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Electrochemical Characterization of $((\eta^5\text{-}C_5H_5)_2VCO)^-$ Anion and Electrochemical Behaviour of $(\eta^5\text{-}C_5H_5)_2VCO$ and $\eta^5\text{-}C_5H_5V(CO)_4$

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With the purpose of synthesizing chiral vanadium(III) complexes of general formula η^5*-Cp*η^5*-Cp'-V(CO)R an electrochemical approach has been made to obtain the* $((\eta^5\text{-}C_5H_5)_2VCO)^-$ *anion. This anion can be generated from the corresponding neutral complex in a one electron reversible process, but it is unstable. A study of electrochemical behaviour of* $(\eta^5\text{-}C_5H_5)_2VCO$ *under CO atmosphere and of* $\eta^5\text{-}C_5H_5V(CO)_4$ *is presented to determine a possible pathway during the ECE decomposition process of the neutral carbonyl dicyclopentadienyl vanadium complex.*

Introduction

Many anions of general formula $(\eta^5\text{-CpM}(CO)_n)^{m-}$, which are 18-electron species, have been well characterized and largely used to prepare organometallic compounds with σ M–C bonding (m = 1 or 2). But, to our knowledge, the 18-electron corresponding anions with two π-cyclopentadienyl ring, $((\eta^5\text{-Cp})_2M(CO)_n)^{m-}$ are not yet known. Of course such possible species would be limited to the element of the first transition elements, $(Cp_2V(CO))^-$ or $(Cp_2Ti(CO))^{2-}$. With the purpose of preparing vanadium complexes surrounded by four different ligands, such as η^5-Cpη^5-Cp'V(CO)R, we have studied the possibility of attaining the anion $((\eta^5\text{-Cp})_2VCO)^-$. The action of the homologous anion $(\eta^5\text{-Cp}\eta^5\text{-Cp'V(CO)})^-$ on an alkyl halide would give directly the expected chiral compound of vanadium(III).

Two carbonylcyclopentadienylvanadium anions have already been prepared. The dianion $(\eta^5\text{-}C_5H_5V(CO)_3)^{2-}$ can be obtained by shaking a solution of $C_5H_5V(CO)_4$ in tetrahydrofuran with 1% sodium amalgam [1]. The anionic vanadium carbonyl hydride $(\eta^5\text{-}C_5H_5V(CO)_3H)^-$ has been prepared recently by the addition of water to a slurry of the preceding dianion in THF [2]. But attempts to transform $(\eta^5\text{-}C_5H_5)_2VCO$ into the corresponding hypothetical 18-electron anion $((\eta^5\text{-}C_5H_5)_2VCO)^-$ by reaction with sodium in THF in the presence of CO at atmospheric pressure gave only tetracarbonyl(η-cyclopentadienyl)vanadium [3].

We have tried to prepare directly the carbonyldicyclopentadienylvanadium anion by electrochemical reduction of the neutral precursor.

The electrochemical behaviour of cyclopentadienyl vanadium compounds has already been studied in some cases and the following electrochemical processes have been characterized:

$$Cp_2V^{2+} \overset{+e}{\rightleftharpoons} Cp_2V^{+} \qquad [4]$$

$$Cp_2VCl_2 \xrightarrow[-Cl^-]{+e} Cp_2VCl \xrightarrow[-Cl^-]{+e} Cp_2V \qquad [5]$$

$$Cp_2V \overset{-e}{\rightleftharpoons} Cp_2V^{+} \xrightarrow{-e} Cp_2V^{2+} \qquad [6]$$

$$Cp_2V \overset{+e}{\rightleftharpoons} Cp_2V^{-} \qquad [6]$$

$$CpVC_7H_7 \overset{-e}{\rightleftharpoons} (CpVC_7H_7)^{+} \qquad [7]$$

For the last process a one electron reversible oxidation is observed in acetonitrile on a platinum electrode and the cation formed is unstable.

Surprisingly enough no reduction wave could be observed for $CpVC_7H_7$. According to the usual 18-electron rule for transition metal π-complexes the mixed complex which contains only seventeen electrons should be reducible. However it is well known that the 18-electron rule does not work well with the transition metal complexes of titanium and vanadium columns. Moreover it is possible that the reduction wave of $CpVC_7H_7$ is beyond the discharge of supporting electrolyte.

Now $CpVC_7H_7$ is isoelectronic with Cp_2VCO and, with our purpose of using $((Cp_2VCO)^-$ anion as a synthetic precursor, it was necessary to know the electrochemical behaviour of Cp_2VCO.

This paper is devoted to the electrochemical study of this compound. We will also give the electrochemical behaviour of $CpV(CO)_4$ as a neces-

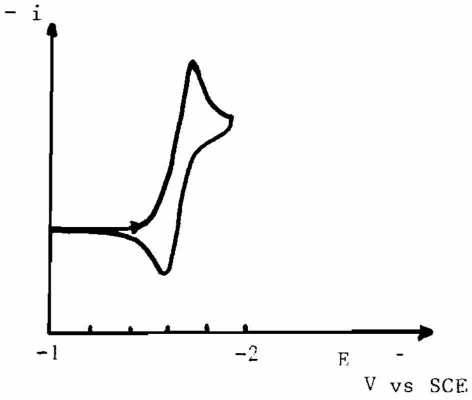

Figure 1. Cyclic voltammogram of Cp_2VCO in THF, 0.1 *M* $Bu_4N^+PF_6^-$, at scan rate of 0.05 V sec^{-1}.

sary contribution to the analysis of the decomposition products of the Cp_2VCO^- anion.

Results and Discussion

Cp_2VCO has been prepared according to [8]. $CpV(CO)_4$ was a commercial product.

Electrochemical Behaviour of Cp_2VCO

The polarographic analysis of a solution of Cp_2VCO in THF with 0.1 *M* $Bu_4N^+PF_6^-$ as supporting electrolyte shows a monoelectronic oxidation wave ($E_{1/2}$ = −0.3V*) and a monoelectronic reduction wave ($E_{1/2}$ = −2.32 V).

The cyclic voltammetry (Figure 1) depends on the scanning rate. For the sweeping speed of 0.05 V/sec the reduction process is reversible but the oxidation process is irreversible. For the sweeping speed of 1 V/sec the oxidation process also becomes reversible.

In thin layer voltammetry on a graphite electrode the reduction process shows reversibility for scanning rates between 0.001 and 0.01 V/sec.

The electrode processes correspond to the transformation of the neutral complex to the corresponding cationic and anionic species:

$$(Cp_2VCO)^+ \underset{(1)}{\overset{e}{\rightleftharpoons}} Cp_2VCO \underset{(2)}{\overset{e}{\rightleftharpoons}} (Cp_2VCO)^-$$

To study the chemical stability of the anion $(Cp_2VCO)^-$ we have tried to make a preparative electrolysis of the species. The electrolysis has been made with a THF solution of Cp_2VCO at −2.2 V using 0.2 *M* $Bu_4N^+PF_6^-$ as supporting electrolyte. It appears that the solution of the $(Cp_2VCO)^-$ obtained is unstable.

Moreover the preparative electrolysis needs two Faradays per mol whereas polarography and thin layer voltammetry show that the first electrochemical process is a one electron process. This clearly shows that the $(Cp_2VCO)^-$ anion is transformed into a decomposition species which is reducible at a potential more positive than −2.2 V.

This hypothesis is supported by the characterization of the decomposition products: in fact a metallic vanadium deposit is observed and cyclopentadienyl anion can be detected in the solution. The formation of Cp^- anion is shown unambiguously by adding $CoBr_2$ to the solution. In these conditions the cobalticinium cation is formed immediately and has been identified as $Cp_2Co^+PF_6^-$.

So the first electrochemical step of the whole ECE process must be followed by one of the three possible pathways a, b or c:

$$\begin{tikzcd}
 & & (CpVCO)^- \arrow[r] & Cp^- + V + CO & (a) \\
(Cp_2VCO)^- \arrow[r] & Cp^- + (CpVCO) \arrow[ur, "e"] \arrow[r] \arrow[dr] & Co + CpV \arrow[r, "e"] & Cp^- + V + CO & (b) \\
 & & Cp^- + CO + V^+ \arrow[r, "e"] & V & (c)
\end{tikzcd}$$

But the electrochemical analysis is unable to differentiate among these three possibilities.

Electrolysis of Cp_2VCO under CO Atmosphere

The chemical step of the ECE process proposed for Cp_2VCO postulates the intermediate (CpVCO) of vanadium(I) which is coordinatively unsaturated. To detect this intermediate we have tried to trap this species by the action of CO ligands. So the electrolysis of Cp_2VCO has been performed under a CO atmosphere with the aim of reaching the well known $CpV(CO)_4$ complex according to $(CpVCO) + 3CO \rightarrow CpV(CO)_4$. The electrolysis has been made at −2.2 V and requires 3 Faradays per mol and the solution obtained is orange. Moreover the infra-red spectra show four characteristic bands: 1891, 1811, 1782 and 1740 cm^{-1}.

The consumption of three Faradays per mol for the electrolysis in our experimental conditions prompted us to reinvestigate the electrochemical behaviour of $CpV(CO)_4$. Indeed Dessy reported that $CpV(CO)_4$ gives an irreversible monoelectronic reduction wave. It seems that such a result is inconsistent with our hypothesis because if the reduction of $CpV(CO)_4$ requires only one electron our whole process would need only 2 Faradays.

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*All potentials refer to the saturated calomel electrode.

Electrochemical Behaviour of $CpV(CO)_4$

In THF $CpV(CO)_4$ gives a monoelectronic reduction wave ($E_{1/2} = -1.97$ V). We have estimated its monoelectronic character by reference to the waves of $C_8H_8Fe(CO)_3$ which are well known [9]. Cyclic voltammetry shows that the electrochemical process is reversible even for slow scanning rates (0.025 V/sec).

$$CpV(CO)_4 + e \rightleftharpoons (CpV(CO)_4)^{\dot{-}}$$

But if the polarographic data corresponds to a one electron wave, preparative electrolysis starting from $CpV(CO)_4$ needs about 1.42 Faraday per mol. This electrolysis gives an orange coloured solution with four specific lines (1890, 1811, 1785 and 1738 cm^{-1}). This means that preparative electrolysis starting from $CpV(CO)_4$ or starting from Cp_2VCO under CO atmosphere gives the same products and this result definitively confirms our hypothesis about the formation of the (CpVCO) complex as a decomposition product of $(Cp_2VCO)^-$.

However we have to explain the complete behaviour of $CpV(CO)_4$ solutions and the contrast between the polarographic analysis and the data obtained by preparative electrolysis starting from $CpV(CO)_4$. It is particularly curious that, in spite of the reversibility of the system $CpVCO_4/CpV(CO)_4$), it is impossible to obtain a stable solution of $(CpV(CO)_4)^{\dot{-}}$*.

The following results allow us to propose a coherent explanation:

– If water is added gradually to the THF solution of $CpV(CO)_4$ the polarographic wave becomes higher and higher and it can reach two electrons.

– In presence of water the electrolysis of $CpV(CO)_4$ requires 2 Faradays and gives an orange coloured solution with only two IR absorptions in the metal carbonyl region (1890 and 1782 cm^{-1}). These two lines have been found for THF solutions of the salt $((Ph_3P)_2N)^+(\eta^5\text{-}C_5H_5V(CO)_3H)^-$ [2].

So the species which are formed in the electrolysis of $CpV(CO)_4$ in presence of water are $(\eta^5\text{-}C_5H_5V(CO)_3H)^-$ anion. The same anion must also be formed in the electrolysis of $Cp_2V(CO)$ under CO atmosphere beside another product (IR absorption at 1811 and 1740 cm^{-1}).

The presence of $(CpV(CO)_3H)^-$ in the solution can be attributed to the action of $(CpV(CO)_3)^{2-}$ dianion on residual water which is contained in THF or in the supporting electrolyte.

We have finally to confirm the formation of $(CpV(CO)_3)^{2-}$ and attribute the two IR absorptions at 1811 and 1740 cm^{-1}.

$CpV(CO)_4$ is chemically reduced by Na/Hg as already described [1] in THF. After one hour reaction time $CpV(CO)_3Na_2$ is partially precipitated. A small quantity of the solid which has been precipitated can be dissolved in an excess of THF. This solution shows four IR absorptions (1890, 1811, 1785 and 1738 cm^{-1}) but the two lines at 1811 cm^{-1} and 1738 cm^{-1} vanish upon addition of a small quantity of water. Obviously this means that the preceding two IR absorptions are specific of $(CpV(CO)_3)^{2-}$ anion and that this anion reacts with traces of water which are present in THF during the electrolysis.

In summarizing we can conclude that the Cp_2VCO complex is electroreducible in a one electron process giving the corresponding anion $(Cp_2VCO)^-$. This anion is unstable at room temperature. The final products of the reduction are Cp^-, V and CO. (CpVCO) or (CpV) can be the transient species. These highly coordinatively unsaturated complexes react with CO to give $CpV(CO)_4$.

Tetracarbonylcyclopentadienylvanadium is reducible in a one electron reversible process to the 19e anion $(CpV(CO)_4)^{\dot{-}}$ which is also unstable and is decomposed in presence of traces of water according to two possible ways (a) or (b):

$$\begin{tikzcd}
 & & CpV(CO)_3^{2-} \arrow[r, "H^+"] & CpV(CO)_3H^- & (a) \\
{[CpV(CO)_4]^{\dot{-}}} \arrow[r, "-CO"'] & {[CpV(CO)_3]^{\dot{-}}} \arrow[ur, "e"] \arrow[dr, "H^+"'] & & & \\
 & & CpV(CO)_3H)\cdot \arrow[r, "e"] & (CpV(CO)_3H)^- & (b)
\end{tikzcd}$$

Moreover, to account for the consumption of current during the electrolysis of $CpV(CO)_4$ (1.42 F per mol), it is necessary to suppose that $(CpV(CO)_3)^{\dot{-}}$ can also be spontaneously decomposed to CO, vanadium and cyclopentadienyl anion.

Experimental

All chemical and electrochemical experiments were carried out in purified nitrogen or argon atmosphere. The solvents were purified by standard methods and were distilled just before use.

Cp_2VCO was prepared by carbonylation of Cp_2V in heptane [8] and the brown solid obtained was crystallized twice in heptane (yield: 80%, ν_{CO}(THF): 1870 cm^{-1}.

The electrochemical experiments were performed in an electrochemical cell which permits one to work

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*This anion cannot be detected by polarography in solutions obtained from preparative electrolysis.

under high-vacuum and inert gas controlled atmosphere.

The reference electrode was a saturated calomel electrode and the auxiliary electrode consisted of a platinum wire; these two electrodes were separated from the solution by a fritted glass disk. The working electrode was a dropping mercury electrode for the polarographic experiments, a glassy carbon electrode for the voltammetry studies and a mercury pool for the controlled-potential electrolysis.

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