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CHIROPTICAL STUDY OF SOME METALLOCENYL(PHENYL)CARBINOLS AND CORRESPONDING α-METALLOCENYLCARBENIUM IONS

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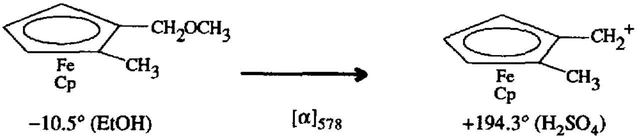
Abstract: The circular dichroism spectra have been reported of ferrocenyl- and ruthenocenyl(phenyl)carbinols with substituents in one or both cyclopentadienyl rings, in acetonitrile (carbinols themselves) and in trifluoroacetic acid (carbenium ions).

Optical activity in α-metallocenylcarbenium ions due to the restricted rotation around the Cp-C$^+$HR bond has been known for some time[2]. Inversion of the sign of optical rotation has been reported in the course of the conversion of α-ferrocenyl- and α-ruthenocenyl(methyl)carbinols to the cations[3]. Similar sign change has also been observed for the simplest carbocation prepared from a precursor also having planar chirality[4]:



That work was the first one, to the best of our knowledge, in which the CD spectra of α-metallocenylcarbenium ions were investigated.

Recently we have described a convenient experimental procedure for preparing metallocenyl(phenyl)carbinols enantiomerically enriched using enantioselective reduction of corresponding ketones[5]. Now we wish to report the CD spectra of these compounds, monosubstituted **A** and **B** as well as1,1'-diols **C** and **D**, in acetonitrile (as carbinols) and in trifluoroacetic acid (as carbocations); Cotton effects (C.E.) are listed in Table 1.

Well-defined C.E. were observed for the ruthenocenyl compound **B**, *viz.*, a positive C.E. of low intensity for the carbinol and a much intensive one for its cation. They correspond to the band II in the absorption spectrum which is composed of two components[6]. In the ferrocene analogue, **A**, the longest wavelength C.E. which is due to band I (see Table 2) does not change the sign when going from the carbinol to the carbocation, although Δε is increased by a factor of 10^2. However, such a sign inversion of Δε does occur in the C.E. near 333 nm which probably corresponds to band III.

Diols **C** and **D** exhibit Δε values whose magnitudes are about twice of those of the corresponding mono carbinols. On the contrary, no optical activity was observed in acidic medium when carbocations were formed. This had been explained in our preceding paper[5] by way of the formation of an achiral ether intermediate.

Table 1. Cotton effects in CD spectra of mono- and 1,1'-di-metallocenyl(phenyl)carbinols and corresponding carbocations

				Solvent					
Substance		CH_3CN (carbinols)				CF_3COOH (cations)			
		λ_{max}	$\Delta\varepsilon$	conc.(mM/L)	d (cm)	λ_{max}	$\Delta\varepsilon$	conc. (mM/L)	d (cm)
A	FcCH(OH)Ph	470	-0.03	2.3	2.0	443	-6.2	1.9	0.05
		384	-0.005			380	-3.8		
		335	+0.02			330	-2.5		
						290	-1.0		
B	RcCH(OH)Ph	324	+0.24	2.6	0.5	315	-14.8	0.7	0.1
		275	+0.05						
C	$Fc(CHOHPh)_2$	448	-0.21	0.65	1.0		zero		
		339	+0.09						
		272	-1.56	0.65	0.2				
		250	+0.17						
D	$Rc(CHOHPh)_2$	331	+0.36	1.8	0.5		zero		
		280	+0.145						

Table 2. This assignment of electronic transitions in ferrocene and ruthenocene according to Sohn, Hendrickson and Gray[6]

		λ_{max}	
band	transition	Cp_2Fe	Cp_2Ru
I	$^1A_{1g}\longrightarrow a^1E_{1g}$	458	384
II	$^1A_{1g}\longrightarrow b^3E^*_{1g}$	417	339
	$^1A_{1g}\longrightarrow {}^1E_{2g}$		307
III	$^1A_{1g}\longrightarrow b^1E_{1g}$	325	273

It is interesting to compare the intensities of these C.E. measured for enantiomeric metallocenes with those observed before for related achiral compounds in the cyclodextrin-induced spectra. For the equilibrium system acetylferrocene - β-cyclodextrin in ethylene glycol[7] the $\Delta\varepsilon$ value was determined −0.047 whereas for compound **A** (Table 1) it is −0.03. This shows that the 'natural' and the cyclodextrin-induced values are of the same order of magnitude.

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