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NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF METAL CYCLOPENTADIENYLS

VII*. A CRITERION FOR DISTINGUISHING THE π- AND σ-STRUCTURES BASED ON AN ANALYSIS OF ^{13}C–H SATELLITES IN THE PMR SPECTRA

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SUMMARY

The ^{13}C–H satellite magnetic resonance spectrum of cyclopentadienyltrimethyltin has been obtained. Its analysis enables the two J(H–H) coupling constants J^1 and J^2 to be determined. If it is assumed that this molecule is fluxional, these two experimentally measured constants may be averaged over six independent constants in a rigid AA'BB'X(C_5H_5) system. By taking four coupling constants, averaged from the literature data, it is possible to estimate the two most important constants J(AX) and J(BX). On the other hand, comparing the values J^1 and J^2 for the compound $C_5H_5Sn(CH_3)_3$ with the respective values for other fluxional σ-cyclopentadienyls, taking averaged values of the appropriate couplings in rigid systems together with the values of J^1 and J^2 in π-complexes, it is possible to choose a criterion for distinguishing between π- and σ-structures. Other criteria (^{1}H and ^{13}C chemical shifts, H–^{13}C, M–H coupling constants where M is magnetic isotope of a metal) are discussed.

The first problem in studying the metal cyclopentadienyls is a definition of the structural types involved. In general, a complete classification which accounts for all the structural parameters and molecular symmetry is rather complicated. If the local symmetry of a particular C_5H_5–M fragment is taken into account it is possible to separate two sufficiently general classes: (I) that of C_{5v} symmetry which corresponds to equivalent bonds in the planar C_5H_5 ring with equal metal–carbon separations, and (II) that of C_{2v} symmetry (or of lower symmetry, for example, C_s^1) with non-equivalent bonds in the ring and with the metal atom located in the vicinity of one carbon atom. In Cotton's terminology[2] compounds of the first type are called *pentahapto*-cyclopentadienyls, while those of the second type are known as *monohapto*-cyclopentadienyls. With such a rough classification it is not always possible to make a sufficiently unequivocal assignment. In particular compounds exist with almost equivalent C–C and C–M bonds [for example $(C_5H_5)_3MoNo^3$], *i.e.* those having "almost C_{5v} symmetry" or "almost π-structure". Following Fritz's classification[4]

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* For Part VI see ref. 14.

the first group should extend to the ionic cyclopentadienides having sharply different properties, and to the central σ-bonded compounds and various π-complexes. Compounds of the second class have properties which are more in common in view of the C_5H_5–M bond. Thus the rough assignment of a C_5H_5–M fragment to a particular symmetry species may be a useful means of classification since it enables compounds of type (II) to be separated from all other complexes. In the following discussion we shall use the traditional term σ-structure for such compounds and the term π-structure for compounds of type (I)*.

Only the diffraction methods (X-ray, electrono- and neutronography) provide absolute criteria for π- or σ-assignments, but their use is limited by the complicated analysis of the respective reflections which they imply and by the difficulty of obtaining single crystals of sufficient size and purity. Thus other methods involving some secondary criteria based on a systematic study of authentically established compounds (*i.e.* established by diffraction methods) are usually more helpful and more widely used. Among such methods IR and NMR techniques have been extensively employed. It should be noted however that some uncertainty which arises in the complete analysis of the C_5H_5 modes, prevents the use of IR methods for unequivocally establishing structural assignments, and only very recently has some interest been shown in the application of IR methods for establishing the structures of mercury [5] and copper[6] cyclopentadienyl derivatives.

The pioneering work of Piper and Wilkinson[7] (see also refs. 8 and 9) has stimulated the intensive NMR study of the metal cyclopentadienyl derivatives. Together with the elucidation of molecular structures, nuclear magnetic resonance spectra also enable the rates of dynamic processes occurring in some C_5H_5 metal derivatives to be determined[7,10]. This property is associated with the life-time of the structural states (τ_l) of these compounds which under certain conditions may be compared to the NMR characteristic time (τ_{NMR}). As a result of dynamic processes the PMR spectrum of the five protons of a σ-bonded C_5H_5 ring should be treated as the AA'BB'X** (monosubstituted ring) spectrum of a stereochemically rigid molecule which transforms to the A_5 spectrum when fast migration occurs ($\tau_l \ll \tau_{NMR}$) and is not different from the respective spectrum of a π-bonded ring. Unfortunately with some σ-bonded C_5H_5 compounds, in spite of the possibility of changing τ_{NMR} (frequency variation, use of the ^{13}C NMR spectroscopy[11,***]) and τ_l (temperature variation), low migration rates cannot be attained. Strictly speaking in such cases other methods having shorter characteristic times, for example IR spectroscopy, should be used, and, in fact, in this way the σ-structure of mercury cyclopentadienyl derivatives has been proved[5].

In the analysis of the A_5 NMR spectra of the relevant π- and σ-structures with fast migration, values of the chemical shifts of H and ^{13}C and of the ^{13}C–H and M–H coupling constants (M is metal magnetic isotope) could also be used as criteria of structural type. Unfortunately such an analysis has not to date been described, and

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* Use of the special terms *monohapto* and *pentaphapto* is also quite reasonable as they avoid a misleading situation which may arise when the terms π- and σ-structures are used in conjunction with the quantum-mechanical models. Separation into π- and σ-electronic functions is correct only for C_5H_5 anion. In all other cases bonding occurs via both the π- and σ-electrons.

** Classification of the C_5H_5 ring proton spectra is given in ref. 1.

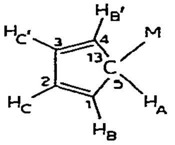
*** On the average $\tau_{NMR}(^{13}C)/\tau_{NMR}(H) \simeq 10^{-2}$ at the fast exchange limit.

in the present study an attempt is made to present such an analysis.

Recently Crecely, Crecely and Goldstein[12] have carried out a theoretical calculation of the ^{13}C–H satellite PMR spectra of ferrocene and cobalticene chloride which has enabled the determination of the coupling constants of the ring protons. An analysis of the ^{13}C–H satellite PMR spectrum of $C_5H_5Sn(CH_3)_3$ is given in this paper and the problem of using the coupling constants J(H–H) for distinguishing the type of bonding is discussed.

ANALYSIS OF THE ^{13}C–H SATELLITE SPECTRA

In the general case when fast exchange occurs the ^{13}C–H satellite spectra of ring protons of the σ-cyclopentadienyl–metal derivatives should be treated as an ABB′CC′X system where X is the magnetic carbon isotope (interaction with magnetic metal isotopes not being taken into account).



When fast rates of metallotropic rearrangement occur, the spectrum shows only two mean values for the spin–spin coupling constants of ring protons: *vicinal* J^1 (H–H) and *diagonal* J^2 (H–H) defined by eqns. (1) and (2) which are valid for a degenerate rearrangement:

$$J^1(\text{H–H}) = \tfrac{1}{5}(J_{12}+J_{23}+J_{34}+J_{45}+J_{15}) \tag{1}$$
$$J^2(\text{H–H}) = \tfrac{1}{5}(J_{13}+J_{14}+J_{24}+J_{25}+J_{35}) \tag{2}$$

From a formal point of view an analysis of the ^{13}C–H satellite spectrum of a σ-cyclopentadienyl compound should not be different from that for the respective spectrum of a π-cyclopentadienyl compound which also exhibits two different spin–spin coupling constants for ring protons. As indicated above, a study of the ^{13}C–H satellites for the π-bonded C_5H_5 metal derivatives (ferrocene, ruthenocene, cobalticene chloride) has been carried out and has been discussed in ref. 12. Theoretical calculations of the ABB′CC′X spectrum taking into account eight parameters [the relative chemical shifts due to the isotopic effect and the J^1(H–H), J^2(H–H), $J(^{13}$C–C–H) and $J(^{13}$C–C–C–H) coupling constants] led to the following spin–spin coupling constants for the ring protons of ferrocene and cobalticene chloride: J^1(H–H) = 2.40, J^2(H–H) = 1.24, J^1(H–H) = 2.58 and J^2(H–H) = 1.46 Hz.

In an attempt to compare these values of J(H–H) with those averaged by the fast exchange occurring in σ-cyclopentadienyl compounds an investigation was made of the ^{13}C–H satellites in the respective silicon, germanium and tin compounds*.

We have been unsuccessful in attempting such an analysis for compounds of Si and Ge since quite high rates for their degenerate rearrangement are observed far above their boiling points. In such a study a narrow resonance signal of the C_5H_5

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* Metallotropic rearrangement in such compounds has been studied and reported in refs. 13 and 14.

group ($\simeq$ 0.3 Hz) should have occurred in the spectra of $C_5H_5Si(CH_3)_3$ and $C_5H_5Ge(CH_3)_3$ at temperatures close to 200°, while the compound $C_5H_5Sn(CH_3)_3$ should have been capable of study at lower temperatures due to its fast metallotropic rearrangement at room temperature.

In order to calculate the ^{13}C–H satellite spectra of the ring protons in cyclopentadienyltrimethyltin it has been necessary to use a simplified model which accounts for the complete six-spin ABB'CC'X spectrum ($X \equiv {}^{13}C$) as an imposition of two AMM'-NN' sub-spectra corresponding to the low- and high-field satellites. Such an approach involving a lowering of the order of the system in the analysis of ^{13}C–H satellites could be used in this case due to the large directly-bonded ^{13}C–H couplings. A similar approach has been successfully used for determining the H–H coupling constants for example in ethylene[15]. The chemical shifts in each sub-spectrum are defined by values of both $\frac{1}{2}J(^{13}C\text{–}H)$ and the ^{13}C isotopic effect (Table 1). Thus, the asymmetry of the spectrum is caused by an isotopic shift.

TABLE 1

THE CHEMICAL SHIFTS IN THE ^{13}C–H SATELLITE SPECTRUM OF THE C_5H_5 GROUP

Spin ^{13}C	Nucleus A	Nucleus M	Nucleus N
$+\frac{1}{2}$	$+\frac{1}{2}J(^{13}C\text{–}H)+\delta^{A}_{isot}$	$+\frac{1}{2}J(^{13}C\text{–}C\text{–}H)+\delta^{M}_{isot}$	$+\frac{1}{2}J(^{13}C\text{–}C\text{–}C\text{–}H)+\delta^{N}_{isot}$
$-\frac{1}{2}$	$-\frac{1}{2}J(^{13}C\text{–}H)+\delta^{A}_{isot}$	$-\frac{1}{2}J(^{13}C\text{–}C\text{–}H)+\delta^{M}_{isot}$	$-\frac{1}{2}J(^{13}C\text{–}C\text{–}C\text{–}H)+\delta^{N}_{isot}$

In examining the possibility of applying such an approach to the molecules under study and for testing the experimental technique, the ^{13}C–H satellites of ferrocene have been measured experimentally and calculated using the data given in ref. 12*. Fig. 1. shows the experimental and calculated 100 MHz spectra of an outer high-field satellite of the ferrocene molecule. The line width in the theoretical spectrum was taken as 0.17 Hz. As seen from Fig. 1, the spectra are virtually identical to those measured at 60 MHz (see ref. 12) due to the weak isotopic effect on the spectral pattern of outer satellites.

In the case of cyclopentadienyltrimethyltin the following values of the isotopic shift of ferrocene[12] were used (converted to 100 MHz): $\delta^{A}_{isot}=0.234$ Hz, $\delta^{M}_{isot}=0.167$ Hz and $\delta^{N}_{isot}=0.133$ Hz. The directly-bonded ^{13}C–H coupling was obtained experimentally from the centres of gravity of the satellites, leaving the constants J^1(H–H), J^2(H–H) and $J(^{13}C\text{–}C\text{–}H)$, $J(^{13}C\text{–}C\text{–}C\text{–}H)$ undetermined. The sum of the constants (J^1+J^2) may be measured with high accuracy ($\pm$0.03 Hz) for the five-spin AMM'NN' system (in our notation) provided that the conditions $J_{MN'}=J_{M'N}$, $J_{AN'}=J_{AN}$, $J_{AM}=J_{AM'}$ and

TABLE 2

THE COUPLING CONSTANTS IN $C_5H_5Sn(CH_3)_3$ (C_5H_5 GROUP)

J^1(H–H)	J^2(H–H)	$J(^{13}C\text{–}C\text{–}C\text{–}H)$	$J(^{13}C\text{–}C\text{–}H)$	$J(^{13}C\text{–}H)$
2.86±0.03	0.97±0.03	8.05±0.06	4.95±0.06	161.3±0.15

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* The spectra were calculated on an M-20 computer using the YaMR-1 program.

$J_{MN}=J_{M'N'}$[16] are satisfied, the separation of the terminal intensive lines in the spectrum of the outer satellite (nucleus A) being equal to the double sum of the constants J^1(H–H)$+J^2$(H–H). This is confirmed by the calculation of an outer ^{13}C–H satellite of ferrocene. Since the directly-bonded coupling is high [$J(^{13}\text{C–H}) \gg J(^{13}\text{C–C–H})$, $J(^{13}\text{C–C–C–H})$, J^1(H–H), J^2(H–H)] the outer satellite spectrum was investigated by varying two parameters *i.e.* the relative chemical shift of the nuclei N and M and the value of the constant J^1(H–H). The values of $J(^{13}\text{C–C–H})$ and $J(^{13}\text{C–C–C–H})$ were found from an analysis of the spectrum of the internal satellites. The results of the analysis of the spectrum of the ^{13}C–H satellites of the ring protons in cyclopentadienyltrimethyltin are presented in Table 2. All the values are given in Hz.

By way of illustration, Figs. 2 and 3 show the experimental and calculated spectra of the outer (high-field) and inner ^{13}C–H satellites in $C_5H_5Sn(CH_3)_3$. In the calculated spectrum the line width was found to be equal to 0.34 Hz.

DISCUSSION

The NMR parameters of some organo-element cyclopentadiene derivatives (data on the C_5H_5–M fragment) are given in Table 3, where the first part of the Table lists "authentic" π-structures. The term "authentic" is used in the sense that the structural type has been confirmed by diffractional methods. Such structures are characterised by a singlet in their PMR spectra [compounds (I)–(X)] and by a ring carbons equivalence in the ^{13}C NMR spectra [compounds (II), (V), (VI)] over a wide temperature range. Compounds with "authentic" σ-structures [compounds (XI)–(XV)] exhibit quite a number of σ-features in their NMR spectra over the same temperature range, *e.g.*, an AA'BB'X type of spectrum for compounds (XI)–(XIV) and singlet broadening for compound (XV). On the other hand, A_5 spectra are very difficult to obtain for some "authentic" σ-structures because of the necessity of working at high temperatures, *i.e.* under conditions which may lead to the occurrence of additional processes [for example, dimerization of compounds (XI) and (XII)]. In such cases the parameters obtained should be presented as the mean values found from relations similar to (1) and (2):

$$\langle \delta\text{H} \rangle = \tfrac{1}{5}[\delta_5+2\delta_1+2\delta_2]\,, \tag{3}$$
$$\langle \delta\text{C} \rangle = \tfrac{1}{5}[\delta\text{C}_5+2\delta\text{C}_1+2\delta\text{C}_2]\,,$$
$$\langle J(^{13}\text{C–H}) \rangle = \tfrac{1}{5}[J(^{13}\text{C–H}_5)+2J(^{13}\text{C–H}_1)+2J(^{13}\text{C–H}_2)]\,, \tag{5}$$
$$\langle J(\text{M–H}) \rangle = \tfrac{1}{5}[J(\text{M–H}_5)+2J(\text{M–H}_1)+2J(\text{M–H}_2)]\,. \tag{6}$$

The class of "unknown structures" includes compounds for which data from structural studies have not been obtained. Among them a σ-structure of $C_5H_5Sn(CH_3)_3$ has been confirmed unequivocally using PMR spectroscopy[14] (an AA'BB'X spectrum being observed at −150° and by ^{13}C–{^{1}H} NMR techniques (essentially singlet broadening at −50°))*,**. The data of West *et al.*[19] as well as the results of an IR study[5] leave no doubt that C_5H_5HgCl and $(C_5H_5)_2Hg$ also possess σ-structures.

The data of Table 3 indicate that in the majority of cases π- and σ-structures are characterised by different values of δH (π-structure from 4.0 to 5.2, σ-structure

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* While this work was being completed, such a conclusion was confirmed from a complete electronographic study[18].

** The ^{13}C NMR data of σ-C_5H_5 compounds will be reported in a future paper.

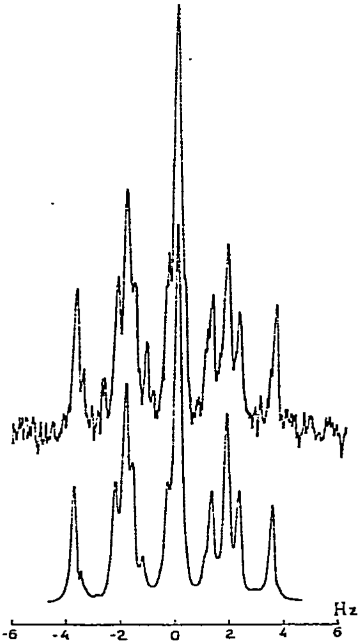
(*continued on* p. 112)

TABLE 3

THE C_5H_5—M NMR PARAMETERS OF THE ORGANOMETALLIC CYCLOPENTADIENYL DERIVATIVES[a]

Nos.	Compounds	Proton chemical shifts (ppm)[b]	Carbon chemical shifs[c] (ppm)	$J(^{13}C-H)$ (Hz)	$J(M-H)$ (Hz)	Ref.
π Compounds						
(I)	$C_5H_5Mn(CO)_3$	$4.65^d(CS_2)$	118^d	175^d		25
(II)	$(C_5H_5)_2Fe$	$4.14^e(CDCl_3)$	123.6^d	174.8^f		26
(III)	π-$C_5H_5Fe(CO)_2$-σ-C_5H_5	$4.40^g(CS_2)$	106.7 ± 0.3^h	180.8 ± 0.5^h		27
(IV)	$[\pi$-$C_5H_5Fe(CO)_2]_2Sn(C_5H_5)_2$	$4.78^h(CS_2)$		178.5 ± 1^h	$5.1^{v,h}$	28
(V)	$C_5H_5Mo(CO)_3C_2H_5$	$5.2^d(CS_2)$	101.1^d	175^d		29
(VI)	$(C_5H_5)_2Ru$	$4.55^e(CDCl_3)$		176.3^f		30
(VII)	C_5H_5Tl	$4.8^i(THF)$			^{j}	31
(VIII)	$(C_5H_5)_2Sn$	5.8^k			$15.5/16.3^k$	32
(IX)	$(C_5H_5)_2TiCl_2$	$6.56^h(THF)$				33
(X)	$(C_1H_5)_2Pb$	$5.77^l(C_6H_6)$			^{j}	32
σ-Compounds						
(XI)	C_5H_6	$5.63^{m,n}$(neat)	$78.9^{m,o}$	$159^{m,o}$		34
(XII)	$C_5H_5Si(CH_3)_3$	$5.87^p(+130°$ neat)	$77.0^{m,o}$			35
(XIII)	$C_5H_5Ge(CH_3)_3$	$5.87^p(+90°$ neat)	$76.1 \pm 0{,}3^{q,h}$	161 ± 1^h		36
(XIV)	$\sigma-C_5H_5Fe(CO)_2$-π-C_5H_5	$5.70^g(+30°, CS_2)$	80.7 ± 0.3^h	161.2 ± 0.6^h		27
(XV)	$(\sigma$-$C_5H_5)_2Sn[Fe(CO)_2C_5H_5]_2$	$6.12^h(+30°, CS_2)$		161 ± 1^h	$13.6/14.2^h$	28
"Unknown" compounds						
(XVI)	$C_5H_5Sn(CH_3)_3$	$5.94^p(+30°, CS_2)$	79.5°	161.3^h	$21.8/22.9^h$	
(XVII)	C_5H_5HgCl	$6.12^r(+22°, THF)$			116^s	
(XVIII)	$(C_5H_5)_2Hg$	$5.95^r(+25°, THF)$		160^s	66.7^s	
(XIX)	$(C_5H_5)_2Cd$	$5.56^t(+30°, C_5D_5N)$				
(XX)	$C_5H_5AuP(C_6H_5)_3$	$6.3^u(+30°, CDCl_3)$				

[a] Principles used in the construction of this Table are described in the text. [b] Measured in δ scale. *c* Measured with respect to CS_2. [d] Ref. 20. [e] Ref. 37. [f] Ref. 12. [g] Ref. 27. [h] This work. [i] Ref. 38. [j] Coupling constants not found. [k] Ref. 39. [l] Ref. 40. [m] Parameters averaged using formulae (3)–(6). [n] Ref. 17. [o] Ref. 11. [p] Ref. 13. [q] At 125°. [r] Ref. 19. [s] Ref. 41. [t] Ref. 42., 19(1969)189. [u] Ref. 43. [v] Constant $J(Sn-Fe-C_5H_5)$.



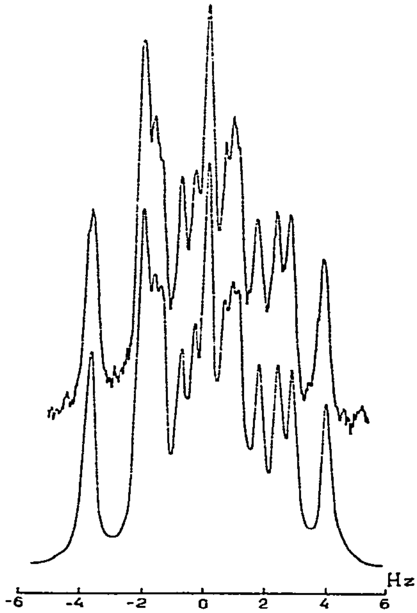


Fig. 1. The experimental and calculated PMR spectra (100 MHz) of the upfield outer ^{13}C–H satellite of ferrocene. The line width of calculated spectrum was taken as 0.17 Hz.

Fig. 2. The experimental and calculated spectra of the upfield ^{13}C–H satellite of C_5H_5 protons in $C_5H_5Sn(CH_3)_3$. The line width of calculated spectrum was taken as 0.34 Hz.

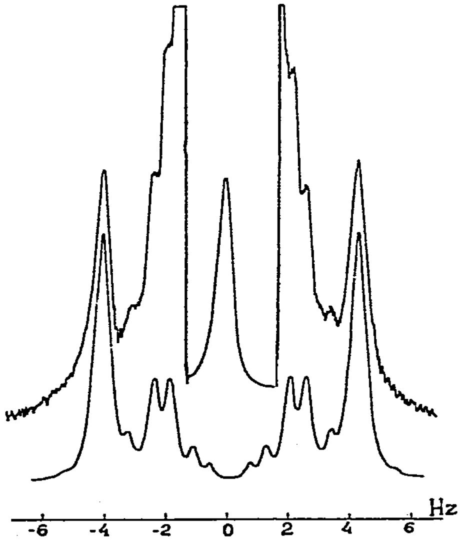


Fig. 3. The experimental and calculated spectra of the inner ^{13}C–H satellites of C_5H_5 protons of $C_5H_5Sn(CH_3)_3$. The line width of calculated spectrum was taken as 0.34 Hz.

from 5.7 to 6.2 ppm) and δC (π-structure from 101 to 123, σ-structure from 76 to 80 ppm). An exception is provided by the compounds (VIII)–(X) which are "bent sandwich" compounds but with chemical shifts typical of σ-structures. Such compounds differ markedly from typical π-complexes in chemical properties and thus the apparent difference between their δH values is not entirely accidental*.

From the data of Table 3, the value of δH is influenced both by the metal and by its substituent nature in both π- and σ-structures. Introduction of electronegative substituents at the metal atom (halogen, carbonyl) results in a down-field shift as may be seen from the data on silicon[17], mercury[19], titanium[7,9] and iron (see also Table 3). A dependence of δH upon the solvent has also been observed[9]. All the above data lead to the conclusion that the parameter δH cannot be used as an unequivocal criterion for determining the type of structure involved. Thus it is not possible from the above data to draw conclusions regarding the structures of the C_5H_5 derivatives of Cd and Au**.

As indicated earlier[11] the values of $J(^{13}C{-}H)$ are different for π- and σ-structures. This may be clearly seen in the spectrum of π-$C_5H_5Fe(CO)_2$-σ-C_5H_5 in which the π- and σ-ligands are bonded to the same metal atom. The values of $J(^{13}C{-}H)$ change from 175 (Table 3, ref. 20) to 185 Hz ($[Co(C_5H_5)_2]^+Cl^-$ ref. 12) for all π-structures. σ-Structures are characterised by $J(^{13}C{-}H)$ values close to or equal to 161 ±1 Hz. This enables the constant $J(^{13}C{-}H)$ to be used as a criterion for the determination of structure. As an example, the structure of $(C_5H_5)_2Hg$ may be designated as of the σ-type by the observation that $J(^{13}C{-}H)$ is equal to 160 Hz.

Experimental data on the spin–spin coupling constants for the cyclopentadienyl ring protons and magnetic metal isotopes are too sparse to allow any reliable conclusions to be drawn. Thus, the absence of the $J(^{205}Tl{-}H)$ constant for C_5H_5Tl might possibly suggest that all π-structures have no M–H coupling. Similar data characterize derivatives of $(C_5H_5)_2Pb$***. The $J(Sn{-}H)$**** constant has however been found in the analogous Sn^{II} derivatives which, as has been mentioned above, may be regarded as "bent sandwich" molecules which are characterised by "abnormal" parameters.

Owing to intramolecular migration, all the σ-cyclopentadienyl compounds of tin[13,14] and mercury[19] exhibit the $J(M{-}H)$ coupling constant. In principle the latter constant can be used as a proof of a particular structure in a comparison of experimental data to those calculated from the averaging formula (6) for the model structures. This procedure has been employed by Kitching *et al.*[21] in the study of indenyl derivatives of mercury. In a similar fashion, it is possible to discuss cyclopentadienyltin derivatives on the basis of the model structures listed in Table 4. Using the data for

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* It would seem reasonable to suggest that a more detailed NMR study of these compounds should be undertaken, perhaps a ^{13}C spectral investigation over a wide range of temperature and employing a variety of solvents.

** In the spectrum of $C_5H_5AuP(C_6H_5)_3$ measured in acetone-d_6 solution at low temperatures, a resonance signal of C_5H_5 protons resolves to a doublet owing to spin–spin coupling with the ^{31}P nucleus (A. V. Kisin and Yu. A. Ustynyuk, unpublished results). In our opinion an intermolecular exchange between the C_5H_5 ligands occurs.

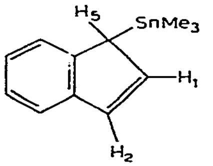
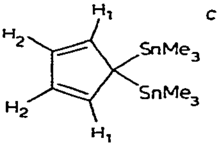
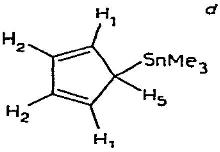
*** The situation regarding the $J(M{-}H)$ constants is not clear possibly due to intermolecular ligand exchange taking place in some cases.

**** The symbol $J(Sn{-}H)$ is used here to specify the average value for the coupling constants $J(^{119}Sn{-}H)$ and $J(^{117}Sn{-}H)$.

the indenyl compound, taking into account the fact that the value of $J(\text{Sn–H}_1)$ is opposite in sign with respect to $J(\text{Sn–H}_5)$ and $J(\text{Sn–H}_2)$, the value of J(Sn–H) for $C_5H_5Sn(CH_3)_3$ has been found to be 21 Hz, close to that obtained experimentally.

TABLE 4

Sn–H COUPLING CONSTANTS OF MODEL COMPOUNDS (Hz)

Compound	$J(\text{Sn–H}_5)$[a]	$J(\text{Sn–H}_1)$	$J(\text{Sn–H}_2)$
 [b]	±91	∓12	±18
 [c]		∓ 6.4	± 8.0
 [d]	91	[e]	[e]

[a] Probably all positive. [b] Ref. 22. [c] A. V. Kisin, private communication. [d] Ref. 14. [e] Not found.

However, some uncertainty regarding the nature of the model structure, and undetermined signs in some cases eliminate any hope of using the J(M–H) constant as proof of a σ-structure. What is possible, however, is that the value of J(M–H) for "authentic" structures can be used for determining the separate coupling constants for a stereochemically rigid system★.

Let us consider the values of J(H–H) for the cyclopentadienyl fragment restricting ourselves to the unsubstituted rings. Because many σ-cyclopentadienyl compounds readily produce rigid structures it is possible to completely analyze the proton spectrum for the determination of J(H–H) constants. Such treatment has been carried out for derivatives of iron and ruthenocene[23], silicon[17] and germanium[14]. However, in the analysis of the spectra of σ-cyclopentadienyl compounds it is necessary to make certain approximations and a knowledge of the coupling constants (averaged by migration) obtained from ananalysis of ^{13}C–H satellites would be helpful in overcoming this difficulty.

From the values of the averaged coupling constants it is possible to estimate two coupling constants corresponding to a stereochemically rigid molecule together with the other four constants given in eqns. (1) and (2). As is evident from the published J(H–H) values of cyclopentadienyl compounds[17], the constant $J_{25(53)}$ undergoes

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★ For example the $J(^{119}\text{Sn–H})$ coupling constant of trimethylindenyltin has been found using this technique[22] the most variation. Since the sign of $J_{15(45)}$ has not been strictly determined* the constants $J_{15(45)}$ and $J_{25(35)}$ must be considered as unknown. Taking for the other constants ($J_{12(34)}$, $J_{13(24)}$, J_{23} and J_{14}) the values obtained from the known data[17], which are respectively equal to 5.0, 1.2, 2.1, 2.1 (all in Hz), from eqns. (1) and (2) it is possible to show that for $C_5H_5Sn(CH_3)_3$, $J_{15(45)} = +1.1$ Hz and $J_{25(35)} = +0.2$ Hz respectively. In spite of the significant error in these values ($\pm$0.6 Hz), each of these values leads to the important conclusion that the value of $J_{15(45)}$ is essentially positive. This may be regarded as a direct proof of the correctness of the sign assumed for this constant earlier[1,17,23]. Furthermore the calculated value of this constant (1.1 Hz) is

Table 5 lists the J^1 and J^2 values. Their experimental values were obtained only for the first three compounds, as for the other substances the J^1 and J^2 values were estimated from eqns. (1) and (2) using the proton coupling constants for stereochemically rigid systems. In addition, the values (J^1+J^2), (J^1-J^2) together with the ratio K equal to $(J^1-J^2)/(J^1+J^2)$ are tabulated. As can be seen from Table 5, the sum of the constants (J^1+J^2) is hardly influenced by the structure and change to a somewhat smaller extent than the difference (J^1-J^2). On the other hand, the parameter K, formally determined as $(J^1-J^2)/(J^1+J^2)$, can be used as an index of the bonding type: $K \geqslant 0.5$ most probably corresponds to a σ-structure while $K \leqslant 0.3$ corresponds to the π-structure.

Attention should be drawn to the apparent relationship between the value of K and the temperature at which the migration rate is equal to 1 sec^{-1} (T_r)[14] and possibly to the free energy of activation of metallotropic rearrangements of σ-structures.

In spite of the experimental difficulties which may arise in the observation and

TABLE 5

THE AVERAGED J^1 AND J^2 CONSTANTS FOR VARIOUS CYCLOPENTADIENYL COMPOUNDS[a]

Compound	J^1	J^2	J^1+J^2	J^1-J^2	K[h]	T_r^i (°C)
$Fe(C_5H_5)_2$[b]	2.40	1.24	3.64	1.16	0.32	
$[Co(C_5H_5)_2]^+Cl^-$[b]	2.58	1.46	4.04	1.12	0.28	
$(C_5H_5)Sn(CH_3)_3$	2.86	0.97	3.83	1.89	0.50	−152[j]
σ-$C_5H_5Fe(CO)_2$-π-C_5H_5[c]	2.73	0.87	3.60	1.86	0.52	− 92[j]
σ-$C_5H_5Ru(CO)_2$-π-C_5H_5[c,d]	2.75	0.84	3.59	1.91	0.53	− 55[j]
	2.75	0.92	3.67	1.83	0.50	
$C_5H_5Ge(CH_3)_3$[e]	2.88	0.78	3.66	2.10	0.57	− 73[j]
$C_5H_5Si(CH_3)_3$[f]	2.88	0.60	3.48	2.28	0.65	− 23[j]
$C_5H_5SiCH_3Cl_2$[f]	2.92	0.52	3.44	2.42	0.70	+ 7[k]
C_5H_6[g]	3.02	0.18	3.20	2.84	0.89	+162[j]

[a] The values of J^1 and J^2 for the first three compounds were measured experimentally, for all other compounds they were calculated using formulae (1) and (2). [b] Ref. 12. [c] Ref. 23. [d] The upper row for $J_{35} = -0.1$ Hz, the lower row for $J_{35} = +0.1$ Hz. [e] Ref. 14. [f] Ref. 17. [g] Refs. 17 and 24. [h] $K \equiv (J^1-J^2)/(J^1+J^2)$. [i] T_r is temperature at which the migration rate is equal to 1 sec^{-1}. [j] From data in ref. 14. [k] From data in ref. 17.

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* In principle, the procedures reported in refs. 1 and 17 do not exclude the possibility that $J_{25(53)} > 0$ and that $J_{15(45)} < 0$ (*cf.* also ref. 24).

analysis of ^{13}C–H satellites in the PMR spectra of cyclopentadienyl compounds, such investigations could prove useful as they require no measurements over wide temperature ranges. It is useful to recall that this has been a long-standing problem in the study of the cyclopentadienyl derivatives of mercury and tin. By taking into account the comparative constancy of the value (J^1+J^2) it is possible to make an approximate guess at the complete variety of possible ^{13}C–H satellites appearing in the PMR spectra of cyclopentadienyl compounds simply by varying the parameter (J^1-J^2) (or K). Such a "catalogue" of the spectra for values of K from 0.2 to 0.7 at intervals of 0.1 is given in Fig. 4. In this case the value (J^1+J^2) was 3.7 Hz (*cf.* Table 5). The relative chemical shifts of effective nuclei M and N were equal to 1.5 Hz (at 100 MHz) in a similar manner to the cases discussed above. At low values of K (π-structures) the spectrum of the satellite has some asymmetry. The latter rapidly enhances with increase of K, *i.e.* in passing to the σ-structures. In addition, an apparent dependence of the appearance of the spectrum upon the relative chemical shift exists, *i.e.* upon $J(^{13}\text{C–C–H})-J(^{13}\text{C–C–C–H})$. This dependence is not so critical however and is not illustrated in the "catalogue" (Fig. 4).

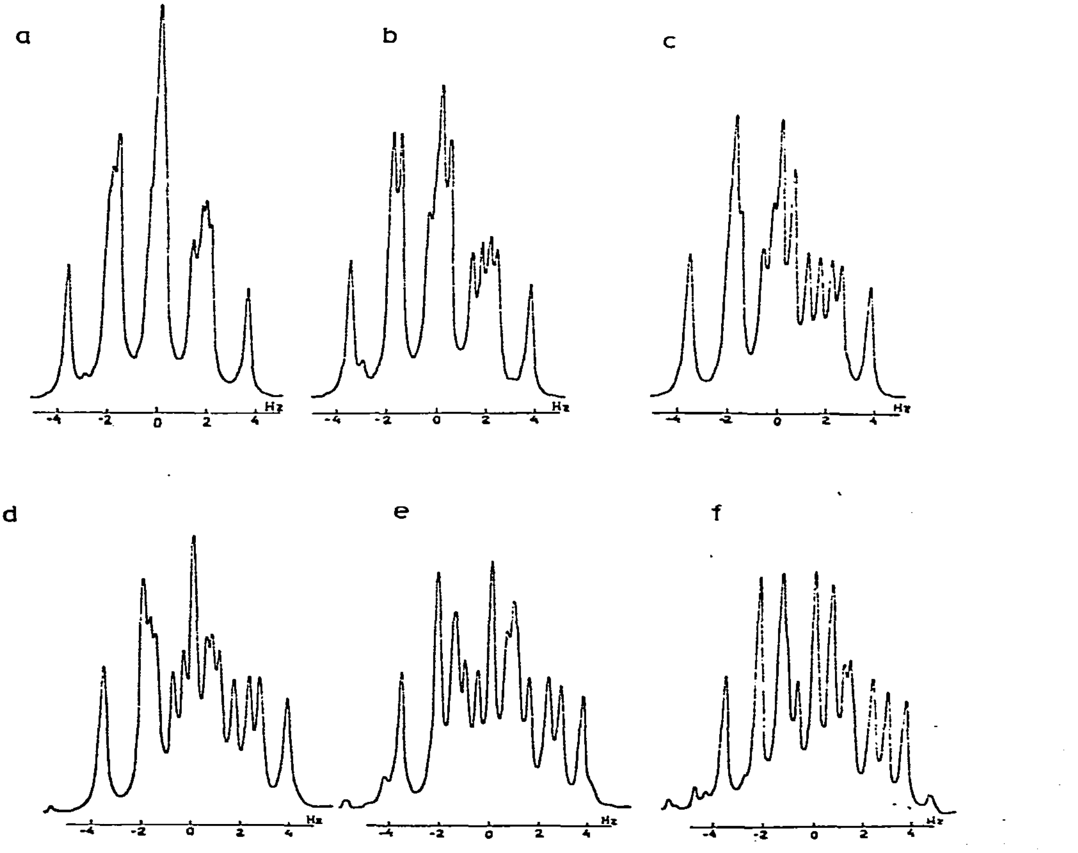

Fig. 4. The calculated spectra of the upfield outer ^{13}C–H satellites at the proton resonance frequency 100 MHz at various $K[\equiv(J^1-J^2)/(J^1+J^2)]$: (a) $K=0.2$, (b) $K=0.3$, (c) $K=0.4$, (d) $K=0.5$, (e) $K=0.6$, (f) $K=0.7$. In all cases $(J^1+J^2)=3.7$ Hz. The line width was equal to 0.3 Hz.

EXPERIMENTAL

Compounds $C_5H_5M(CH_3)_3$ (M = Si, Ge, Sn) were synthesized by Miss I. M. Pribytkova, σ-$C_5H_5Fe(CO)_2$-π-C_5H_5 was obtained by Dr. I. V. Polovyanyuk and $(\sigma\text{-}C_5H_5)_2Sn\,[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$ was kindly supplied by Dr. N. E. Kolobova, ferrocene being commercially available.

The ^{13}C–H satellite PMR spectra of cyclopentadienyltrimethyltin were measured in the neat liquid state, those of the cyclopentadienyl derivatives of Si and Ge in 25% decaline solution and octamethylcyclotetrasiloxane while the ferrocene spectrum was measured using a saturated solution of carbon disulphide. Since $(\sigma\text{-}C_5H_5)_2Sn\,[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$ is poorly soluble (10% in CS_2) the ^{13}C–H satellites were observed in the time-averaged spectra. In some solvents the solubility of σ-C_5H_5-$Fe(CO)_2$-π-C_5H_5 was insufficient for the direct study of ^{13}C–H satellites corresponding to the fast exchange in the σ-C_5H_5 ligand (temp. ≃ 70–80°) and for these cases time-averaging was also necessary. Measurements of $J(^{13}C\text{–}H)$ were performed using carbon disulphide and acetone solutions. The chemical shifts of σ-C_5H_5 and π-C_5H_5 ligands in acetone were equal to 5.8 and 4.8 ppm respectively. Prior to each investigation, all compounds were degassed and sealed *in vacuo*. The proton-decoupled ^{13}C NMR spectrum of the ring carbons of σ-$C_5H_5Fe(CO)_2$-π-C_5H_5 measured at room temperature in acetone shows a narrow signal corresponding to the π-C_5H_5 ligand and a broadened signal corresponding to the σ-C_5H_5 ring which is markedly narrowed at 60°.

PMR spectra were measured on an HA-100D spectrometer (Varian) operating at 100 MHz for protons in the field/frequency sweep mode.

The proton-decoupled ^{13}C NMR spectra were measured on a JNM-4H-100-(JEOL) instrument operating at 25.14 MHz for carbons in the field sweep mode. Double resonance conditions were maintained while the irradiation frequency was swept synchronously with the field sweep by means of frequency synthesizer Ch 1–9.

CONCLUSIONS

It seems reasonable to summarize the results of the present investigation. First, it should be pointed out that the experimental NMR data on the metal cyclopentadienyl derivatives are rather restricted and in many cases deserve careful scrutiny. However even with this restriction it is possible to conclude that in the majority of cases the type of structure (π- or σ- in the sense of local symmetry as defined in the Introduction) may be established using the NMR spectra. The most unequivocal criteria are provided by the carbon shifts (in ^{13}C spectra), by the coupling constants ^{13}C–H (in the ^1H and ^{13}C spectra) and by the proton coupling constants (in the ^{13}C–H satellites and ^1H spectra).

From the above discussion, it also follows that in certain cases NMR spectroscopy cannot give an unequivocal answer regarding the type of structure present. Such a situation exists with the "bent sandwich" structures whose detailed study is desirable. Another problem that demands further study is the case of "almost π-structures" as well as systems in which the symmetry is distorted by ligand interaction or by substituents in the cyclopentadienyl ring. Studies of this kind should clearly demonstrate the range of compounds to which the criteria advanced in this paper may be applied.

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REFERENCES

1 N. M. Sergeyev, G. I. Avramenko and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 22 (1970) 63.
2 F. A. Cotton, *J. Amer. Chem. Soc.*, 90 (1968) 6230.
3 J. L. Calderon, F. A. Cotton and P. Legzdins, *J. Amer. Chem. Soc.*, 91 (1969) 2528.
4 H. P. Fritz, *Advan. Organometal. Chem.*, 1 (1964) 240.
5 E. Maslowsky Jr. and K. Nakamoto, *Inorg. Chem.*, 8 (1969) 1108.
6 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 7281.
7 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.
8 W. Strohmeier and R. M. Lemmon, *Z. Naturforsch. A*, 14 (1959) 109.
9 M. L. Maddox, S. L. Stafford and H. D. Kaesz, *Advan. Organometal. Chem.* 3 (1965) 1.
10 G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, 89 (1967) 2855.
11 Yu. K. Grishin, N. M. Sergeyev and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 22 (1970) 361.
12 R. W. Crecely, K. M. Crecely and J. H. Goldstein, *Inorg. Chem.*, 8 (1969) 252.
13 A. Davison and P. E. Rakita, *Inorg. Chem.*, 9 (1970) 289.
14 A. V. Kisin, V. A. Korenevsky, N. M. Sergeyev and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 34 (1972) 93.
15 N. Sheppard and R. M. Lynden-Bell, *Proc. Roy. Soc., Ser. A*, 269 (1962) 385.
16 R. E. Richards and T. Schaefer, *Proc. Roy. Soc., Ser. A*, 246 (1958) 429.
17 N. M. Sergeyev, G. I. Avramenko, A. V. Kisin, V. A. Korenevsky and Yu. A. Ustynyuk, *J. Organometal. Chem.*, in press.
18 N. N. Veniaminov, Yu. A. Ustynyuk, Yu. T. Struchkov, N. V. Alekseev and I. A. Ronova, *Dokl. Akad. Nauk SSSR*, in press.
19 P. West, M. C. Woodvill and M. D. Rausch, *J. Amer. Chem. Soc.*, 91 (1969) 5649.
20 P. C. Lauterbur and R. B. King, *J. Amer. Chem. Soc.*, 87 (1965) 3266.
21 W. Kitching and B. F. Hegarty, *J. Organometal. Chem.*, 21 (1970) 29.
22 P. E. Rakita and A. Davison, *Inorg. Chem.*, 8 (1969) 1164.
23 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 7523.
24 M. A. Cooper, D. D. Elleman, C. D. Pearce and S. L. Manatt, *J. Chem. Phys.*, 53 (1970) 2343.
25 A. F. Berndt and E. R. Marsh, *Acta Crystallogr.*, 16 (1963) 118.
26 J. D. Dunitz, L. E. Orgel and A. Rich, *Acta Crystallogr.*, 9 (1956) 373.
27 M. J. Bennett Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard and S. M. Morehouse, *J. Amer. Chem. Soc.*, 88 (1966) 4371.
28 B. P. Biryukov and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 10 (1969) 95.
29 M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, (1963) 273.
30 G. L. Hardgrove and D. H. Templeton, *Acta Crystallogr.*, 12 (1959) 28.
31 E. Frasson, F. Menegus and C. Paunattoni, *Nature*, 199 (1963) 1087.
32 A. Almenningen, A. Haaland and T. Motzfeldt, *J. Organometal. Chem.*, 7 (1967) 97.
33. I. A. Ronova and N. V. Alekseev, *Dokl. Akad. Nauk SSSR*, 174 (1967) 614.
34 L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 43 (1965) 2765.
35 N. N. Veniaminov, Yu. A. Ustynyuk, Yu. T. Struchkov, N. V. Alekseev and I. A. Ronova, *Zh. Strukt. Khim.*, 11 (1970) 127.

36 N. N. VENIAMINOV, YU. A. USTYNYUK, YU. T. STRUCHKOV, N. V. ALEKSEEV AND I. A. RONOVA, *J. Organometal. Chem.*, 22 (1970) 551.
37 M. D. RAUSCH AND V. MARK, *J. Org. Chem.*, 28 (1963) 3225.
38 A. N. NESMEYANOV, R. B. MATERIKOV, E. I. FEDIN, N. S. KOCHETKOVA, P. V. PETROVSKII, L. A. FEDOROV AND E. V. LEONOVA, *Dokl. Akad. Nauk SSSR*, 177 (1967) 586.
39 L. D. DAVE, D. F. EVANS AND G. WILKINSON, *J. Chem. Soc.*, (1969) 3684.
40 H. P. FRITZ AND K.-E. SCHWARZHANS, *Chem. Ber.*, 97 (1964) 1390.
41 A. N. NESMEYANOV, L. A. FEDOROV, R. B. MATERIKOVA, E. I. FEDIN AND N. S. KOCHETKOVA, *Dokl. Akad. Nauk SSSR*, 183 (1968) 356.
42 J. LORBERTH, *J. Organometal. Chem.*, 19 (1969) 189.
43 R. HÜTTEL, U. RAFFAY AND H. REINHEIMER, *Angew. Chem.*, 79 (1967) 859.