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Preliminary communication

BOND IONICITY IN TlC_5H_5

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Summary

^{19}F NMR spectra of *m*- and *p*-fluorophenylcyclopentadienylthallium have been measured. The resulting $\delta(F)$ values have been converted into the constants σ_I and σ_R^0. The chemical shifts and the constants are collated with the respective values for alkali cyclopentadienyls and for metallocenes. The thallium—cyclopentadienyl bond "ionicity" has been estimated to be at least 40 to 50%.

The nature of the bonding in some cyclopentadienylmetals such as $Be(C_5H_5)_2$, $Mg(C_5H_5)_2$, InC_5H_5 and TlC_5H_5 is a point of controversy, e.g. in some papers the metal—ring bond in InC_5H_5 and TlC_5H_5 is claimed to be covalent and in other papers to be ionic.

Bond ionicity in TlC_5H_5 was said to follow from the fact that there is no absorption due to the metal—cyclopentadienyl bond in the crystalline TlC_5H_5 IR spectra [1], no $^{(203)205}Tl$—^1H spin—spin coupling from the ^1H NMR spectra of TlC_5H_5 solutions [2] and from X-ray data on InC_5H_5 and TlC_5H_5 which reveal that the rings and the metal atoms between them are arranged in chains, with the metal atom being distanced identically from the adjacent rings [3].

Covalence of the bonds in InC_5H_5 and TlC_5H_5 was argued by electron-diffraction data on gaseous InC_5H_5 which demonstrate that the metal—carbon bond is 0.4 Å shorter than is a sum of the ionic radii, and by the calculation [4] of overlap integrals as a function of the In—C distance (2.3, 2.6 and 2.9 Å); as for the absence of thallium—proton spin—spin coupling, adherents of the covalent hypothesis say that there is no *s*-admixture in the valent Tl orbital which implements the bond with the ring [5]. Polarography of TlC_5H_5 in DMF, as well as a low conductivity of the compound (5×10^{-4} in DMF) suggest that the bond is not "purely ionic" [6].

The discrepancy outlined above suggests that the bond in InC_5H_5 and TlC_5H_5 is of an intermediate nature, that is, some covalent bonding coexists with some ionicity.

We wanted to find a parameter satisfying the following conditions. It should change proportionally across the entire series of cyclopentadienyl compounds, from "ionic" derivatives of alkali metals to covalent compounds such as ferrocene. It should be measurable under identical (or very similar) conditions in the whole group. Such a parameter may serve as a quantitative measure of ionicity (or covalence) of the bonds.

We believe that useful information on the bond nature in cyclopentadienyl metals may be obtained by studying ^{19}F NMR spectra of *m*- and *p*-fluorophenylcyclopentadienyl compounds of univalent thallium and collating these with the spectra of the respective alkali metal derivatives and h^5 metallocenes. The advantage over the ^{1}H and ^{13}C NMR approach is evident. Firstly, the direct effect of the metal on the neighbouring nuclei is eliminated; further, ^{19}F nuclei as compared with ^{1}H are more sensitive to electron structure alterations [7] and, finally, ^{19}F NMR data may allow one to estimate induction and resonance components of the total electron effect of the cyclopentadienylmetal group as substituent in the benzene ring, cf. Taft et al. [8].

We have synthetised a number of *m*- and *p*-fluorophenylcyclopentadienyl compounds, measured the ^{19}F NMR chemical shifts and calculated the constants σ_I and σ_R^0. The results are summarised in Table 1.

TABLE 1

^{19}F NMR DATA, σ_I AND σ_R^0 VALUES FOR *m*- AND *p*-FLUOROPHENYLCYCLOPENTADIENYL DERIVATIVES [a]

Compound	Solvent	$\delta(m\text{-F})$	$\delta(p\text{-F})$	σ_I	σ_R^0
LiC_5H_4—C_6H_4F-*m*(-*p*) [b]	CH_3CN	2.20	10.65	—0.22	—0.29
NaC_5H_4—C_6H_4F-*m*(-*p*)	THF	2.62	12.60	—0.29	—0.34
$BrMgC_5H_4$—C_6H_4F-*m*(-*p*)	THF	1.17	7.77	—0.08	—0.22
TlC_5H_4—C_6H_4F-*m*(-*p*)	THF	1.50	7.40	—0.13	—0.20
$C_3H_5PdC_5H_4$—C_6H_4F-*m*(-*p*)	CCl_4	1.00	4.65	—0.06	—0.12
$C_5H_5FeC_5H_4$—C_6H_4F-*m*(-*p*) [c]	THF	0.65	4.00	—0.01	—0.11

[a] Satisfactory spectra and analyses were obtained for all new compounds. The chemical shifts δ(F) were measured from a C_6H_5F internal standard. [b] See ref. 10. [c] The compounds were reportedly synthetised in [10].

It is apparent that δ(F) and σ values of alkali cyclopentadienyls differ significantly from those of the transition metal compounds; cyclopentadienyl-thallium and -magnesium compounds are in an intermediate position.

Evidently, a correct h^5 standard is provided by ferrocene or allylcyclopentadienylpalladium rather than compounds of the cyclopentadienylmetal tricarbonyl type containing strong electron-withdrawing CO ligands. Calculations and the chemical properties suggest that the metal—ring bond is not so polar in ferrocene. The a priori calculations performed for ferrocene disagree on the sign of the charge built up on the rings and the metal, however, a conventional assumption is that the negative charge is on the rings [9].

Now, let us assume that the bond is 100% ionic in the sodium derivative*, 0% in ferrocene. Collate δ(F) and σ values of these compounds with the values obtained for the cyclopentadienylthalliums the TlC_5H_5 ionicity may thus be estimated to be at least 40 to 50%.

Consequently, the main conclusion from the data in Table 1 is that the

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*The chemical shift δ(F) depends on the alkali metal cation, however, the sodium derivative ionicity may well be assumed to be ~100%. The cation effect in various solvents and/or in the presence of chelating diamines or crown-ethers is under study now and the results will be published in due course.

metal—ring bond in TlC_5H_5 (and in $BrMgC_5H_5$) is neither purely ionic nor purely covalent. It belongs to an intermediate type, in other words, the bond polarity is high enough to permit a significant contribution of the ionic component to be assumed in the metal—cyclopentadienyl bonding.

The discussion above is concerned just with a solution of TlC_5H_5 in THF; indeed, the literature data allow one to assume that the metal—ring bond ionicity may strongly depend on the phase (crystal, vapour) state of the molecule. Accordingly, the covalent component of the metal—ring bond may rise, while the ionic one fall, on going from crystalline InC_5H_5 and TlC_5H_5 to the vapours.

Probably, the metal—ring bond ionicity may vary with temperature, the aggregate state, and with solvent in other cyclopentadienylmetals for which "essentially ionic" bonding was admitted[*].

The method proposed here for estimating the metal—ring bond polarity may be used with other cyclopentadienylmetals as well. The study of fluorophenylcyclopentadienyls of transition or non-transition metals is in progress.

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[*] There are some examples for inorganic compounds. E.g., CaO is assumed to be covalent in the gas state, ionic in the crystal state [11].