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CARBON-13 AND PROTON MAGNETIC RESONANCE SPECTRA OF CYCLOPENTADIENYLCYCLOHEPTATRIENYLMETAL COMPOUNDS

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Summary

Carbon-13 and proton magnetic resonance spectra of the compounds $(C_5H_5)M(C_7H_7)$ (M = Ti, Zr, Mo, Cr) and of some methyl derivatives of the Ti compound have been studied. In the Ti and Zr compounds the C-13 resonance of the C_7H_7 ring is observed to higher field than that of the C_5H_5 ring; the opposite applies to the Cr compound, while for the Mo compound the two signals lie close together. This is taken to indicate that the C_7H_7 ring is more negatively charged than the C_5H_5 ring in the Ti and Zr compounds, while the reverse is true for the Cr compound; these results agree with those of metallation experiments. Proton magnetic resonance spectra indicate hindered rotation of the rings in the Cr and Mo compounds, but not in the Ti and Zr compounds.

Introduction

In a recent study on the properties of $(C_5H_5)M(C_7H_7)$ (M = Ti, V and Cr) compounds, we reported [1] that $(C_5H_5)Ti(C_7H_7)$ was easily metallated and that metallation predominantly took place in the seven-membered ring. Experiments with $(C_5H_5)V(C_7H_7)$ showed that substitution in this compound is more difficult, and occurs only in the five-membered ring [2]. Substitution reactions of $(C_5H_5)Cr(C_7H_7)$ with n-butyllithium were unsuccessful [2]; only with amylsodium could substitution of this compound be brought about, probably again mainly in the five-membered ring [3].

We have attempted to explain the different behaviour of $(C_5H_5)M(C_7H_7)$ (M = Ti, V and Cr) in terms of differences in the charge distribution in these compounds [1]. By qualitative molecular orbital arguments it was shown that the charge of the seven-membered ring becomes more negative in the sequence M = Cr < V < Ti. For the five-membered ring the same sequence was derived, but the change in the charge of this ring is expected to be much less pronounced.

A valuable technique for obtaining information about the charge on carbon atoms is carbon-13 NMR (CMR). This technique is preferred to proton NMR (PMR), since local magnetic anisotropies and shieldings which complicate the interpretation of PMR spectra are of less importance in CMR [4]. In the present communication we report a study of the CMR spectra of $(C_5H_5)M(C_7H_7)$ (M = Ti, Cr, Zr, Mo) and of some methyl derivatives of the Ti compound.

Results and discussion

Carbon-13 chemical shifts

The CMR chemical shifts of cyclic olefins strongly depend on the charge on the carbon atoms of the compounds. Comparison of the chemical shifts of C_5H_6 and $(C_5H_5)^-Na^+$, for instance, shows an upfield shift for the latter compound of about 30 ppm [5]. A downfield shift of the same order is found when C_7H_8 and $C_7H_7^+Br^-$ are compared [5]. It is found, therefore, that an increase in the negative charge gives rise to an upfield shift (i.e. a decrease in δ) of the ^{13}C resonance, indicating an increase in the shielding of the carbon atoms.

Chemical shifts of carbon atoms in hydrocarbons are mainly determined by changes in the paramagnetic shielding contribution σ_p [6] (eqn. 1).

$$(\sigma_p^{AA})_{zz} = -\frac{e^2\cdot\hbar^2}{2m^2\cdot c^2}\cdot\frac{\langle r^{-3}\rangle_{2p}}{\Delta E}\cdot[(\varphi_{AA})_{zz}+\Sigma_{B\neq A}(\varphi_{AB})_{zz}] \qquad (1)$$

The term φ_{AA} and the factor $\langle r^{-3}\rangle_{2p}$ primarily depend on the local electron density on the carbon atom. An increase of the electron density on carbon atom A causes an expansion of the $2p_z$ orbital and, therefore, a decrease of $\langle r^{-3}\rangle_{2p}$, leading to an increase of σ_p and a decrease of δC. The terms involving φ_{AB} depend on the multiple bond order between the atoms A and B while ΔE means an average electronic excitation energy.

The CMR data of the compounds $(C_5H_5)M(C_7H_7)$ (M = Cr, Mo, Ti, Zr) are collected in Table 1. In all cases the most intense signal was assigned to the seven-membered ring. The intensities of the signals are not exactly proportional to the number of carbon atoms, due to differences in relaxation times of the two ligands. To check the assignment of the signals, the methyl-substituted titanium compounds were also studied (Table 1). The signals of the various

TABLE 1

CARBON-13 CHEMICAL SHIFTS (IN δ RELATIVE TO TMS) FOR SOME CYCLOPENTADIENYL-CYCLOHEPTATRIENYLMETAL COMPOUNDS

Compound	Solvent	δ C(C_5H_5)	δ C(C_7H_7)	$\Delta\delta$ C (C_7H_7-C_5H_5)	δ C(CH_3)
$(C_5H_5)Cr(C_7H_7)$	CS_2	75.4	86.9	11.5	
$(C_5H_5)Mo(C_7H_7)$	C_6D_6	83.8	80.0	− 3.8	
$(C_5H_5)Ti(C_7H_7)$	CS_2	96.5	86.1	−10.4	
$(C_5H_5)Zr(C_7H_7)$	C_6H_6	100.6	80.2	−20.4	
$(C_5H_5)Ti(C_7H_6CH_3)$	CS_2	97.2	96.8(C_1) 87.2($C_{2,7}$) 88.3($C_{3,6}$) 85.1($C_{4,5}$)		28.6
$(CH_3C_5H_4)Ti(C_7H_7)$	CS_2	107.3(C_1) 99.0($C_{2,5}$) 96.0($C_{3,4}$)	86.8		15.9

carbon atoms of the substituted rings in these compounds were assigned by analogy with results for substituted aromatic rings, such as in toluene [7].

It is seen that for $(C_5H_5)Ti(C_7H_7)$ and $(C_5H_5)Zr(C_7H_7)$ the signal at highest field is due to the seven-membered ring, while for $(C_5H_5)Cr(C_7H_7)$ it is due to the five-membered ring. This indicates that in the Ti and Zr compounds the electron density of the carbon atoms of the seven-membered ring is larger than that of the five-membered ring, while the reverse is true for the chromium compound. This result is in agreement with the findings in metallation reactions with the titanium and chromium compounds [1, 3].

When comparing the compounds given in Table 1 it is seen that the signal due to the cyclopentadienyl carbons shift to higher fields with increasing group number of the central metal. The same trend is found in other π-cyclopentadienyl complexes [8, 9], but as far as we know, no convincing explanation has yet been given. Probably, the same trend also affects the shifts of the carbon atoms of the seven-membered ring, but it is opposed by the charge on this ring which becomes more positive with increasing group number of the central metal [1]. It seems to be fortuitous that these two effects nearly cancel, so that the shifts of the C_7H_7 carbons in $(C_5H_5)M(C_7H_7)$ are virtually the same for M = Ti and Cr and for M = Zr and Mo.

Proton resonance spectra and fluxional behaviour

The data from the PMR spectra of $(C_5H_5)M(C_7H_7)$ (M = Cr, Mo, Ti, Zr) and the methyl-substituted titanium compounds are collected in Table 2. In general, the PMR signals follow the same trends as the CMR signals (Fig. 1) and a roughly linear relation between δ ^{1}H and δ ^{13}C holds for the five-membered rings. Such a relation has also been observed for π-cyclopentadienyl ligands in complexes of other metals [8].

It is seen from Table 2 that a change of the solvent affects the PMR signal of the C_7H_7 ring more than that of the C_5H_5 ring in the case of $(C_5H_5)Cr(C_7H_7)$, while the reverse is true for the titanium compound. This agrees with the general experience that PMR signals of more positive groups are more affected by a change of solvent than those of more negative groups [10].

The PMR spectrum of $(C_5H_5)Cr(C_7H_7)$ in various solvents (CS_2, C_6D_6, $C_6D_5CD_3$), recorded at room temperature, shows two rather broad singlets. On

TABLE 2

PMR CHEMICAL SHIFTS (IN δ RELATIVE TO TMS) FOR SOME CYCLOPENTADIENYLCYCLOHEPTATRIENYL METAL COMPOUNDS[a]

Compound	Solvent	δ H(C_5H_5)	δ H(C_7H_7)	δ H(CH_3)
$(C_5H_5)Cr(C_7H_7)$	C_6D_6	3.71	5.48	
	CS_2	3.75	5.58	
$(C_5H_5)Mo(C_7H_7)$	$C_6D_5CD_3$	5.00	4.84	
$(C_5H_5)Ti(C_7H_7)$	C_6D_6	4.97	5.47	
	CS_2	5.07	5.43	
$(C_5H_5)Zr(C_7H_7)$	C_6D_6	5 31	5.23	
$(C_5H_5)Ti(C_7H_6CH_3)$	C_6D_6	4.96	5.43 m	2.52
	CS_2	5.06	5.36 m	2.58
$(CH_3C_5H_4)Ti(C_7H_7)$	C_6D_6	4.90 m	5 46	1.81
	CS_2	4 98 m	5 40	1.97

[a] m = multiplet.

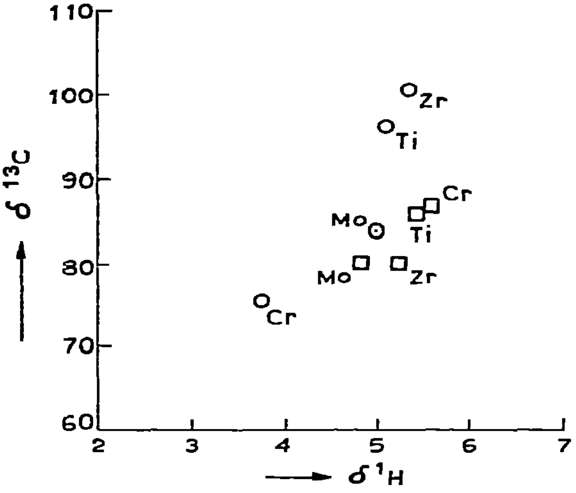

Fig. 1. Relationship between carbon (δ ^{13}C) and proton (δ ^{1}H) chemical shifts (in ppm relative to TMS) of the five- (○) and seven-membered (□) ring of some $(C_5H_5)M(C_7H_7)$ compounds.

cooling the solution in deuterotoluene, the width of the lines increases rapidly, and below 0° no signals are observed. Upon heating of the solution the line broadening decreases and at 100° two sharp singlets are observed. Similar behaviour was found for the Mo compound [11]. The corresponding Ti and Zr compounds do not show line broadening at room temperature, and no changes of the line width were observed on heating (up to 100°) or cooling (down to —70°) the Ti compound.

The difference in behaviour between the Cr and Ti compounds in solution is also reflected in the solid state. In his determination of the crystal structure of $(C_5H_5)Cr(C_7H_7)$ Russell [12] observed orientational disorder (rotation in the ring plane) of the five-membered ring at room temperature. No such disorder was found by Zeinstra and De Boer [13] in their study of $(C_5H_5)Ti(C_7H_7)$. It seems reasonable to assume that in solution the mutual orientation of the two rings of $(C_5H_5)Cr(C_7H_7)$ is fixed at low temperature, that there is hindered rotation at room temperature and free rotation at high temperature. From the change in line shape of the PMR signal with temperature, an activation energy of about 5 kcal mol^{-1} was calculated for the rotation of the rings in (C_5H_5)-$Cr(C_7H_7)$.

Spin—spin coupling constants

The ^{13}C—^{1}H spin—spin coupling constants are given in Table 3. These data show that $J(CH)$ is virtually constant for the five-membered ring, whereas for the seven-membered ring there is a slight increase in the sequence Cr < Mo, Ti < Zr. Although such small differences are difficult to interpret, they may indicate a small increase in *s*-character of the C—H bonding in the sequence given. Long-range coupling constants could only be determined for the five-membered ring. Because so many possibilities for long-range coupling exist for the seven-membered ring, disentangling of the two observed multiplets is not

TABLE 3

$^{13}C-^{1}H$ SPIN—SPIN COUPLING CONSTANTS (IN Hz) FOR SOME CYCLOPENTADIENYLCYCLOHEPTATRIENYLMETAL COMPOUNDS

Compound	C_5H_5				C_7H_7
	J(CH)	*J*(CCH)	*J*(CCCH)	*J*($CCCH_3$)	*J*(CH)
$(C_5H_5)Cr(C_7H_7)$	170	7			159
$(C_5H_5)Mo(C_7H_7)$	172	7			164
$(C_5H_5)Ti(C_7H_7)$	172	7			164
$(C_5H_5)Zr(C_7H_7)$	172	6			168
$(C_5H_5)Ti(C_7H_6CH_3)$	172	7	9		166
$(CH_3C_5H_4)Ti(C_7H_7)$	170	6	8	3	166

feasable. The large solubility of $(C_5H_5)Ti(C_7H_6CH_3)$ made possible a detailed investigation of the coupling constants in the five-membered ring. Two long-range coupling constants were found, namely 9 and 7 Hz. By analogy with results for benzene (where *J*(CCCH) > *J*(CCH) [14]), these two coupling constants were assigned to *J*(CCCH) and *J*(CCH), respectively.

Experimental

All experiments were carried out under purified nitrogen. Solvents were purified by conventional methods, and oxygen removed by repeated degassing. The compounds $(C_5H_5)Ti(C_7H_7)$ [15], $(CH_3C_5H_4)Ti(C_7H_7)$ [16] and $(C_5H_5)Ti(C_7H_6CH_3)$ [16] were prepared according to published procedures. The synthesis of $(C_5H_5)Zr(C_7H_7)$ will be described in a separate paper, together with the improved synthesis of the compounds $(C_5H_5)M(C_7H_7)$ (M = Cr, Mo). The CMR spectra of the titanium and chromium compounds were recorded in CS_2 solution, the spectra of the zirconium and molybdenum compounds in C_6D_6 ; for the PMR spectra both solvents were used. The solvent for the measurements on the compounds $(C_5H_5)M(C_7H_7)$ (M = Ti, Cr, Mo) at variable temperatures was $C_6D_5CD_3$.

The PMR spectra were recorded on a Varian A-60 high-resolution instrument The CMR spectra were obtained on a Varian XL-100/15 Fourier Transform spectrometer with proton decoupling at 25.2 MHz. A 12 mm sample tube fitted with a coaxial capillary containing D_2O for ^{2}H field/frequency stabilization was used. Spectra with a good signal-to-noise ratio were obtained by collecting the Fourier Transform resulting from 1000 to 3640 repetitive R.F. pulses of 80 μs duration at intervals of 1.8 s. Undecoupled spectra were obtained by the gated decoupler technique.

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