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FERROCENYL DERIVATIVES OF DICYCLOPENTADIENYL-TITANIUM, -ZIRCONIUM AND -HAFNIUM

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Summary

Ferrocenyl compounds $(C_5H_5FeC_5H_4)_2M(C_5H_5)_2$ ($M = Ti, Zr, Hf$) were synthesized by treatment of dicyclopentadienylmetal dichloride with ferrocenyllithium. These air-sensitive, strongly coloured crystalline solids are sublimed at $120^\circ C$ in vacuum (10^{-2} Torr). IR, UV and PMR spectra confirm the structure of these derivatives.

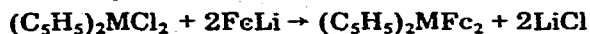
Introduction

The ferrocenylation reactions of organic compounds with ferrocenyllithium are of great interest in synthetic organic chemistry [1]. The ferrocenylation reactions of various organometallic non-transition metal compounds have been well studied. Yet, the reactions of ferrocenyllithium with organometallic transition metal compounds, particularly with other metallocenes, have not been studied.

In this work the syntheses of diferrocenyl derivatives of dicyclopentadienyl-titanium, -zirconium and -hafnium are described and some of their physico-chemical properties are discussed.

Results and discussion

The compounds studied are obtained by treatment of ferrocenyllithium (FcLi) with the dichlorides of the corresponding metallocenes in a mixture of THF, ether and hexane.



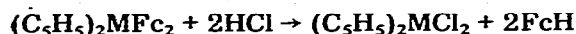
$M = Ti, Zr, Hf$; $Fc = (C_5H_4FeC_5H_5)$

The complexes obtained were completely purified from lithium compounds by recrystallization from benzene, or by sublimation.

TABLE I
DTA DATA FOR $(C_5H_5)_2MFC_2$ COMPLEXES

Metal	Ti	Zr	Hf
Decomposition temperature ($^{\circ}C$)	156	154	137

Diferrocenyltitanocene is isolated as dark green crystals which are rather stable in air but decompose in solution. Diferrocenylzirconocene and diferrocenylhafnocene are bright red crystalline substances. They are less stable than the titanium analogue when exposed to moisture or oxygen in the air. All the complexes obtained react readily with dry HCl with quantitative isolation of ferrocene and the corresponding metallocene dichlorides:



Differential thermal analysis

In every case thermograms show one irreversible exothermal effect, which is due to decomposition by heat. The decomposition temperatures are listed in Table 1.

Thermolysis of compounds

On heating the complexes to a temperature close to the decomposition temperatures, the compounds decompose with ferrocene isolation and formation of an M-containing residue, which has lost its Cp_2M structure. These results agree well with the data of ref. 2, in which the decomposition is proved to occur through intramolecular hydrogen atom abstraction either from the Cp ring or from another R group. Yet, with decomposition of the diferrocenyltitanocene diferrocenyl formation is observed as the more complicated decomposition mechanism of the given compound. The detailed data on the thermal decomposition of the compounds obtained will be published in a subsequent paper.

On the basis of the chemical behavior of the Cp_2MFC_2 complexes obtained, the presence of metal-carbon σ -bonds of the ferrocene cyclopentadienyl ring may be expected, as with the $(Et_2N)_2TiFc_2$ compound recently obtained [3].

This assumption is confirmed by spectral investigations. The comparative analysis of the electron spectra of ferrocene [4], titanocene and zirconocene dichlorides [5] and of the complexes obtained shows the presence of an intensive absorption band, typical only for Cp_2MFC_2 , in the visible spectrum region at 665 nm (max) for Cp_2TiFc_2 and at 480 nm (max) for Cp_2ZrFc_2 . This band may be assigned to an electron transition with charge transfer between the ferrocene and metallocene fragment orbitals, that is, to an electron transition from the upper occupied ferrocene molecular orbital into the lowest vacant Cp_2M fragment orbitals (Fig. 1).

The location of the ferrocenyl and Cp_2M -fragment orbitals is such that at their interaction ferrocenyl behaves as a donor in a complex molecule and Cp_2M as an electron acceptor. This is seen from the participation of the vacant MO of the Cp_2M fragment in the formation of the upper occupied MO of the Cp_2MFC_2 .

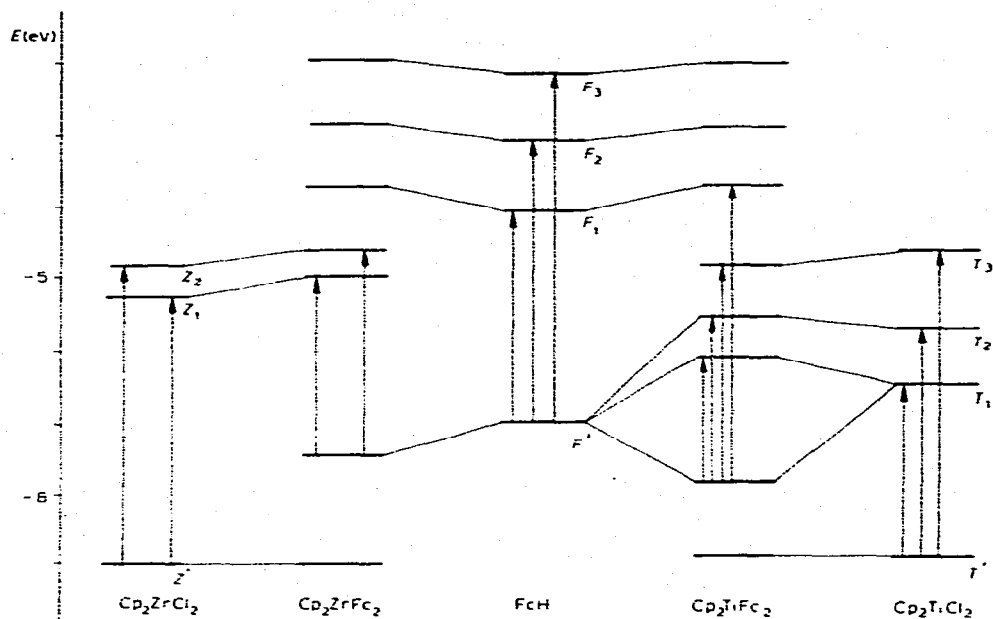


Fig. 1. Interaction scheme of $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$ and Cp_2M fragment molecular orbitals. F , T and Z values for correlation were selected to be equal ionization potentials of Cp_2Fe , Cp_2MCl_2 from mass-spectral data [7].

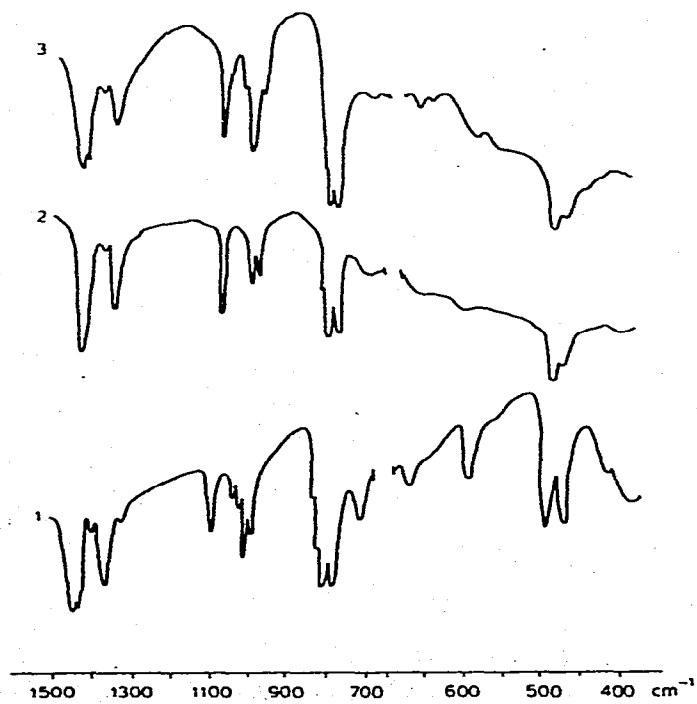


Fig. 2. IR spectra of (1) Cp_2TiFc_2 , (2) Cp_2ZrFc_2 and (3) Cp_2HfFc_2 (in Nujol).

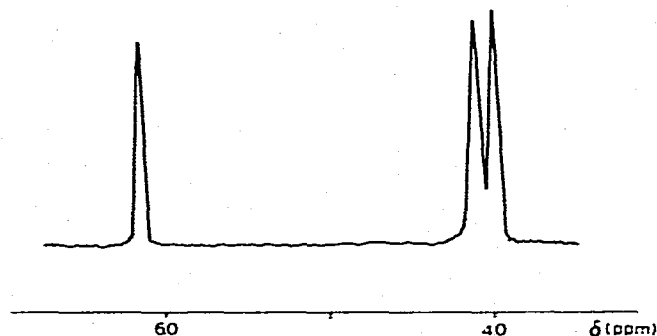


Fig. 3. PMR spectrum of Cp_2TiFc_2 in deuterioethene.

The most interesting region of the IR spectra of the complexes obtained (Fig. 2) is a deformation vibration region of C—H bonds of the Cp rings ($900\text{--}1100\text{ cm}^{-1}$). The spectrum of Cp_2TiFc_2 in this region is rich in absorption bands, this being indicative of perturbations either in the titanium Cp rings or in the ferrocene Cp rings due to Ti—C bond formation in the ferrocene Cp rings. These perturbations may be associated: (1) with steric factors caused by the ferrocenyl ligands in Cp_2Ti oscillations; (2) with charge transfer from ferrocenyl onto titanium orbitals, and this may lead to changes in π -electron delocalization of ferrocene Cp rings; (3) with peculiarities of the crystalline packing of Cp_2TiFc_2 .

The absence of such perturbations in IR spectra of similar zirconium and hafnium compounds having a large metal radius points in favor of the first and the third factors.

The conclusion about proton equivalency of the titanium Cp rings is deduced from the PMR spectrum of Cp_2TiFc_2 (Fig. 3). Ferrocenyl proton signals correspond to the literature data for monosubstituted ferrocenes [6].

Experimental

Dicyclopentadienyldiferrocenyl titanium

1 g of Cp_2TiCl_2 (4.05 mmol) was added with stirring to a ferrocenyllithium solution, obtained by metallation of 5.6 g ferrocene in a mixture of ether and tetrahydrofuran (1/1) by *n*-butyllithium (48 ml, 0.65 *N* in hexane) under argon. After stirring for 1 h the reaction mixture was carefully decanted from the residue, which was then washed several times with warm hexane. The residue is extracted many times then with benzene, and the solvent removed under vacuum. 1.1 g of fine dark-green crystals of Cp_2TiFc_2 (yield 50%) are isolated. A more purified substance can be obtained by sublimation of these ($120^\circ\text{C}/10^{-2}$ Torr). Analysis Found: C, 65.4; H, 5.1; Ti + Fe, 29.2. $\text{C}_{20}\text{H}_{20}\text{FeTi}$ calcd.: C, 65.6; H, 5.1; Ti + Fe, 29.2%.

The action of hydrogen chloride on diferrocenyltitanocene

A stream of dry HCl was passed for some minutes into a suspension of Cp_2TiFc_2 (0.674 g, 1.350 mmol) in absolute hexane. After filtration and washing

the residue with hexane 0.301 g (1.200 mmol) of Cp_2TiCl_2 was obtained (m.p. 284°C) and 0.490 g (2.630 mmol) of ferrocene (m.p. 172°C) was isolated from the filtrate.

Diferrocenylzirconocene and diferrocenylhafnocene

These compounds were prepared by an analogous procedure. After purification by sublimation the substances obtained are red crystalline compounds, readily soluble in benzene and tetrahydrofuran and insoluble in hexane.

On treatment with dry HCl in hexane 0.320 g (0.540 mmol) of Cp_2ZrFc_2 , 0.150 g (0.514 mmol) of Cp_2ZrCl_2 (m.p. 244°C) and 0.202 g (1.070 mmol) of ferrocene (m.p. 171°C) were formed.

Similarly, from 0.674 g (0.994 mmol) of Cp_2HfFc_2 , 0.370 g (0.992 mmol) of Cp_2HfCl_2 (m.p. 230°C) and 0.360 g (1.938 mmol) of ferrocene (m.p. 171°C) were formed.

All the substances were also identified by IR spectroscopy.

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