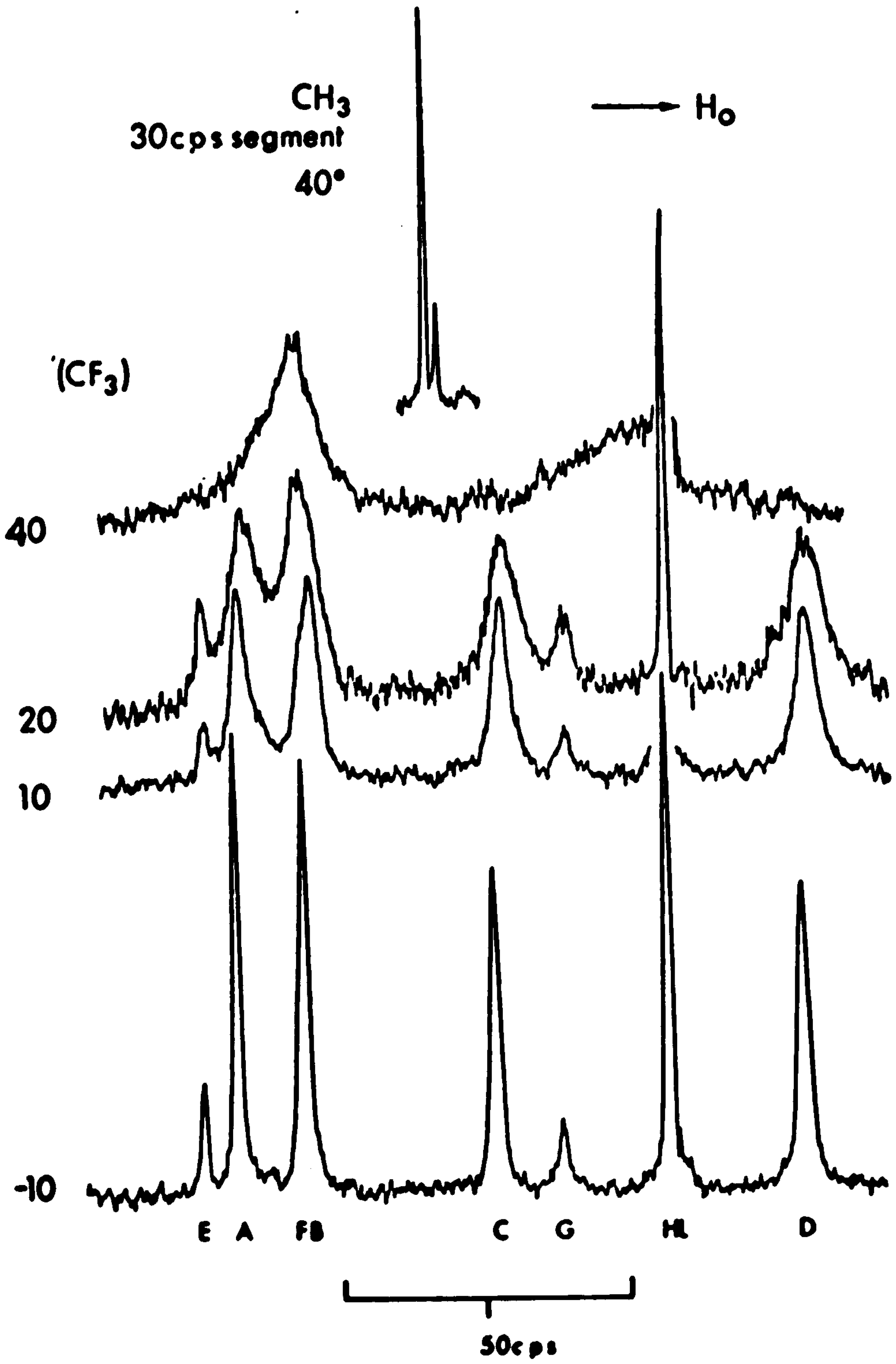
π-$CH_3C_5H_4Ti(hfac)_2Cl$.

The presence of two isomers in solution for this compound was indicated by the low temperature ^{19}F nmr spectrum and by the observation of two methyl resonances of the correct abundances at 40^0 Fig.12. The position of some overlapped resonances in the CF_3 region were inferred by integration, and in some cases it was possible to resolve the resonances in question by use of a different solvent. Thus, resonances F and B overlapped in dichloromethane or $CDCl_3$ but were resolved using bromobenzene. The methyl resonances were also shifted by this solvent.

The temperature dependence of the ^{19}F nmr spectra was very similar to that of the π-C_5H_5 analogue, apart from an apparent temperature difference for a particular stage of coalescence of about 10^0. The methyl substituent appeared to slow down the intramolecular exchange of hfac chelates compared with the unsubstituted π-C_5H_5 derivative, possibly due to an extra steric effect.

The high temperature spectrum , recorded using bromobenzene as solvent, was almost free of decomposition at 90^0, much different from that of the π-C_5H_5 derivative which decomposed in benzene at about 60^0. The spectra were indicative of an unselective intramolecular exchange process in which the environments of all four CF_3 groups in each isomer were averaged.

Figure 12.



Variable temperature ^{19}F nmr spectra of π-$CH_3C_5H_4Ti(hfac)_2Cl$, $CDCl_3$ solvent.

The overlapping coalescences precluded observation of chelate exchange between isomers, but the amount of broadening of the methyl resonances, which were still separate at 80^0, and the unsymmetrical ^{19}F nmr resonance at this temperature (which could be due to an averaging of ABCD separated from EFGH resonances by a small amount) indicated that this process occurred only slowly, if at all, on the nmr time scale. Fig. 13.

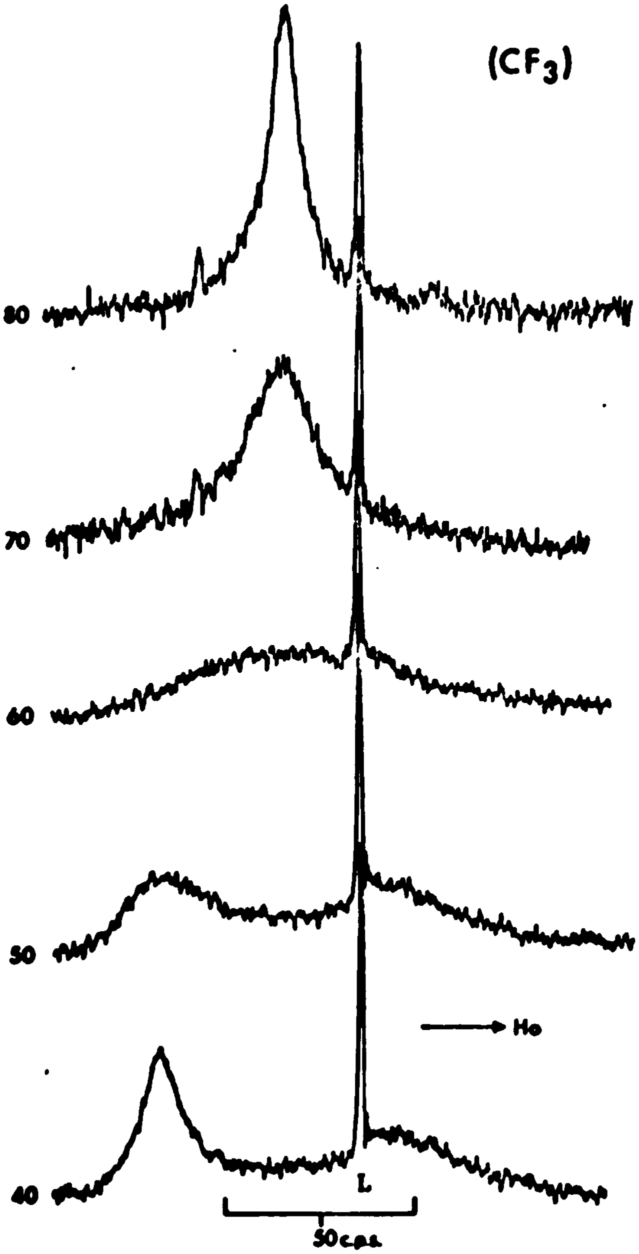
π-$C_5(CH_3)_5Ti(hfac)_2Cl$

The presence of two isomers was confirmed in this compound by observation of two sharp methyl resonances (ratio 3 : 2) and by the observation of two sets of four equal intensity trifluoromethyl resonances in the same 3 :2 ratio. Fig. 14.

The simultaneous broadening of resonances ABCD paralleled the observed behaviour of the bis hfac chelate compounds previously investigated. In the present compound, however, broadening of the EFGH resonances occurred about 15^0 lower than those of the corresponding ABCD resonances. This was a strong indication of intramolecular exchange, since an isomer conversion via chelate exchange would involve either an intermolecular chelate exchange or an intramolecular rearrangement of the π-C_5H_5MCl skeleton. This process would be characterized by a simultaneous coalescence of resonances A,B,C,D,E,F,G, and H. Prior to the investigation of this compound, intra-chelate exchange had been a possibility due to similar coalescence temperatures of minor and major isomers.

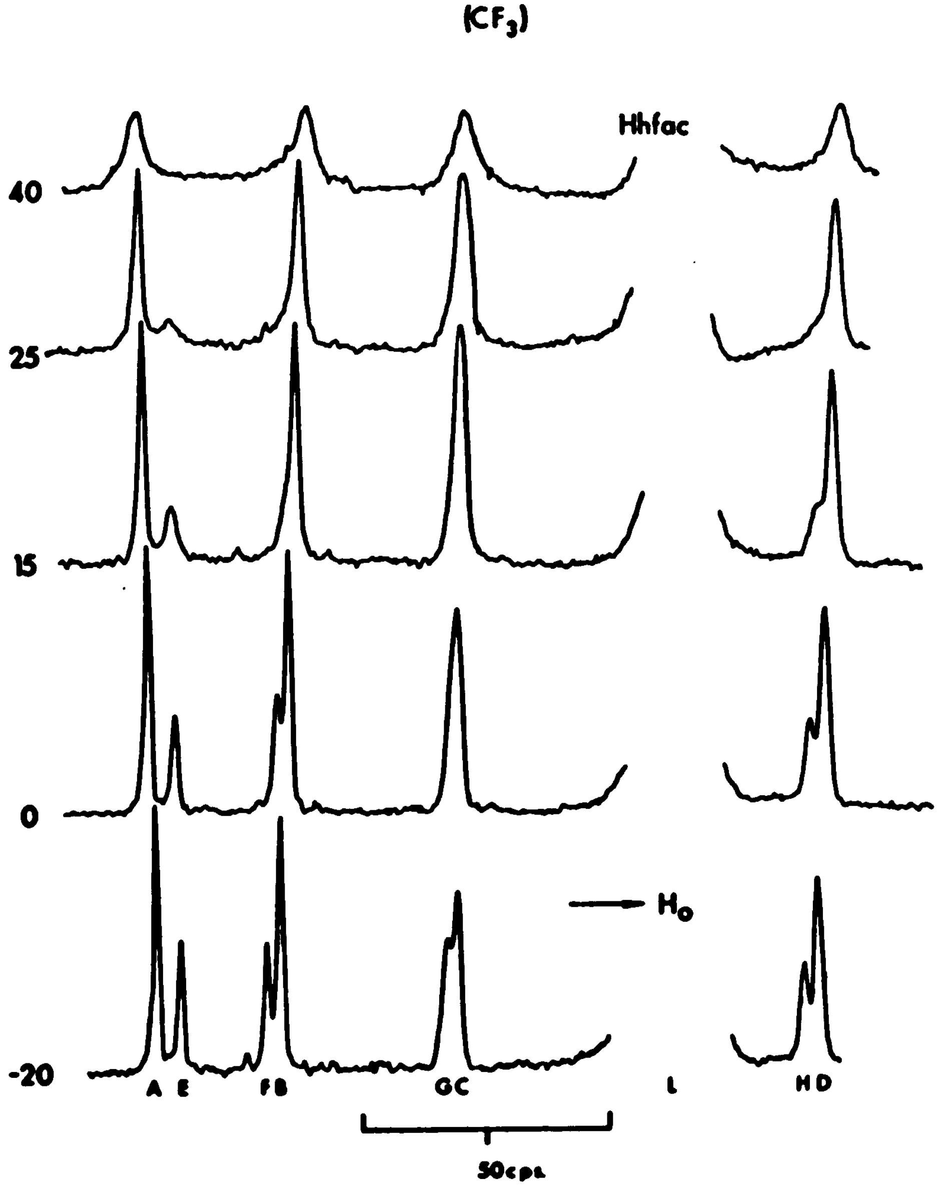
The bulky π-$C_5(CH_3)_5$ ligand slowed intramolecular chelate

Figure 13.



High temperature spectra of π-$CH_3C_5H_4Ti(hfac)_2Cl$ indicating an unselective exchange and slow exchange with free HHfac(L). Bromobenzene solvent.

Figure 14.



Variable temperature ^{19}F nmr spectra of π-$C_5(CH_3)_5Ti(hfac)_2Cl$ using $CDCl_3$ as solvent.

exchange still further than the π-$CH_3C_5H_4$ ligand. The trend, in order of rapidity of chelate exchange was π-C_5H_5 > π-$CH_3C_5H_4$ > π-$C_5(CH_3)_5$ for the π-system $Ti(hfac)_2Cl$ compounds investigated.

π-$C_5H_5Ti(tfac)_2Cl$, π-$C_5H_5Ti(bztfac)_2Cl$, π-$C_5H_5Ti(ttfac)_2Cl$.

The spectra of these compounds showed many similarities to those recorded for the isoelectronic zirconium analogues. The most striking spectral similarity was the intensity and distribution of the CF_3 resonances which indicated the presence of two major forms of the system comprising about 60% of the total. Other unassigned resonances were also observed.

The titanium chelate compounds appeared to have two arrangements of π-C_5H_5 and Cl giving two sets of possible edges for π-$C_5H_5Ti(hfac)_2Cl$ and thus two isomers each with four sets of edges for the compound π-$C_5H_5Ti(tfac)_2Cl$. If the compound followed the distribution of forms in π-$C_5H_5Zr(tfac)_2Cl$ and of isomers in π-$C_5H_5Ti(hfac)_2Cl$ then the overall distribution in $\pi C_5H_5Ti(tfac)_2Cl$ may be quantitatively predicted.

π-$C_5H_5Zr(tfac)_2Cl$	
A	50%
B	35%
C	10%
D	5%

π-$C_5H_5Ti(hfac)_2Cl$	
I	75%
II	25%

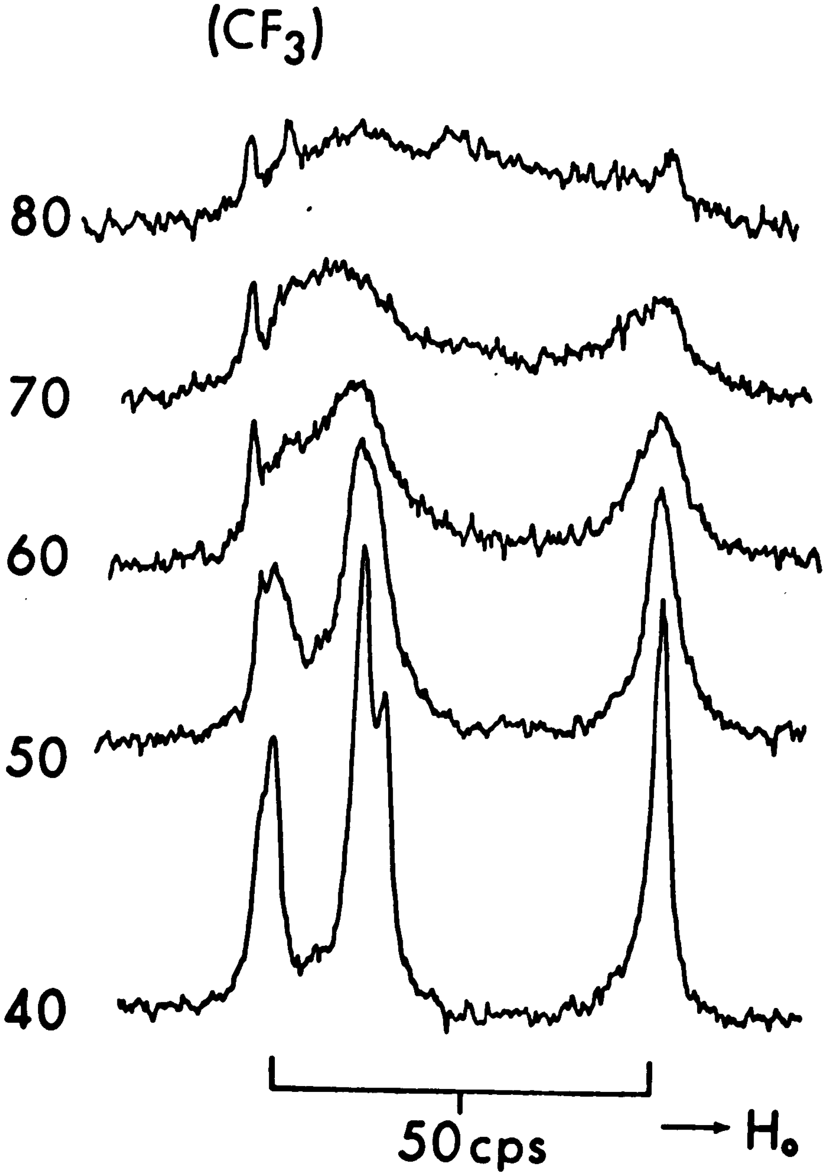
π-$C_5H_5Ti(tfac)_2Cl$

Form AI	37.5%	AII	12.5%
Form BI	26.3%	BII	8.5%
Form CI	7.5%	CII	2.5%
Form DI	3.7%	DII	1.5%
Total	75.0%		25.0%

The ^{19}F nmr spectrum of π-$C_5H_5Ti(tfac)_2Cl$ (Table IV) could be rationalized on the basis of the presence of the forms AI and BI. These forms were similar to the A and B forms of π-$C_5H_5Zr(tfac)_2Cl$ both from considerations of chemical shift and abundance. The CF_3 spectrum of π-$C_5H_5Ti(tfac)_2Cl$ at -20° was similar to that of π-$C_5H_5Ti(bztfac)_2Cl$ at 40°.(Fig.15). The resonances due to forms AII,BII and CI were not assigned and the resonances due to forms DI,CII and DII would be on the limits of detection.

These compounds showed environmental exchange of the major isomers at lower temperatures than the zirconium analogues. Studies were limited by sample decomposition at 80°. For a π-$C_5H_5M(tfac)_2Cl$ system, the non-rigid behaviour increases in the order $Zr < Ti$, (i.e. zirconium compounds are more stereochemically rigid than the corresponding titanium analogues) and for the π-$C_5H_5Ti(chelate)_2Cl$ system tfac < bztfac ≃ ttfac. Fig.15 shows the temperature behaviour of π-$C_5H_5Ti(bztfac)_2Cl$.

Figure 15.



Variable temperature ^{19}F nmr spectra of π-$C_5H_5Ti(bztfac)_2Cl$. CH_2Br_2 solvent.

CHAPTER V

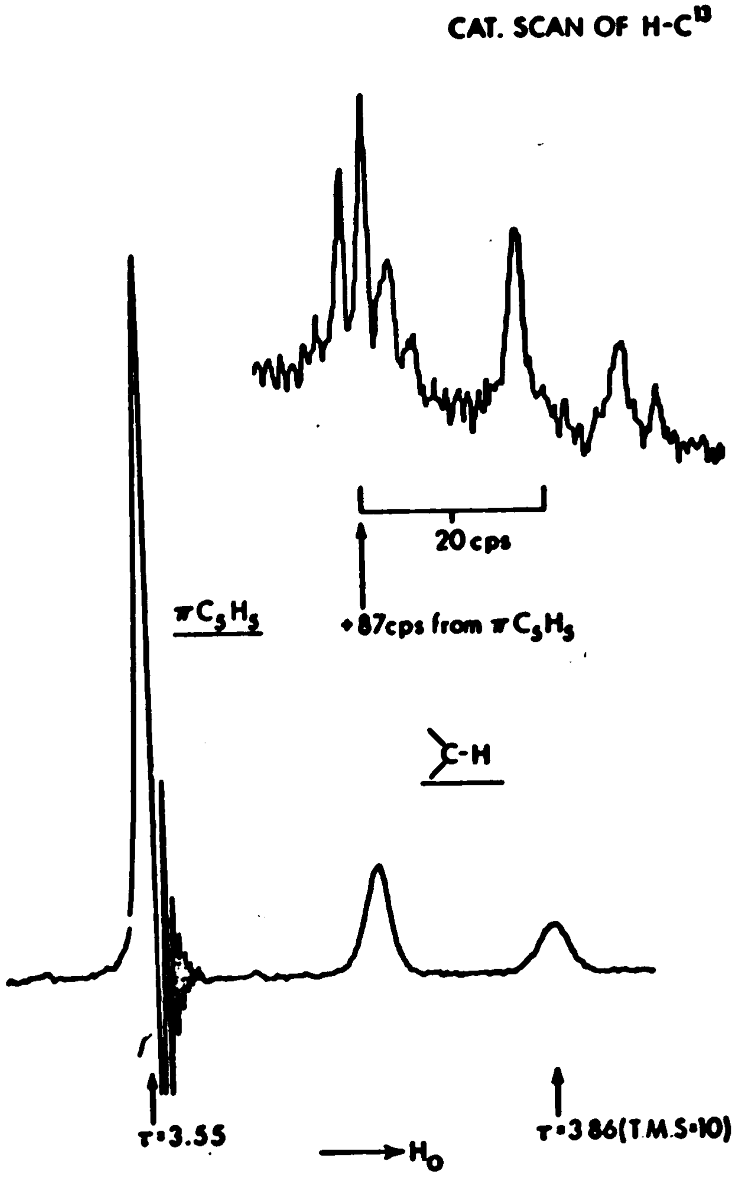
Results and Discussion of Tris Chelate Compounds.

π-$C_5H_5Zr(hfac)_3$

The compound was shown by both ^{19}F and ^{1}H nmr to contain two equivalent hfac chelates and one unique chelate. The chelation of the hfac moieties was indicated by the low carbonyl stretching frequencies of the coordinated compared with the free chelate. The results of a C.A.T. (Computer Averaging of Transients) scan of the ^{1}H nmr couplings indicated a ^{13}C- H coupling constant for both types of methine protons and the π-C_5H_5 ring protons of 173±2 cps, a value close to that observed for sp^2 hybridized carbon.(75). The ^{13}C- H couplings of the π-C_5H_5 ring could be classified as an AA'BB' system and were similar to those found for the π-C_5H_4 systems of $(\pi\text{-}CH_3C_5H_4)_2MCl_2$ where M = Ti, Zr. The appearance and magnitude of the ^{13}C- H couplings were similar to those found for other π-C_5H_5 systems. (76) (77). Figure 16.

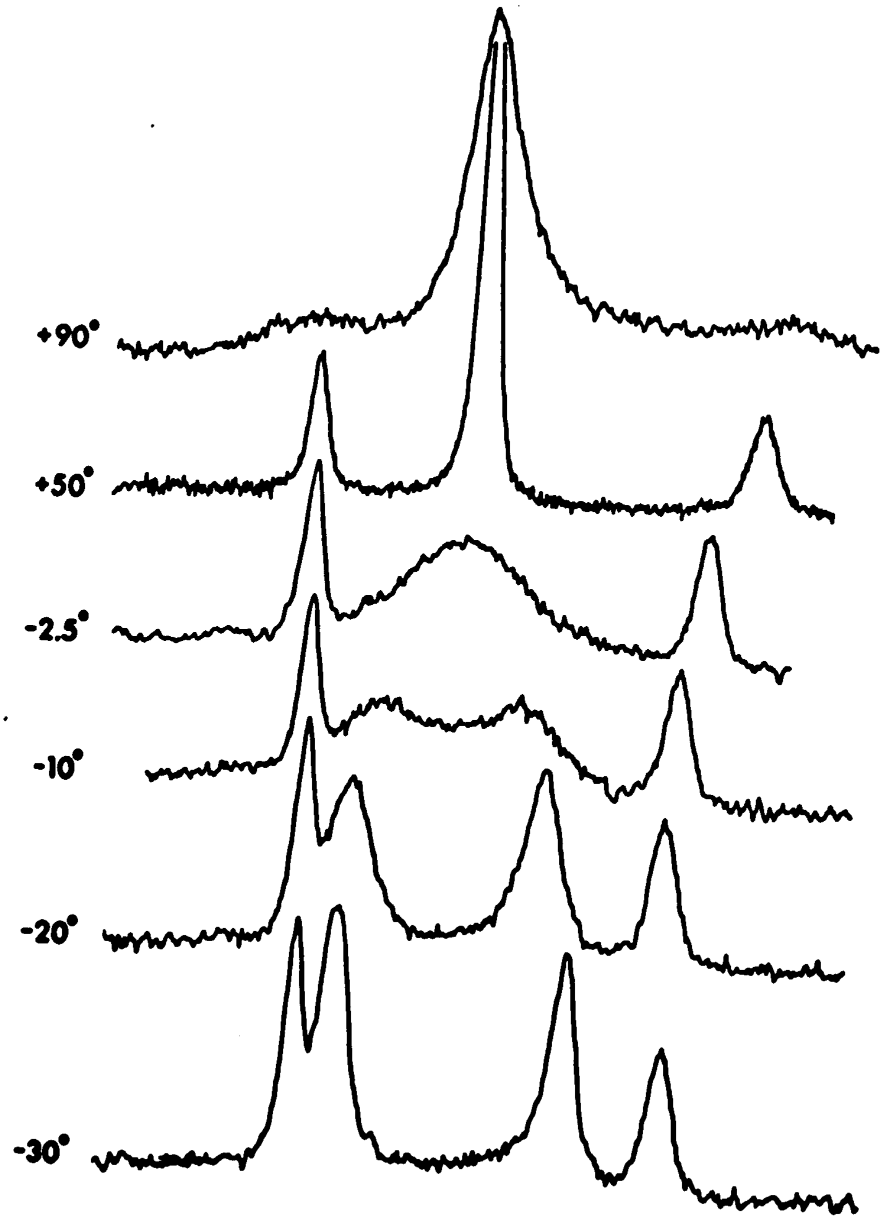
An interpretation of the observed spectra was not possible in terms of a simple structure based on possible seven or nine coordinate zirconium. The low temperature ^{19}F nmr spectra resolved the apparent difficulty since the 1:4:1 distribution of resonances at 40° changed to a 1:2:2:1 distribution (Figure 17) with no change in the ^{1}H spectra. The π-C_5H_5 resonance remained as a sharp singlet at all temperatures. This additional information led to the consideration of a structure based on a pentagonal bipyramid ,

Figure 16.



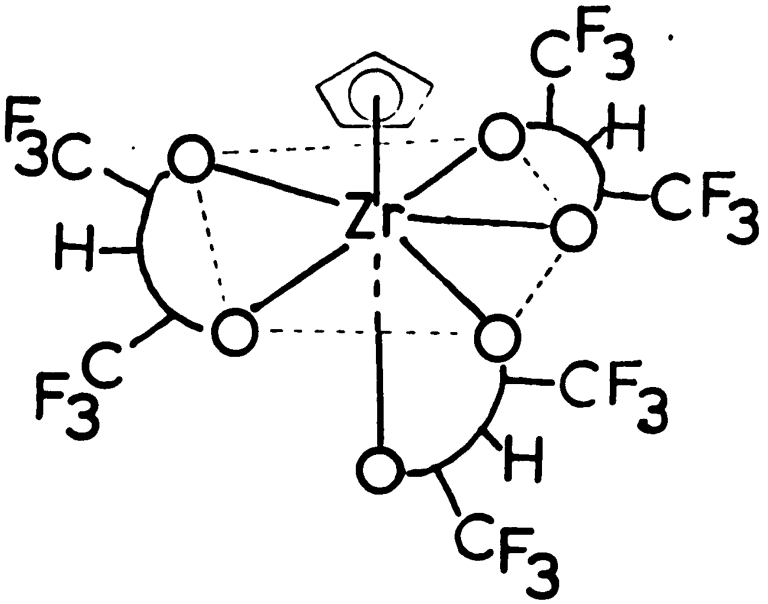
^1H nmr spectrum at 40^0 of π-$C_5H_5Zr(hfac)_3$, measured at 60.0 Mcs. with $CDCl_3$ as solvent. CAT scan insert was obtained at 100.0 Mcs. with acetone as solvent, from 17 scans of the ^{13}C-H couplings.

Figure 17.



Variable temperature nmr spectra of π-$C_5H_5Zr(hfac)_3$ (^{19}F only). Spectra at 50^0 and 90^0 recorded in methylcyclohexane, remainder in acetone-d^6.

substituted axially by the π-cyclopentadienyl group. The three remaining hfac chelates span the six available sites in the only way possible. Two hfac chelates span equatorial- equatorial sites and one unique chelate spans an equatorial and the remaining axial site.(XII).



(XII)

The fluxional behaviour observed at ambient temperatures was a reflection of the environmental exchange of the equatorial CF_3 groups. The CF_3 groups of the equatorial-axial (unique) chelate were uninvolved, on the nmr time scale, in any exchange up to about 90° when a coalescence of both methine and CF_3 resonances indicated that a general chelate exchange process was operative.

The stages of exchange are shown in Figure 18.

The nmr spectral behaviour in both ^{19}F and proton regions was independent of concentration, solvent (similar in methylcyclohexane, bromobenzene, chloroform, dichloromethane and acetone) and also independent of quantities of added Hhfac up to about 90^0, when some broadening of the Hhfac signals occurred. The exchanges were thus intramolecular.

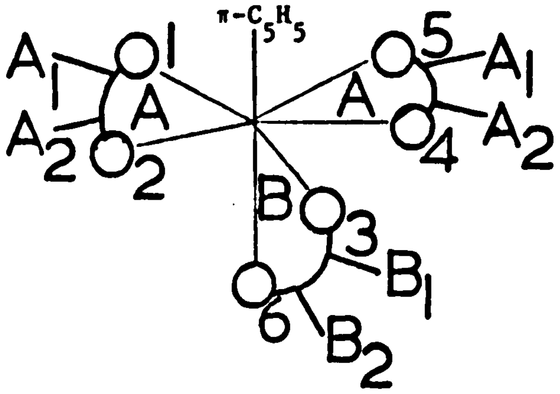
The solid state structure was undertaken by M. Elder (63),(64) (Fig. 19) in order to completely classify this formally nine-coordinate structure (the π-C_5H_5 occupying three coordination sites). The most pertinent conclusions were that the structure could be visualized as a pentagonal bipyramid, substituted axially by the π-C_5H_5 group, and that there were significant differences in the zirconium-oxygen bond lengths. The difference between Zr-O(6) and Zr-O(3) was 0.1Å or sixteen times the standard deviation on either bond length. Zr-O(6) was also shorter and presumably stronger than Zr-O(1), Zr-O(2), Zr-O(4) and Zr-O(5). The possibility of internal compensation by the unique chelate was investigated by comparison of Zr-O(3) with Zr-O(1), Zr-O(2), Zr-O(4) and Zr-O(5). Observed differences, although all in the direction of lengthening the Zr-O(3) bond, were not as significant as the shortening of the Zr-O(6) bond.

A simple orbital treatment for the bonding in this molecule was carried out as follows. The orbitals available for the π-C_5H_5Zr-O(6) system were the following:- s, p_z, d_{xz}, d_{yz} and d_{z^2} ; those for the Zr-O(1-5) system the s, p_x, p_y, d_{xy}, $d_{x^2-y^2}$ and d_{z^2}. The p_z, d_{xz} and d_{yz} orbitals are involved exclusively in the π-C_5H_5Zr-O(6) bonding

Figure 18.

Zr-O (1-5) are equatorial bonds.

Zr-O (6) is an axial bond



<u>**No exchange:-**</u> ^1H. π-C_5H_5 : 2 A >CH : 1 B >CH

Intensity 5 : 2 : 1

^{19}F CF_3B_2 : $2CF_3A_1$: $2CF_3A_2$: CF_3B_1

Intensity 1 : 2 : 2 1

<u>**Selective A chelate exchange:-**</u>

^1H π-C_5H_5 : 2 A >CH : 1 B >CH

Intensity 5 : 2 : 1

^{19}F CF_3B_2 : $4CF_3(A_1+A_2)$: CF_3B_1

Intensity 1 : 4 : 1

<u>**A and B chelate exchange:-**</u>

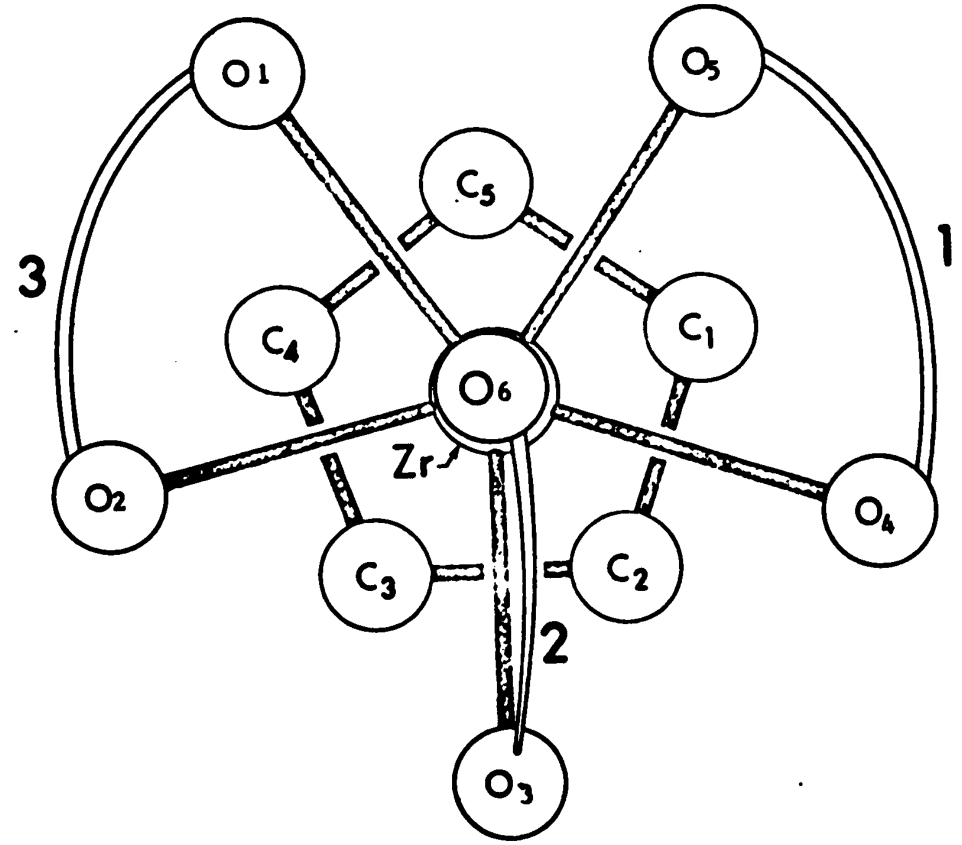
^1H π-C_5H_5 : 2A+1B >CH

Intensity 5 : 3

^{19}F $2CF_3(B_1+B_2)$+ $4CF_3(A_1+A_2)$

Intensity 6

Figure 19.



Structure of π-$C_5H_5Zr(hfac)_3$ viewed along the Zr-O(6) bond, showing the approximately pentagonal bipyramidal arrangement. (63),(64).

system, while the p_x, p_y, d_{xy} and $d_{x^2-y^2}$ orbitals are exclusively involved in Zr-O(1-5) bonding. The remaining two orbitals, s and d_{z^2}, may be involved in bonding to both axial and equatorial oxygen atoms. The different hybridization of axial and equatorial Zr-O bonds could well cause the observed differences in Zr-O bond lengths.

The presence of a selective chelate environment exchange in this molecule was an unprecedented occurrence. In all chelate compounds studied previously only non-selective environmental exchange had been found. (23 - 28). The factors which led to selective intramolecular exchange could well be the crowded stereochemistry of the molecule together with a unique separation of the bonding orbitals into two differently hybridized sets.

π-$C_5H_5Hf(hfac)_3$

This compound, as prepared, contained about 10% of the easily identified zirconium analogue due to the contamination of $(\pi\text{-}C_5H_5)_2$-$HfCl_2$ by $(\pi\text{-}C_5H_5)_2ZrCl_2$ in the starting material. The compound had similar properties and nmr behaviour to the zirconium analogue, indicating a similar structure and exchange process. The resonances due to the two sets of equatorial trifluoromethyl groups became averaged at about -30^0 compared with -10^0 in the zirconium case.

π-$CH_3C_5H_4Zr(hfac)_3$

This compound was prepared to investigate the steric effect of cyclopentadienyl substituents in the tris hfac system. The behaviour of the ^{19}F nmr spectra was similar to that of the π-C_5H_5 analogue, the resonances corresponding to equatorial trifluoromethyl groups

being averaged at ca 10^0. Fig. 20. The rates of exchange in the tris hfac system for equatorial chelates were in the order:-
$\pi-C_5H_5Hf > \pi-C_5H_5Zr > \pi-CH_3C_5H_4Zr$.

The methine resonances and $\pi-C_5H_4$ resonances overlapped considerably, and it was determined that weak coupling existed between the methyl resonance and one half of the AA'BB' or ABCD spectrum by irradiation experiments. A similar situation has been postulated for both $(\pi-CH_3C_5H_4)_2TiCl_2$ and $(\pi CH_3C_5H_4)_2ZrCl_2$.

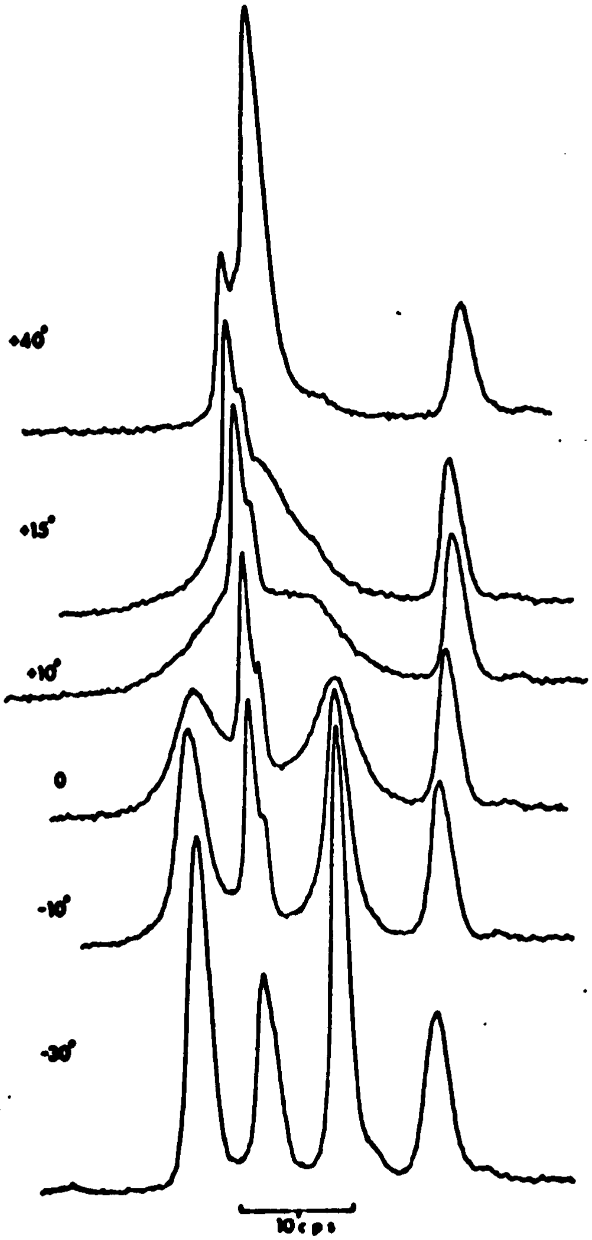
$\pi-C_5H_5Zr(tfac)_3$.

The spectral characteristics of this compound together with some similarities drawn from the study of the hfac derivatives led to the identification of two isomers in the nmr spectrum at 40^0. The two isomers were caused by the two different orientations of the unique chelate (which spans an equatorial and an axial site) combined with a fast exchange process which averaged the CH_3 and CF_3 environments of the equatorial chelates. There were other possible explanations to account for the observed resonances; these will be discussed more fully at a later stage. The major isomer (60%) and the minor isomer (40%) were not interconverted on the nmr time scale at ambient temperatures. Figures 21-23.

The high temperature spectra indicated that the unique chelate was involved in an intramolecular unselective exchange with the equatorial chelates, indicated by the observation of single resonances in the $\pi-C_5H_5$, methine, methyl and trifluoromethyl regions.

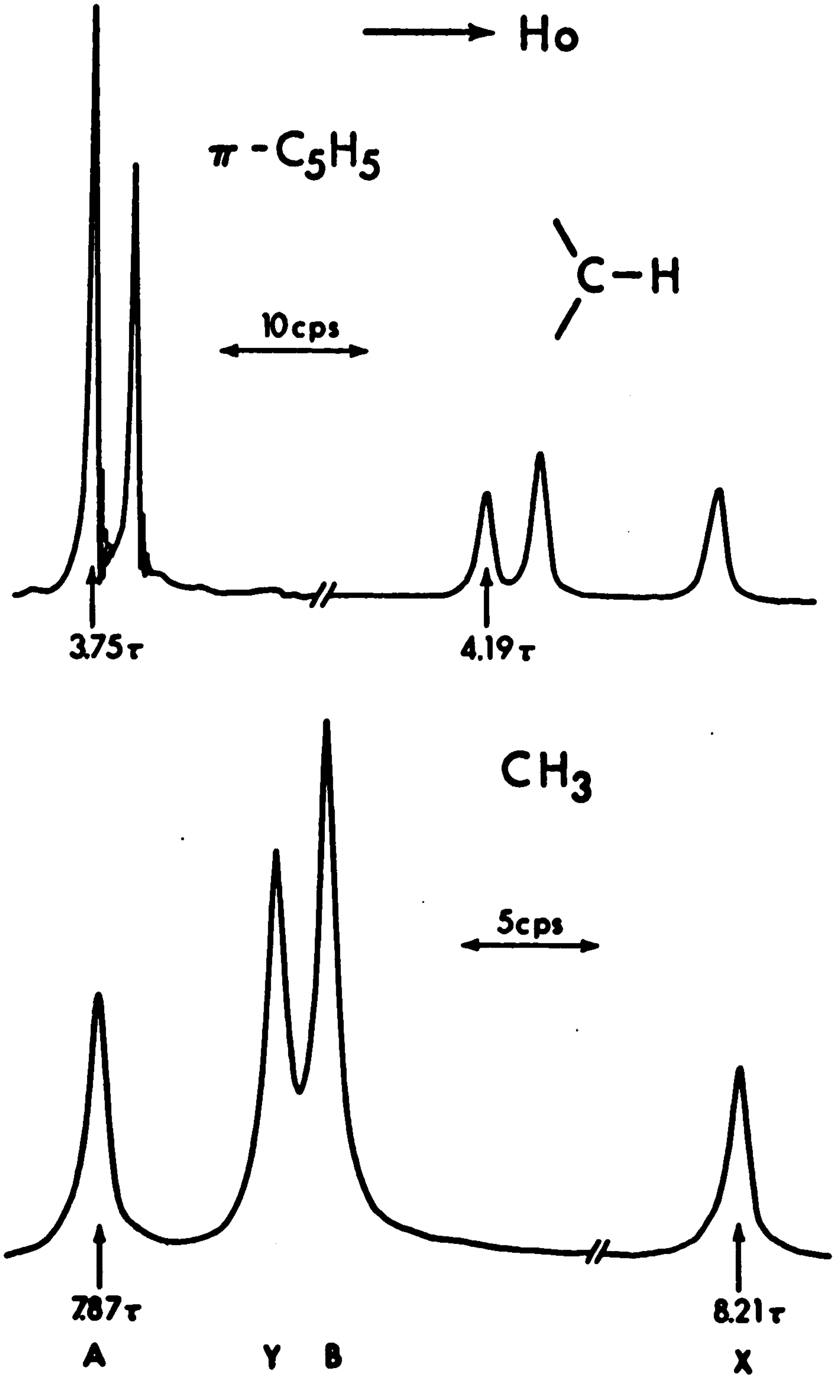
The spectral changes observed in the ^{19}F spectra on cooling

Figure 20.



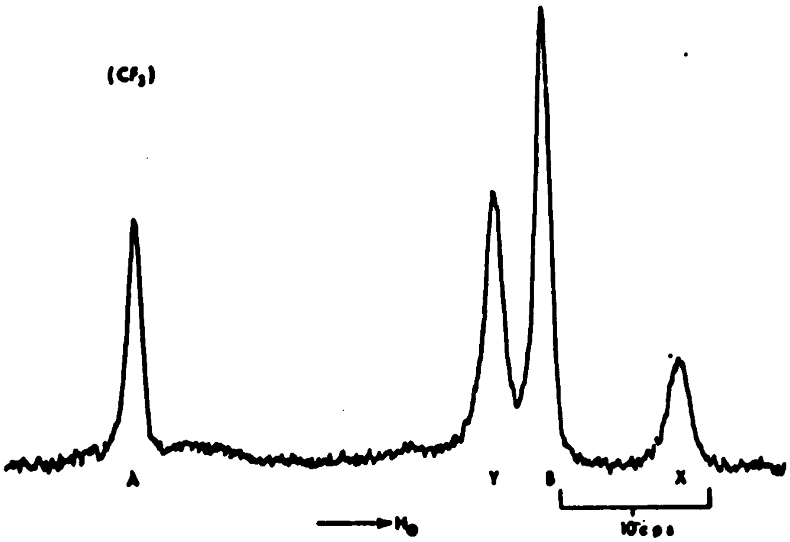
Variable temperature ^{19}F nmr spectra of π-$CH_3C_5H_4Zr(hfac)_3$ in acetone-d^6.

Figure 21.



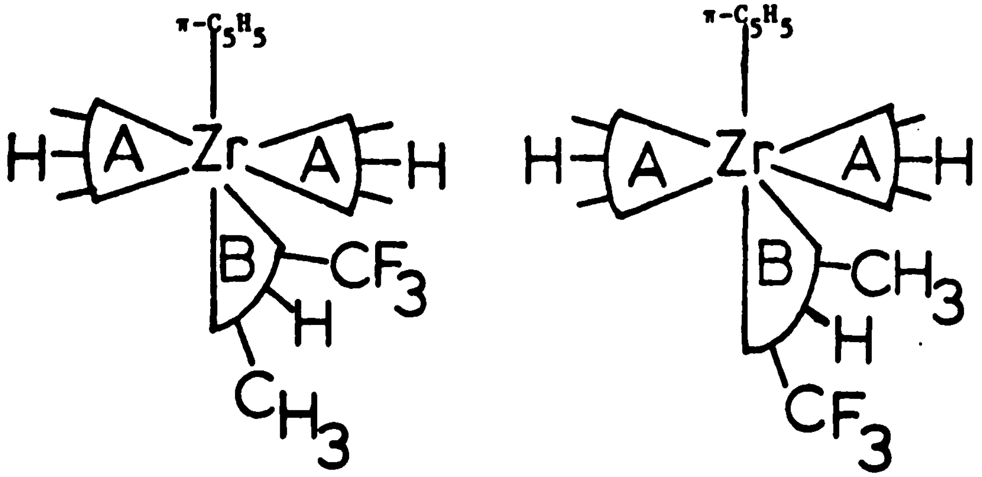
Ambient temperature ^1H nmr spectrum of π-$C_5H_5Zr(tfac)_3$ recorded at 100.0 Mcs. $CDCl_3$ solvent.

Figure 22.



Ambient temperature (40^0) ^{19}F nmr spectrum of π-$C_5H_5Zr(tfac)_3$ in $CDCl_3$, recorded at 56.4 Mcs. The labelled resonances may be associated with similarly labelled resonances in the CH_3 region. (Fig. 21).

Figure 23.



Nmr characteristics (fast averaging of A environments)

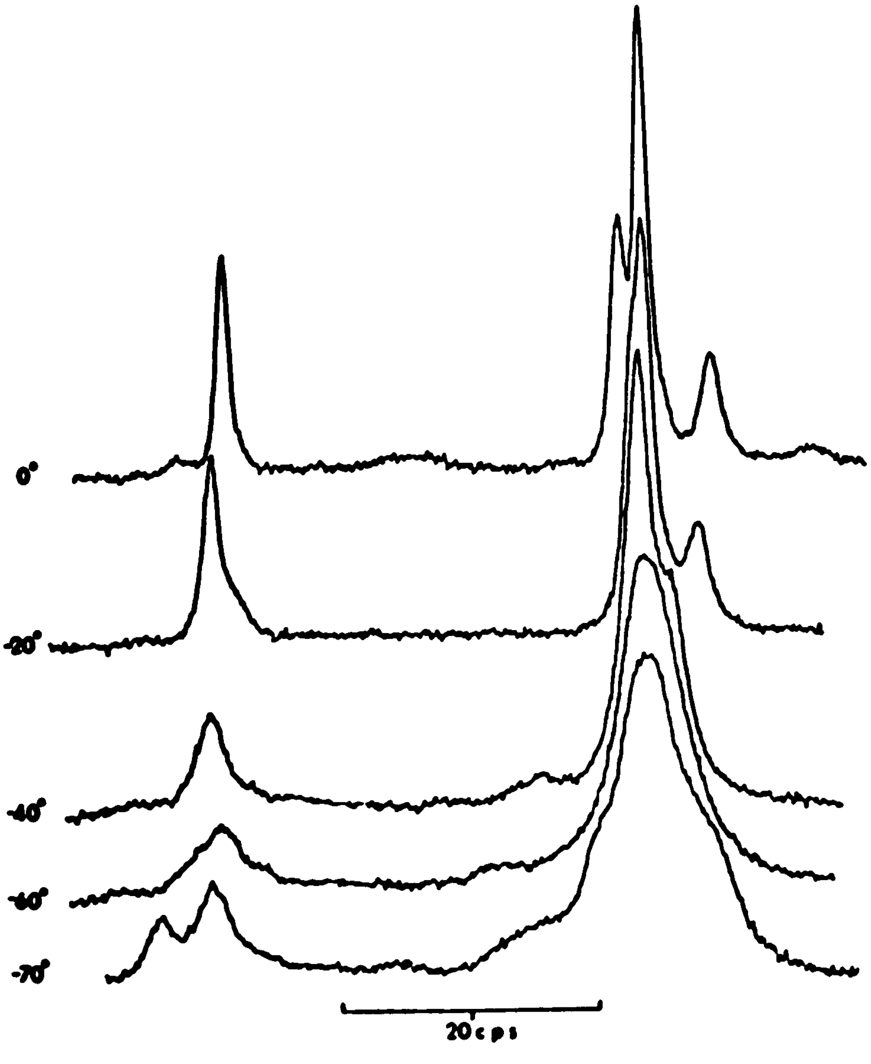
1 π-C_5H_5	1 π-C_5H_5
1 CH_3 Axial (B)	1 CH_3 Equatorial (B)
2 CH_3 Equatorial (A)	2 CH_3 Equatorial (A)
2 CF_3 Equatorial (A)	2 CF_3 Equatorial (A)
1 CF_3 Equatorial (B)	1 CF_3 Axial (B)
2 >CH Equatorial (A)	2 >CH Equatorial (A)
1 CH Axial (B)	1 CH Axial (B)

Fig. 24 indicated that the exchange of equatorial chelate environments was being retarded, and the chelates were being 'frozen out' in particular configurations. There was a possibility of observing six isomers at low temperature Fig. 25. arising from a three fold possibility of equatorial chelate environment for each unique chelate environment. Assuming a statistical distribution of equatorial environments, each averaged equatorial resonance was expected to split into four equal intensity resonances and each unique chelate resonance was expected to split into a 1 :2 :1 triplet. The fourteen possible resonances expected would have been closely grouped and it was found that the overlap of resonances made for a difficult complete assignment. It was noted that a CF_3 resonance attributed to a CF_3 group associated with the unique chelate did split into two unequal intensity resonances. Fig. 25.

The overall spectral change and the above observation indicated that exchange of equatorial environments was being slowed by a temperature decrease, but unfortunately no correlation of the statistical predictions with observations was possible due to overlap in both CF_3 and CH_3 regions and the inability to resolve the closely spaced π-C_5H_5 resonances at low temperatures. The spectra were independent of concentration, indicating intramolecular exchange. The equatorial lability for intramolecular exchange was greater for tfac chelates than hfac chelates at similar temperatures <u>i.e.</u> tfac > hfac.

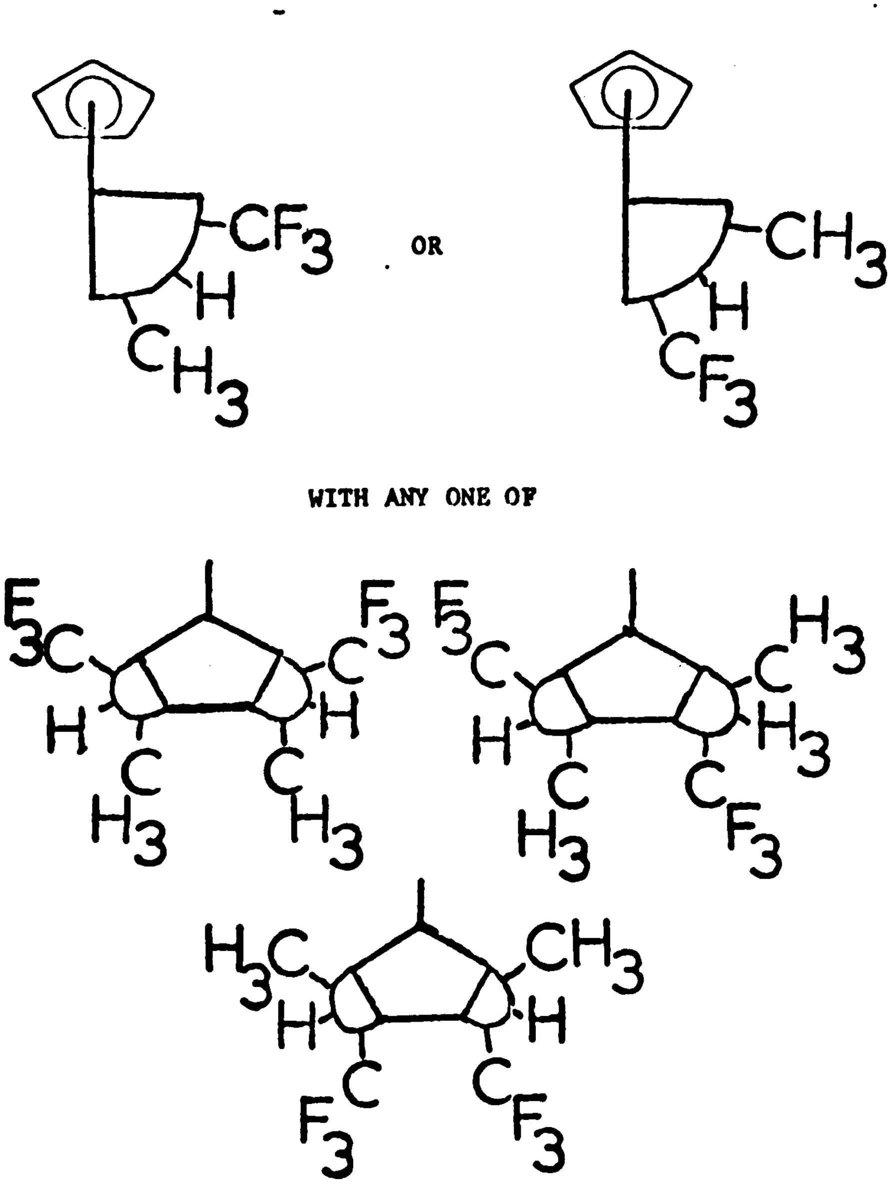
<u>π-$CH_3C_5H_4Zr(tfac)_3$.</u>

Figure 24.



Low temperature ^{19}F nmr spectra of π-$C_5H_5Zr(tfac)_3$ indicating slowing down of the exchange of equatorial chelate substituents. Acetone-d^6 solvent.

Figure 25.



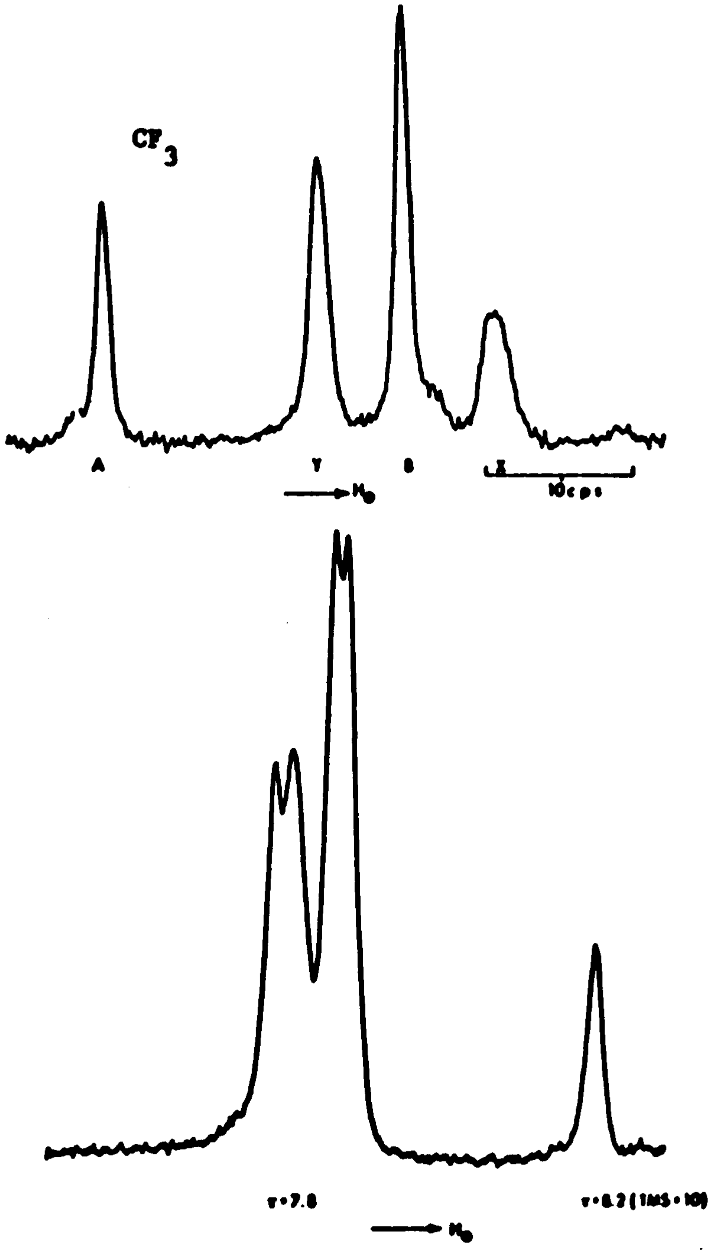
Six form possibility for structures of formula π-$C_5H_5Zr(tfac)_3$, derived from two possible orientations of the unique chelate (top) and from three orientations of the non-unique chelates (bottom).

The presence of two isomers at room temperature was demonstrated by the distribution of CF_3resonances in the ^{19}F spectrum. Fig.26. The relative amounts of each isomer were very similar to the corresponding π-C_5H_5 analogue. The study of the methyl region indicated overlap of methyl resonances attributed to the chelates and of methyl resonances attributed to the π-$CH_3C_5H_4$ system in solvents such as $CDCl_3$. The compound, when dissolved in benzene or bromobenzene, showed good resolution of the two sets of methyl resonances. Similar phenomena have been previously described (61) (70).

The spectral similarity of the limiting low temperature spectra of the π-$CH_3C_5H_4$ and the π-$C_5H_5Zr(tfac)_3$ compounds could be due to the presence of favoured orientations of the equatorial chelates. Figure 27.

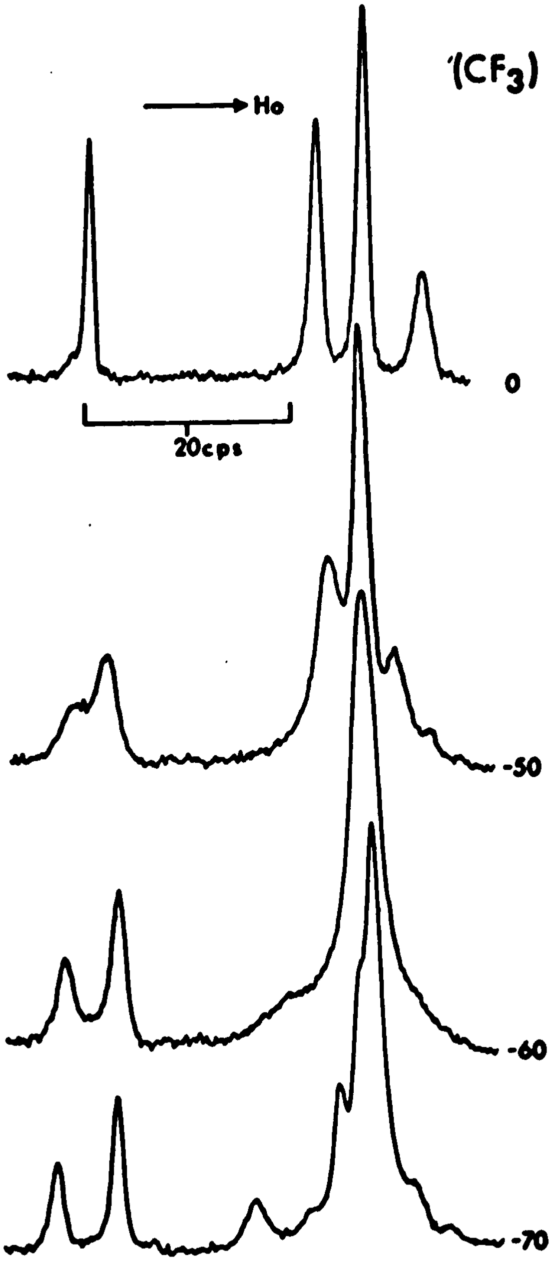
The high temperature ^{19}F and ^1H nmr spectra indicated that an unselective exchange of all chelates was occurring, as shown by coalescence of CF_3 resonances with simultaneous coalescences of chelate resonances (both CH_3 and methine) and coalescence of the two methyl resonances of the π-$CH_3C_5H_4$ groups. The spectra rule out exchange between chelate CH_3 groups and π-$CH_3C_5H_4$ substituents, a not unexpected result. Comparison of intramolecular exchanges indicated that these exchanges, whether selective or unselective were faster for the π-C_5H_5 derivative at a given temperature. i.e., π-C_5H_5 > π-$CH_3C_5H_4$. Figure 28.

Figure 26.



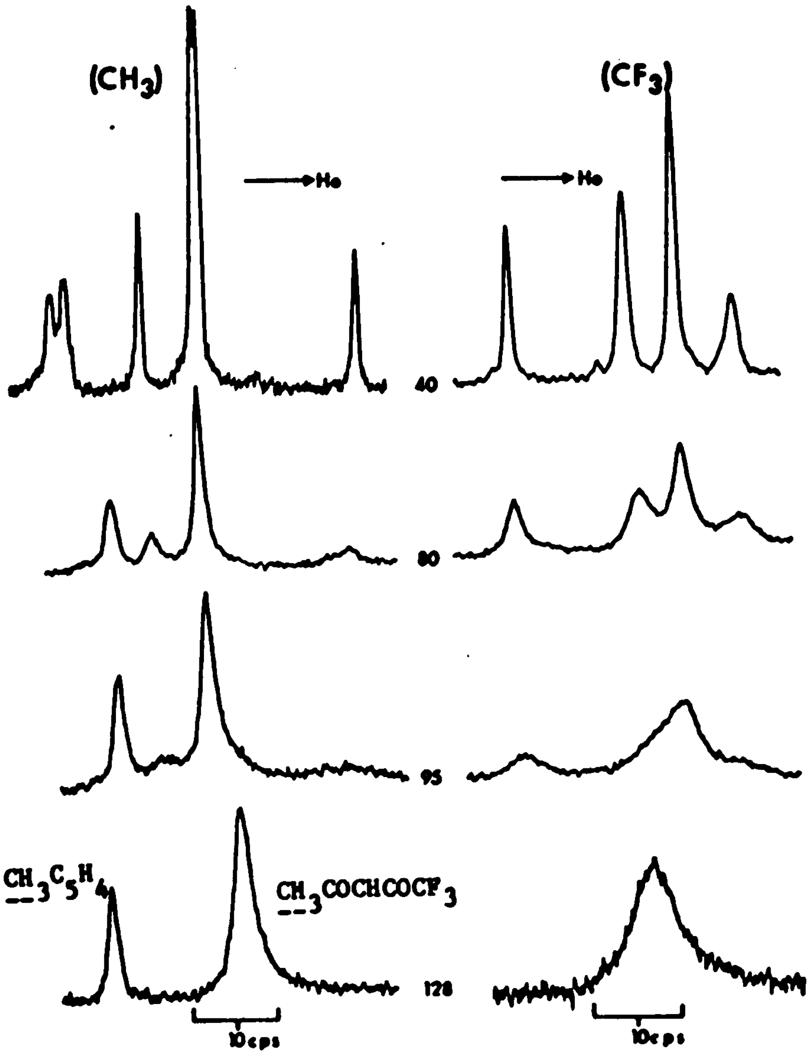
Ambient temperature (40^0) nmr spectrum of π-$CH_3C_5H_4Zr(tfac)_3$ (^1H nmr at 60.0 Mcs, ^{19}F nmr at 56.4 Mcs.). $CDCl_3$ solvent.

Figure 27.



Low temperature ^{19}F nmr spectra of π-$CH_3C_5H_4Zr(tfac)_3$ showing retarded equatorial chelate environment exchange.

Figure 28.



High temperature CH$_3$ and CF$_3$ region nmr spectra of π-CH$_3$C$_5$H$_4$Zr(tfac)$_3$ in bromobenzene. Recorded at 60.0 and 56.4 Mcs respectively.

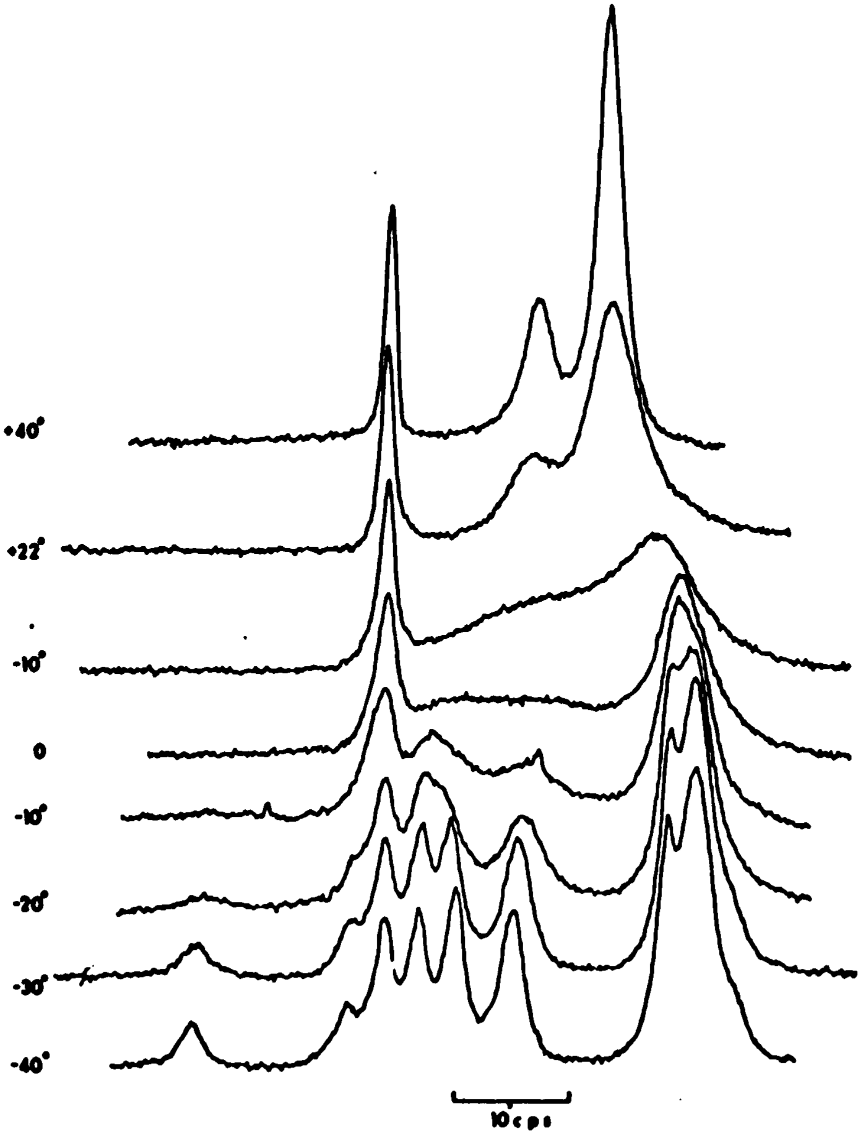
π-$C_5H_5Zr(bztfac)_3$.

The two sharp π-C_5H_5 resonances observed at 40^0 indicated that a mixture of two isomers was present in solution. The spectacular changes in the ^{19}F nmr spectra as the temperature was lowered (Figure 29) were accompanied by splitting of the π-C_5H_5 resonances into two sets of two resonances. The intramolecular interconversion of the equatorial chelate substituent environments was retarded by cooling giving 'frozen out' isomers having preferred orientations of the equatorial chelates. The expected six π-C_5H_5 resonances were not observed as the temperature was lowered and the spectrum showed no change below -50^0. Unselective chelate exchange also occurred in this compound at elevated temperatures. (Figure 30).

π-$CH_3C_5H_4Zr(bztfac)_3$.

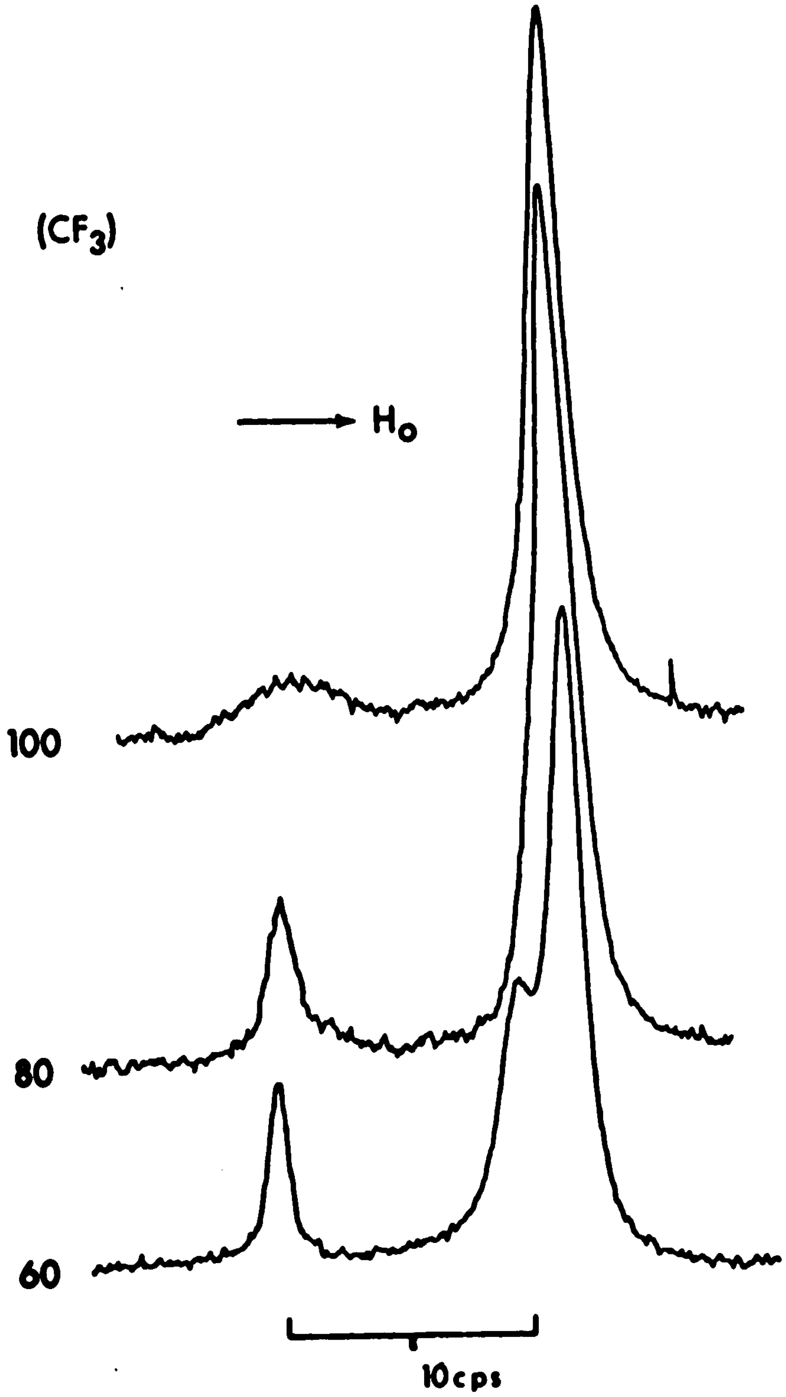
Similar ^{19}F nmr spectra were obtained from the study of this compound as for the π-C_5H_5 analogue described above. The methyl region indicated that this compound also existed as a mixture of two isomers in solution.

Figure 29.



Variable temperature ^{19}F nmr spectra of π-$C_5H_5Zr(bztfac)_3$.
Recorded in acetone-d^6 at 56.4 Mcs.

Figure 30.



High temperature ^{19}F nmr spectra of π-C_5H_5 Zr(bztfac)$_3$ in methylcyclohexane.

Intermolecular Exchange.

By analogy with some of the π-$C_5H_5Zr(chelate)_2Cl$ systems, the possibility of intermolecular exchange was studied for certain tris chelate systems and found to occur. The systems studied were chosen so as to provide maximum information with minimum overlap of resonances.

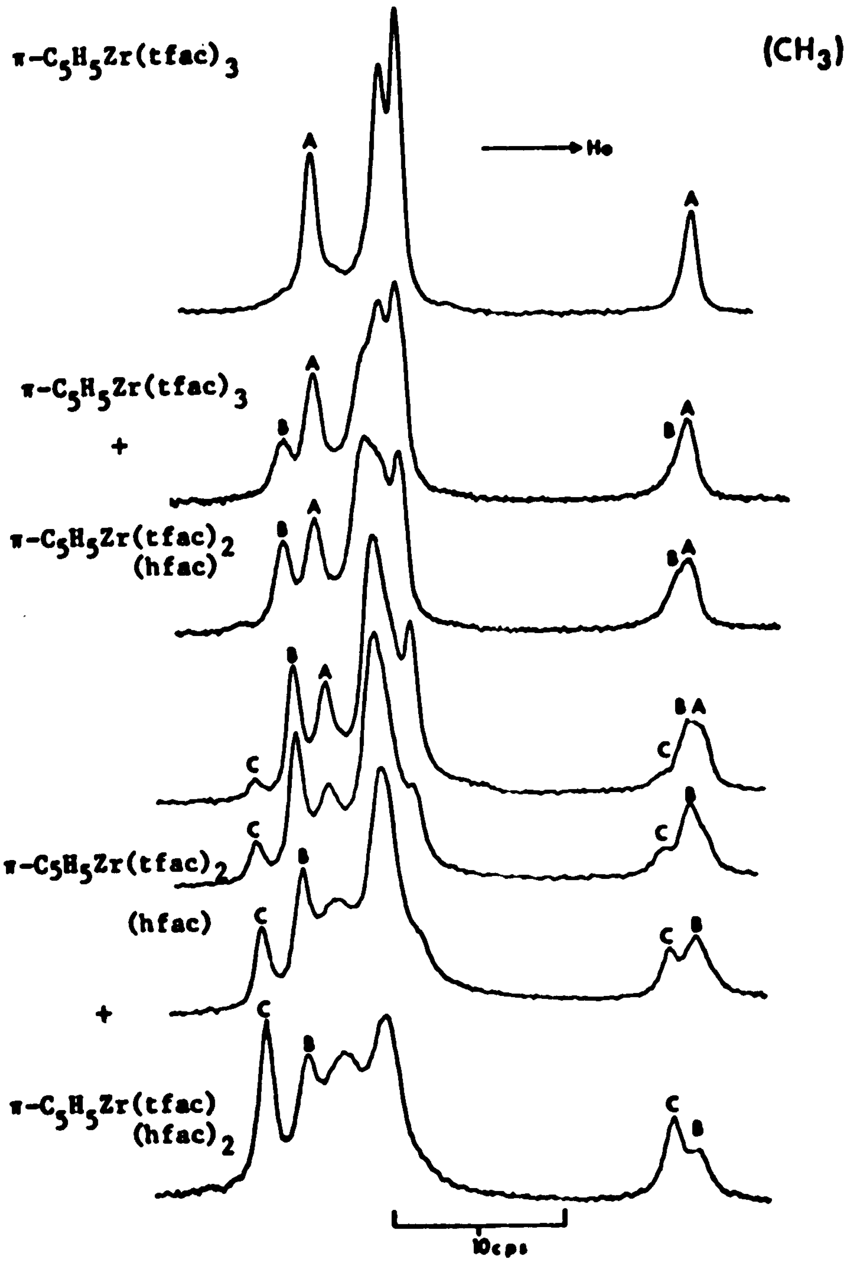
π-$C_5H_5Zr(tfac)_2(hfac)$ and π-$C_5H_5Zr(tfac)(hfac)_2$.

In the successive addition of small quantities of π-$C_5H_5Zr(hfac)_3$ to π-$C_5H_5Zr(tfac)_3$, the methyl region was followed in order to determine the fate of the tfac ligand. In this addition (Fig.31.) the following changes were expected by analogy to similar systems.(23),(24).

1) Starting material.
2) Starting material and π-$C_5H_5Zr(tfac)_2(hfac)$.
3) Decrease of π-$C_5H_5Zr(tfac)_3$, increase of π-$C_5H_5Zr(tfac)_2(hfac)$ and production of π-$C_5H_5Zr(tfac)(hfac)_2$.
4) Eventual disappearance of π-$C_5H_5Zr(tfac)_3$ followed by π-$C_5H_5Zr(tfac)_2(hfac)$ and increase to a constant quantity of π-$C_5H_5Zr(tfac)(hfac)_2$.

The spectral changes could be rationalized on the basis of the above changes, the resonances denoted by A (Fig.31) indicating CH_3 substituents of the unique chelates in π-$C_5H_5Zr(tfac)_3$, B indicating these substituents in π-$C_5H_5Zr(tfac)_2(hfac)$ and C these substituents in π-$C_5H_5Zr(tfac)(hfac)_2$. Each of A, B or C would have two possible positions, CH_3 up or CH_3 down. The assignment of equatorial CH_3 resonances was not attempted. The relative intensities of the methyl

Figure 31.



Study of the intermolecular exchange between π-$C_5H_5Zr(tfac)_3$ (top) and small added amounts of π-$C_5H_5Zr(hfac)_3$. The formation of mixed chelate compounds in $CDCl_3$ solution is followed.

resonances of tfac chelates did not change appreciably as hfac was substituted for tfac. This gave no positive information as to the possibility of dissociation of the axial ZrO bond in the intermolecular rearrangement. If this bond did dissociate then the steric effects of tfac and hfac chelates in the equatorial position were of the same order.

π-$C_5H_5Zr(tfac)_2(bztfac)$ and π-$C_5H_5Zr(tfac)(bztfac)_2$.

The behaviour of the unique tfac chelate was very similar positionally to the previous case. In this study, however, the distribution of the unique tfac chelate was altered appreciably as the exchange of tfac chelates proceeded. It was noted that different isomer ratios existed for π-$C_5H_5Zr(bztfac)_3$ and π-$C_5H_5Zr(tfac)_3$ and thus it was not surprising that substitution of bztfac for tfac in the equatorial chelates could cause alteration in the distibution of tfac in the unique chelate.

This situation suggests that both axial and equatorial zirconium-oxygen bonds may be involved in dissociation steps in the intermolecular exchange.

The reactions of π-$C_5H_5Zr(tfac)_3$ and π-$C_5H_5Zr(hfac)_3$ with free β-diketones were studied. Intermolecular exchange occurred in many cases but complexity and overlapping resonances precluded a detailed study. The unfluorinated β-diketones Hacac, Hdpm ,Hbzbzac and Hbzac displaced fluorinated β-diketones with difficulty.

Redistribution Studies of π-$C_5H_5Zr(hfac)_3$ and π-$C_5H_5Zr(tfac)_3$.

Using the π-cyclopentadienyl region of the nmr spectra of mixtures of the above compounds, it was possible to infer relative equilibrium concentrations of all the species in solution by 'counting squares' under the envelope of the resonances. These relative equilibrium concentrations were insensitive to concentration of the chelates over the range studied and also independent of temperature in the range 30^0- 40^0. The spectra were recorded using $CDCl_3$ as a solvent at a probe temperature of $33^0 \pm 1^0$.

The π-C_5H_5 resonances of the following chelates were assigned from previous studies.

π-$C_5H_5Zr(hfac)_3$	H_3
π-$C_5H_5Zr(hfac)_2(tfac)$	H_2T
π-$C_5H_5Zr(hfac)(tfac)_2$	HT_2
π-$C_5H_5Zr(tfac)_3$	T_3

The usual presentation of distributions was to investigate the mole fraction of each chelate compound as it varied with mole fraction of a particular chelating agent. (23).(24). In the present case, the mole fraction of tfac in the mixture was given by:-

$$\underline{f}\ \text{tfac} = \frac{(3T_3 + 2T_2H + TH_2)}{(3T_3 + 3T_2H + 3TH_2 + 3H_3} = \frac{\underline{f}\ \text{tfac}}{\underline{f}\ \text{tfac} + \text{hfac}}$$

$$\text{or} \quad \underline{f}\,\text{tfac} = \frac{T_3 + {}^2/3T_2H + {}^1/3TH_2}{T_3 + T_2H + TH_2 + H_3}$$

where T_3, T_2H, TH_2, H_3 refer to the measured areas of the particular chelate.

The mole fractions of total solute as

$$\underline{f}\ \pi\text{-}C_5H_5Zr(tfac)_n(hfac)_{3-n} = \frac{\pi\text{-}C_5H_5Zr(tfac)_n(hfac)_{3-n}}{\pi\text{-}C_5H_5Zr(tfac)_n}$$

$$= \frac{T_3}{T_3 + T_2H + H_3}$$

for π-$C_5H_5Zr(tfac)_3$

were plotted as a function of $\underline{f}$ tfac above. Theoretical curves which gave calculated values of $\underline{f}$ π-$C_5H_5Zr(tfac)_n(hfac)_{3-n}$ assuming a random distribution of ligands were also plotted by application of probability considerations , following the approach evolved by Calingaert and Beatty (<u>79</u>) and Van Wazer (<u>80</u>) and used in the $Zr(tfac)_4$, $Zr(acac)_4$ system by Pinnavaia and Fay (<u>24</u>):-

$$\underline{f}\ \pi\text{-}C_5H_5Zr(tfac)_n(hfac)_{3-n} = \underline{f}\ (tfac)^n(hfac)^{3-n}\ 3!/n!(3-n)!$$

where *f* hfac = 1- *f* tfac.

The result (Figure 32) indicated that the mixed chelates were favoured at the expense of π-$C_5H_5Zr(hfac)_3$ and π-$C_5H_5Zr(tfac)_3$.

The chelate exchange equilibria were described by specifying two equilibrium constants defined by the reactions:-

$$\pi\text{-}C_5H_5Zr(tfac)_3 + \pi\text{-}C_5H_5Zr(tfac)(hfac)_2 \overset{K_1}{\rightleftharpoons} 2\ \pi\text{-}C_5H_5Zr(tfac)_2(hfac).$$

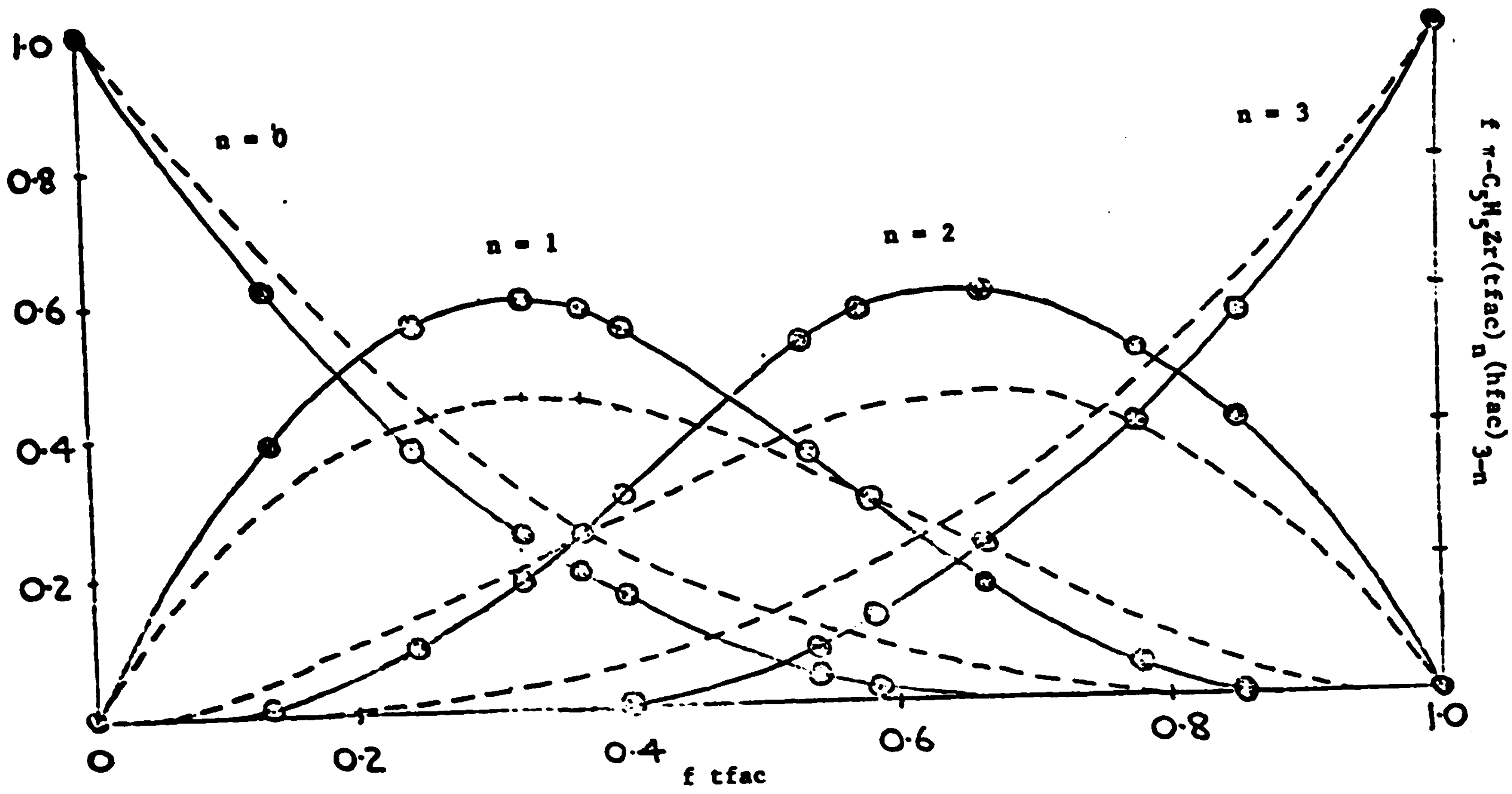
$$\pi\text{-}C_5H_5Zr(hfac)_3 + \pi\text{-}C_5H_5Zr(hfac)(tfac)_2 \overset{K_2}{\rightleftharpoons} 2\ \pi\text{-}C_5H_5Zr(hfac)_2(tfac).$$

The equilibrium constants K_1 and K_2 were calculated in the regions of greatest accuracy. These equilibrium constants were in the order of 10±1 compared with the statistically predicted value of 3. *i.e.*, when *f* tfac = 0.5, *f* hfac = 1-0.5 = 0.5

$$f\ \pi\text{-}C_5H_5Zr(tfac)_3 = 0.5^3 .\ 1\ .\ 3!/3! = 0.5^3.$$

$$f\ \pi\text{-}C_5H_5Zr(tfac)_2(hfac) = 0.5^2 . 0.5\ . 3!/2!1! = 3\ .\ 0.5^3.$$

Figure 32.



n = 0
n = 1
n = 2
n = 3
1·0
0·8
0·6
0·4
0·2
0
0·2
0·4
0·6
0·8
1·0
f tfac
f π-$C_5H_5Zr(tfac)_n(hfac)_{3-n}$

$$\underline{f}\ \pi\text{-}C_5H_5Zr(tfac)(hfac)_2 = 0.5\ .\ 0.5^2\ .\ 3!/1!2! = 3\ .\ 0.5^3.$$

$$\underline{f}\ \pi\text{-}C_5H_5Zr(hfac)_3 = 1\ .\ 0.5^3\ .\ 3!/3! = 0.5^3.$$

$$K_1 = \frac{\{\ \pi\text{-}C_5H_5Zr(tfac)_2(hfac)\ \}^2}{\{\ \pi\text{-}C_5H_5Zr(tfac)_3\ \}\ \{\ \pi\text{-}C_5H_5Zr(tfac)(hfac)_2\ \}}$$

$$K_1 = \frac{\{\ 3\ .\ 0.5^3\ \}^2}{\{\ 0.5^3\ \}\{3\ .\ 0.5^3\}} = 3.$$

Similarly $K_2 = 3.$

Note that $\sum_n\ \underline{f}\ \pi\text{-}C_5H_5Zr(tfac)_n(hfac)_{3-n}\ \ (\ n = 0,1,2,3)$

$$= 0.5^3\ .(\ 1 + 3 + 3 + 1\ )$$

$$= 1.0\ .$$

The results obtained for the chelate redistribution were similar to those determined for the $Zr(tfac)_4$-$Zr(acac)_4$ system (23), (24). The mixed complexes were favoured in both cases and the equilibrium constants were in all cases larger than those predicted on the basis of a random statistical ligand distribution. The reason for a favouring of the mixed chelate compounds is not known. Certain authors have suggested that the favouring may arise from a difference in the solvation entropies of reactants and products.(24), (81),(82),(83).

CHAPTER VI

Resonance Characteristics of Nmr Spectra.

The basis of assignment of the ^1H nmr spectra of many of these compounds was founded on several qualitative assumptions. The major of these were the similarities in shielding properties of the π-C_5H_5 ring system to the well studied benzene ring system (84), (85), (86) and that similar shifts may arise from electron circulation in the π-systems associated with the chelating groups.

From the known structure of π-$C_5H_5Zr(hfac)_3$ (63), (64), it was possible to measure distances of methine protons from the centroid of the π-C_5H_5 ring and to predict the relative shielding of these protons according to the treatment of Johnson and Bovey (86).

The methine resonance of the unique chelate (intensity 1) in both π-$C_5H_5Zr(hfac)_3$ and π-$C_5H_5Hf(hfac)_3$ was unambiguously located to high field of the methine resonances attributable to the methine environments of the equatorial chelates (intensity 2). Fig. 16. This ordering was in complete agreement with the treatment outlined previously. The ^1H nmr spectrum of π-$C_5H_5Zr(tfac)_3$ had indicated the existence of two forms in solution at ambient temperature on the basis of the two sharp π-C_5H_5 resonances observed (60 : 40).

Several possibilities were considered in order to explain the distribution of resonances. A similar exchange to that observed for π-$C_5H_5Zr(hfac)_3$ (in which rapid averaging of the environments of the equatorial chelates was occurring) was a possibility. In this case the two isomers arise from different orientations of the unique rigid chelate. Other possibilities involved a preferential orientation of this chelate with a particular exchange mechanism operating to selectively average equatorial environments.

The resolution of these possibilities was effected by consideration of the ^{19}F spectra of several of the compounds available.

The ^{19}F nmr resonances of intensity 1 in π-$C_5H_5Zr(hfac)_3$, π-$CH_3C_5H_4Zr(hfac)_3$ and π-$C_5H_5Hf(hfac)_3$ were assigned unambiguously to unique chelate CF_3 environments, one of which is an axial CF_3 and the other an equatorial CF_3 group. The averaged equatorial CF_3 environments (intensity 4) of the non-unique chelates in all cases lie between these resonances. The ^{19}F nmr spectra of π-$C_5H_5Zr(tfac)_3$ and π-$CH_3C_5H_4Zr(tfac)_3$ could be associated into two sets of unequally intense 1 : 2 resonances. Figs. 22 and 26. The resonances of intensity 1 occurred at high and low field, indicating an axial and an equatorial CF_3 environment associated with the unique chelate. The resonances of intensity 2 occurred between the resonances of intensity 1, indicating an averaged equatorial CF_3 environment.

The observation of both axial and equatorial CF_3 environments for π-$C_5H_5Zr(tfac)_3$ indicated that a unique chelate preference was not operative to any great extent and indirectly that the first exchange possibility was the most likely. The exchange processes will be discussed later.

The ambient temperature nmr spectrum of π-$C_5H_5Zr(tfac)_3$ may be completely assigned as follows. The low field methine resonances were assigned to averaged equatorial methine environments. These resonances were of the correct intensity relative to each other (60 : 40) and relative to the high field methine resonance (2 : 1) to be so assigned. The high field asymmetric methine resonance was assigned to the two methine environments of the unique chelate. Fig. 21.

The averaging of equatorial chelate environments produced CH_3 and CF_3 spectra consisting of two sets of 1 : 2 resonances as mentioned previously. The application of arguments used for the prediction of the relative shielding of methine environments was extended to methyl environments and indicated that the resonance of a methyl group in an axial position (i.e., in closest proximity to the axial oxygen atom or 'trans' to the π-C_5H_5 group) occurs at high field, while that in an equatorial position (i.e., in close proximity to an equatorial oxygen atom or 'cis' to the π-C_5H_5 group) occurs at low field. The low field grouping of resonances A, Y and B provides some evidence for these conclusions since both Y and B (intensity 2) resonances must arise from equatorial CH_3 groups.

The form of π-$C_5H_5Zr(tfac)_3$ giving rise to the associated resonances A and B (total 60%) is thought to be I, and the form giving rise to resonances X and Y (total 40%) is thought to be II.

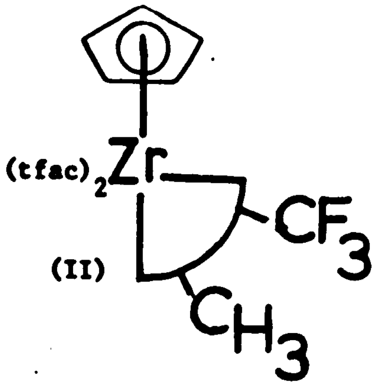
A comparison of ^1H and ^{19}F spectra on the basis of relative intensities allowed a direct association of corresponding CH_3 and CF_3 resonances(Figures 21 and 22). The comparison was critically dependent on intensity measurements which have been checked by different techniques such as peak integration, peak weighing and counting squares on different samples. The relative area measurements differ by ±2% in both ^{19}F and ^{1}H nmr spectra. The small magnitude of this variation in comparison with the difference in abundance of each form (20% for π-$C_5H_5Zr(tfac)_3$, and 12% for π-$CH_3C_5H_4Zr(tfac)_3$) enables intensity comparisons to be made with confidence.

The orientation of the unique chelate giving rise to I (60%) i.e., resonances AB, is CH_3 equatorial (low field) and CF_3 axial (low field); the orientation giving rise to II (40%) i.e., resonances XY, is CH_3 axial (high field) and CF_3 equatorial (high field). The close grouping of the equatorial CF_3 resonances Y, B and X to high field provides some support for these conclusions. Fig.33.

The similar distribution of both CH_3 and CF_3 resonances indicates a reversal of assignment for CF_3 groups compared with corresponding CH_3 groups. This effect presumably has as its basis the fact that ^{19}F shifts are primarily paramagnetic in origin while ^{1}H shifts are mainly diamagnetic in origin.

Extension of the preceding conclusions to the dodecahedral system of π-$C_5H_5Zr(diketone)_2Cl$ with an AAB face occupied by the π-C_5H_5 group indicated that CF_3 groups 'trans' to the π-C_5H_5 ring would appear as low field resonances - these correspond to CF_3 groups proximate to A sites (i.e., A_1. A_2 in Fig.1) and that CF_3 groups 'cis' to the π-C_5H_5 ring would appear as high field resonances - these correspond to CF_3 groups adjacent to B sites.

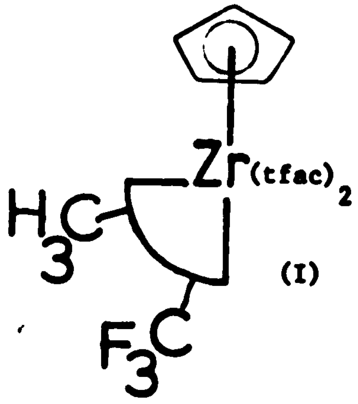
Figure 33.



(II)

CH_3 axial (high field)

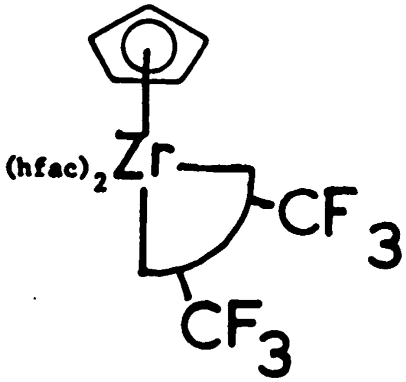
CF_3 equatorial (high field)



(I)

CF_3 axial (low field)

CH_3 equatorial (low field)



CF_3 axial (high field)

CF_3 equatorial (low field)

Several examples lend credence to the treatment so far outlined.

1) The distributional similarity of the isomers of π-$C_5H_5Ti(hfac)_2Cl$ and similar compounds, in particular the coincidence in chemical shift of the low field or A site resonances. The two isomers each have CF_3 resonances in close proximity to the same A sites; the isomerism occurs in the B sites.

2) The almost inverse relationship between the ^{19}F spectrum of π-$C_5H_5Ti(hfac)_2Cl$ and the CH_3 spectrum of π-$C_5H_5Zr(acac)_2Cl$ indicates the operation of different shieldings in these compounds.

3) The ^{19}F spectrum of π-$C_5H_5Zr(hfac)(acac)Cl$ indicates the presence of two forms of unequal abundance. The two available positions of the hfac chelate (which must span an AB edge <u>viz</u>., A_1B_2 or A_2B_1 for Cl at B_3 or A_1B_1 or A_2B_3 for Cl at B_2) indicates that separation of A and B CF_3 resonances by large shifts is possible (55 cps major form, 32 cps minor form).

The predominance of low field CF_3 resonances in the spectra of π-$C_5H_5Zr(tfac)_2Cl$, π-$C_5H_5Zr(bztfac)_2Cl$ and π-$C_5H_5Zr(ttfac)_2Cl$ indicated, together with the spectral characteristics of π-$C_5H_5Zr(acac)(tfac)Cl$, π-$C_5H_5Zr(acac)(bztfac)Cl$ and π-$C_5H_5Zr(acac)(ttfac)Cl$ (with a maximum intensity low field singlet CF_3 resonance in each case) that the favoured orientation of a fluorinated chelate occurs with the CF_3 group of the chelate adjacent to <u>one</u> A site of the dodecahedron. The other available sites also compete for proximity to CF_3 groups as indicated by the isomer distributions.

Distribution of Forms in the π-$C_5H_5Zr(tfac)_2Cl$ System.

The evaluation of distributions was considered using the spectra of π-$C_5H_5Zr(tfac)(acac)Cl$ and π-$C_5H_5Zr(hfac)(acac)Cl$ and , subject to the use of dodecahedral coordination, each site was allocated a preference for proximity to CF_3 groups.

If the chelate rings are identified as ξ and ψ and the sites of the dodecahedron are labelled as A and B, then the CF_3 environments in π-$C_5H_5Zr(tfac)(acac)Cl$ are as follows:-

$CF_3A\xi$, $CF_3B\xi$, $CF_3A\psi$, $CF_3B\psi$.

indicating a mixture of four forms, each with one CF_3 resonance. Similarly the CF_3 environments in π-$C_5H_5Zr(hfac)(acac)Cl$ were as follows for the two forms:-

Form 1:- $CF_3A\xi$, $CF_3B\xi$.
Form 2:- $CF_3A\psi$, $CF_3B\psi$.

The CF_3 environments for the four forms of π-$C_5H_5Zr(tfac)_2Cl$ were as follows:-

Form 1:- $CF_3A\xi$, $CF_3A\psi$.
Form 2:- $CF_3A\xi$, $CF_3B\psi$.
Form 3:- $CF_3B\xi$, $CF_3A\psi$.
Form 4:- $CF_3B\xi$, $CF_3B\psi$.

The lowest field resonance in π-$C_5H_5Zr(hfac)(acac)Cl$ was assigned to a $CF_3A\xi$ site and the corresponding high field resonance to a $CF_3B\xi$

site. The two remaining resonances were assigned to a $CF_3A\psi$ site (low field) and a $CF_3B\psi$ site (high field).

The most intense lowest field resonance in π-$C_5H_5Zr(tfac)(acac)Cl$ was assigned as $CF_3A\psi$ site with the $CF_3A\xi$ site the least preferred. The site preference (P) for π-$C_5H_5Zr(tfac)(acac)Cl$ was based on form distributions. <u>i.e.</u>

$P\ (CF_3A\psi) = 60$

$P\ (CF_3A\xi) = 0 - 10$

$P\ (CF_3B\psi) = 10$

$P\ (CF_3B\xi) = 20$

where $B\psi$ and $B\xi$ have been assigned by comparison with π-$C_5H_5Zr(hfac)(acac)Cl$.

For π-$C_5H_5Zr(hfac)(acac)Cl$

$P(CF_3A\psi) + P(CF_3B\psi) = 70$

$P(CF_3A\xi) + P(CF_3B\xi) = 30$

A comparison of the above equations gave a revised estimate for $P(CF_3A\xi)$ of 10.

For π-$C_5H_5Zr(tfac)_2Cl$, assuming the CF_3 preferences are operative.

Form 1:- $P(CF_3A\psi) + P(CF_3A\xi) = 60 + 10 = 70$

Expected low field doublet. (35%). Found 35%.

Form 2:- $P(CF_3A\psi) + P(CF_3B\xi) = 60 + 20 = 80$

Expected doublet of large separation. (40%). Found 50%.

Form 3:- P(CF_3Bψ) + P(CF_3Aξ) = 10 + 10 = 20

Expected doublet of large separation.(10%). Found 5%.

Form 4:- P(CF_3Bψ) + P(CF_3Bξ) = 10 + 20 = 30

Expected high field doublet. (15%). Found 10%.

A comparison of predicted and observed spectra showed a correct correlation of chemical shifts with relative abundances. The above assignment, derived from the study of π-C_5H_5Zr(tfac)(acac)Cl and π-C_5H_5Zr(hfac)(acac)Cl was almost independent of the interpretation of the spectrum of π-C_5H_5Zr(tfac)$_2$Cl.

Correlation of observed and predicted spectra were possible by reversing both AξAψ and BξBψ assignments. Reversal of one of the pairs produced a mis-match of observed and predicted spectra.

Reversal of Aξ and Aψ gave the following result.

Form 1:- P(CF_3Aψ) + P(CF_3Aξ) = 60 + 10 = 70

Expected low field doublet (35%). Found 35%.

Form 2:- P(CF_3Aψ) + P(CF_3Bξ) = 10 + 20 = 30

Expected large separation doublet (15%). Found 50% or 5%

Form 3:- P(CF_3Bψ) + P(CF_3Aξ) = 10 + 60 = 70

Expected large separation doublet.(35%). Found 50% or 5%.

Form 4:- P(CF_3Bψ) + P(CF_3Bξ) = 10 + 20 = 30

Expected high field doublet (15%). Found 10%.

Reversal of Bξ and Bψ only gave the following result.

Form 1:- P(CF_3Aψ) + P(CF_3Aξ) = 60 + 10 = 70

Expected low field doublet (35%). Found 35%.

Form 2:- P(CF_3Aψ) + P(CF_3Bξ) = 60 + 10 = 70

Expected large separation doublet (35%). Found 50%.

Form 3:- P(CF_3Bψ) + P(CF_3Aξ) = 20 + 10 = 30

Expected large separation doublet (15%). Found 5%.

Form 4:- P(CF_3Bψ) + P(CF_3Bξ) = 20 + 10 = 30

Expected high field doublet (15%). Found 10%.

Expected correlations of CH_3 and CF_3 resonances were observed, although less clearly due to resolution problems in the methyl region. The corresponding CH_3 environments in π-$C_5H_5Zr(tfac)_2Cl$ were as follows:-

Form 1:- CH_3Bψ , CH_3Bξ . Form 2:- CH_3Bψ , CH_3Aξ .
Form 3:- CH_3Aψ , CH_3Bξ . Form 4:- CH_3Aψ , CH_3Aξ

While the spectrum was weighted in favour of high field CH_3 resonances, an indication of equatorial or B site CH_3 groups, the assignments were not as definite as for CF_3 resonances. The CH_3 environments of π-C_5H_5Zr(hfac)(acac)Cl were as follows:-

$CH_3A\xi$ and $CH_3B\xi$ (70%)
$CH_3A\psi$ and $CH_3B\psi$ (30%)

The main doublet observed in the CH_3 region was an indication of the correlation between ^1H and ^{19}F spectra.

The extension of shielding arguments to the π-$C_5H_5Zr(tfac)_2Cl$ system indicated a definite preference for fluorinated chelates such that the CF_3 group was located in close proximity to one A site of the dodecahedron. The reasons for this effect are not directly obvious but the A site preference may be related to a destabilizing effect of CF_3 groups proximate to B sites, if the CF_3 reduces the π-bonding capacity of the B site O atom (72) by electron-withdrawal.

Line Widths in ^{19}F Nmr Spectra.

In the course of this study, the ^{19}F nmr spectra of many compounds were available and certain trends were noted. High field ^{19}F nmr resonances were generally much broader than low field resonances, the peak width at half peak height was taken as a measure of this broadening. It may be noted that in Tables 3 and 4, the highest field nmr resonance had a peak width at half-height ($\nu_{\frac{1}{2}}$) of 1.8 - 2.5 cps., while the low field CF_3 nmr resonances had $\nu_{\frac{1}{2}}$ 0.8-1.4 cps.

The ^{19}F nmr spectrum of π-$C_5H_5Ti(hfac)_2Cl$ showed this trend well in that a constant increase of $\nu_{\frac{1}{2}}$ to high field was noted for resonances attributable to the compound. The resonance due to Hhfac, even though at higher field than other resonances did not follow the trend of broadening ($\nu_{\frac{1}{2}}$ Hhfac = 1 cps.)

The CF_3 nmr resonances which were broadened have been assigned as CF_3 groups in equatorial positions on the equatorial chelates or unique chelate in the π-$C_5H_5Zr(chelate)_3$ system or CF_3 groups located in close proximity to B sites in the π-$C_5H_5Zr(chelate)_2Cl$ system. In both cases the CF_3 groups were also in reasonably close proximity to the π-C_5H_5 ring and hence to the magnetic influence of this moiety.

The rotation of the CF_3 group in the varying magnetic field of the π-C_5H_5 group could lead to an additional mode of relaxation of the ^{19}F nuclei. Any additional relaxation shortens the spin-spin relaxation time T_2 and broadens the resonance in question since

$\nu_{\frac{1}{2}}$ is proportional to $1/T_2$. The resonances have identical peak widths at half height when the spectra are recorded at 94.1 Mcs. instead of the most used 56.4 Mcs.

The possibility that this broadening to high field was due to an instrumental artifact was discounted in several ways.

a). Broadening did not occur uniformly to high field. This was most evident in mixtures of π-$C_5H_5Ti(hfac)_2Cl$ or π-$CH_3C_5H_4Ti(hfac)_2Cl$ and Hhfac (Figs. 10 and 12), where the resonance due to Hhfac (L), although at high field, was always sharp. Several instances in which the broadening varies between forms of a compound have also been noted. (Figs.5,7,20,22 and 26).

b). Similar spectra showing similar high-field broadening have been recorded on different instruments.

CHAPTER VII

Exchange Mechanisms.

The interpretation of certain aspects of the variable-temperature nmr spectra of both the bis and tris chelate compounds has indicated the presence of a process or processes which interconvert the environments of the chelate substituents. This mechanism, which has been alluded to in certain explanations of spectral behaviour, is now discussed more fully.

A. Bis chelate compounds.

Several possibilities of intramolecular chelate exchange mechanisms have been suggested. (26),(27),(28). These were as follows:-

1. Non-selective exchange *via* successive 'twisting' of chelates or by non-selective dissociation of metal-oxygen bonds wich subsequent rearrangement to the starting stereochemistry. This mode of exchange involves an averaging of the environments of the chelate substituents.

2. Selective twisting of one chelate ring with rearrangement to the starting stereochemistry involves averaging of the environments of that chelate only.

3. Selective twisting of both chelate rings involves averaging of two sets of chelate substituent environments with no averaging between these environments.

4. Selective dissociation of metal-oxygen bonds with subsequent rearrangement may involve some form of selective averaging dependent

on the bond which is dissociated.

The behaviour of the nmr spectrum of π-$C_5H_5Zr(acac)_2Cl$ on raising the temperature indicated that process 1. was operative for the one solution isomer of the compound at high temperatures. This was shown by the averaging of the four CH_3 resonances and by the averaging of the two methine resonances. Studies on the hfac compounds π-$C_5H_5Ti(hfac)_2Cl$ and π-$CH_3C_5H_4Ti(hfac)_2Cl$ indicated that intramolecular chelate exchange occurred at elevated temperatures by process 1.

In several cases, a selective site dissociation or a selective twisting mechanism was considered to be a strong possibility. For dodecahedral coordination, metal- O_A site bonds have been shown to be longer and presumably weaker than metal- O_B site bonds (<u>72</u>). If bond dissociation mechanisms were important, dissociation of metal- O_A sites followed by later dissociation of metal- O_B sites at higher temperatures was expected. The final stage of dissociation of both metal- O_A and metal- O_B sites corresponds to process 1. The behaviour of the major isomer of π-$C_5H_5Ti(hfac)_2Cl$ was compared with the predicted behaviour from each of the possible exchange mechanisms.

1. Simultaneous exchange of CF_3 resonances proximate to A and B sites <u>viz</u>., coalescence of four CF_3 resonances. As this occurs, exchange of the two magnetically non-equivalent methine environments also proceeds giving coalescence of the methine resonances.

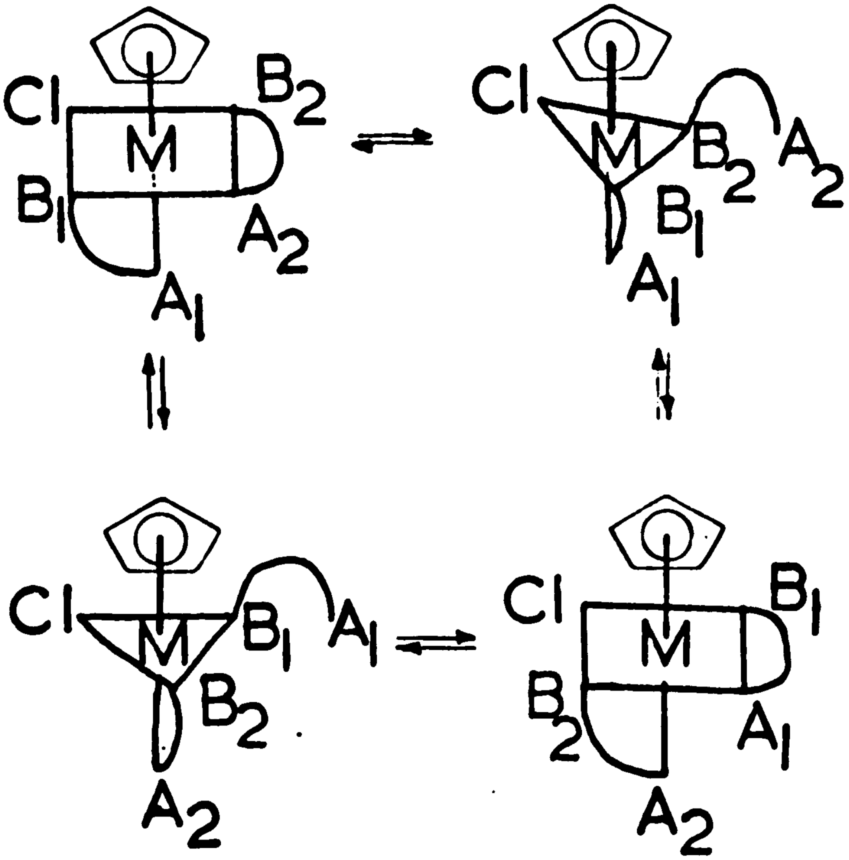
2. Selective twisting of one chelate exchanges only one CF_3 A site resonance with one CF_3 B site resonance, this would be indicated by a coalescence of only two of the four CF_3 resonances. These resonances would be expected at low (A site) and high (B site) field. No exchange of methine environments is required for this mode of exchange.

3. Selective twisting of both chelate rings exchanges two sets of CF_3 A and B site environments. This would reflect in coalescence of these two sets of resonances to produce two singlets. No exchange of methine environments is required for this exchange mechanism.

4. Dissociation of a metal- O_A site with retention of coordination at the metal- O_B site throughout the exchange process may, in certain circumstances, average only CF_3 A environments with a simultaneous averaging of CF_3 B environments. This process would be observed as a coalescence of CF_3 A resonances to give a singlet with a similar coalecsence of the CF_3 B resonances. The process, although similar in some respects to process 3. vide supra., does differ in the gross feature that methine environments are averaged in this case only. Fig. 34 .

The possibility of contributions from processes 2 and 3 cannot be discounted at lower temperatures but these processes cannot fully account for the observed variable-temperature nmr spectra. The possibilitv of contributions from process 4 also cannot be discounted, the nmr spectra of this form of exchange being similar at low temperatures to that expected for process 1.

Figure 34.



Possible selective exchange mechanism for bis chelate compounds <u>via</u> dissociation of A_1 or A_2 sites.

It is not possible to distinguish, on the basis of the nmr spectra, between non-selective bond-breaking mechanisms and non-selective successive chelate twist mechanisms (26),(27),(28).

B. Tris chelate compounds.

Two forms of exchange have been noted in the study of these novel compounds.

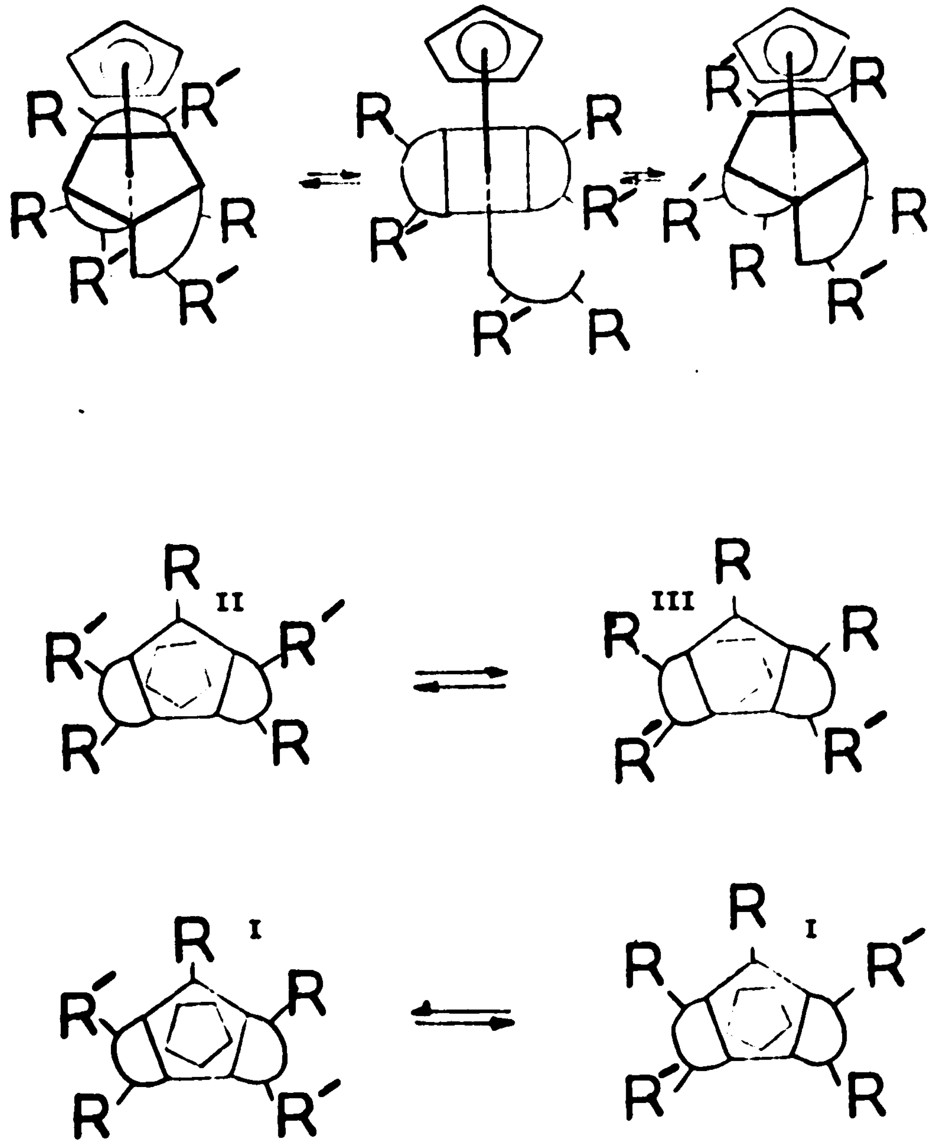
1. A non-selective exchange of chelates which could occur by successive chelate twisting or by a bond-breaking mechanism involving both equatorial and axial zirconium-oxygen bonds. The nmr technique cannot distinguish between these high temperature exchange mechanisms.

2. A selective exchange which averages only the environments of the equatorial (non-unique) chelate substituents. This exchange mechanism may be investigated by the nmr technique, considering both chelate twisting and metal-oxygen bond-breaking.

Bond dissociation mechanisms.

a) The short axial zirconium-oxygen bond in π-$C_5H_5Zr(hfac)_3$ could well have significance in the selectivity of chelate exchange between processes 1 and 2 *vide supra*. The longest and presumably weakest Zr-O bond was considered to have the greatest tendency for dissociation. The choice of this bond was not clear and the possibilities of both unique and non-unique equatorial Zr-O bond dissociations are considered. The dissociation and subsequent rearrangement of the species formed by dissociation of the unique equatorial zirconium-oxygen bond is shown in Figure 35 .

Figure 35.



Rearrangement process of π-$C_5H_5Zr(R'COCHCOR)_3$ via a selective dissociation of the unique Zr-O equatorial bond with subsequent rearrangement.

The averaging of the equatorial chelate environments of forms II and III with the averaging of the environments of form I was expected to lead to the observation of four nmr forms (two for each orientation of the unique chelate) compared with the six forms expected in a limiting low temperature spectrum. Fig. 25 .

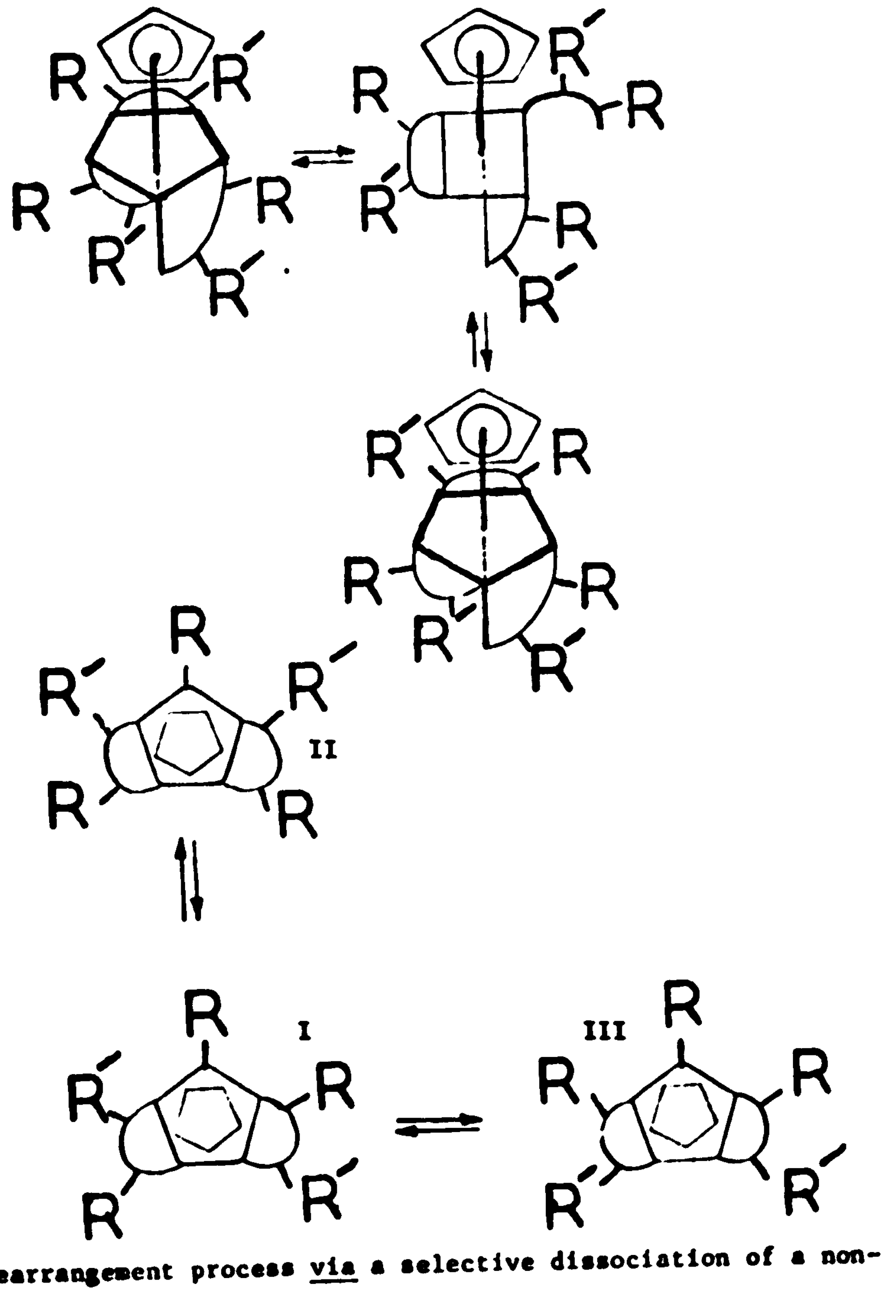
b) The possibility of a selective dissociation of a non-unique Zr-O bond in an asymmetric chelate compound was next considered and the treatment shown in Figure 36. This random equatorial Zr-O bond breaking averages the equatorial chelate environments of forms I, II and III and would lead to the observation of two nmr forms (one for each orientation of the unique chelate).

The observation of a limiting low temperature ^{19}F nmr spectrum for π-$C_5H_5Zr(hfac)_3$ which could be related to the X-ray crystal structure combined with the exchange of equatorial CF_3 environments could be explained by either or both the above processes , viz., the ^{19}F nmr spectra cannot distinguish between these two bond-breaking processes.

In the case of π-$C_5H_5Zr(tfac)_3$, the ambient temperature nmr spectra were closely comparable to the predictions of process 2 or by processes 1 and 2 combined, in that two nmr forms were observed. Two forms were also observed in the ambient temperature nmr spectra of π-$CH_3C_5H_4Zr(tfac)_3$, π-$C_5H_5Zr(bztfac)_3$and π-$CH_3C_5H_4Zr(bztfac)_3$.

The low temperature ^{19}F nmr spectra of π-$C_5H_5Zr(tfac)_3$ and the well-resolved nmr spectra of π-$CH_3C_5H_4Zr(tfac)_3$ and π-C_5H_5Zr $(bztfac)_3$ showed considerably less resonances than the expected

Figure 36.



Rearrangement process via a selective dissociation of a non-unique equatorial Zr–O bond.

14 CF_3 resonances (from a mixture of six forms). The low field CF_3 resonance of π-$CH_3C_5H_4Zr(tfac)_3$ appeared to split into two singlets of unequal intensity as the temperature was lowered. Similar behaviour was noted for the low field resonance of π-$C_5H_5Zr(tfac)_3$. Only four of the expected six π-C_5H_5 resonances were observed in the ^1H nmr spectrum of π-$C_5H_5Zr(bztfac)_3$ at all attainable temperatures below -50^0.

Several possibilities exist to explain these observations.

a). The resonances expected from the six forms may be coincident or almost so.

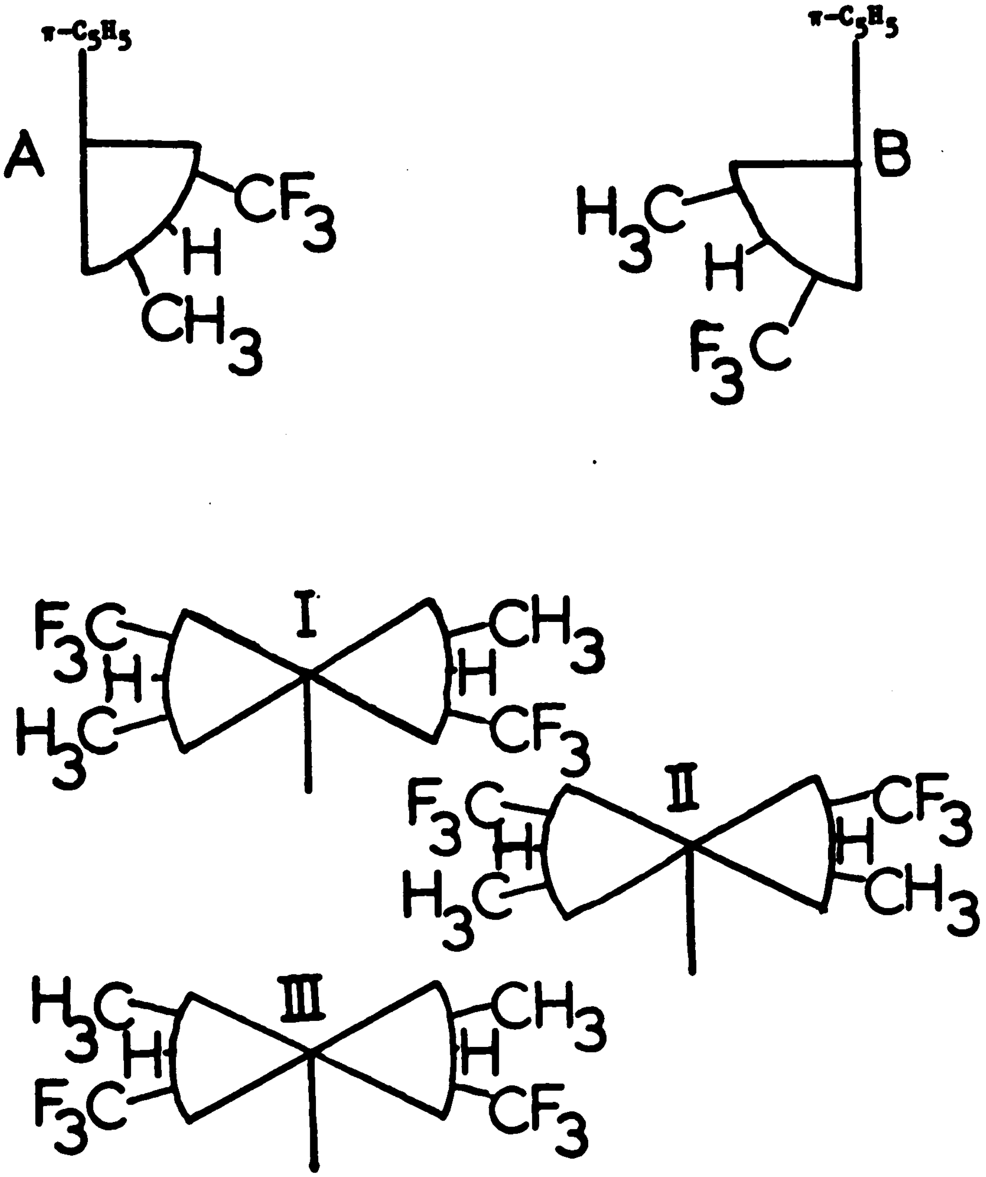
b). The use of an asymmetric chelate should theoretically distinguish between processes 1 and 2 and if there exists an appreciable temperature difference between these processes (as there does between process 2 and the unselective exchange) then process 1 may not be observable if the limiting low temperature spectrum is not attained.

c). The possibility of preferred chelate orientations for the 'frozen out' forms in the limiting low temperature spectrum could not be discounted. This preferred orientation has been observed for bis chelate compounds containing asymmetric chelates.

A definitive choice of mechanism is not possible on the basis of the observed spectra.

The theoretical treatment of the differing exchanges of a statistical distribution of the six forms of π-$C_5H_5Zr(tfac)_3$ is presented. Fig. 37.

Figure 37.



Six form possibility in the π-$C_5H_5Zr(tfac)_3$ system. A or B refer to orientations of the unique chelate. I-III refer to orientations of the equatorial chelates.

No exchange.	Form AI	3 CF_3	(1:1:1)	Total 2.
	Form AII	2 CF_3	(1:2)	Total 1.
	Form AIII	2 CF_3	(1:2)	Total 1.
	Form BI	3 CF_3	(1:1:1)	Total 3.
	Form BII	2 CF_3	(1:2)	Total 1.5.
	Form BIII	2 CF_3	(1:2)	Total 1.5.

The relative totals are derived from a statistical distribution combined with the relative abundances of the unique chelate orientations. The predicted nmr spectrum of this compound was as follows:-

6 π-C_5H_5 (ratio 2:1:1:3:1.5:1.5)
14 CF_3 (ratio 1:1:1.5:1.5:2:2:2:2:2:3:3:3:3:3)
14 CH_3 (ratio as for CF_3)
14 CH (ratio as for CF_3)

Process 1.	Form AI	2 CF_3	(1:2)	Total 2.
	Form AII-AIII	2 CF_3	(1:2)	Total 2.
	Form BI	2 CF_3	(1:2)	Total 3.
	Form BII-BIII	2 CF_3	(1:2)	Total 3.

The predicted nmr spectrum was as follows:-

4 π-C_5H_5 (ratio 2:2:3:3)
8 CF_3 (ratio 1:1:2:2:1.5:1.5:3:3)
Similar CH_3 and methine.

Process 2.	Form AI-AII-AIII	2 CF_3	(1:2)	Total 2.
	Form BI-BII-BIII	2 CF_3	(1:2)	Total 3.

The predicted nmr spectrum was as follows:-

2 π-C_5H_5 (ratio 2:3)

4 CF_3 (ratio 1:1.5:2:3)

Similar CH_3 and methine.

<u>Chelate twist mechanisms</u>.

Twisting of an equatorial chelate with subsequent rearrangement would give similar nmr behaviour as process 2 of the bond-breaking study. A distinction between these processes cannot be made on the available evidence. The detection of a chelate dissociation mechanism for the exchange could arise by observation of process 1 in the absence of process 2.

CHAPTER VIII.

Mass Spectrometry.

This technique was used in the study of different compound types and fragmentation patterns in the process of compound identification.

The mass spectra of $Zr(acac)_4$ (87), $Zr(hfac)_4$ (25) and several fluorinated and unfluorinated β-diketone compounds have been reported. (88),(89). The metallocene compounds $(\pi\text{-}C_5H_5)_2MCl_2$ (where M = Ti or Zr) have been comprehensively studied. (15).

Several simple compounds prepared in this study were examined by mass spectrometry to provide a link between the above systems. Metal-containing fragments were indicated by known isotope patterns and chlorine-containing fragments by combination patterns. Organic fragments were abundant in all cases; from $\pi\text{-}C_5H_5$ compounds the ions $C_5H_5^+$ and $C_3H_3^+$ were observed, while acac compounds produced CH_3CO^+. Compounds containing fluorinated β-diketones gave CF_3^+ and CF_2^+.

Unfluorinated β-diketones.

The compounds $Zr(acac)_2Cl_2$ and $Zr(acac)_3Cl$ were the subject of a mass spectrometric investigation. Considerable rearrangement was observed but the spectra were significantly different and could be assigned using the data for $Zr(acac)_4$(87). Table VII.

The mass spectra of $(\pi\text{-}C_5H_5)_2MCl_2$ (M = Ti, Zr.) , $\pi\text{-}C_5H_5TiCl_3$ and $(\pi\text{-}CH_3C_5H_4)_2ZrCl_2$ were recorded for comparison purposes. The breakdown patterns of these compounds were very similar to those reported (15). Of special interest was the observation of $C_3H_3MCl_2^+$ ions in the fragmentation processes of several of these compounds. The observation of $C_3H_3M^+$ ions in the fragmentation of $\pi\text{-}C_5H_5$ metal carbonyl compounds has also been noted (90).

The mass spectrum of $\pi\text{-}C_5H_5Zr(acac)_2Cl$ was recorded at 70 eV and showed no molecular ion but many of the ions observed in the fragmentations in Table VII. No ion corresponding to $C_5H_5Zr(acac)Cl^+$ was observed. This indicated a preferred loss, at 70 eV, of C_5H_5 or of Cl rather than acac. In several instances rearrangement ions were detected, possibly due to thermal decomposition during evaporation from the ion source.

TABLE VII MASS SPECTRAL DATA FOR UNFLUORINATED CHELATE COMPOUNDS.

$Zr(acac)_2Cl_2$.		$Zr(acac)_3Cl$.		$Zr(acac)_4$ (87).	
		$Zr(acac)_3Cl^+$	422(0.5)		
		$Zr(acac)_3^+$	387(100)	$Zr(acac)_3^+$	387
$Zr(acac)_2Cl_2^+$	358(4)				
$Zr(acac)_2Cl^+$	323(100)	$Zr(acac)_2Cl^+$	323(87)		
				$Zr(acac)_2OH^+$	305
$Zr(acac)Cl_2^+$	259(21)				
$Zr(acac)OHCl^+$	241(8)	$Zr(acac)OHCl^+$	241(15)		
				$^+Zr(acac)(OH)_2$	223
$O = Zr(acac)^+$	205(7)	$O = Zr(acac)^+$	205(18)	$O = Zr(acac)^+$	205

$(\pi-C_5H_5)Zr(acac)_2Cl$.	$Zr(acac)_3^+$	387 (1)
	$C_5H_5Zr(acac)_2^+$	353 (4)
	$Zr(acac)_2Cl^+$	323 (100)
	$Zr(acac)OHCl^+$	241 (6)
	$O = Zr(acac)^+$	205 (4)

Ions are described by chemical formulae. Mass (% base)

Fluorinated β-diketones.

The mass spectrum of $Zr(hfac)_4$ was recorded to aid in the assignment of C_5H_5 and C_6H_7-containing ions in the mass spectra of π-$C_5H_5Zr(hfac)_3$ and $\pi CH_3C_5H_4Zr(hfac)_3$ respectively. Table VIII. The breakdown of the above compounds indicated the preferential formation of the following ions at 70 eV., with loss of CF_2 and/or F from these ions as an additional process.

$$Zr(hfac)_pF_q \quad \text{where } p + q = 3.$$

Similar losses have been observed for the $Cs^+ \; Y(hfac)_4^-$ compound. This behaviour has been taken as indicative of migration of fluorine to the central metal atom (91), and has also been observed in other systems containing the trifluoromethyl group. (92). Secondary fragmentation was indicated by the ions:-

$$C_5H_5Zr(hfac)_rF_s \quad \text{where } r + s = 2.$$

Studies of π-$C_5H_5Zr(tfac)_3$ and $Zr(tfac)_4$ indicated similar trends. Table IX .

Comparison of the ions formed in the breakdown of π-$C_5H_5Zr(hfac)_3$ and π-$C_5H_5Zr(tfac)_3$ showed similarities as did those formed in the breakdown of $Zr(hfac)_4$ and $Zr(tfac)_4$. Isoelectronic fragments were observed in all cases except for the m/e 266 ion for the hfac chelate compounds.

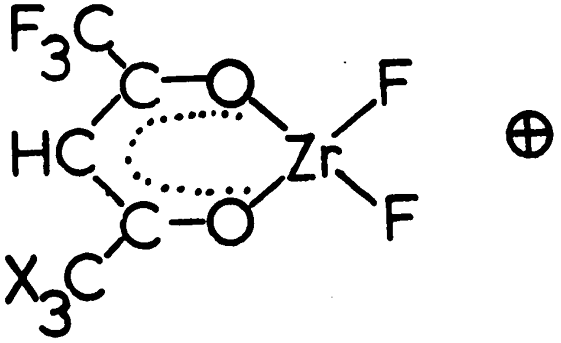
TABLE VIII MASS SPECTRAL DATA FOR HFAC CHELATE COMPOUNDS.

π -$C_5H_5Zr(hfac)_3$	$Zr(hfac)_4$	Ion
776 (0.2)		$C_5H_5Zr(hfac)_3^+$
757 (5.4)		$(C_5H_5Zr(hfac)_3 - F)^+$
711 (100)	711 (23.1)	$Zr(hfac)_3^+$
569 (10.7)	-	$C_5H_5Zr(hfac)_2^+$
523 (79.2)	523 (87.2)	$Zr(hfac)_2F^+$
473 (55.1)	473 (100)	$(Zr(hfac)_2F-CF_2)^+$
381 (4.7)		$C_5H_5Zr(hfac)F^+$
335 (21.0)	335 (42.5)	$Zr(hfac)F_2^+$
316 (8.8)	316 (15.2)	$(Zr(hfac)F_2-F)^+$
285 (35.2)	285 (97.0)	$(Zr(hfac)F_2-CF_2)^+$
266 (16.8)	266 (42.4)	$(Zr(hfac)F_2-CF_2 -F)^+$
193 (9.2)		$C_5H_5ZrF_2^+$
147 (0.3)	147 (0.5)	ZrF_3^+

TABLE IX MASS SPECTRAL DATA FOR TFAC CHELATE COMPOUNDS.

π-$C_5H_5Zr(tfac)_3$	$Zr(tfac)_4$	Ion.
614 (0.1)		$C_5H_5Zr(tfac)_3^+$
595 (1.4)		$(C_5H_5Zr(tfac)_3-F)^+$
549 (100)	549 (53.6)	$Zr(tfac)_3^+$
461 (6.0)		$C_5H_5Zr(tfac)_2^+$
415 (33.2)	415 (59.1)	$Zr(tfac)_2F^+$
365 (21.6)	365 (83.2)	$(Zr(tfac)_2F-CF_2)^+$
327 (1.6)		$C_5H_5Zr(tfac)F^+$
281 (6.8)	281 (42.5)	$Zr(tfac)F_2^+$
262 (18.6)	262 (31.5)	$(Zr(tfac)F_2-F)^+$
231 (18.6)	231 (100)	$(Zr(tfac)F_2-CF_2)^+$

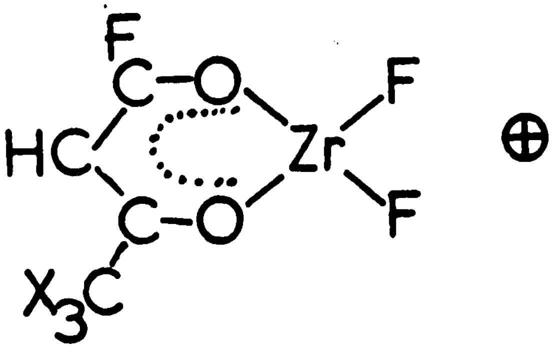
The m/e 281 ion in the tfac case and the m/e 335 ion in the hfac case may be:-



X = F m/e 335

X = H m/e 281

These may lose CF_2 to form



X = F m/e 285

X = H m/e 231

The further loss of F from this ion was more probable with X = F, retaining the apparently stable skeleton of the ion. If X = H, this skeleton would have to be restructured in order to lose F. This explanation may well explain the different base ions formed in the breakdown of $Zr(hfac)_4$ and $Zr\ (tfac)_4$ (m/e 473 and m/e 231 respectively).

Clastographic analysis of the mass spectrum of π-$C_5H_5Zr(hfac)_3$ at a source temperature of 100^0 and under different excitation voltages indicated several interesting trends. As the voltage was raised, the base ion corresponded to $C_5H_5Zr(hfac)_2^+$ and accounted for over 80% of the metal-containing fragments at 5eV. An increase in voltage decreased the amount of this ion to 3% while the amount of $Zr(hfac)_3^+$ increased from 7 to 85%. Still further increase in excitation voltage caused $Zr(hfac)_3^+$ to decrease to a constant value which was reached at 50-60 eV.

Relative ion abundances of most species were constant to within ±3% from 40-70 eV. All ions, except $C_5H_5Zr(hfac)_2^+$, showed unusual behaviour in the 10-30 eV region, the clastogram indicating the occurrence of consecutive reactions in the ion source (<u>93</u>). The interpretation of the clastogram was derived from the work of King and Long (<u>94</u>) and Kiser (<u>15</u>),(<u>93</u>)

Type I ions- these are only observed for parent ions or ions of low activation energy. More favourable higher energy processes do not favour these ions. Observed- $C_5H_5Zr(hfac)_2^+$.

Type II ions- these are primary products of slightly higher energy than Type I ions, usually exhibiting an intensity decrease at high excitation voltages due to secondary processes or decomposition. Observed- $Zr(hfac)_3$.

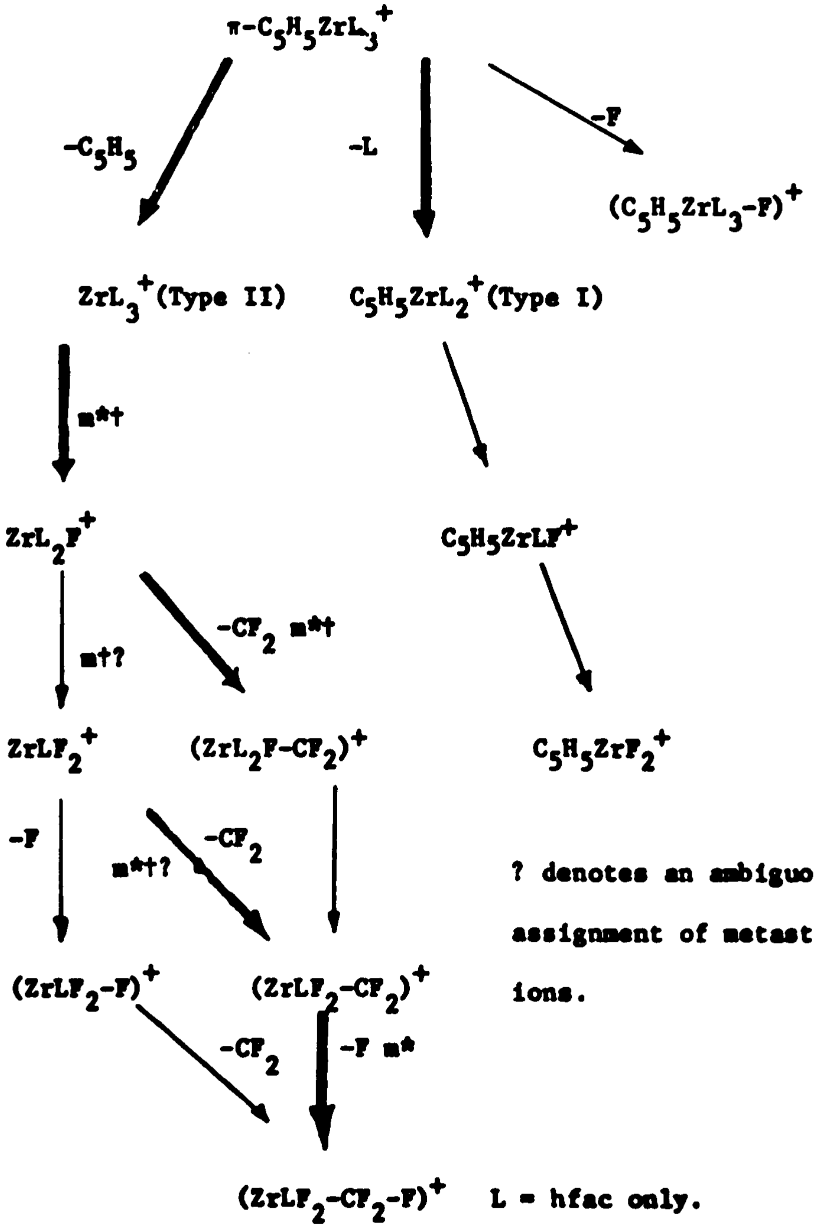
Type III ions- these are high energy ions or ions formed by complex fragmentation. Observed- $Zr(hfac)_2F^+$, $Zr(hfac)F_2^+$, $(Zr(hfac)F_2-CF_2)^+$ and several minor ions .

The possible breakdown pattern was constructed from knowledge of the clastogram and from the assignment of several metastable ions. Fig. 38 .

The fragmentation pattern of π-$C_5H_5Ti(hfac)_2Cl$ was complex due to large amounts of rearrangement ions. Rearrangement during evaporation from the source has been noted in other Ti(IV) compounds (95).

Figure 38.

Observed breakdowns in heavy lines.



? denotes an ambiguous assignment of metastable ions.

m* metastable ion observed for hfac case

m† metastable ion observed for tfac case

CHAPTER IX.

Infra-red Spectra.

The infra-red spectra of many of the more symmetrical compounds were recorded. Positions of bands are reported in cm^{-1} and the bands are classified as weak (w), medium (m), strong (s), shoulder (sh) and broad (br).

$(\pi\text{-}C_5H_5)_2TiCl_2$:- 3108m, 3100w, 1435m, 1016m, 835s, 795m, 460m, 422m, 330m, 293m.

$\pi\text{-}C_5H_5TiCl_3$:- 3100m, 1440m, 1027m, 1016m, 872m, 819s, 414w, 399m, 359m, 300m, 243m, 204m.

$(\pi\text{-}C_5H_5)_2ZrCl_2$:- 3100w, 3097w, 1435w, 1018m, 1010m, 851m, 845m, 811s, 808s, 358m, 335m, 308m, 268m.

$(\pi\text{-}C_5H_5)_2ZrI_2$:- Far IR region. 850m, 811s, 357m, 270m.

The IR spectra of $(acac)_2ZrCl_2$ and $(acac)_3ZrCl$ were similar to those reported by Fay and Pinnavaia (96).

$\pi\text{-}C_5H_5Ti(hfac)_2Cl$:- 3070w, 1665m br, 1615sh, 1560m,1545m, 1478m, 1440m,1360m, 1260s br, 1151s br, 1110m br, 1024w, 846s, 814s, 745m, 665s, 593m, 530w, 500w, 387m, 366m, 349m, 271w, 252w.

$\pi\text{-}C_5H_5Zr(hfac)_3$:- 3075w, 1661m, 1645m, 1615sh, 1562m, 1545m,1476m, 1444m, 1362w, 1260s br, 1215s br, 1150s br, 1115m, 1105m, 1024w, 845w, 831m, 809m, 745m, 665m, 661m, 590m, 531w, 506w, 488w, 381w, 342m, 250m, 235m.

$\pi\text{-}CH_3C_5H_4Zr(hfac)_3$:- 3070w, 1661m, 1642m, 1615sh, 1560m, 1543m, 1478m, 1440m, 1360w, 1260s br, 1150s br, 1112w, 1106w, 884w, 828m, 803m, 742w, 663m, 659m, 596m, 590m, 530w, 506w, 483w, 383w, 366w, 250m, 235m.

π-$CH_3C_5H_4Zr(hfac)_3$:- 3070w, 1661m, 1642m, 1615sh, 1560m, 1543m, 1478m, 1440m, 1360w, 1260s br, 1150s br, 1112w, 1106w, 864w, 828m, 803m, 742w, 663m, 659, 596m, 590m, 530w, 506w, 483w, 383w, 366w, 343m, 240m br.

π-$C_5H_5Hf(hfac)_3$:- because of contamination with the isostructural zirconium compound, this material was not suitable for I.R. investigation. The spectra recorded in the range 4000cm^{-1} to 300cm^{-1} were essentially similar to that of the zirconium analogue while the region below 300cm^{-1} indicated several differences, presumably due to different Zr - 0 and Hf - 0 stretching frequencies.

π-$C_5H_5Zr(acac)_2Cl$:- Low region. 830m, 820m, 810s, 798w, 665m, 560w, 541m, 444m, 432m, 405m, 331m, 315m br, 253w.

π-$C_5H_5Zr(bzac)_2Cl$:- Low region. 820m, 812m, 789w, 777m, 770m, 712m, 684m, 569w, 550m, 440, 417m, 330m, 308m, 243w.

By comparison of spectra, it was observed that correlations of structure and I.R. spectra did exist in certain cases Characteristic frequencies of the π-C_5H_5, acac and hfac moieties appeared in most compounds containing these groups. Metal-chlorine stretching frequencies appeared in the range 300 - 350 cm^{-1} i.e. 314 cm^{-1} $Zr(acac)_3Cl$, 336 cm^{-1} $Zr(acac)_2Cl_2$ (96). 335 cm^{-1} π-$C_5H_5ZrCl_2$, 308 cm^{-1}? π-$C_5H_5ZrCl_2$ and possibly 308, 330 cm^{-1} for π-$C_5H_5Zr(bzac)_2Cl$ and 315, 331 cm^{-1} for π-$C_5H_5Zr(acac)_2Cl$. Titanium - chlorine frequencies appeared to be at higher wave number than the zirconium-chlorine fequencies. Metal - oxygen vibrations have been assigned from 260 - 440 cm^{-1} in chelate compounds of zirconium (96). In the compounds investigated many I.R. bands were observed in this region.

CHAPTER X.

Exchange Rates.

The results of Gutowsky and Holm(44) for moderate exchange rates between two environments of equal population have been described in the following form:-

$$1/\tau = \pi\sqrt{2}\,\{(\nu_A{}^0 - \nu_B{}^0)^2 - (\nu_A - \nu_B)^2\}^{1/2}$$

where $\tau = \tau_A\ (= \tau_B)\ /2$, $\nu_A{}^0 - \nu_B{}^0$ = separation in cps between A and B sites for large τ, $\nu_A - \nu_B$ = separation in cps between A and B sites.

Application of this relation and the relations described earlier (p.8,9) to the environmental averaging of the equatorial CF_3 groups in π-$C_5H_5Zr(hfac)_3$ and π-$CH_3C_5H_4Zr(hfac)_3$ was complicated by several factors.

1. The methanol-filled capillary produced some broadening of resonances due to extra inhomogeneity in the magnetic field.
2. The resonances did not have equal T_2 values.
3. The Gutowsky-Holm relation (above) was valid only in conditions of minimum overlap of components. The small separation of the resonances would only allow this relation to be used over a small temperature range.
4. Considerable overlap of 'inner' and 'outer' spectral components during the coalescence of 'inner' (major) components.
5. Investigation of the ^{19}F nmr spectra of π-$C_5H_5Zr(hfac)_3$, π-$CH_3C_5H_4Zr(hfac)_3$ and π-$C_5H_5Hf(hfac)_3$ over the temperature range -80^0 to $+80^0$ indicated a temperature-dependent

behaviour of 'inner' and 'outer' components. The outer or minor intensity components expanded for all three compounds by about 0.1 cps per degree, while the inner or major intensity components expanded in the region of observation by about 0.03 cps per degree.(Figs.39,40).

The region of coalescence was not used for the determination of rate constants. Instead, the regions of slow and rapid exchange were used, employing an extrapolated value of $(\omega_A - \omega_B)$ for a particular temperature. Measurements of spectra were made at 2^0 temperature differences in these regions and a plot of $\log_{10}k$ (= $1/\tau_A$) against $1/T^0K$ gave activation energies for the selective exchange process. These values were 16.0±2.0 Kcals. mole^{-1} for the π-C_5H_5 compound and 15.5± 2.0 Kcals. mole^{-1} for the π-$CH_3C_5H_4$ compound. These values compare favourably with that reported by Pinnavaia (<u>100</u>) for π-$C_5H_5Zr(hfac)_3$ (a value of 15.8± 0.5 Kcals . mole^{-1} was reported). These activation energies are slightly higher than those reported for the octahedral $(acac)_2TiX_2$ compounds , where X = F,Cl,Br. (<u>24</u>).

The determination of activation energies for other processes appeared possible for other compounds such as π-$C_5H_5Zr(acac)_2Cl$ and π-$C_5H_5Ti(hfac)_2Cl$. In these cases, analysis of the methyl or trifluoromethyl coalescences was of too complex a nature for treatment, while the small separation of methine resonances precluded treatment.

A comparison of rate constants was possible using coalescence temperatures to provide a good estimate of k.

Figure 39.

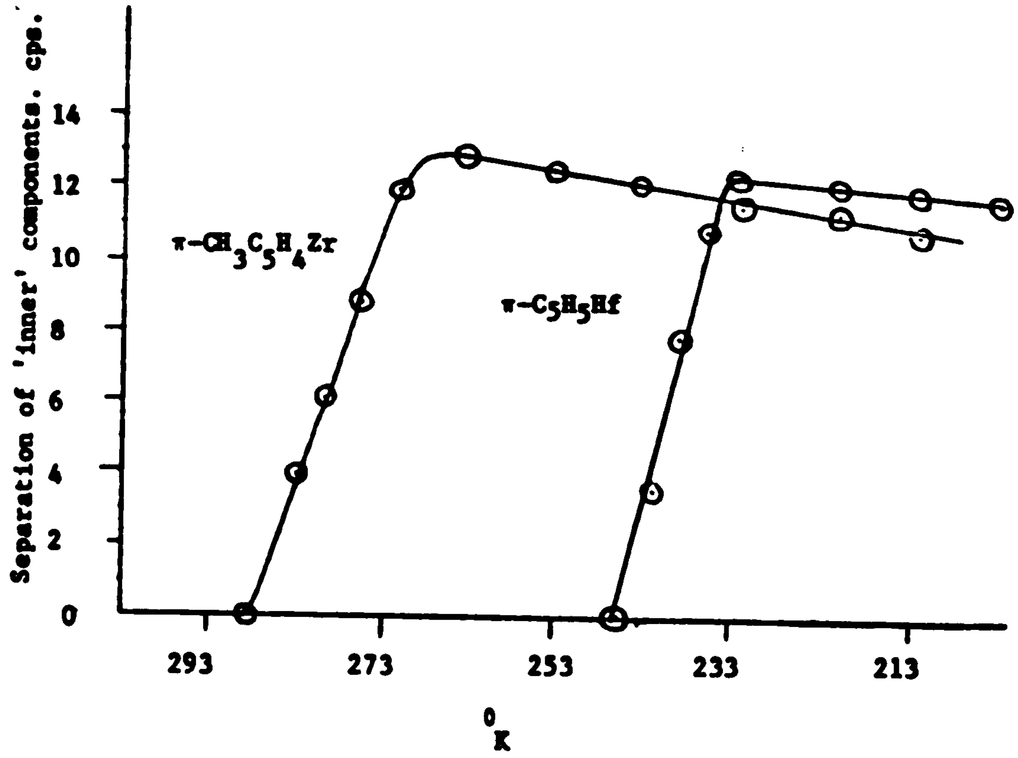
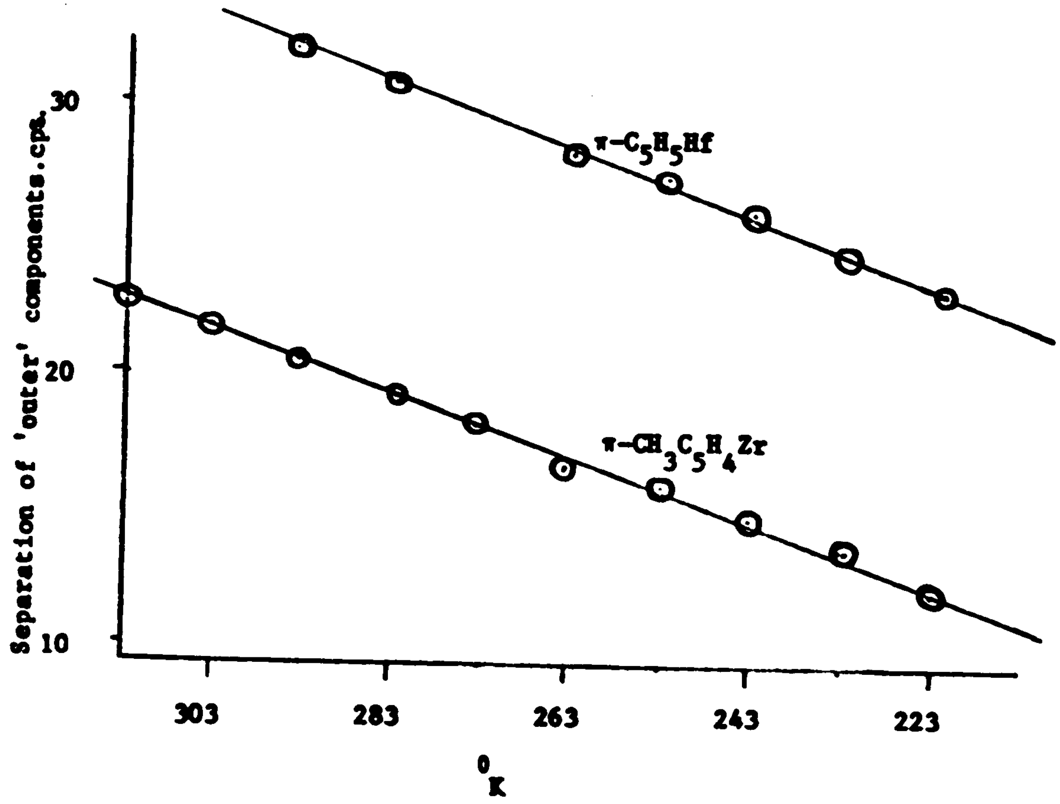

Separation of 'inner' components. cps.
14
12
10
8
6
4
2
0
293
273
253
233
213
0K
π-$CH_3C_5H_4Zr$
π-C_5H_5Hf

Figure 40.


Separation of 'outer' components.cps.
30
20
10
303
283
263
243
223
^{0}K
π-C_5H_5Hf
π-$CH_3C_5H_4Zr$

At coalescence $\nu_A - \nu_B = 0$

and $$k = \frac{\sqrt{2}\pi}{2}(\nu^0_A - \nu^0_B)$$

For the π-$C_5H_5Zr(hfac)_3$ system at 258 ± 2^0K, $\nu^0_A - \nu^0_B$(extrapolated)= 13.1 cps giving k = 29.1 sec^{-1}.

For the π-$C_5H_5Hf(hfac)_3$ system at 243 ± 2^0K, $\nu^0_A - \nu^0_B$(extrapolated)= 13.5 cps giving k = 30.0 sec^{-1}.

For the π-$CH_3C_5H_4Zr(hfac)_3$ system at 279 ± 2^0K, $\nu^0_A - \nu^0_B$(extrapolated) = 15.5 cps giving k = 34.4 sec^{-1}.

Using these figures and assuming an Arrhenius relationship with an activation energy of 16 Kcal. $mole^{-1}$, it was possible to extrapolate the rate constants to 260^0K giving the following ordering

	π-$C_5H_5Hf(hfac)_3$	>	π-$C_5H_5Zr(hfac)_3$	>	π-$CH_3C_5H_4Zr(hfac)_3$
k ($sec.^{-1}$)	2.8×10^2	>	3.7×10^1	>	3.7

This ordering for environmental exchange of equatorial CF_3 groups in the tris hfac system has already been inferred from qualitative comparison of spectra. This is clearly shown by Figs. 17 and 19.

At 90^0 the exchange of equatorial and axial chelates of π-$C_5H_5Zr(hfac)_3$ occurred at a rate of about 5 sec^{-1}. The extrapolated rate constant for equatorial exchange only was in the order of

10^4 sec^{-1} at 90^0. This demonstrated the different time scales of each exchange, again previously noted by qualitative spectral comparison.

The exchange of equatorial chelates in π-$C_5H_5Zr(tfac)_3$ was estimated as 10 sec^{-1} at -60^0 while the that for π-$CH_3C_5H_4Zr(tfac)_3$ was estimated as 10 sec^{-1} at -50^0. The exchange of equatorial and axial chelates, as estimated from the coalescence of the π-C_5H_5 resonances was slower than $k = 11$ sec^{-1} at 60^0, again demonstrating the very different time scales of equatorial and equatorial-axial exchange.

Equatorial chelate exchange in π-$C_5H_5Zr(bztfac)_3$ was in the order of 5 sec^{-1} at -20^0, while at 100^0 this rate corresponded to that of equatorial-axial chelate exchange. Both of these estimations were obtained from inspection of the π-C_5H_5 region.

The rate of intramolecular averaging of chelate environments in π-$C_5H_5Ti(hfac)_2Cl$ was estimated as about 2 sec^{-1} at 0^0. A similar rate was obtained for π-$C_5H_5Zr(acac)_2Cl$ at $+60^0$. These rates were calculated, in each case, from the coalescence of the methine proton doublet.

Exchange with free ligand has been shown to occur slowly in comparison with intramolecular exchange. The ^{19}F peak width at half height for Hhfac measured in the absence of exchange was 0.8 - 1.0 cps, while the corresponding width at elevated temperature in the presence of exchange was never more than 1.2 cps. Using the slow exchange approximation (97), it could be shown that the maximum rate constant, observable with this data,was in the order of 0.5 sec^{-1}.

This value, the upper limit of intermolecular exchange with free ligand, was much slower than most rates for environmental averaging at much lower temperatures. The difference between the rates of unselective chelate exchange in π-$C_5H_5Zr(hfac)_3$ and intermolecular exchange with free ligand at the same temperature was at least a factor of ten.

CHAPTER XI.

Conclusions.

The present study has revealed several interesting aspects of the chelate chemistry of Ti(IV) and Zr(IV).

The first case of selective exchange of chelate environments was detected for the compound $\pi\text{-}C_5H_5Zr(hfac)_3$ and correlated with relative bond distances derived from a structural study. Similar exchanges were found for the $\pi\text{-}C_5H_5Hf(hfac)_3$ and $\pi\text{-}CH_3C_5H_4Zr(hfac)_3$ compounds. Both selective and non-selective exchanges were found in the above compounds and in the compounds containing asymmetric chelates i.e., $\pi\text{-}RC_5H_4Zr(chelate)_3$. R = H, CH_3., chelate = tfac, bztfac.

An nmr study of the mixed chelate compounds $\pi\text{-}C_5H_5ZrL_nL'_{3-n}$, where L = hfac, bztfac., L' = tfac, indicated that these mixed complexes were favoured over the pure tfac or hfac complexes.

The rates of intramolecular selective and non-selective exchange were, for a particular tris chelate , in the order

$$\pi\text{-}C_5H_5Hf > \pi\text{-}C_5H_5Zr > \pi\text{-}CH_3C_5H_4Zr$$

and for a particular π-system at a given temperature.

$$\text{tfac} > \text{hfac} \approx \text{bztfac}$$

The observed differences could be due to steric effects in the transition state, different metal-oxygen bond distances and different electronic properties of the chelate substituents.

The study of π-cyclopentadienyl chelate compounds of Ti(IV) e.g. π-$C_5H_5Ti(hfac)_2Cl$, indicated the possibility of the existence of isomers in solution. The existence of only two isomers was rationalized using a dodecahedral model for the coordination polyhedron, with the π-C_5H_5 ring visualized as occupying three coordination sites. Two isomers were also detected in the low temperature ^{19}F and ambient temperature ^1H nmr spectra of the related compounds π-$CH_3C_5H_4Ti(hfac)_2Cl$ and π-$C_5(CH_3)_5Ti(hfac)_2Cl$.

The exchange of chelate environments by an intramolecular, apparently unselective,exchange process was demonstrated for these Ti(IV) compounds. The exchange rates at a given temperature were in the order:-

$$\pi\text{-}C_5H_5 \quad > \quad \pi\text{-}CH_3C_5H_4 \quad > \quad \pi\text{-}C_5(CH_3)_5$$

for the $Ti(hfac)_2Cl$ system.

The study of the chelate compounds of Zr(IV) indicated that for symmetric chelates only one solution isomer existed in solution. Compounds with asymmetric chelates were found to exist in solution as a mixture of four forms due to the two possible orientations of the two chelate rings. Examination of the compounds containing fluorinated chelates indicated a preferred orientation of the chelate with a CF_3 group proximate to one A site of the dodecahedron, a position 'trans' to the π-C_5H_5 ring.

Mixed chelate compounds e.g., π-$C_5H_5Zr(acac)(tfac)Cl$, prepared by *in situ* reaction in an nmr tube, further demonstrated this preference. The CF_3 preferences were found to be additive, the prediction of the ^{19}F nmr spectrum of the four form mixture of π-$C_5H_5Zr(tfac)_2Cl$ was possible from consideration of the spectra of the related compounds π-$C_5H_5Zr(acac)(tfac)Cl$ and π-$C_5H_5Zr(acac)(hfac)Cl$.

The recent structural study of π-$C_5H_5Ti(quinoline)_2Cl$ (98) indicated that Ti–O bonds were shorter than Zr–O bonds, a fact which may explain the formation of different compounds in the π-C_5H_5Ti and π-C_5H_5Zr systems.

The structural characteristics of dodecahedral coordination as examined may be applied with some success to other systems containing the π-cyclopentadienyl group. One of the first π-C_5H_5 compounds to be structurally examined was $(\pi\text{-}C_5H_5)_2TiCl_2$ (2) ; this compound has been regarded as pseudo-tetrahedral. The application of the arguments for dodecahedral coordination for this formally eight coordinate compound indicated that the π-C_5H_5 rings occupy equivalent AAB faces while the two Cl ligands occupy the remaining two B sites.

Comparison of the hard-sphere model of the dodecahedron with the pseudo-tetrahedral arrangement on the basis of the interplanar angle between the π-C_5H_5 rings gave the following results:-

Pseudo-tetrahedral $\approx 71^0$ $(180^0 - 109^0)$

Dodecahedral $\approx 36^0$

The above values may be compared with the values determined for $(\pi\text{-}C_5H_5)_2TiCl_2$, (59^0) (2), and $(\pi\text{-}C_5H_5)_2ZrCl_2$, (46 ± 5^0) (99).

Study of the exchange of chelate environments was effective in the elimination of certain mechanisms. There remain, however, several alternatives which cannot be distinguished by the nmr technique. A very recent paper by Howe and Pinnavaia (<u>100</u>) reports activation energies for π-$C_5H_5Zr(hfac)_3$ and a superficial study of π-$C_5H_5Zr(tfac)_3$. The results and conclusions bear close resemblance to the results cited in this work for the tris chelate systems.

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VITA.

PERSONAL.

Name:- John Gerald Evans.

Date of Birth:- 17 October 1944.

Place of Birth:- Watford, Herts. U.K.

Nationality:- Citizen of the U.K., Canadian Landed Immigrant.

Marital Status:- Married.

EDUCATIONAL.

Institutions attended:-Watford Technical High School. Watford, Herts., U.K. 10 G.C.E. 'O' levels, 3 G.C.E. 'A' levels.

University of Bristol. U.K. B.Sc. Special Honours Chemistry. Class 2, Division 2. 1963-1966. M.Sc. in Advanced Instrumentation in Analytical Chemistry. 1967.

University of Alberta. Edmonton. Canada. Proposed Ph.D. 1971.

THESES and PUBLICATIONS.

B.Sc. Some Stereochemical Studies of Platinum and Palladium Complexes. M.Sc. Metal Additives in Gas Chromatography. Ph.D. π-cyclopentadienyl Compounds of Titanium and Zirconium Containing Chelated β-diketones.

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AWARDS.

County Grant. U.K. 1963-1966. U.K.Science Research Council Studentship. 1966-1967. Teaching Assistantship. U.of A. 1967-1969, 1970-1971. National Research Council of Canada Bursary. 1969-1970.