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SOME COMPLEXES CONTAINING THE DICYCLOPENTADIENYLVANADIUM(III) GROUP

F. W. SIEGERT AND H. J. DE LIEFDE MEIJER
Laboratorium voor Anorganische Chemie, Rijksuniversiteit, Bloemsingel 10, Groningen (The Netherlands)

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SUMMARY

The complexes $(C_5H_5)_2V^{III}R$, where R = pentafluorophenyl, cyclopentadienyl, allyl, 2-methylallyl and 2-butenyl, were prepared by reaction of one mole of $(C_5H_5)_2$-$V^{III}Cl$ with one mole of C_6F_5Li, C_5H_5Na, or (methyl)allylmagnesium halide in tetrahydrofuran or diethyl ether. The pentafluorophenyl complex is very stable, but the other complexes had to be prepared and stored below room temperature. The complexes are very sensitive to oxygen. They have two unpaired electrons per molecule. The infrared and proton magnetic resonance spectra indicate that the ligands R are σ-bonded to the metal.

INTRODUCTION

A number of derivatives of dicyclopentadienylvanadium of the type $(C_5H_5)_2$-$V^{III}R$ (R = methyl, phenyl and benzyl) were reported by H. J. de Liefde Meijer *et al.*[1,2]. This paper describes the syntheses, properties and structure of the compounds $(C_5H_5)_2$-$V^{III}R$ with R = pentafluorophenyl, cyclopentadienyl, allyl, 2-methylallyl, and butenyl-2.

EXPERIMENTAL

All experiments were carried out in an atmosphere of purified nitrogen[2]. Solvents were purified by conventional methods; before use, they were freed from oxygen by repeated degassing and saturating with nitrogen. Tetrahydrofuran was distilled from $LiAlH_4$ under nitrogen. C_5H_5Na was prepared by reaction of cyclopentadiene(monomer) with sodium sand in tetrahydrofuran. The solution was cooled to −78°. Colourless crystals separated. The mother liquor was removed and the crystals freed from tetrahydrofuran in vacuum (0.1 mm) at 80°. All other starting materials were prepared according to published procedures[3,4,5]. Elementary analyses of C, H and V were carried out at the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg; V was weighed as V_2O_5. F was analysed in our laboratory according to Schöniger's method. The (uncorrected) melting points were observed in sealed glass capillaries. Spectra in the visible range were recorded by a Unicam SP 800 Spectrophotometer; cyclohexane was used as solvent. Infrared spectra were measured by means of a Hitachi EPI-G Spectrophotometer. The samples were embedded in KBr discs excluding oxygen as described previously[4]. Magnetic susceptibilities were determined by the Faraday method. The measurements were carried out by Miss A. H. C. Bruining. The derived magnetic moments (corrected for induced diamagnetism) are given in Table 1; their accuracy is about 3%. PMR spectra were measured by Drs. C. Migchelsen on a wide-line instrument (Varian V 4210/V-FR 2503).

Pentafluorophenyldicyclopentadienylvanadium(III)

A solution of pentafluorophenyllithium (27.6 mmoles) in 60 ml of ether (from 52 g of 1% Li-amalgam and 6.7 g of C_6F_5Br[6]) was added to a mixture of 5.75 g (26.6 mmoles) of DCV monochloride* and 40 ml of tetrahydrofuran and kept at −5°. After stirring for one hour the solvents were removed at reduced pressure. The residue was stirred with 150 ml of pentane; pentane was evaporated and the resulting solid material extracted with benzene. The benzene solution was evaporated to dryness and the blue-black residue recrystallized from ether. Pentafluorophenyl-DCV was isolated as blue-black crystals; yield 6.83 g (75%); m.p. 208°; λ_{max} 490 and 665 mμ. (Found: C, 55.19, 55.57; H, 2.88, 3.00; V, 14.3; F, 27.2. $C_{16}H_{10}F_5V$ calcd.: C, 55.19; H, 2.89; V, 14.6; F, 27.3%.).

*Tricyclopentadienylvanadium(III)***

DCV monochloride (1.34 g, 6.2 mmoles) was mixed with 50 ml of tetrahydrofuran at 0°, contained in the first bulb of a double-Schlenk-type vessel. White solid C_5H_5Na (0.75 g, 8.5 mmoles) was added. The reaction mixture was stirred during 15 minutes. The solvent was removed at 0° in vacuum and the residue evaporated to complete dryness. 100 ml of ether (0°) were added. The mixture was stirred for 15 minutes, the solution filtered into the second bulb and concentrated to 40 ml. On slowly (duration three hours) cooling to −78° $(C_5H_5)_3V$ separated as black crystals. The mother liquor was removed and 0.73 g of $(C_5H_5)_3V$ were isolated; yield 48%; m.p. 98°. (Found: C, 73.30; H, 6.30; V, 20.29. $C_{15}H_{15}V$ calcd.: C, 73.17; H, 6.14; V, 20.69%.)

Allyldicyclopentadienylvanadium(III)

DCV monochloride (2.90 g, 13.4 mmoles) was mixed with 50 ml of tetrahydrofuran and kept at 0°. A solution of allylmagnesium chloride (14.3 mmoles) in 12 ml of tetrahydrofuran was added dropwise under stirring. The solvent was evaporated at 0° and the residue dried in vacuum (0.1 mm) during half an hour. 100 ml of pentane (0°) were added. The mixture was stirred during 15 minutes, warmed quickly to room temperature, filtered and immediately cooled to −78°. Black crystals separated. The mother liquor was removed and 1.25 g of allyl-DCV were isolated; yield 42%; m.p. 49°; λ_{max} 696 mμ. (Found: C, 69.88; H, 6.70. $C_{13}H_{15}V$ calcd.: C, 70.26; H, 6.80%.)

(2-Methylallyl)dicyclopentadienylvanadium(III)

DCV monochloride (3.29 g, 15.1 mmoles) was mixed with 50 ml of tetrahydro-

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* DCV = dicyclopentadienylvanadium(III)

** Some exploratory experiments directed towards the synthesis of C_5H_5–DCV were carried out by one of us (H.J. de Liefde Meijer) at the Institute for Organic Chemistry, TNO, Utrecht, the Netherlands, under the supervision of Prof. G. J. M. van der Kerk.

furan and cooled to $-15°$. A solution of 2-methylallylmagnesium chloride (15.8 mmoles) in 17 ml of tetrahydrofuran was dropwise added. The isolation of the reaction product was carried out as described for allyl-DCV. Yield 1.44 g (40%) of black crystals of 2-methylallyl-DCV; m.p. 65°; λ_{max} 708 mμ. (Found: C, 71.37; H, 7.24; V, 21.70. $C_{14}H_{17}V$ calcd.: C, 71.15; H, 7.25; V, 21.56%.)

(2-Butenyl)dicyclopentadienylvanadium(III)

DCV monochloride (1.61 g, 7.5 mmoles) was mixed with 50 ml of diethyl ether at $-15°$. A solution of 2-butenylmagnesium bromide (7.9 mmoles) in 15 ml of diethyl ether was dropwise added. The solvent was evaporated at $-15°$. Cold pentane (50 ml) was added; the mixture was stirred, filtered and the filtrate concentrated in vacuum. The residue consisted of a black oil; λ_{max} 700 mμ. The infrared spectrum of the oil was analogous to the spectra of allyl-DCV and 2-methylallyl-DCV.

Dicyclopentadienylvanadium (4.16 g, 23.0 mmoles) was mixed with 75 ml of pentane at 0°. Freshly distilled crotyl bromide (1.62 g, 12.0 mmoles) was dropwise added under stirring. The following reaction occurred: $2\,(C_5H_5)_2V^{II}+RX \rightarrow (C_5H_5)_2V^{III}R+(C_5H_5)_2V^{III}X$ (*cf.* ref. 1). Solid DCV monobromide separated. The mixture was filtered and pentane evaporated in vacuum. The residue consisted of a black oil. The infrared spectrum of this oil was identical with that of the product of the first synthesis.

At room temperature 2-butenyl-DCV decomposed to $(C_5H_5)_2V$ within 24 h.

Attempted synthesis of (2-tert-butylallyl)dicyclopentadienylvanadium(III)

DCV monochloride (0.90 g, 4.1 mmoles) was mixed with 30 ml of diethyl ether at 0°. A solution of 2-tert-butylallylmagnesium bromide (4.2 mmoles) in 50 ml of diethyl ether was dropwise added. The solvent was evaporated. 80 ml of cold pentane were added. The mixture was stirred for 15 minutes, filtered and the filtrate cooled to $-78°$. Violet crystals separated. Isolation gave 0.13 g of solid material, that was identified as $(C_5H_5)_2V$ by its melting point and infrared spectrum[7]; yield 17%.

Attempted synthesis of (3-methyl-2-butenyl)dicyclopentadienylvanadium(III)

DCV monochloride (2.26 g, 10.4 mmoles) was mixed with 50 ml of tetrahydrofuran at 0°. A solution of 3-methyl-2-butenylmagnesium chloride (11.0 mmoles) in 18 ml of tetrahydrofuran was dropwise added. The solvent was removed in vacuum. 100 ml of cold pentane were added. The mixture was stirred for 15 minutes, filtered and the brown-black filtrate cooled to $-78°$. Violet crystals separated. Isolation gave 0.27 g of solid material, that was identified as $(C_5H_5)_2V$ by its melting point and infrared spectrum; yield 15%.

Analysis of the R content of the complexes $(C_5H_5)_2V^{III}R$

The complexes $(C_5H_5)_2V^{III}R$ react with hydrogen chloride with formation of RH and DCV monochloride. The latter compound was oxidized by an excess of hydrogen chloride and oxygen:

$$(C_5H_5)_2V^{III}R+HCl \rightarrow (C_5H_5)_2V^{III}Cl+RH$$

$$2\,(C_5H_5)_2V^{III}Cl+2\,HCl+\tfrac{1}{2}\,O_2 \rightarrow 2\,(C_5H_5)_2V^{IV}Cl_2+H_2O$$

The gaseous compounds RH were quantitatively determined by gas-volumetric methods[4] and identified by their infrared spectra. The liquids RH were quantitatively determined by gas chromatography and identified by their retention times. $(C_5H_5)_2$-$V^{IV}Cl_2$ was identified by its infrared spectrum. The following results were obtained:

R	RH (%)
C_6F_5	97
C_5H_5	92
C_3H_5	100
C_4H_7 (2-methylallyl)	97

PHYSICAL PROPERTIES

The infrared spectra of the complexes $(C_5H_5)_2V^{III}R$ all show the expected frequencies of π-bonded cyclopentadienyl ligands and the CH, CC and CF frequencies of the ligands R (Fig. 1).

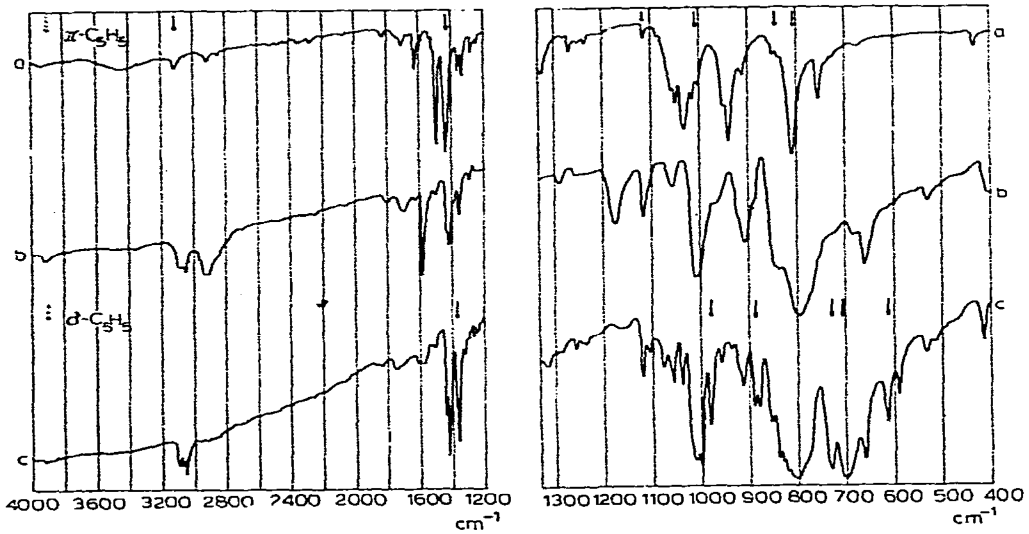

Fig. 1. Infrared spectra of (a) $(\pi\text{-}C_5H_5)_2VC_6F_5$; (b) $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_3H_5)$; (c) $(\pi\text{-}C_5H_5)_2V(\sigma\text{-}C_5H_5)$ in KBr discs. Some characteristic vibrations of π- and σ-bonded C_5H_5 ligands are indicated.

In the spectrum of tricyclopentadienylvanadium all frequencies for π-bonded and σ-bonded cyclopentadienyl groups are present, just as with tetracyclopentadienyl niobium[7]. C_6F_5-DCV shows an infrared spectrum analogous to that of $(C_5H_5)_2$-$Ti(C_6F_5)_2$[8]. The infrared spectra of allyl-, 2-methylallyl- and 2-butenyl-DCV are very similar. The most important frequencies are the C=C stretching frequencies: 1588 (allyl-), 1598 (2-methylallyl-) and 1610, 1625 cm^{-1} (2-butenyl-DCV); the observation of two C=C stretching bands for 2-butenyl-DCV is ascribed to *cis-trans* isomerism of the 2-butenyl group.

The absorption spectra in the visible range of allyl-DCV and its homologues in cyclohexane are also very similar. They show a broad and weak absorption at about

700 mμ and strong absorption below 450 mμ. Pentafluorophenyl-DCV shows an absorption spectrum very much like that of phenyl-DCV[2].

The complexes $(C_5H_5)_2V^{III}R$ are paramagnetic compounds; their magnetic moments (Table 1) correspond to two unpaired electrons per unit of $(C_5H_5)_2V^{III}R$ (calculated for spin only: 2.83 B.M.)

TABLE 1

MAGNETIC MOMENTS OF THE COMPLEXES $(C_5H_5)_2V^{III}R$, CORRECTED FOR INDUCED DIAMAGNETISM

$(C_5H_5)_2V^{III}C_6F_5$		$(C_5H_5)_2V^{III}CH_2\text{-}C(CH_3)\text{=}CH_2$		$(C_5H_5)_3V^{III}$	
T (°K)	μ_{eff}(B.M.)	T (°K)	μ_{eff}(B.M.)	T (°K)	μ_{eff}(B.M.)
273.6	2.738	275.6	2.672	277.9	2.593
218.3	2.746	214.4	2.691	223.9	2.609
172.5	2.773	170.1	2.723	168.6	2.638
126.6	2.800	124.7	2.758	125.8	2.672
94.7	2.813	93.2	2.766	93.9	2.713

Proton magnetic resonance spectra of cyclohexane solutions of allyl-DCV and tricyclopentadienylvanadium were measured on a wide-line instrument. The first compound showed two broad absorptions at 120 and 194 ppm with an intensity ratio of about 2/1. The second compound showed two broad absorptions at 94 and 123 ppm with an intensity ratio of about 1/2. The shifts were measured relative to the solvent cyclohexane.

DISCUSSION

The chemical and physical properties of the complexes $(C_5H_5)_2V^{III}R$ strongly suggest that they have a di-π-cyclopentadienylvanadium structure. They are prepared by substitution of the chlorine atom in DCV monochloride and react with hydrogen chloride under regeneration of the starting material. All compounds show the normal vibrations of π-cyclopentadienyl groups at their usual wave numbers. The absence of vibrations of σ-cyclopentadienyl groups in pentafluorophenyl-DCV, allyl-DCV and its homologues exclude the possibility of σ-bonded cyclopentadienyl groups in these compounds. The intensity ratio of the absorptions in the PMR spectrum of allyl-DCV of 2 (120 ppm)/1 (194 ppm) allows the assignment of the absorption at 120 ppm to the two π-bonded cyclopentadienyl groups. The two absorptions in the PMR spectrum of tricyclopentadienylvanadium show that the cyclopentadienyl groups are bonded in two different ways. Comparison with the PMR spectrum of allyl-DCV indicates that the absorption at 123 ppm is due to the π-bonded cyclopentadienyl groups. Moreover, the intensity ratio ~2 (123 ppm)/1 (94 ppm) shows that the complex has two π-bonded cyclopentadienyl groups and one σ-bonded cyclopentadienyl group per molecule.

The bonding in the complexes $(\pi\text{-}C_5H_5)_2MR_n$ ($n = 1,2,3$) has been discussed by Ballhausen and Dahl[10]; three orbitals of the metal are available for combining with orbitals of the ligands R. In the complex C_6F_5-DCV one of these orbitals is used for σ-bonding with the C_6F_5 ligand; the two unpaired electrons occupy the two remaining orbitals. In allyl-DCV and cyclopentadienyl-DCV the possibility that the ligands R are π-bonded to vanadium must be considered; in the case of allyl-DCV this would imply that allyl-DCV is diamagnetic ("inert-gas rule"). Actually, however, the compound is paramagnetic, containing two unpaired electrons per molecule, as is the case with pentafluorophenyl-DCV indicating the σ-bonding of the allyl group. In accordance with this view the C=C stretching frequency in allyl-DCV and homologues is observed at about 1600 cm^{-1}. A more detailed discussion of the infrared spectra of the allyl compounds has been given elsewhere[11].

The PMR spectrum of tricyclopentadienylvanadium indicates (see above) that one of the cyclopentadienyl groups is σ-bonded to the metal. Indeed, the infrared spectrum shows the characteristic frequencies for both π- and σ-bonded cyclopentadienyl groups; it is analogous to the infrared spectrum of $(\pi\text{-}C_5H_5)_2Nb(\sigma\text{-}C_5H_5)_2$[7]. Tricyclopentadienylvanadium gives three frequencies in the 1400–1500 cm^{-1} range *viz.* at 1410, 1426 and 1440 cm^{-1}, while tri-π-cyclopentadienyltitanium has only one frequency in this range, *viz.* at 1447 cm^{-1} (Ref. 9). Just as allyl-DCV and pentafluorophenyl-DCV, tricyclopentadienylvanadium contains two unpaired electrons per molecule.

In general, the thermal stability of aryl and alkyl compounds of transition metals decreases in the sequence: perfluoroaryl > aryl > methyl > alkyl[12]. It has been reported previously[1,2] that aryl-DCV complexes melt without decomposition at about 100°; methyl-DCV melts at about 100° with decomposition starting at about 80°; solutions of ethyl-DCV are stable for days but isolation of the compound fails because of decomposition[2]. If the ligands R of the new compounds $(C_5H_5)_2V^{III}R$ reported are σ-bonded, it is expected that pentafluorophenyl-DCV is very stable and that the thermal stability of allyl-DCV and homologues and tricyclopentadienylvanadium is less than that of methyl-DCV. This is exactly what has been observed. The pentafluorophenyl complex is stable up to its melting point (208°); allyl-DCV, 2-methylallyl-DCV, 2-butenyl-DCV and tricyclopentadienylvanadium had to be prepared and stored at about 0°; 2-tert-butylallyl-DCV and 3-methyl-2-butenyl-DCV could not be isolated.

Combining all evidence we conclude that the compounds $(C_5H_5)_2V^{III}R$ reported here all have the structure $(\pi\text{-}C_5H_5)_2V^{III}\text{-}\sigma\text{-}R$.

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