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INTERACTION OF BIS(CYCLOPENTADIENYL)VANADIUM WITH ORGANOCADMIUM COMPOUNDS

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Summary

The reactions of bis(cyclopentadienyl)vanadium with organocadmium compounds in toluene solution at 20°C have been investigated. These reactions lead to the formation of metallic cadmium and vanadium(IV) compounds. The derivatives Cp_2VR_2 (where R = Et, Ph, CH_2Ph) decompose at 20°C to yield Cp_2VR. Cp_2VMe_2 is stable at 20°C for some months.

Introduction

It is known from literature data that electron-deficient bis(cyclopentadienyl)-vanadium readily exhibits carbenoid ability to insert into single oxygen—oxygen, carbon—halogen and metal—metal bonds. In our previous work it was shown that bis(cyclopentadienyl)vanadium in reaction with $(R_3Ge)_2Cd$ (where R = Et, Ph) inserts into a cadmium—germanium bond [1].

Results and discussion

For this reason we have studied reactions of bis(cyclopentadienyl)vanadium with a number of organocadmium compounds of the type R_2Cd, (where R = Me, Et, Ph, CH_2Ph), in which insertion of bis(cyclopentadienyl)vanadium into a covalent cadmium—carbon bond could be expected. Reactions were carried out in toluene or xylene solutions at room temperature in vacuum ampoules. On mixing the solutions of bis(cyclopentadienyl)vanadium and organocadmium compounds (molar ratio 1 : 1) a change of colour from violet to black-green was observed. Experiments showed that under these conditions organocadnium compounds readily decomposed to quantitatively yield metallic cadmium in 1—2 h.

A characteristic spectrum of the derivatives Cp_2VR_2 was recorded in the reaction mixture of bis(cyclopentadienyl)vanadium with dimethylcadmium, diethylcadmium and dibenzylcadmium by ESR methods [2]. It indicates that in the

course of reaction, initial bis(cyclopentadienyl)vanadium is oxidized to vanadium(IV) compounds of the type Cp_2VR_2. The ESR spectra of Cp_2VMe_2, Cp_2VEt_2 and $Cp_2V(CH_2Ph)_2$ in toluene at room temperature consist of eight equidistant lines of equal intensity. The values of the isotropic parameters show that they do not depend on the nature of the R-substituent at the vanadium atom (Table 1).

A peculiarity of the ESR spectrum of Cp_2VMe_2 is the presence of an additional superfine structure in which each of the eight spectrum components splits into seven lines with an intensity ratio close to binomial (1 : 6 : 15 : 20 : 15 : 6 : 1); the superfine interaction constant of additional splitting is 4.8 eV. The character of the superfine structure points to the interaction of an unpaired electron with the six protons of the two methyl groups (Fig. 1).

The additional superfine structure in Cp_2VEt_2 and $Cp_2V(CH_2Ph)_2$ is not observed, probably due to the small value of the superfine interaction constant with protons of the methylene group ($A_H(CH_2)$). This value was measured for iso-electronic titanium derivatives $(Cp_2TiR_2)^-$. The constant $A_H(CH_2)$ for the $[Cp_2Ti(CH_2Ph)_2]^-$ and $(Cp_2TiEt_2)^-$ anions are 2.6 eV and 2.3 eV respectively [3,4]. These values are nearly twice as low as that for $(Cp_2TiMe_2)^-$ which has $A_H(CH_2)$ 4.2 eV [4]. Therefore, superfine structure with a superfine interaction constant of 2.5 eV is not resolved in the ESR spectra of Cp_2VR_2, in which the individual line width is far more than that in the ESR spectra of titanium complexes.

The thermal stability of the derivatives Cp_2VR_2 was studied by ESR. It turned out that at room temperature the signal intensity of Cp_2VMe_2 does not change for some months. A slow decrease in the signal intensity of vanadium(IV) is observed in the ESR spectrum of Cp_2VEt_2, while the signal intensity of $Cp_2V(CH_2Ph)_2$ decreases much faster.

The half-lives of Cp_2VEt_2 and $Cp_2V(CH_2Ph)_2$ at 20°C, determined by ESR techniques, are about 90 h and 30 min respectively.

In the system $Cp_2V + Ph_2Cd$ it is quite impossible to record the ESR signal of vanadium(IV) at room temperature, this indicates the extreme instability of Cp_2VPh_2. Simultaneously with the decrease in the signal intensity an increase in the amount of the decomposition products of Cp_2VR_2 in the reaction mixture occurs (Table 2).

For the reaction of bis(cyclopentadienyl)vanadium with diethylcadmium no balance in ethyl groups is observed: only 30% of ethane and traces of ethylene are evolved. In this case polymerization of the ethylene formed due to disproportionation of ethyl groups probably occurs. In earlier work [5] such proc-

TABLE 1

ESR ISOTROPIC SPECTRAL PARAMETERS OF Cp_2VR_2

Cp_2VR_2	g_i	A_i^{51V} (eV)
Cp_2VMe_2	1.9915	−63.0
Cp_2VEt_2	1.9920	−62.7
$Cp_2V(CH_2Ph)_2$	1.9910	−64.0

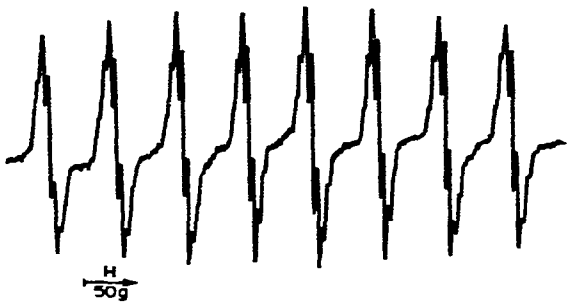

Fig. 1. Solution ESR spectrum of $Cp_2V(CH_3)_2$ in toluene recorded at room temperature.

esses have been convincingly proved to occur on decomposition of Et_4V. Toluene and dibenzyl were found in the decomposition products of $Cp_2V(CH_2Ph)_2$, whereas only benzene was found for Cp_2VPh_2.

The amounts of the products obtained indicate the cleavage of only one V—R bond and formation of diamagnetic Cp_2VR. Organovanadium(IV) compounds which we have isolated are black substances sensitive to oxygen and air moisture [6]. The vanadium—carbon bond is readily cleaved by hydrogen chloride giving about 1 mol of RH and blue crystals of Cp_2VCl (0.95 mol) (eq. 1)

$$Cp_2VR + HCl \xrightarrow[20°C]{toluene} Cp_2VCl + RH \quad (1)$$

It has been shown previously [7], that the reaction of Cp_2VR with acetic acid leads to the decay of the biscyclopentadienyl structure and formation of the dimeric acylate $[CpV(OAc)_2]_2$ according to eq. 2.

$$Cp_2VR + 2\,CH_3COOH \xrightarrow[20°C]{toluene} RH + CpH + \tfrac{1}{2}[CpV(OCOCH_3)_2]_2 \quad (2)$$

From the data obtained we can conclude that the interaction of bis(cyclopen-

TABLE 2

PRODUCTS OF THE REACTIONS OF Cp_2V WITH R_2Cd

System	Reaction time (h)	Reaction products (mols/mol of Cp_2V)			
		Cd	R—H	R—R	Cp_2VR
$Cp_2V + (C_2H_5)_2Cd$	24	0.99	0.07	none	mixture
	48	0.98	0.24	none	$Cp_2VEt + Cp_2VEt_2$ [b]
	576 [a]	0.99	0.30	none	Cp_2VEt (0.60)
$Cp_2V + (CH_2Ph)_2Cd$	12	0.98	0.22	0.12	mixture
	24	0.99	0.28	0.26	$Cp_2V(CH_2Ph)_2 + Cp_2VCH_2Ph$ [b]
	48 [a]	0.98	0.30	0.33	$Cp_2V(CH_2Ph)$ (0.66)
$Cp_2V + Ph_2Cd$	24 [a]	0.99	0.99	none	Cp_2VPh (0.88)
$Cp_2V + Me_2Cd$	576	0.98	none	none	Cp_2VMe_2 (0.70)

[a] During this period the ESR signal for vanadium(IV) has disappeared and Cp_2VR has been separated out. [b] Unseparable mixture of vanadium(IV) and vanadium(III) derivatives.

tadienyl)vanadium with organocadmium compounds is a complicated process which proceeds in several steps. The first step seems to be the insertion of bis-(cyclopentadienyl)vanadium into a cadmium—carbon bond. This is confirmed by the reactions carried out at various molar ratios of starting components. In all cases only equimolar quantities of bis(cyclopentadienyl)vanadium and organocadmium compounds reacted. The excess of the corresponding substances was isolated from the reaction mixture in unaltered form. From these data it is possible to represent the first step of this process by eq. 3.

$$Cp_2V + R_2Cd \rightarrow \left[Cp_2V\begin{matrix}\diagup CdR \\ \underset{(I)}{} \\ \diagdown R\end{matrix} \right] \qquad (3)$$

However, the ESR signal corresponding to complex I with a vanadium—cadmium bond was not recorded. It follows that complex I is extremely unstable and the second stage of the process includes its decay:

$$I \xrightarrow{20^\circ C} Cd + Cp_2VR_2 \qquad (4)$$

(R = Me, Et, Ph, CH_2Ph)

The quantitative separation of metallic cadmium being complete before the signal of vanadium(IV) derivatives begins to decrease. Experimental results show that compounds Cp_2VR_2, except for Cp_2VMe_2, decompose at room temperature. Hence the third step of the process involves decomposition of Cp_2VR_2 and formation of vanadium(III) compounds which are stable under conditions of the reactions studied:

$$Cp_2VR_2 \xrightarrow{20^\circ C} Cp_2VR + [R] \qquad (5)$$

(R = Et, Ph, CH_2Ph)

The half-life of compounds Cp_2VR_2, determined by ESR, shows that their thermal stability depending on a one-electron substituent decreases in the following sequence: Me > Et > CH_2Ph > Ph. In a series of bicovalent derivatives of bis(cyclopentadienyl)vanadium, Cp_2VMe_2 turned out to be the most stable. It was prepared in the form of black crystals sensitive to oxygen and moisture. The composition of Cp_2VMe_2 has been confirmed by the reaction with hydrogen chloride which proceeds with the quantitative formation of methane and Cp_2VCl_2 (eq. 6).

$$Cp_2VMe_2 + 2\,HCl \rightarrow Cp_2VCl_2 + 2\,MeH \qquad (6)$$

The composition of Cp_2VMe_2 is also proved by the appearance of a superfine structure in the ESR spectrum owing to the interaction of an unpaired electron of the methyl groups. Cp_2VMe_2 can be stored without decomposition at 20°C for a long time. It was shown by the DTA method that its decay occurs at 135°C. The study of chemical properties of Cp_2VMe_2 is in progress.

Experimental

All reactions were carried out in vacuum sealed ampoules or in an argon atmosphere. Melting points were measured in vacuum capillaries. The radiospec-

trometric measurements were taken using a EPA-2M spectrometer. As a pattern for calibration of the magnetic field we used the Mn^{2+} samples in the crystal lattice of MgO. For measuring the values of *g*-factor 2,2,6,6-tetramethylpiperidinoxyl was used. When determining the values of *g*-factors we took into account the correction of the second order for term A_i.

Preparation of bis(cyclopentadienyl)dimethylvanadium
(a) A mixture of Cp_2V (1.53 g, 8.30 mmol) and $(CH_3)_2Cd$ (1.32 g, 9.30 mmol) in toluene (20 ml) was kept at 20°C for 72 h. The colour of the reaction solution changed from violet to black-green. 0.91 g (8.10 mmol) of metallic cadmium separated out. Crystallization from hexane/toluene mixture at —78°C gave black crystals of Cp_2VMe_2 (1.22 g, 5.80 mmol), m.p. 130—132°C (dec.). (Found: C, 68.20; H, 7.57; V, 24.40; mol.wt. (cryoscopy in benzene) 208. $C_{12}H_{16}V$ calcd: C, 68.24; H, 7.58; V, 24.17%; mol.wt. 211.)
(b) Dry gaseous HCl in dioxane was added to Cp_2VMe_2 solution (0.38 g, 1.80 mmol) in toluene (10 ml) at 20°C. Methane (81 ml, 3.60 mmol) was isolated. The colour of the reaction mixture changed from black to green, and a precipitate of Cp_2VCl_2 (0.40 g, 16.00 mmol) formed.

Reaction of bis(cyclopentadienyl)vanadium with diethylcadmium
A mixture of Cp_2V (2.79 g, 16.00 mmol) and $(C_2H_5)_2Cd$ (2.72 g, 16.00 mmol) in toluene (30 ml) was kept at 20°C for a month. The colour of the reaction solution changed from violet to black-green and metallic cadmium (1.68 g, 15.00 mmol) separated out. The reaction mixture was analyzed by ESR and GLC methods at certain periods of time. After 24 h 1.00 mmol of ethane was found and a mixture of Cp_2VEt_2 and Cp_2VEt isolated. After 576 h 4.80 mmol of ethane was determined. The ESR vanadium(IV) signal disappeared completely. The solvent was removed from the reaction mixture under vacuum and the residue was washed by hexane. Black crystals of Cp_2VEt (2.00 g, 9.60 mmol), m.p.dec. ~100°C were separated out. (Found: C, 68.20; H, 7.09; V, 25.10. $C_{12}H_{15}V$ calcd: C, 68.67; H, 7.14; V, 24.28%.)

Reaction of bis(cyclopentadienyl)ethylvanadium with HCl and CH_3COOH
(a) Dry gaseous HCl in dioxane was added to Cp_2VEt (0.50 g, 2.38 mmol) in hexane (15 ml) at 20°C. Ethane (53 ml, 2.36 mmol) was isolated. The colour of the reaction mixture changed from black to blue and a precipitate of Cp_2VCl (0.49 g, 2.30 mmol) formed.
(b) CH_3COOH (10 ml) was added to Cp_2VEt (1.07 g, 5.10 mmol) in toluene (15 ml). Ethane (100 ml, 4.90 mmol) and C_5H_6 (2.00 mmol) were detected by chromatography. The reaction mixture turned blue and crystals of $CpV(OCOCH_3)_2$ (1.20 g, 5.10 mmol) precipitated. (Found: C, 46.39; H, 4.65; V, 21.80. $C_9H_{10}O_4V$ calcd: C, 46.20; H, 4.70; V, 21.80%.)

Reaction of bis(cyclopentadienyl)vanadium with dibenzylcadmium
A mixture of Cp_2V (0.39 g, 2.10 mmol) and $(CH_2Ph)_2Cd$ (0.62 g, 2.10 mmol) in xylol (15 ml) was kept at 20°C for one hour. Metallic cadmium (0.22 g, 2.00 mmol) separated out. The reaction mixture was analyzed at certain periods of time by ESR and GLC methods. A mixture of $Cp_2V(CH_2Ph)_2$ and Cp_2VCH_2Ph

was isolated. $C_6H_5CH_3$ (0.58 mmol) and $(CH_2Ph)_2$ (10.54 mmol) were determined after 24 h, $C_6H_5CH_3$ (0.67 mmol) and $(CH_2Ph)_2$ (0.69 mmol) were determined after 48 h. The solvent was removed under vacuum and the residue was recrystallized from hexane/toluene at −78°C. Black crystals of Cp_2VCH_2Ph (0.16 g, 0.58 mmol), m.p. 107—109°C, were isolated [6]. (Found: C, 75.30; H, 6.44; V, 18.40. $C_{16}H_{15}V$ calcd: C, 75.00; H, 6.25; V, 18.75%.)

Dry gaseous HCl in dioxane was added to a solution of 0.24 g (0.90 mmol) Cp_2VCH_2Ph in xylol (10 ml). Toluene (0.66 mmol) was determined by chromatography. The colour of the solution changed from black to blue and Cp_2VCl (0.14 g, 0.64 mmol) precipitated.

Reaction of bis(cyclopentadienyl)vanadium with diphenylcadmium

A mixture of Cp_2V (1.03 g, 5.90 mmol) and Ph_2Cd (1.43 g, 5.40 mmol) in toluene (30 ml) was kept at 20°C for 24 h. The colour of the reaction solution changed from violet to green, metallic cadmium (0.58 g, 5.20 mmol) was separated out. Benzene (2.10 mmol) was determined in the reaction mixture by GLC. The solvent was removed under vacuum, and the residue washed with hexane to yield Cp_2VPh, m.p. 90—92°C [6].

Dry gaseous HCl in dioxane was added to a solution of Cp_2VPh (0.34 g, 1.31 mmol) in toluene (10 ml). Benzene (1.11 mmol) was determined by chromatography. Blue crystals of Cp_2VCl (0.26 g, 1.20 mmol) were isolated.

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