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2-(DIMETHYLAMINOMETHYL)PHENYLDICYCLOPENTADIENYLTITANIUM(III) AND -VANADIUM(III)

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Summary

The preparation of the air-sensitive complexes $Cp_2M[2\text{-}\{(CH_3)_2NCH_2\}\text{-}C_6H_4]$ (M = Ti, V) is described. Their physical and chemical properties demonstrate the presence of the Cp_2M group and a M—C σ-bond. In the titanium compound the amino group is internally coordinated to the metal atom, in contrast to the vanadium analogue. The thermal stabilities of the compounds are considered along with those of other compounds Cp_2MR (M = Ti, V; R = aryl).

Introduction

Investigations of the thermal stability of compounds of the type Cp_2TiR (R = aryl) have led to the assumption that an empty titanium orbital plays an active role in the thermal decomposition [1]. Enhancement of the thermal stability could be achieved by blocking this active site sterically [1, 2] or by complexation with a donor molecule (e.g. molecular nitrogen [1, 3]). Increase in thermal stability is also expected for compounds Cp_2TiR in which R is a group capable of intramolecular coordination, such as 2-[(dimethylamino)-methyl]phenyl [4].

In this paper we describe the synthesis and properties of $Cp_2Ti[2\text{-}\{(CH_3)_2\text{-}NCH_2\}C_6H_4]$ and the corresponding vanadium compound. The latter was prepared for comparison because internal coordination is unlikely in it. The compounds were also compared with $Cp_2Ti(o\text{-}CH_3C_6H_4)$ and $Cp_2V(o\text{-}CH_3C_6H_4)$ in order to estimate the contribution of coordination to the increase in thermal stability.

Experimental and results

All experiments were performed under nitrogen using Schlenk-type glassware. Details on equipment and methods were given before [1—3]. EPR spectra were recorded with a Varian E3 X-band EPR spectrometer. ^1H NMR spectra were obtained with a Varian A-60 instrument. Benzyldimethylamine (Fluka) and n-butyllithium (20% in hexane, Merck) were obtained commercially. 2-[(Dimethylamino)methyl]phenyllithium was prepared according to ref. 5. Molecular weights were determined cryoscopically in benzene.

2-[(dimethylamino)methyl]phenyldicyclopentadienyltitanium(III), $Cp_2Ti[2-\{(CH_3)_2NCH_2\}C_6H_4]$

Solid 2-[(dimethylamino)methyl]phenyllithium (2.26 g, 16.0 mmoles) was added at room temperature to a well-stirred suspension of Cp_2TiCl (3.20 g, 15.0 mmoles) in 50 ml of toluene. After 1.5 h stirring the reaction mixture was concentrated to 25 ml and filtered. Upon cooling the filtrate to —78°, brown-purple crystals separated. After decanting of the mother liquor, the product was dried in vacuum, and isolated. More product was obtained by extracting the evaporated liquor with hexane. Yield 3.16 g (10.1 mmoles, 67%). The compound was purified by recrystallization from hexane; m.p. 134°. (Found: C, 73.15, 73.17; H, 7.24, 7.30; N, 4.41, 4.41; Ti, 15.27, 15.30; Mol. wt., 313. $C_{19}H_{22}NTi$ calcd.: C, 73.07; H, 7.10; N, 4.49; Ti, 15.33% Mol. wt., 312.3).

2-[(dimethylamino)methyl]phenyldicyclopentadienylvanadium(III), $Cp_2V[2-\{(CH_3)_2NCH_2\}C_6H_4]$

Solid 2-[(dimethylamino)methyl]phenyllithium (1.57 g, 11.1 mmoles) was added at —78° to a well-stirred suspension of Cp_2VCl (2.17 g, 10.0 mmoles) in 200 ml of ether. After warming to room temperature (3.5 h) the reaction mixture was filtered, and the filtrate concentrated to 50 ml and slowly cooled to —78°. Glittering black crystals separated. After decanting of the mother liquor, the product was washed three times with small amounts of ether (—78°), dried in vacuum (room temperature) and isolated. Yield 2.21 g (7.02 mmoles, 70%). The compound was recrystallized from hexane; m.p. 112°. (Found: C, 72.23, 72.37; H, 7.17, 7.09; N, 4.51, 4.58; V, 16.24, 16.28; Mol. wt., 311. $C_{19}H_{22}NV$ calcd.: C, 72.37; H, 7.03; N, 4.44; V, 16.15%. Mol. wt., 315.3.)

Physical properties

The IR spectra of the compounds are shown in Fig. 1. Absorption spectra (340—1000 nm) were taken in toluene. The following data were obtained: $Cp_2Ti[2-\{(CH_3)_2NCH_2\}C_6H_4]$, 548 nm ($\epsilon = 25$ l mol^{-1} cm^{-1}), 820 (41); $Cp_2V[2-\{(CH_3)_2NCH_2\}C_6H_4]$, 436 (140), 518 (89), 696 (130). EPR spectra were also recorded in toluene (10^{-4}—10^{-3} *M*) between 130—300 K. For $Cp_2Ti[2-\{(CH_3)_2NCH_2\}C_6H_4]$ only a singlet was observed ($g = 1.983$, width 2.8 G). The vanadium compound gave no signal. The magnetic susceptibility of $Cp_2V[2-\{(CH_3)_2NCH_2\}C_6H_4]$ was measured between 100—300 K. Found: $\mu = 2.6$ B.M., corresponding to two unpaired electrons per molecule (calcd. for spin only $\mu = 2.83$ B.M.).

Chemical properties

No reaction was observed upon exposing the compounds (both in solution and in the solid state) to molecular nitrogen at temperatures down to —80°. With oxygen, reaction took place immediately to give unidentified products.

The compounds reacted with HCl in ether at —78° quantitatively according to eqn. 1. After the mixture had warmed to room temperature Cp_2MCl was oxidized with an excess of HCl and air (eqn. 2).

$$Cp_2M[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4] + 2\ HCl \rightarrow Cp_2MCl + [C_9H_{14}N]^+Cl^- \qquad (1)$$

$$2\ CpMCl + 2\ HCl + \tfrac{1}{2}O_2 \rightarrow 2\ Cp_2MCl_2 + H_2O \qquad (2)$$

(M = Ti, V)

In ether at 0° the compounds slowly reacted with D_2O. After 24 h the ether layer was separated and investigated by GLC. The major product was isolated and identified as (2-deuterobenzyl)dimethylamine by IR [ν(C—D) 2250 cm^{-1}, characteristic group frequencies for 1,2-disubstituted phenyl group at 1700—2000 cm^{-1}, at 849 cm^{-1} and at 732 cm^{-1} (C—H def.) [6, 7]] and NMR [(THF-d_8, TMS internal): δ 2.17 (s, 6 H, $N(CH_3)_2$) 3.38 (s, 2 H, $—CH_2—N$) and 7.29 ppm (m, 4 H, C_6H_4D)].

Thermal decomposition

The compounds were investigated by DTA [1]. Thermograms showed two thermal effects for each of the compounds ($Cp_2V[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ 111°, 199°; $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ 134°, 226°), the first one being endothermic, that at higher temperature exothermic. The endothermic effects were due to melting as was confirmed by melting point determinations using a silicon oil bath. The exothermic effects indicated thermal decomposition. The products of the thermal decomposition were analyzed. $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ decomposed at 230—240° giving benzyldimethylamine (90%), and a black titanium-containing residue formulated as "$C_9H_{10}Ti$", similar to the decomposition of other compounds of the type Cp_2TiR (R = aryl) [1]. The vanadium compound decomposed in a different way giving benzyldimethylamine (63%), Cp_2V (60%), and two more V-containing products which are under investigation.

Discussion

The very air sensitive compounds were prepared following a general method [8]:

$$Cp_2MCl + RLi \rightarrow Cp_2MR + LiCl$$

(M = Ti, V; R = $C_9H_{12}N$)

Elementary analyses and molecular weight determinations in benzene are in accordance with the formulation as monomeric compounds with the composition $Cp_2MC_9H_{12}N$ (M = Ti, V). Details concerning the structure of the compounds are derived from the chemical and physical properties.

The IR spectra (Fig. 1) of both compounds show absorption characteristic for π-bonded cyclopentadienyl groups (absorptions at 3100—3080, 1430, 1370, 1120, 1010 and 800 cm^{-1}) [9]. For $Cp_2TiC_9H_{12}N$ the bands at 3100 cm^{-1}

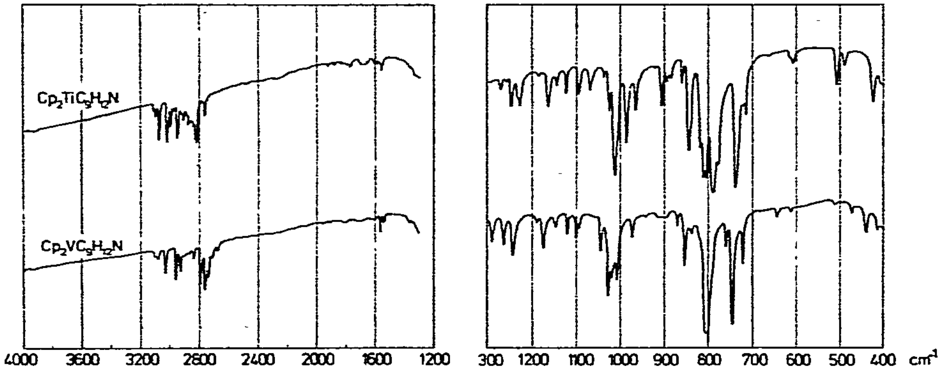
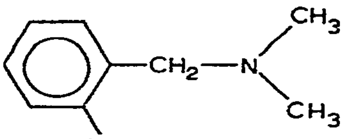


Fig. 1. IR spectra of $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ and $Cp_2V[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ (4000—1200 cm^{-1} in Voltralef -3S; 1300—400 in Nujol).

(C—H stretch) and at 800 cm^{-1} (C—H def. ⊥) are split into several components. Characteristic group frequencies of moiety A are also observed, e.g. 740—750



(A)

cm^{-1} C—H def. ⊥ for 1,2-disubstituted phenyl [6], 840—850 cm^{-1} band diagnostic for the aryl—CH_2—$N(CH_3)_2$ group [7].

The presence of the Cp_2M (M = Ti, V) moiety and of M—C σ-bonds is illustrated by the reaction with HCl in ether, Cp_2MCl_2 and RH being formed as expected [2]. The position of the metal substituent on the aromatic ring *ortho* to the methylene group is demonstrated by the reaction with D_2O which yields (2-deuterobenzyl)dimethylamine.

For $Cp_2V[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ internal coordination of the nitrogen atom at vanadium is unlikely. Firstly, the electronic spectrum is closely similar (both in position as in extinction coefficients of the peaks) with that of related compounds Cp_2VR (R = aryl) in which internal coordination is not possible [10]. Secondly, the observed magnetic behaviour (μ = 2.6 B.M.) indicates two unpaired electrons per vanadium atom, whereas the coordination of the amino-group would force the electrons into one metal orbital and hence produce a diamagnetic molecule*.

On the other hand, coordination of the nitrogen atom at the metal does take place in $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ and is consistent with the observed free electron per molecule. The rather complex structure of the Cp-bands in the IR spectrum at 3100 and at 800 cm^{-1} indicates non-equivalent

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* For a bonding model for bent dicyclopentadienylmetal compounds see ref. 11.

TABLE 1

MELTING POINTS AND DECOMPOSITION TEMPERATURES OF SOME COMPOUNDS OF THE TYPE Cp_2MR (M = Ti, V)

Compound	M.p. (°C)	Decomp. (°C)
$Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$	134	226
$Cp_2Ti(o\text{-}CH_3C_6H_4)$[a]	69	95
$Cp_2V[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$	112	199
$Cp_2V(o\text{-}CH_3C_6H_4)$[b]	78	204

[a] Data from ref. 1. [b] Data from ref. 10.

ring hydrogen atoms. This non-equivalence is probably caused by the steric interaction of the methyl group of the coordinated amino group with the cyclopentadienyl rings. The decrease of the symmetry of the molecule by internal coordination is also reflected in the electronic spectrum of $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$, which shows two absorptions (at 548 and 820 nm), in marked contrast with other compounds Cp_2TiR (R = aryl) where a single absorption at about 620 nm is observed [2]. Another argument for internal coordination is the fact that in contrast with another *ortho*-substituted aryl compound, viz. $Cp_2Ti(o\text{-}CH_3C_6H_4)$, $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ does not form a dinitrogen complex of the type $(Cp_2TiR)_2N_2$ [1, 3].

The internal coordination has a marked effect on the thermal stability of the titanium compound. Table 1 shows that $Cp_2Ti[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ decomposes at a temperature about 130° above the decomposition temperature of the comparable compound $Cp_2Ti(o\text{-}CH_3C_6H_4)$. This stabilization is apparently caused by the donation of the electron pair on the amino nitrogen atom to the empty metal orbital normally used in the thermal decomposition [1].

For $Cp_2V[2\text{-}\{(CH_3)_2NCH_2\}C_6H_4]$ this type of stabilization does not take place, and the compounds shows the same thermal stability as $Cp_2V(o\text{-}CH_3C_6H_4)$. The higher stability of these vanadium compounds compared to $Cp_2Ti(o\text{-}CH_3C_6H_4)$ probably is related with the occupacy of the metal orbital used in thermal decomposition by an unpaired electron.

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