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## STEREOCHEMICAL APPROACH TO THE PROBLEM OF BONDING IN $\text{TlC}_5\text{H}_5$ . $^{13}\text{C}$ NMR STUDY OF DIASTEREOTOPY OF CYCLOPENTADIENYL CARBON ATOMS IN THE $\text{C}_5\text{H}_4\dot{\text{C}}\text{H}(\text{Me})\text{Ph}$ LIGAND

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### Summary

A stereochemical approach to the problem of bonding in  $\text{TlC}_5\text{H}_5$  is proposed, which consists of a  $^{13}\text{C}$  NMR study of the diastereotopy of cyclopentadienyl carbon atoms in  $\text{TlC}_5\text{H}_4\dot{\text{C}}\text{H}(\text{Me})\text{Ph}$ ,  $\text{KC}_5\text{H}_4\dot{\text{C}}\text{H}(\text{Me})\text{Ph}$  and  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\dot{\text{C}}\text{H}(\text{Me})\text{Ph}$ . Results obtained indicate the absence of a stable covalent metal—ring bond in  $\text{TlC}_5\text{H}_5$ . These data along with the results of a  $^{19}\text{F}$  NMR study of  $\text{TlC}_5\text{H}_4\text{C}_6\text{H}_4\text{F}$  *m(-p)*,  $\text{MC}_5\text{H}_4\text{C}_6\text{H}_4\text{F}$  *m(-p)* ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) and of  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}_6\text{H}_4\text{F}$  *m(-p)* suggest that the thallos compound exists in THF predominantly in the form of tight ion pairs.

### Introduction

The nature of bonding in indium(I) and thallium(I) cyclopentadienyl compounds is still unclear. Electron diffraction [1], IR [2] and microwave spectroscopic [3] studies have established that in the gas phase  $\text{InC}_5\text{H}_5$  and  $\text{TlC}_5\text{H}_5$  exist in the form of half-sandwiches with the metal atom arranged in the centre over a cyclopentadienyl ring. On the other hand, X-ray studies showed that in the solid state the structure of  $\text{TlC}_5\text{H}_5$  is characterized by a chain arrangement of the metal atoms and of the rings enclosed between them, at the same distance from both metals [4].

Fischer [5] postulated that the bonding in  $\text{TlC}_5\text{H}_5$  is covalent and such as to give a structure of  $C_{5v}$  symmetry. According to the proposed scheme  $s^2$  lone pair Tl electrons remain in the 6s orbital, while three 6p orbitals are used for bonding. Conversely, Cotton and Reynolds [6] came to the conclusion after studying the IR spectra of gaseous  $\text{TlC}_5\text{H}_5$  and  $\text{Mg}(\text{C}_5\text{H}_5)_2$  that these compounds are essentially ionic. Subsequently, various physical and chemical arguments

TABLE 1

$^{19}\text{F}$  CHEMICAL SHIFTS <sup>a</sup> AND VALUES OF  $\sigma_{\text{I}}$  AND  $\sigma_{\text{R}}^{\circ}$  FOR *m*- AND *p*-FLUOROPHENYLCYCLOPENTADIENYL DERIVATIVES

Compound	Solvent	<i>m</i> -F	<i>p</i> -F	$\sigma_{\text{I}}$	$\sigma_{\text{R}}^{\circ}$
$\text{LiC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	$\text{CH}_3\text{CN}$	2.0	10.6	-0.20	-0.29
	$\text{CH}_3\text{CN/TMEDA}^b$	1.7	9.9	-0.18	-0.27
	THF	2.5	11.1		
	HMPA	4.2	17.9	-0.51	-0.50
$\text{NaC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	THF		12.3		
	HMPA		17.9		
$\text{KC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	THF	3.2	12.7	-0.37	-0.32
	THF/18-crown-6 <sup>b</sup>	4.1	15.1	-0.50	-0.35
$\text{TlC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	THF	1.5	7.4	-0.13	-0.20
$\text{BrMgC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	THF	1.2	7.8	-0.08	-0.22
$\text{C}_3\text{H}_5\text{PdC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	$\text{CCl}_4$	1.0	4.6	-0.06	-0.12
$\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$	THF	0.6	4.0	-0.01	-0.11

<sup>a</sup> Measured for  $\sim 0.1$  M solutions, in  $\delta$  ppm upfield from  $\text{C}_6\text{H}_5\text{F}$ . <sup>b</sup> Complexing agents *N,N*-tetramethylethylenediamine (TMEDA) and 1,4,7,10,13,16-hexaoxocyclooctadecane (18-crown-6) were added in quantities of 100% in relation to the carbanion salt.

have been proposed in favour of both ionic and covalent bonding (see ref. 7 and references therein) \*.

## Results and discussion

The recently proposed approach to the elucidation of the nature of the bonding in  $\text{TlC}_5\text{H}_5$  is based on an estimation of the negative charge in the cyclopentadienyl ring by comparing it with the charge on obviously ionic alkali cyclopentadienides on the one hand, and with covalent iron and palladium cyclopentadienyls on the other [7]. Accordingly, we synthesised *m*- and *p*-fluorophenylcyclopentadienyl derivatives of these metals and measured their  $^{19}\text{F}$  chemical shifts. The values of  $^{19}\text{F}$  chemical shifts and calculated constants  $\sigma_{\text{I}}$  and  $\sigma_{\text{R}}^{\circ}$  are given in Table 1.

The values of  $^{19}\text{F}$  chemical shifts, which are a measure of the polarity of metal-cyclopentadienyl bonds, vary considerably. For ionic cyclopentadienyls they depend strongly on the "donor number" [11] of the solvent and on the nature of the alkali cation, due to the equilibrium between tight and solvent-separated ion pairs in solutions.

On passing from solvent-separated to tight ion pairs perturbation of the carbanion electron shell caused by the proximity of the cation increases. As a result the ionicity of the bond decreases leading to smaller  $^{19}\text{F}$  chemical shifts. Conversely, on passing to a solvent-separated ion pair the ionicity increases: this would be enhanced by higher donor strength of the solvent. Thus, for  $\text{LiC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}p$  the  $^{19}\text{F}$  chemical shifts in acetonitrile, tetrahydrofuran (THF) and in hexamethylphosphoramide (HMPA) are 10.6, 11.1 and 17.9 ppm, respectively, which agrees with the increase of the "donor number" of these solvents in the same

\* Cyclopentadienylthallium(I) is sometimes [8-10] erroneously depicted as  $\text{Tl}-\text{C}_5\text{H}_5$ , with the cyclopentadienyl ring  $\eta^1$ -bonded to the metal atom.

series: 14.1, 20.0 and 38.8 [11]. It is assumed that in HMPA the carbanion salt is completely in the form of solvent-separated ion pairs, whereas in acetonitrile and THF a considerable fraction of the ion exists as tight ion pairs [12].

For salts of fluorophenylcyclopentadienide carbanions in THF the shielding of  $^{19}\text{F}$  nuclei increases in the order  $\text{Li} < \text{Na} \lesssim \text{K}$ . Usually the smaller cation promotes formation of solvent-separated ion pairs since it is better solvated but it is also found that the smaller and the more highly charged the cation, the more charge distribution in the neighbouring carbanion is distorted. Comparison of the  $^{19}\text{F}$  shielding in carbanions in THF and HMPA solutions shows that in THF a substantial fraction of ions exists in the form of tight ion pairs.

The  $^{19}\text{F}$  chemical shifts of the thallos and magnesium derivatives occupy an intermediate position between alkali cyclopentadienides and covalent iron and palladium derivatives and are close to the values of the lithium derivative in THF and acetonitrile. Therefore, it is reasonable to assume that  $\text{TlC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$  and  $\text{BrMgC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-}m(-p)$  exist predominantly as tight ion pairs in THF.

To verify this assumption we used a stereochemical approach which consists of a  $^{13}\text{C}$  NMR study of the diastereotopy of cyclopentadienyl carbon atoms in a suitably substituted ring.

In the carbanion  $\text{C}_5\text{H}_4\overset{\star}{\text{C}}\text{H}(\text{Me})\text{Ph}$  (I) the cyclopentadienyl ring contains two pairs of prochiral [13] carbons,  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$ . In the  $^{13}\text{C}$  NMR spectrum of ionic carbanion derivatives, e.g.  $\text{KC}_5\text{H}_4\overset{\star}{\text{C}}\text{H}(\text{Me})\text{Ph}$  (II),  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  carbons will be isochronous, since in solution various types of ion pairs are in a rapid (on a NMR time scale), dynamic equilibrium and as a result, the averaged stereochemical environment of these nuclei will be similar to that in a "free" carbanion.

With formation of a stable bond between the metal and ligand I, such as the covalent bond in the ferrocene derivative  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\overset{\star}{\text{C}}\text{H}(\text{Me})\text{Ph}$  (III), the prochiral nuclei of the substituted cyclopentadienyl ring become chiral (planar chirality). Even in the case of free rotation about the  $\text{C}_1-\text{C}_6$  bond  $\text{C}_2$  and  $\text{C}_5$  nuclei (as well as  $\text{C}_3$  and  $\text{C}_4$ ) will always have different stereochemical environments. In the  $^{13}\text{C}$  spectra diastereotopic  $\text{C}_{2,5}$  carbons will be anisochronous, i.e. each will have a separate resonance signal. Bearing this in mind, we compared



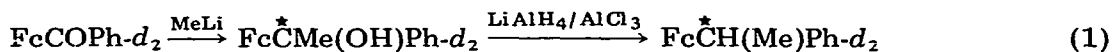
(I)

(III)

the spectrum of the thallos derivative  $\text{TlC}_5\text{H}_4\overset{\star}{\text{C}}\text{H}(\text{Me})\text{Ph}$  (IV) with those of the ionic (II) and covalent (III) compounds.

The ferrocene derivative III was obtained by reduction of the hydroxy compound  $\text{C}_5\text{H}_5\text{FeC}_5\overset{\star}{\text{C}}\text{Me}(\text{OH})\text{Ph}$  (V) with a  $\text{LiAlH}_4/\text{AlCl}_3$  mixture in ether. To make unequivocal assignments of the signals of  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  carbons in V and III 2,5-dideutero analogues were prepared from 2,5-dideuterobenzoylferrocene

(eq. 1).



(Fc = ferrocenyl)

By reduction of 6-methyl-6-phenylfulvene with lithium aluminium hydride the diene  $\text{C}_5\text{H}_5\overset{\star}{\text{C}}\text{H(Me)Ph}$  was obtained (which consists of a mixture of isomers according to its  $^{13}\text{C}$  NMR spectrum). Treatment of the diene with sodium-potassium alloy,  $\text{NaK}_{2,8}$ , and with thallos ethoxide rendered II and IV respectively. The thallos compound is an oily, viscous, brown substance which rapidly decomposes in air. The potassium (II) and thallos (IV) compounds were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and by conversion into the respective ferrocene derivatives by treatment with ferrous chloride.

$^{13}\text{C}$  NMR chemical shifts of II–V are given in Table 2. As expected, in the ferrocene derivative III (as in V)  $\text{C}_2$ – $\text{C}_5$  carbons display four separate signals, while in the ionic derivative II  $\text{C}_{2,5}$ , as well as  $\text{C}_{3,4}$ , carbons are isochronous. The thallos compound IV is similar to the potassium compound II in that the  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  carbons of these derivatives display two signals. This unequivocally indicates the absence of a stable covalent metal–ligand bond in  $\text{TlC}_5\text{H}_5$ . This is also indicated by the similar values of  $\text{C}_2$ – $\text{C}_5$  chemical shifts in IV and II.

Comparison of  $\delta$  values in the  $^{13}\text{C}$  NMR spectra of cyclopentadienyl carbons in IV and II shows that carbons in the thallos compound are less shielded\*. This indicates that the bonding in IV is less ionic in nature than in II and agrees with the results of a  $^{19}\text{F}$  NMR study of *m*- and *p*-fluorophenylcyclopentadienyl derivatives of these metals.

The predominance of tight ion pairs of IV in THF solution is supported by comparison with data obtained for II in benzene in the presence of macrocyclic polyether 18-crown-6. In this case the difference in chemical shifts of  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  carbons in II and IV is only 2.0–2.5 ppm. The effect of solvent on the chemical shifts of cyclopentadienyl carbons in IV is in accord with the substantial ionic contribution to metal–ring bonding: on going from  $\text{CH}_2\text{Cl}_2$  to THF the increased thallos ion solvation causes the polarity of the metal–ring bond to increase and  $^{13}\text{C}$  NMR  $\delta$  values are shifted upfield.

Although the diameters of potassium and thallos ions are similar (2.66 and 2.80 Å, respectively), the polarity of the bond in the cyclopentadienyl derivatives of these metals differs markedly. Evidently this is due to the presence of a “stereochemically active” [14] lone pair of electrons on the thallos ion which repels the solvent molecules. The possibility of distortion of the  $6s^2$  pair by partial mixing with the  $6p$  orbitals was shown by X-ray analysis of TlF [15].

Data obtained in the  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR studies of thallos cyclopentadienyl compounds lead us to the conclusion that in THF solution these compounds exist mainly in the form of tight ion pairs. At the same time, the covalent contribution to metal–ring bonding competes with the ionic contribution, and evidently increases on going from solution to gaseous phase.

\* The large number of factors (the relative importance of which is still unclear) which determines the upfield shift of organic ligand nuclei upon coordination with a transition metal makes it impossible to compare shielding of cyclopentadienyl nuclei in ionic compounds and ferrocene derivatives.

TABLE 2  
<sup>13</sup>C CHEMICAL SHIFTS OF METAL CYCLOPENTADIENYL DERIVATIVES

Compound	Solvent	<sup>13</sup> C chemical shifts, in ppm from TMS										
		C <sub>1</sub>	C <sub>2,5</sub>	C <sub>3,4</sub>	C <sub>5</sub> H <sub>5</sub>	C <sub>6</sub>	CH <sub>3</sub>	C <sub>i</sub>	C <sub>o</sub>	C <sub>m</sub>	C <sub>p</sub>	
* TiC <sub>5</sub> H <sub>4</sub> CH(Me)Ph	C <sub>6</sub> H <sub>6</sub>	136.7	106.6	107.8		40.5	22.7	151.3	a	a	a	
	CH <sub>2</sub> Cl <sub>2</sub>	136.8	106.8	107.4		40.1	23.7	151.1	127.3	128.6	126.8	
* KC <sub>5</sub> H <sub>4</sub> CH(Me)Ph	THF	135.5	104.9	106.6		40.2	a	150.9	127.3	128.1	125.5	
	THF	125.9	102.2	103.7		40.3	22.6	151.3	126.5	128.1	124.5	
C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CH(Me)Ph	C <sub>6</sub> H <sub>6</sub> /E <sup>b</sup>	124.7	102.9	104.1		42.2	26.1	153.9	a	a	124.5	
	ClCH <sub>2</sub> CH <sub>2</sub> Cl	94.2	65.9	67.3	68.4	39.5	22.0	147.5	126.6	127.9	125.6	
C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CMe(OH)Ph <sup>c</sup>	C <sub>6</sub> H <sub>6</sub>		66.7	67.6								
	ClCH <sub>2</sub> CH <sub>2</sub> Cl	100.3	65.6	67.6	68.3	72.1	31.1	148.1	124.8	127.5	126.1	
C <sub>5</sub> H <sub>5</sub> FeC <sub>5</sub> H <sub>4</sub> CMe(OH)Ph <sup>c</sup>	CCl <sub>4</sub>	100.6	67.1	68.0	68.1	71.9	31.8	147.6	124.4	127.3	125.9	
	CCl <sub>4</sub>		66.0	67.2								
			66.9	67.8								

<sup>a</sup> The solvent signal overlaps the resonance signal of the given nucleus. <sup>b</sup> E is a macrocyclic polyether, 18-crown-6, amount ~100% in relation to the carbanion salt.  
<sup>c</sup> Assignment of C<sub>2,5</sub> and C<sub>3,4</sub> signals given in [16] is incorrect.

## Experimental

All operations connected with the preparation of polar cyclopentadienyls were carried out under argon. Lithium, sodium and potassium derivatives of *m*- and *p*-fluorophenylcyclopentadienyl anions were obtained by reacting the corresponding dienes with *n*-butyllithium, sodium hydride and sodium-potassium alloy respectively [12]. Solutions of *m*- and *p*-fluorophenylcyclopentadienylmagnesium bromide were prepared by treating dienes with ethylmagnesium bromide in THF as proposed for the synthesis of  $C_5H_5MgBr$  [17]. The synthesis and properties of the ferrocene derivatives studied in this work will be described in a separate report.

The  $^1H$  (60 MHz) and  $^{19}F$  (56.4 MHz) NMR spectra were recorded on an R 20 Hitachi-Perkin-Elmer spectrometer and the  $^{13}C$  NMR spectra with a HX-90 Bruker instrument (22.635 MHz) at 34°C.

### *m*-Fluorophenylcyclopentadienylthallium

5 g of  $Tl_2SO_4$  and 2 g of potassium hydroxide were dissolved with heating in 40 ml of distilled water. After cooling, 2.4 g of *m*-fluorophenylcyclopentadiene was added to the  $TlOH$  solution obtained and the mixture was stirred for 4 h. A small amount of ethanol was then added, the light coloured precipitate which formed was filtered, washed with cooled ethanol and dried in vacuo over KOH. A cream-coloured (almost white) crystalline substance was obtained (yield 3.92 g, 73%), m.p. 123–125°C (dec.). Found: C, 36.37; H, 2.15.  $C_{11}H_8FTl$  calcd.: C, 36.34; H, 2.22%. The product is poorly soluble in  $CCl_4$  and acetonitrile, moderately soluble in methanol, acetone and pyridine and better soluble in THF. In contrast with alkyl derivatives of  $TlC_5H_5$ , the product obtained and its *p*-isomer are quite stable in air and darken slowly on storage.

### *p*-Fluorophenylcyclopentadienylthallium

This was obtained in the same way as the *m*-isomer (yield 74%), m.p. 149–151°C (dec.). Analysis found: C, 35.93; H, 2.32.  $C_{11}H_8FTl$  calcd.: C, 36.34; H, 2.22%. The light-yellow substance is less soluble than the *m*-isomer and is crystallized from dimethylsulphoxide in the form of needles, m.p. 157–160°C (dec.).

### $\alpha$ -Methylbenzylcyclopentadienylthallium

1.87 g of thallos ethoxide in 40 ml of pentane were added dropwise to a stirred solution of 1.37 g  $\alpha$ -methylbenzylcyclopentadiene in 40 ml pentane. After heating the solution for 30 min it was cooled and the heavy oily product which was precipitated was removed with a syringe. The brown product obtained was identified by its NMR spectrum and by conversion into its ferrocene derivative,  $C_5H_5FeC_5H_4\dot{C}H(Me)Ph$  [18], by treating it with anhydrous ferrous chloride in a mixture with  $TlC_5H_5$ .

$^1H$  NMR spectrum ( $C_6H_6$ ):  $\delta$  (ppm); 1.54 (d,  $J$  7 Hz,  $CH_3$ ); 3.89 (q, CH); 5.57 (t,  $H_{2,5}$  or  $H_{3,4}$ ) and 5.81 (t,  $H_{2,5}$  or  $H_{3,4}$ ); phenyl proton signals overlap with those of the solvent. As  $TlC_5H_4Me$  the substance rapidly decomposes in air.

*(p-Fluorophenylcyclopentadienyl)-π-allylpalladium*

3.5 g of crystalline  $\text{TiC}_5\text{H}_4\text{C}_6\text{H}_4\text{F-p}$  was added to a solution of 1.69 g of bis( $\pi$ -allylpalladium chloride) in THF. The solution instantly turned red. The solution was stirred for an hour at room temperature after which the solvent was removed on a rotary evaporator and the residue extracted with light petroleum ether. Removal of the solvent and crystallisation of the residue from pentane yielded 2.5 g (88.5%) of dark-red crystals, m.p. 72–74°C (dec.). Analysis found: C, 55.16; H, 4.34.  $\text{C}_{14}\text{H}_{13}\text{FPd}$  calcd.: C, 54.76; H, 4.27%.

*(m-Fluorophenylcyclopentadienyl)-π-allylpalladium*

This was prepared in the same way as the *p*-isomer. Dark-red crystals were obtained, yield 60%, m.p. 41–43°C (dec.). Analysis found: C, 54.37; H, 4.04.  $\text{C}_{14}\text{H}_{13}\text{FPd}$  calcd.: C, 54.76; H, 4.27%.

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