

## VANADIUM METALLOCYCLES CONTAINING THE $Cp_2V$ GROUP

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### Summary

The preparation and characterization of three new vanadium-containing metallocycles are reported viz. 2,2'-(di- $\pi$ -cyclopentadienylvanadium)octafluorobiphenyl, 2,2'-(di- $\pi$ -cyclopentadienylvanadium)biphenyl and 1,4-(di- $\pi$ -cyclopentadienylvanadium)tetraphenylbutadiene. The thermal stabilities of the complexes, which are about the same as those of the titanium analogues, are discussed in the light of previous failures to prepare complexes of the type  $Cp_2VR_2$  (R = aryl).

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### Introduction

Various compounds of the type  $Cp_2TiR_2$  (R = alkyl, aryl) have been studied extensively [1,2]. Attempts to prepare the corresponding vanadium complexes,  $Cp_2VR_2$ , failed (except for R =  $C_6H_5C\equiv C$ ) [3]; in most cases a reduction of the metal was observed and compounds of the type  $Cp_2VR$  were obtained [4]. The failure to prepare derivatives of the type  $Cp_2VR_2$  was thought to result from the thermal instability of these complexes, which was ascribed to steric factors rather than to an instability of the  $Cp_2V^{IV}$  group. In order to check this, we decided to prepare  $Cp_2V^{IV}$ -containing complexes of the type  $Cp_2VR'$  with one bidentate ligand R'.

This paper describes the syntheses and properties of some compounds  $Cp_2VR'$ , viz.: 2,2'-(di- $\pi$ -cyclopentadienylvanadium)octafluorobiphenyl, 2,2'-(di- $\pi$ -cyclopentadienylvanadium)biphenyl and 1,4-(di- $\pi$ -cyclopentadienylvanadium)tetraphenylbutadiene, and compares them with the corresponding titanium compounds.

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## Experimental and results

All experiments were performed under nitrogen using Schlenk-type glassware. Ether and hydrocarbon solvents were distilled from  $\text{LiAlH}_4$ .  $\text{Cp}_2\text{VCl}_2$ , 2,2'-dibromooctafluorobiphenyl and 2,2'-dibromobiphenyl were prepared by published methods [5,6,7]. Elemental analyses were carried out in the Microanalytical Department of this University under the supervision of Mr. A.F. Hamminga. Gas-chromatographic analyses were performed with a Hewlett—Packard model 7620 gas chromatograph. Spectra in the visible range were recorded with a Perkin—Elmer EPS-3T spectrophotometer, and IR spectra with a Hitachi EPI-G spectrophotometer. Magnetic susceptibilities were determined by the Faraday method. EPR spectra were recorded with a Varian E3 X-band EPR spectrometer. Melting points and thermal decomposition temperatures were observed in sealed glass capillaries. Mass spectra were recorded by Mr. A. Kiewiet with an AEI mass spectrometer type MS9 operating at 70 eV.

### 2,2'-(Di- $\pi$ -cyclopentadienylvanadium)octafluorobiphenyl, $\text{Cp}_2\text{VC}_{12}\text{F}_8$ (I)

2,2'-Dibromooctafluorobiphenyl (4.39 g, 9.6 mmol) was dissolved in 25 ml of ether and cooled to  $-78^\circ\text{C}$ . A solution of *n*-BuLi in hexane (20.2 mmol) was added dropwise and the mixture stirred for 1.5 h. Finely powdered  $\text{Cp}_2\text{VCl}_2$  (9.6 mmol) was added.

The mixture was allowed to warm 0.5 h to  $-10^\circ\text{C}$  and filtered. The residue was washed twice with ether ( $-78^\circ\text{C}$ ) and then extracted with  $\text{CH}_2\text{Cl}_2$ , and the extract was filtered. The filtrate was dried in vacuum and the product crystallized from ether. The green crystalline material was sublimed ( $200^\circ\text{C}$ , 0.1 mmHg). Yield 0.30 g (0.63 mmol, 7%); dec.  $252^\circ\text{C}$ ; mass spec. (70 eV)  $M^+$  at  $m/e$  477; magn. moment 1.74 B.M.; absorption spectrum ( $\text{CH}_2\text{Cl}_2$ , visible range): 440 nm (sh), 640 nm (max). (Analysis: Found: C, 55.20, 55.19; H, 2.08, 2.16.  $\text{C}_{22}\text{H}_{10}\text{F}_8\text{V}$  calcd.: C, 55.36; H, 2.11%.)

### 2,2'-(Di- $\pi$ -cyclopentadienylvanadium)biphenyl, $\text{Cp}_2\text{VC}_{12}\text{H}_8$ (II)

2,2'-Dibromobiphenyl (1.5 g; 4.8 mmol) in 50 ml of ether was stirred at  $0^\circ\text{C}$  with 9.7 mmol of *n*-BuLi and 1 mmol of tetramethylethylenediamine in hexane. After 0.5 h the mixture was added dropwise to a suspension of 1.2 g (4.8 mmol) of  $\text{Cp}_2\text{VCl}_2$  in 50 ml of ether ( $0^\circ\text{C}$ ), and stirred for 65 h. After warming to room temperature, the solvent was removed in vacuum and the residue extracted with 30 ml of benzene. The benzene extract was filtered through a column of  $\text{Al}_2\text{O}_3$  (Merck, Aktivitätstufe II-III) and the filtrate dried and washed with 5 ml of pentane ( $2 \times$ ). The green product was crystallized from pentane; yield 0.22 g (0.67 mmol, 14%). Decomp.  $154^\circ\text{C}$ ; mass spec.:  $M^+$  at  $m/e$  333; magn. moment 1.96 B.M.; absorption spectrum (toluene, visible range) 450 nm (sh), 700 nm (max); EPR (toluene,  $25^\circ\text{C}$ ): eight-line signal at  $g$  2.00, splitting 47 G. (Analysis: Found: C, 79.15, 78.98; H, 5.67, 5.75; V, 15.21, 15.16.  $\text{C}_{22}\text{H}_{18}\text{V}$  calcd.: C, 79.27; H, 5.44; V, 15.28%.)

### 1,4-(Di- $\pi$ -cyclopentadienylvanadium)tetraphenylbutadiene, $\text{Cp}_2\text{VC}_{28}\text{H}_{20}$ (III)

A solution of 10.0 mmol of 1,4-dilithiotetraphenylbutadiene in 100 ml of ether (prepared according to [4]) was added dropwise to a suspension of 10.0

mmol of  $\text{Cp}_2\text{VCl}_2$  in 150 ml of ether kept at  $0^\circ\text{C}$ . After stirring for 20 h at room temperature the solvent was removed in vacuum and the residue worked up as described for compound II. After crystallization from ether a small amount (0.1 g) of a mixture of green and colourless crystals was isolated. The colourless crystals were identified (IR, mass spectrum) as 1,2,3,4-tetraphenylbutadiene. Attempts to separate the components were unsuccessful, and so measurements were performed on the mixture. The absorption spectrum in the visible range showed a maximum at 700 nm (toluene). The EPR spectrum (toluene,  $25^\circ\text{C}$ ) showed an eight-line signal at  $g$  2.00 with a splitting of 29 G. Treatment with HCl in ether produced  $\text{Cp}_2\text{VCl}_2$ ; the organic part of the products consists for the greater part of 1,2,3,4-tetraphenylbutadiene.

## Discussion

The physical and chemical properties of the compounds I and II are in agreement with their formulation as derivatives of the type  $\text{Cp}_2\text{VR}'$ , where  $\text{R}'$  is a bidentate ligand with two  $\text{V}-\text{C}$   $\sigma$ -bonds. The magnetic susceptibility measurements and the EPR spectrum of II confirm the presence of one unpaired electron

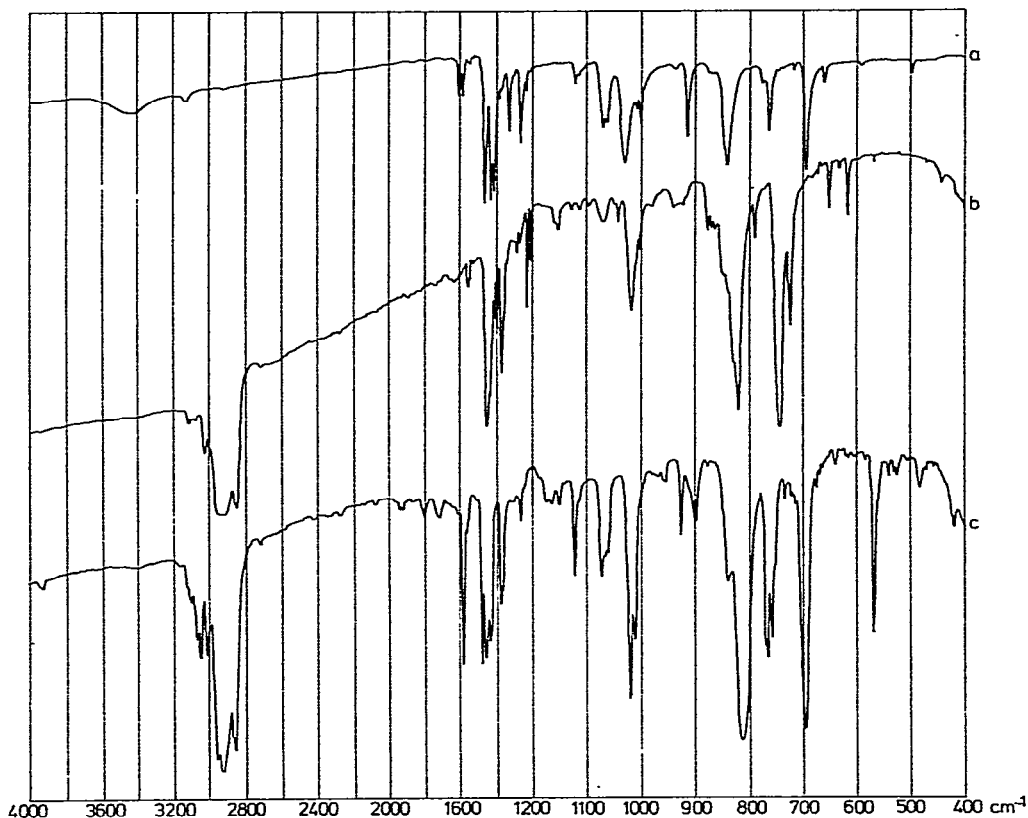


Fig. 1. IR-spectra of (a) 2,2'-(di- $\pi$ -cyclopentadienylvanadium)octafluorobiphenyl (in KBr disc), (b) 2,2'-(di- $\pi$ -cyclopentadienylvanadium)biphenyl (Nujol), and (c) 1,4-(di- $\pi$ -cyclopentadienylvanadium)tetraphenylbutadiene (Nujol).

per vanadium atom, as expected for compounds of tetravalent vanadium [8]. The mass spectra indicate that the compounds are monomeric; ions at  $m/e$  values higher than those of the molecular ions are absent.

Evidence for the existence of the tetraphenylbutadiene complex III is incomplete. However, the spectral analogies with II, (visible spectrum, EPR) and with the corresponding titanium compound (IR) confirm its presence in the isolated product.

The IR spectra of all compounds (Fig. 1) strongly resemble those of the corresponding titanium compounds [4,6], and not only show the presence of cyclopentadienyl groups and the bifunctional group  $R'$ , but also emphasize the close structural resemblance.

The complexes described here are new examples of the limited group of compounds containing a dicyclopentadienylvanadium(IV) group, and are in fact the first vanadium-containing metallocycles; I and II are vanadafluorenes, III is a vanadacyclopentadiene.

An interesting aspect of these compounds is that their thermal stabilities are about the same as those of the corresponding titanium analogues [4,9,10]. This means that the stability of the  $Cp_2V^{IV}$  group is similar to that of the  $Cp_2Ti^{IV}$  group. If the failure to prepare compounds of the type  $Cp_2VR_2$  ( $R = aryl$ ) is indeed due to steric factors, as suggested previously [2,4], they are not operative here. In fact, neither the difference in size of the metal atom (the vanadium atom is about 10% smaller than Ti) nor the difference in the number of electrons in the valence shell (the vanadium compound has one electron more) seem to affect the thermal stability.

In conclusion we note that the investigations described here have not solved the problem of the non-existence of other compounds of the type  $Cp_2VR_2$ . Possibly a detailed study of the reactions between  $Cp_2VCl_2$  and Grignard or lithium reagents would give the answer.

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## References

- 1 F.C. Wailes, R.S.P. Coutts and H. Weigold, *Organic Chemistry of Titanium, Zirconium and Hafnium*, Academic Press, New York, 1974.
- 2 H.J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, 4 (1970) 651.
- 3 J.H. Teuben and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 17 (1969) 87.
- 4 F.W. Siegert and H.J. de Liefde Meijer, *Rec. Trav. Chim. Pays-Bas*, 89 (1970) 764.
- 5 G. Wilkinson and J.M. Birmingham, *J. Amer. Chem. Soc.*, 76 (1954) 4281.
- 6 S.C. Cohen, D.E. Fenton, A.J. Tomkinson and A.G. Massey, *J. Organometal. Chem.*, 6 (1966) 301.
- 7 H. Gilman and B.J. Gaj, *J. Org. Chem.*, 22 (1957) 447.
- 8 A.T. Casey and J.R. Thackeray, *Aust. J. Chem.*, 25 (1972) 2085.
- 9 M.P. Rausch and L.P. Klemann, *J. Chem. Soc., Chem. Commun.*, (1971) 354.
- 10 J.H. Teuben and H. Scholtens, unpublished results.