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SYNTHESIS AND PROPERTIES OF ALKYLDICYCLOPENTADIENYLVANADIUM(III) COMPOUNDS

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Summary

The compounds Cp_2VR (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, $CH_2C(CH_3)_3$ or $CH_2Si(CH_3)_3$) have been prepared from Cp_2VCl and RMgX in n-pentane. The air-sensitive compounds are stable at room temperature, but decompose between 65 and 138° C. The thermal stability decreases in the order R = $CH_3 \sim CH_2Si(CH_3)_3 > C_2H_5 > CH_2C(CH_3)_3 >$ n-$C_5H_{11} >$ n-$C_4H_9 >$ n-C_3H_7. Compounds with R = i-C_3H_7 or t-C_4H_9 could not be obtained.

Introduction

Recent investigations on the thermal decomposition of dicyclopentadienyl derivatives of Ti and V viz. Cp_2TiR_2 (R = aryl or benzyl) [1,2], Cp_2TiR (R = aryl or benzyl) [3] and Cp_2VR (R = aryl) [4] showed some interesting properties of the Cp ligands. Substitution of a hydrogen atom of the Cp ligand and formation of $Cp(C_5H_4R)V$ compounds was observed for Cp_2VR together with the abstraction of hydrogen from these ligands and formation of RH. A similar study of the corresponding alkyl compounds Cp_2VR seemed interesting, but little is known about these compounds. The compounds Cp_2VR with R = CH_3, $CH_2C_6H_5$ have been reported by De Liefde Meijer, who could not, however, isolate $Cp_2VC_2H_5$, probably because of its marginal thermal stability [5]. On the other hand, a number of allyl compounds Cp_2VR, stable at room temperature, have been described by Siegert [6]. This prompted us to reinvestigate the preparation of Cp_2VR compounds with R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, n-C_5H_{11}, $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$. The results are desribed below.

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Experimental

General remarks

All experiments were carried out under nitrogen, using Schlenk-type glassware. Solvents were distilled and dried over sodium wire prior to use. Alkyl halides for Grignard reagents were commercially obtained and used without further purification. Cp_2VCl was prepared from $VCl_3 \cdot 3THF$ (THF = tetrahydrofuran) and CpNa in THF and purified by sublimation (160°C, 0.1 mmHg).

Elemental analyses were performed at the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. IR spectra (Nujol) were obtained using a Hitachi EPI-G spectrophotometer; UV visible spectra were recorded with a Perkin—Elmer EPS-3T spectrophotometer. Mass spectra were recorded by Mr. A. Kiewiet on an AEI MS9 instrument. Magnetic susceptibilities (between 100—300 K) were determined by Miss H. Scholtens by the Faraday method. Melting points and decomposition temperatures were measured using a silicone oil bath.

Synthesis of Cp_2VR with R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11}, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$

All compounds were prepared in essentially the same way. The synthesis of Cp_2V-n-C_3H_7 is described in detail; experimental and analytical data for the other compounds are given in Table 1.

Preparation of n-propyldicyclopentadienylvanadium. Cp_2VCl (2.75 g, 12.7 mmol) and 100 ml of n-pentane were stirred at 0°C and n-C_3H_7MgBr in ether (12.4 ml, 12.8 mmol) was added dropwise in 0.25 h. Stirring (0°C) was continued until all the Cp_2VCl had disappeared. The dark-green solution was filtered and slowly cooled to —78°C. Black crystals separated. The mother liquor

TABLE 1

EXPERIMENTAL AND ANALYTICAL DATA FOR THE ALKYLDICYCLOPENTADIENYLVANADIUM COMPOUNDS

R	Reaction time [a] (h)	Yield (%)	M.p. (°C)	Decomp. temp. (°C)	Analytical data: Found (calcd.) (%)		
					C	H	V
CH_3	0.25	60	52	138	66.45, 66.16 (67.34)	6.73, 6.78 (6.63)	25.93, 25.84 (25.93)
C_2H_5	0.25	60	27	94	67.97, 68.20 (68.57)	7.11, 7.05 (7.19)	24.18 (24.23)
n-C_3H_7	0.25	63	41	65	69.12, 68.98 (69.64)	7.63, 7.61 (7.64)	22.58, 22.59 (22.71)
n-C_4H_9	0.25	65	30	71	70.14, 70.25 (70.58)	7.86, 7.92 (8.04)	21.62, 21.62 (21.38)
n-C_5H_{11}	0.25	30	20	78	70.50, 69.36 (71.41)	8.36, 8.77 (8.39)	20.21, 20.17 (20.19)
$CH_2C(CH_3)_3$	24 [b]	80	71	86	70.59, 70.84 (71.41)	8.34, 8.29 (8.39)	20.11, 20.03 (20.19)
$CH_2Si(CH_3)_3$	24 [b]	84	51	135	62.79, 62.75 (62.66)	7.98, 7.95 (7.89)	19.05, 19.04 (18.98)

[a] Reaction at 0°C. [b] Reaction at room temperature.

was removed and the product was washed twice (at —78° C) with 30 ml of n-pentane. After drying in vacuo 1.80 g (8.06 mmol, 63%) was isolated and sealed in ampoules, Table 1.

Attempted preparation of alkyldicyclopentadienylvanadium compounds with alkyl = i-propyl, t-butyl

The reaction of Cp_2VCl with $i\text{-}C_3H_7MgCl$ (and also with $t\text{-}C_4H_9MgBr$) under the conditions described above, resulted in the formation of a violet solution from which only Cp_2V (IR, subl. 80° C, 0.1 mmHg) was obtained. The yields were 60 and 36% respectively.

Results and discussion

The very air-sensitive compounds Cp_2VR (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$) were obtained in good yield according to

$$Cp_2VCl + RMgX \xrightarrow[\text{n-pentane}]{0°C} Cp_2VR + MgXCl \qquad (1)$$

(X = Cl, Br)

eq. 1. The compounds were obtained analytically pure by recrystallization from n-pentane.

Elemental analyses, physical and chemical properties are in agreement with the formulation as Cp_2VR.

The IR spectra are all very similar and show absorptions due to π-bonded cyclopentadienyl groups at 3100, 1120, 1020, 1010, 800 cm^{-1} [7]. Absorptions due to the σ-bonded alkyl group partly coincide with those of Nujol. For $Cp_2VCH_2Si(CH_3)_3$, the alkyl group shows characteristic absorptions at 1250, 1240, 852, 842, 740, 713, and 675 cm^{-1}. A weak absorption in the range 465—440 cm^{-1} was observed for a number of compounds and is assigned to a V—C stretching frequency [8]. The IR spectra of $Cp_2VCH_2Si(CH_3)_3$ and $Cp_2VCH_2C(CH_3)_3$ are almost identical with those of the analogous Ti compounds [8,9] and suggest a close structural relationship.

The electronic spectra (n-pentane, 340—1000 nm) of all compounds (except R = $CH_2Si(CH_3)_3$) show three absorptions: at 720—730 nm ($\epsilon \sim 90$ l mol^{-1} cm^{-1}), at 530—540 nm ($\epsilon \sim 55$ l mol^{-1} cm^{-1}) and at 430—440 nm ($\epsilon \sim 120$ l mol^{-1} cm^{-1}). These values are similar to those reported for Cp_2VCH_3 and $Cp_2VC_2H_5$ [5]. For R = $CH_2Si(CH_3)_3$ the absorptions are shifted to longer wavelengths (760, 570 and 455 nm).

The magnetic properties of the compounds (Curie—Weiss behaviour between 100—300 K, magnetic moment close to the spin-only value of 2.83 BM, R = $n\text{-}C_3H_7$: 2.94 BM, R = $CH_2Si(CH_3)_3$: 2.63 BM), are as expected for vanadium(III) compounds.

The mass spectra (recorded for R = $n\text{-}C_3H_7$ and $CH_2Si(CH_3)_3$) show low-intensity signals due to the parent ions and intense peaks ascribed to Cp_2V^+ and to its degradation products, indicating facile splitting of the V—alkyl bond.

The Cp_2V entity is quite stable, but the V—C σ-bond is easily split by HCl and Br_2 (eq. 3,4):

$$Cp_2VR + HCl \xrightarrow[\text{n-pentane}]{-78°C} Cp_2VCl + RH \qquad (3)$$

$$Cp_2VR + 1.5Br_2 \xrightarrow[\text{n-pentane}]{-78°\rightarrow 20°C} Cp_2VBr_2 + RBr \qquad (4)$$

The compounds discussed above are thermally quite stable and can be handled at room temperature. They all melt at the temperatures given and decompose at higher temperatures (Table 1). Assuming that the failure to prepare the compounds with R = i-C_3H_7 and t-C_4H_9 is due to their low thermal stability, the stability order is R = $CH_3 \sim CH_2Si(CH_3)_3 > C_2H_5 > CH_2C(CH_3)_3 >$ n-C_5H_{11} $>$ n-$C_4H_9 >$ n-$C_3H_7 >$ t-C_4H_9, i-C_3H_7. The high stability of the ethyl compound is quite unexpected, and cannot be explained at present. With the exception of R = C_2H_5, the stability seems to correlate with the total number of β-hydrogen atoms in the alkyl group, but the possibility that the thermal stability is mainly governed by the steric properties of the alkyl groups cannot be excluded. Coordinating solvents, such as ethers [5], decrease the thermal stability of the compounds Cp_2VR. For R = CH_3, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, the yields were the same whether the synthesis was carried out in diethyl ether or in n-pentane. For the other compounds, vanadocene was the only product obtained in diethyl ether; a result which is in agreement with the experiments of De Liefde Meijer [5].

The thermal decomposition of the compounds Cp_2VR is now being studied and will be described in a forthcoming paper.

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