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Synthesis, Characterization and Mass Spectra of the Titanocene Derivatives $Cp_2Ti(XC_6F_5)_2$ (X = O, S)

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Abstract

Two different methods of preparation and the ^1H NMR and mass spectra of the titanocene complexes, $Cp_2Ti(XC_6F_5)_2$ (X = O, S; Cp = η^5-C_5H_5), are discussed. The mass spectra indicate a loss of cyclopentadienyl and pentafluorophenylchalcogeno radicals and, in the case of the thiolate derivative, a rearrangement to Cp_2TiF_2. Overmore, neutral particle eliminations of HF and CpH are observed. The ion genesis of the phenolate complex was proven by persecution of metastable transitions using the linked scan technique. The ^1H NMR chemical shifts are interpreted in terms of electronegativity and donor ability of the coordinated chalcogen atoms.

Introduction

Numerous bis(phenolato) complexes of the titanocene system, $Cp_2Ti(OR)_2$ (R = aryl), were prepared by reaction of the free phenol with Cp_2TiCl_2 in 2:1 molar ratio in the presence of an excess of $NaNH_2$ [1–3].

The $Cp_2Ti(SR)_2$ compounds are considerably more stable than the corresponding oxygen-coordinated derivatives [4]. The following general methods are suitable for the preparation of titanocene bis(thiophenolato) complexes:

- Reaction of Cp_2TiCl_2 with RSH in the presence of triethylamine [6, 7].
- Reaction of Cp_2TiCl_2 with the appropriate sodium thiolate RSNa [8].
- Treating of an organic disulfide with $Cp_2Ti(CO)_2$ [9].
- Reaction of Cp_2TiCl_2 with an excess of $RSSi(CH_3)_3$ [10].

We now describe the synthesis, ^1H NMR and mass spectra of two pentafluorophenylchalcogeno compounds as a part of our investigation of chalcogen-coordinated titanocene complexes. These fluorine-containing derivatives are interesting because of their catalytic activity in the polymerization of alkenes [5].

Experimental

All reactions were carried out in an inert gas atmosphere by using the Schlenk technique. The solvents were purified, dried and argon-saturated.

Titanocene dichloride was prepared as cited in the literature [11]. Commercially available reagents C_6F_5OH (Merck) and C_6F_5SH (Alfa) were used without further purification.

Mass spectra were measured (Varian MAT 311 A) with an electron impact source; the metastable transitions were observed by the linked scan technique. ^1H NMR spectra were recorded on a Bruker WP 80 spectrometer. Elemental analysis was performed on a Perkin-Elmer C, H, N analyser 185.

Preparation of Complexes

Bis(η^5-cyclopentadienyl)bis(pentafluorophenolato)titanium(IV) (I)

Into a solution of 1.65 g (8.96 mmol) C_6F_5OH and 1.12 g (4.48 mmol) Cp_2TiCl_2 in 100 ml dry benzene 1.52 ml (11.0 mmol) of NEt_3 were dropped and stirred overnight. The red solution was evaporated and the remaining residue extracted with boiling benzene. After concentrating the extract to 10 ml the solution was allowed to stand for 12 h and the precipitate was collected by filtration and dried *in vacuo*. Yield 0.60 g (24.7%). *Anal.* Calc. for $C_{22}H_{10}F_{10}O_2Ti$ [544.20]: C, 48.6; H, 1.9. Found: C, 48.4; H, 1.6%. ^1H NMR ($CDCl_3$), δ (ppm): 6.37 s. MS (135 °C), m/z (rel. int.): 544(8) M^+, 525(1) $M^+ - F$, 479(9) $M^+ - Cp$, 414(4) $M^+ - 2Cp$, 361(100) $M^+ - OC_6F_5$, 341(10) $M^+ - OC_6F_5{-}HF$, 295(24) $M^+ - OC_6F_5{-}CpH$, 178(92) $M^+ - 2OC_6F_5$, 167(78) $C_6F_5{}^+$.

Bis(η^5-cyclopentadienyl)bis(pentafluorothiophenolato)titanium(IV) (II)

Method A. 0.93 g (3.74 mmol) Cp_2TiCl_2 were reacted, as described for **I**, with 1.50 g (7.50 mmol) C_6F_5SH in the presence of 1.39 ml (10.0 mmol) NEt_3. Yield 1.00 g (46.5%). *Anal.* Calc. for $C_{22}H_{10}F_{10}S_2Ti$ [576.33]: C, 45.8; H, 1.7. Found: C, 46.0;

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H, 2.0%. ^{1}H NMR ($CDCl_3$), δ (ppm): 6.10 s. MS (190 °C), m/z (rel. int.): 576(3) M^+, 557(6) $M^+ - F$, 556(5) $M^+ - HF$, 511(4) $M^+ - Cp$, 377(24) $M^+ - SC_6F_5$, 311(7) $M^+ - SC_6F_5 - CpH$, 216(28) $Cp_2TiF_2^+$, 197(7) Cp_2TiF^+, 178(100) $M^+ - 2SC_6F_5$.

Method B. n-Butyllithium (11.50 mmol) was dropped into a solution of 2.30 g (11.50 mmol) C_6F_5SH in 100 ml dry benzene. After stirring the mixture for 1 h 1.43 g (5.74 mmol) Cp_2TiCl_2 were added. The deep red solution was allowed to react for 4 h, after which it was filtered and the solution was concentrated to 20 ml under reduced pressure. The precipitated red product was collected by filtration and recrystallized from benzene/methanol. Yield 2.25 g (68.0%). Analytical and spectroscopical results were in agreement with the data reported with method A.

Results and Discussion

By the reaction of titanocene dichloride with the free ligand acid pentafluorophenol or pentafluorothiophenol in the presence of a base (e.g. triethylamine), both chloro ligands could be substituted (eqn. (1)):

$$Cp_2TiCl_2 + 2C_6F_5XH + 2NEt_3 \longrightarrow Cp_2Ti(XC_6F_5)_2 + 2NEt_3 \cdot HCl \quad (1)$$

(X = O, **I**; S, **II**)

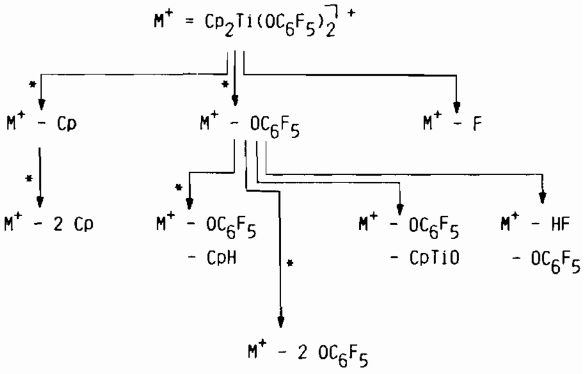
The thiophenolato derivative **II** was also prepared by treating Cp_2TiCl_2 with the lithium ligand salt, yielded from C_6F_5SH and n-butyllithium (eqn. (2)):

$$Cp_2TiCl_2 + 2LiSC_6F_5 \longrightarrow \mathbf{II} + 2LiCl \quad (2)$$

The identities of **I** and **II** were proved by elemental analysis, ^{1}H NMR, and mass spectra. Both complexes are red, they are thermally stable (**II** more than **I**), and quite stable in air, but their solutions decompose on standing in air for a period of several days. The complexes **I** and **II** are soluble in benzene, chloroform and methylene chloride; they are moderately soluble in alcohols but quite insoluble in pentane and water.

The ^{1}H NMR spectra of **I** and **II** only show one sharp singlet, according to the presence of ten chemically equivalent cyclopentadienyl protons. In comparison to Cp_2TiCl_2 the Cp resonances are shifted to a higher field. Because of the different donor ability of the coordinating chalcogen atoms, the singlet of **II** appears at 6.10 ppm and is more high-field shifted than that of **I** (6.37 ppm). The Cp resonance of **II** was found in the same region as published for the Cp singlets in $Cp_2Ti(SC_6H_5)_2$ (6.13 ppm), $Cp_2Ti(SC_6H_4NH_2\text{-}p)_2$ (6.00 ppm), and $Cp_2Ti(SC_6H_4Cl\text{-}p)_2$ (6.05 ppm) [6, 12]. Due to this result the chemical shifts in the ^{1}H NMR spectra of $Cp_2Ti(XPh)_2$ (X = O, S; Ph = C_6H_5, C_6H_4Cl, $C_6H_4NH_2$, C_6F_5) depend on the nature of the chalcogen atom coordinated directly to the titanocene system; this effect is of more significant influence than mesomeric or inductive effects of substituents at the phenyl rings.

The mass spectra of **I** and **II** show, as signal of highest m/z value, a peak of the molecule ion and, with high intensity in both cases, fragmentation of one or both XC_6F_5 (X = O, S) ligands. While the base peak in the mass spectrum of **I** accords with the ion $M^+ - OC_6F_5$, it is given in the spectrum of **II** by the $M^+ - 2SC_6F_5$ ion. In addition to a Cp elimination of **I** and **II**, the thiophenolato derivative **II** shows, under fragmentation, a rearrangement to $Cp_2TiF_2^+$, followed by the elimination of F to Cp_2TiF^+. The ion genesis of **I** was proven by the persecution of metastable transitions (Scheme 1).



Scheme 1. Fragmentation pattern of **I** in the mass spectrum, * transitions proven by metastable transitions (linked scan technique).

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