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SYNTHESIS AND PROPERTIES OF ALKYLDICYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

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Summary

The preparation and characterization of the compounds Cp_2TiR (R = $(CH_2)_3OCH_3$, $(CH_2)_4OCH_3$, $(CH_2)_3SCH_3$ and $(CH_2)_4SCH_3$) are described. Their physical and chemical properties demonstrate the presence of the Cp_2Ti group and a Ti-C σ-bond. In the compounds the O or S atom is internally coordinated to the metal atom. The thermal stability decreases in the order R = $(CH_2)_3OCH_3 > (CH_2)_3SCH_3 \sim (CH_2)_4OCH_3 > (CH_2)_4SCH_3$.

Introduction

Compounds of the type Cp_2TiR, where R = alkyl, have been decribed only recently [1]. There are indications that they are thermally unstable [2], and decompose to hydridic complexes, e.g. $[Cp_2TiH_2]^-$, presumably by β-hydrogen elimination [1]. With R groups containing no β-hydrogen, the stability is higher, and a number of compounds can be isolated and characterized, e.g. those with R = $CH_2C_6H_5$ [3], $CH_2C(CH_3)_3$ [2] and $CH_2Si(CH_3)_3$ [4].

Studies on the related aryl compounds Cp_2TiR showed that the thermal stability can be enhanced by blocking the reactive site on the metal, either sterically (as in Cp_2Ti-*o*-tolyl [5]) or by internal coordination (as in the compound Cp_2TiR with R = 2-$\{(CH_3)_2NCH_2C_6H_4\}$* [6,7]). We have explored the use of this concept of internal complexation in the synthesis of thermally stable, β-hydrogen-containing alkyl derivatives of the type: $Cp_2\underline{Ti \leftarrow Y(C}H_2)_n$ (Y = $N(CH_3)_2$, OCH_3, SCH_3; n = 3, 4).

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* The coordination of the N atom to the metal was confirmed by X-ray analysis [7].

Results and discussion

The preparation of the compounds by the Grignard method was attempted (eq. 1). For each group R, the temperature (between −40 and +25°C) and the

$$Cp_2TiCl + RMgCl \rightarrow Cp_2TiR + MgCl_2 \qquad (1)$$

solvent (THF, ether or pentane) were varied, until optimal conditions were reached. Reactions aimed at $Cp_2Ti(CH_2)_3N(CH_3)_2$ gave deep-green to black products, apparently polymeric. Bands in the IR spectrum around 1200 cm^{-1} indicate the presence of Ti—H—Ti bridges [8]. Nitrogen was also present, but the Ti—N ratios never reached an acceptable stoichiometry. Thus the experiments with amino-group-functionalized Grignards were discontinued.

The Grignard method was successful for the preparation of Cp_2TiR with R = $(CH_2)_3OCH_3$ (I), $(CH_2)_4OCH_3$ (II), $(CH_2)_3SCH_3$ (III) and $(CH_2)_4SCH_3$ (IV), which were obtained in low to moderate yields and purified by recrystallization from n-pentane (Table 1).

Elemental analyses, chemical and physical properties are in agreement with the formula: $Cp_2\underline{Ti \leftarrow Y(C}H_2)_n$ (Y = OCH_3, SCH_3; n = 3, 4);

The IR spectra all are very similar, showing the characteristic η^5-C_5H_5 bands at about 3100w, 1120w, 1010s and 790s cm^{-1}. For I and II a band at 1075 cm^{-1} (I) and at 1065 cm^{-1} (II) is assigned to the ν(COC) of the coordinated ether group. These frequencies are lowered by 40 and 55 cm^{-1}, respectively, compared with the starting chloro ethers, a shift quite normal for a complexed ether group [9,10]. Due to the low intensity of the ν(CSC) frequencies and the problematic assignment of these bands, no such comparison can be made between the free and complexed thioethers [10—12]. However a small upward shift of the CH_3 rocking modes in the titanium compounds is in line with observations reported for thio ether adducts of vanadium halides [11]. In all spectra a peak at about 450 cm^{-1} is assigned as ν(Ti—σ-C) [4].

TABLE 1

PREPARATION AND PHYSICAL DATA OF Cp_2TiR COMPOUNDS

Compound	Reaction conditions	Yield (%)	Colour	Decomp. point [b] (°C)	Analysis (Found (calcd.) (%))		
					C	H	Ti
I, R = $(CH_2)_3OCH_3$	ether, 0°C 60 min	22	Reddish-brown	104	66.49 66.13 (66.94)	7.59 7.33 (7.62)	19.26 19.13 (19.07)
II, R = $(CH_2)_4OCH_3$	ether, −35°C [a] 10 min	10	Light-brown	67	66.98 66.71 (67.92)	8.09 7.90 (7.98)	17.93 18.22 (18.07)
III, R = $(CH_2)_3SCH_3$	ether, 0°C 60 min	15	Purple	67	62.49 62.67 (62.91)	7.13 7.14 (7.16)	17.96 18.16 (17.92)
IV, R = $(CH_2)_4SCH_3$	ehter, −35°C [a] 10 min	6	Dark-brown	54	63.57 63.94 (64.05)	7.38 7.53 (7.52)	17.19 17.16 (17.03)

[a] The temperature was kept below −35°C during synthesis and recyrstallization. [b] Determined by DTA [5].

The molecular weight of I shows it to be monomeric, and the observed magnetic moment of 1.69 BM is close to the spin-only value of 1.72 BM calculated for a titanium(III) compound Cp_2TiR.

The chemical properties also agree with the proposed structure, as is demonstrated by the reactions with HCl and Br_2 (eq. 2, 3).

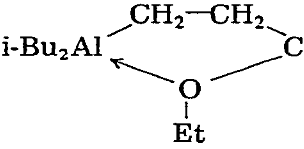
$$Cp_2TiR + HCl \rightarrow Cp_2TiCl + RH \qquad (2)$$

$$Cp_2TiR + \tfrac{3}{2}Br_2 \rightarrow Cp_2TiBr_2 + RBr \qquad (3)$$

Internal coordination of the ligand blocks a vacant site on the metal which would otherwise be available for coordination with another ligand e.g. N_2 (cf. [2,13]). So, when solutions of the compounds in pentane are cooled (even to —110°C) under nitrogen no deep-blue-colour characteristic for the formation of the dinitriogen complexes $(Cp_2TiR)_2N_2$ [2,13] is observed.

The thermal stabilities of the four compounds show some interesting aspects. The synthesis of II and IV had to be carried out below —30°C to avoid decomposition of the products and formation of methylallyldicyclopentadienyltitanium [14]. The latter was the main product at higher temperatures. Methanol (or methanethiol) was also formed and the decomposition can be rationalized as in eq. 4.

$$Cp_2Ti(CH_2)_4OCH_3 \rightarrow Cp_2Ti(CH_3C_3H_4) + CH_3OH \qquad (4)$$

This elimination of a methoxy group in a δ-position of the alkyl chain is surprising compared with e.g. the decomposition of  , in which cyclopropane is formed and the alkoxy group transferred to the metal [15,16].

In contrast, the compounds I and III can be prepared and kept in solution at about 0°C without decomposition.

The isolated compounds I, II, III and IV are thermally fairly stable (Table 1), the stability order being I > II ~ III > IV. In this respect they are very similar to corresponding vanadium compounds Cp_2VR, where R is a normal alkyl group without a substituent donor [17]. In contrast to our observations on the thermal decomposition in solution, no allylic complexes and CH_3SH or CH_3OH were formed in the decomposition of the solid compounds.

This variation in thermal stability of this series of compounds, both in the solid state and in solution, probably is related to the size of the metallocycle $\underline{Y \rightarrow Ti(CH_2)_n}$ the systems with $n = 3$, being more stable than with $n = 4$. An explanation may be found in the relative position of the reactive site of the metal and hydrogen or oxygen (sulphur) of the alkyl group, which depends strongly on the ring size, see e.g. [18,19].

A more detailed investigation of the thermal decomposition as a function of the ring size is being carried out in our laboratory.

Experimental

All experiments were performed under Ar. Solvents were distilled from $LiAlH_4$. Elemental analyses were carried out in the Analytical Department of this University under the supervision of Mr. A.F. Hamminga. IR-Spectra (Nujol mulls) were recorded using a Hitachi EPI-G spectrophotometer. Molecular weights were determined by cryoscopy (benzene), and magnetic susceptibilities by the Faraday method.

Starting materials were prepared by published methods: $Cl(CH_2)_3OCH_3$ [20], $Cl(CH_2)_4OCH_3$ [21], $Cl(CH_2)_3SCH_3$ [22], $Cl(CH_2)_4SCH_3$ [23].

Preparation of the compounds

All the compounds were prepared in essentially the same way on 2—5 mmole scale. A typical example is given below. Relevant data for the preparation of the other compounds can be found in Table 1.

3-Methoxypropyldicyclopentadienyltitanium(III). $MgCl(CH_2)_3OCH_3$ (4.00 mmol) in ether was added at 0°C to a well-stirred suspension of Cp_2TiCl (4.00 mmol) in ether. After stirring for 1 h the ether was pumped off at 0°C and pentane added. The red-brown solution was filtered at 0°C and cooled to −80°C. Red-brown crystals separated. The product was washed with pentane, dried in vacuum, and isolated. Yield 0.222 g (0.88 mmol; 22%). The molecular weight was 271 (calcd. 251) and the magnetic moment (100—300 K) 1.69 BM.

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