SYNTHESIS AND PROPERTIES OF ALKYLDICYCLOPENTADIENYLVANADIUM(III) COMPOUNDS
BOUMAN, H; TEUBEN, JH

Published in:
Journal of Organometallic Chemistry

DOI:
10.1016/S0022-328X(00)82492-4

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1976

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
SYNTHESIS AND PROPERTIES OF ALKYLDICYCLOPENTADIENYL-VANADIUM(III) COMPOUNDS

H. BOUMAN and J.H. TEUBEN *
Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Zernikelaan, Groningen (The Netherlands)
(Received December 2nd, 1975)

Summary

The compounds Cp₂VR (R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, CH₂C(CH₃)₃, or CH₂Si(CH₃)₃) have been prepared from Cp₂VCl 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 = CH₃ ~ CH₂Si(CH₃)₃ > C₂H₅ > CH₂C(CH₃)₃ > n-C₃H₁₁ > n-C₄H₉ > n-C₅H₇. Compounds with R = i-C₃H₇ or t-C₄H₉ could not be obtained.

Introduction

Recent investigations on the thermal decomposition of dicyclopentadienyl derivatives of Ti and V viz. Cp₂TiR₂ (R = aryl or benzyl) [1,2], Cp₂TiR (R = aryl or benzyl) [3] and Cp₂VR (R = aryl) [4] showed some interesting properties of the Cp ligands. Substitution of a hydrogen atom of the Cp ligand and formation of Cp(C₂H₅)₅V compounds was observed for Cp₂VR together with the abstraction of hydrogen from these ligands and formation of RH. A similar study of the corresponding alkyl compounds Cp₂VR seemed interesting, but little is known about these compounds. The compounds Cp₂VR with R = CH₃, CH₂C₂H₅ have been reported by De Liefde Meijer, who could not, however, isolate Cp₂VC₂H₅, probably because of its marginal thermal stability [5]. On the other hand, a number of allyl compounds Cp₂VR, stable at room temperature, have been described by Siegert [6]. This prompted us to reinvestigate the preparation of Cp₂VR compounds with R = CH₃, C₂H₅, n-C₃H₇, i-C₃H₇, n-C₄H₉, t-C₄H₉, n-C₅H₁₁, CH₂C(CH₃)₃, and CH₂Si(CH₃)₃. The results are described below.

* To whom correspondence should be addressed.
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. Cp₂VCl was prepared from VCl₃ - 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 Cp₂VR with R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, CH₂C(CH₃)₃, CH₂Si(CH₃)₃

All compounds were prepared in essentially the same way. The synthesis of Cp₂V-n-C₃H₇ is described in detail; experimental and analytical data for the other compounds are given in Table 1.

Preparation of n-propyldicyclopentadienylvanadium. Cp₂VCl (2.75 g, 12.7 mmol) and 100 ml of n-pentane were stirred at 0° C and n-C₃H₇MgBr in ether (12.4 ml, 12.8 mmol) was added dropwise in 0.25 h. Stirring (0° C) was continued until all the Cp₂VCl 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 ALKYLICYCLOPENTADIENYLVANADIUM COMPOUNDS

<table>
<thead>
<tr>
<th>R</th>
<th>Reaction time a (h)</th>
<th>Yield (%)</th>
<th>M.p. (° C)</th>
<th>Decomp. temp. (° C)</th>
<th>Analytical data: Found (calcd.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>CH₃</td>
<td>0.25</td>
<td>60</td>
<td>52</td>
<td>138</td>
<td>66.45-66.16 (67.34)</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>0.25</td>
<td>60</td>
<td>27</td>
<td>94</td>
<td>67.97, 68.20 (68.57)</td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>0.25</td>
<td>63</td>
<td>41</td>
<td>65</td>
<td>69.12, 68.98 (69.64)</td>
</tr>
<tr>
<td>n-C₄H₉</td>
<td>0.25</td>
<td>65</td>
<td>30</td>
<td>71</td>
<td>70.14, 70.25 (70.58)</td>
</tr>
<tr>
<td>n-C₅H₁₁</td>
<td>0.25</td>
<td>30</td>
<td>20</td>
<td>78</td>
<td>70.50, 69.36 (71.41)</td>
</tr>
<tr>
<td>CH₂C(CH₃)₃</td>
<td>24 b</td>
<td>80</td>
<td>71</td>
<td>86</td>
<td>70.59, 70.84 (71.41)</td>
</tr>
<tr>
<td>CH₂Si(CH₃)₃</td>
<td>24 b</td>
<td>84</td>
<td>51</td>
<td>135</td>
<td>62.79, 62.75 (62.66)</td>
</tr>
</tbody>
</table>

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 alkylidicyclopentadienylvanadium compounds with alkyl = i-propyl, t-butyl**

The reaction of Cp2VCl with i-C3H7MgCl (and also with t-C4H9MgBr) under the conditions described above, resulted in the formation of a violet solution from which only Cp2V (IR, subl. 80°C, 0.1 mmHg) was obtained. The yields were 60 and 36% respectively.

**Results and discussion**

The very air-sensitive compounds Cp2VR (R = CH3, C2H5, n-C3H7, n-C4H9, n-C5H11, CH2C(CH3)3, CH2Si(CH3)3) were obtained in good yield according to

\[
\text{Cp}_2\text{VCl} + \text{RMgX} \xrightarrow{\text{C}} \text{Cp}_2\text{VR} + \text{MgCl} \\
(X = \text{Cl, Br})
\]

(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 Cp2VR.

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 Cp2VCH2Si(CH3)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 Cp2VCH2Si(CH3)3 and Cp2VCH2C-(CH3)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 = CH2Si(CH3)3) show three absorptions: at 720—730 nm (ε ~ 90 l mol\(^{-1}\) cm\(^{-1}\)), at 530—540 nm (ε ~ 55 l mol\(^{-1}\) cm\(^{-1}\)) and at 430—440 nm (ε ~ 120 l mol\(^{-1}\) cm\(^{-1}\)). These values are similar to those reported for Cp2VCH3 and Cp2VCH2H3 [5]. For R = CH3Si(CH3)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-C3H7: 2.94 BM, R = CH2Si(CH3)3: 2.63 BM), are as expected for vanadium(III) compounds.

The mass spectra (recorded for R = n-C3H7, and CH3Si(CH3)3) show low-intensity signals due to the parent ions and intense peaks ascribed to Cp2V\(^+\) and to its degradation products, indicating facile splitting of the V—alkyl bond.

The Cp2V entity is quite stable, but the V—C σ-bond is easily split by HCl and Br\(_2\) (eq. 3,4):

\[
\text{Cp}_2\text{VR} + \text{HCl} \xrightarrow{\text{n-pentane}} \text{Cp}_2\text{VCl} + \text{RH}
\]
\[ \text{Cp}_2\text{VR} + 1.5\text{Br}_2 \xrightarrow{-78^\circ \text{ to } 20^\circ \text{C}} \text{n-pentane} \rightarrow \text{Cp}_2\text{VBr}_2 + \text{RBr} \]  

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 \( R = \text{t-C}_3\text{H}_7 \) and \( \text{t-C}_4\text{H}_9 \) is due to their low thermal stability, the stability order is \( R = \text{CH}_3 \sim \text{CH}_2\text{Si(CH}_3)_3 > \text{C}_2\text{H}_3 > \text{CH}_2\text{C(CH}_3)_3 > \text{n-C}_3\text{H}_11 > \text{n-C}_2\text{H}_9 > \text{n-C}_2\text{H}_7 > \text{t-C}_3\text{H}_7, \text{i-C}_3\text{H}_7 \). The high stability of the ethyl compound is quite unexpected, and cannot be explained at present. With the exception of \( R = \text{C}_2\text{H}_3 \), the stability seems to correlate with the total number of \( \beta \)-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 \( \text{Cp}_2\text{VR} \). For \( R = \text{CH}_3, \text{CH}_2\text{C(CH}_3)_3, \text{CH}_2\text{Si(CH}_3)_3 \), the yields were the same whether the synthesis was carried out in diethyl ether or in \( \text{n-pentane} \). For 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 \( \text{Cp}_2\text{VR} \) is now being studied and will be described in a forthcoming paper.

References