Electron Spin Resonance Studies of Ziegler-Type Catalysts. 3.[1] The Complex Derived from Dichlorobis(η-cyclopentadienyl)vanadium and Diethylaluminum Chloride

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Abstract: The reaction between Cp_2VCl_2 in CH_2Cl_2 and Et_2AlCl in *n*-heptane yields a paramagnetic product giving the ESR parameters $A_{iso} = 4.11$ mT, $g_{iso} = 1.996$ at room temperature. At 77 K a frozen solution spectrum was obtained having the parameters $A_x = -6.37$ mT, $A_y = -7.05$ mT, $A_z = +1.09$ mT, $g_x = 2.001$, $g_y = 1.987$, $g_z = 2.000$. Analysis of this spectrum indicates that the complex is $Cp_2VH(\mu\text{-}Cl)_2AlX_2$ (where X is Cl or Et), having a distorted trigonal bipyramidal structure and C_{2v} symmetry about the vanadium. The spectrum of the complex corresponds to species II in part 1 of this series.[2]

Introduction

The interpretation of Cossee[3] of the mechanism of Ziegler–Natta catalysis has gained wide acceptance. Henrici-Olivé and Olivé[4] have extended this scheme to homogeneous catalysts such as that obtained from the reaction between Cp_2TiCl_2 and R_3Al, R_2AlCl, or $RAlCl_2$ in which they envisage a vacancy in the octahedral coordination sphere of the suggested complex $RCp_2Ti(\mu\text{-}Cl)_2AlR'_2$ (R = alkyl, R′ = alkyl or Cl) filled by the coordinated ethylene group.

Armstrong et al.[5] have carried out a theoretical investigation based on the hypothetical complex $MeTiCl_2(\mu\text{-}Cl)_2AlCl_2$ and argue that the most theoretically favorable conformation for a homogeneous catalyst of this type is one where the site symmetry of the Ti center is trigonal bipyramidal.

All the catalytic species proposed have been Ti(IV), which is not amenable to examination by ESR, as it is d^0 and thus diamagnetic. In part 1[2] of this series the catalytic system obtained by mixing Cp_2VCl_2 and $EtAlCl_2$ was found to contain three paramagnetic species with hyperfine splitting constants $A(^{51}V) = 7.39$, 4.14, and 7.38 mT for species I, II, and III, respectively. In that paper experiments were described which established species I to be a noncatalytic 1:1 complex between Cp_2VCl_2 and $AlCl_3$. The work described in the present paper concerns the reaction between Cp_2VCl_2 in methylene chloride and Et_2AlCl in *n*-heptane which gives a paramagnetic species having (within 10%) the same V(IV) concentration as the starting material. This species has the same $A(^{51}V)_{iso}$ value as that obtained for species II in the $Cp_2VCl_2/EtAlCl_2$ system.[2] Examination of the ESR spectra obtained for this complex gives strong experimental evidence that the site symmetry of the vanadium center is trigonal bipyramidal as suggested by Armstrong's theoretical calculations for the hypothetical titanium complex.[5]

Experimental Section

Materials. All reactions were carried out under an atmosphere of dry dinitrogen. Diethylaluminum chloride in *n*-heptane was obtained from I. C. I. Ltd., Plastics Division. Dichlorobis(η-cyclopentadienyl)vanadium was prepared by the method of Wilkinson and Birmingham.[6]

Procedure. Electron spin resonance spectra were measured on a Varian E-109 spectrometer, fitted with a Varian E-4557 variable temperature controlling unit.

Computer simulated spectra were calculated from the empirically determined values, correct to second order, by the method of Evans, Morgan, and Renaud[7] on an ICL system 4-70 computer and plotted on a Calcomp drum plotter.

Preparation of $HCp_2V(\mu\text{-}Cl)_2AlX_2$. Equimolar amounts of diethylaluminum chloride in toluene and a suspension of Cp_2VCl_2 in toluene were mixed at −30 °C and then brought to 0 °C. Immediately the bright green solution became pale brown, and the ESR spectrum of Cp_2VCl_2 disappeared and was simultaneously replaced by an ESR spectrum of a species having (within 10%) the same spin concentration as the original Cp_2VCl_2. Since ESR shows no remaining Cp_2VCl_2, we conclude that a 1:1 complex has been formed. A similar result is obtained when Cp_2VCl_2 in dichloromethane was mixed with excess diethylaluminum chloride in *n*-heptane. Excess diethylaluminum chloride is required in the latter case because it reacts with the methylene dichloride.

Results and Discussion

ESR Spectra. The solution produced above was examined by ESR spectroscopy. At room temperature an eight-line solution spectrum was obtained (Figure 1A), having $A(^{51}V)_{iso} = 4.11$ mT and $g_{iso} = 1.996$, identical in appearance with the simulated spectrum for species II in part 1 of this series.[2] No superhyperfine structure was apparent until the fifth derivative spectrum was examined (Figure 1B). Computer simulation of this fifth derivative showed the presence of a doublet, indicating interaction between the odd electron on the vanadium and a single proton. A value of 0.57 mT is obtained for this proton hyperfine coupling. The line shape displays Gaussian inhomogeneous broadening[8] and accurate simulation can only be achieved by the inclusion of a hyperfine coupling of 0.16 mT for each of the ten cyclopentadienyl protons (Figure 1C). (The slight differences, marked by an arrow, between Figures 1B and 1C are due to modulation distortions not accounted for in the simulation program. This was checked using strong pitch. Chebychev expansions of the Fourier function are being included in the program to eliminate this problem.) We would not expect these cyclopentadienyl protons to be resolved in the observed spectrum, because in Cp_2VCl_2, where the unpaired electron is primarily in a nonbonding orbital,[9] and the line shape approximates to the Lorentzian function, the line width for vanadium is 0.8 mT.

Figure 2A shows the frozen solution spectrum at 77 K from which the parameters $A_x = -6.37$ mT, $A_y = -7.05$ mT, $A_z = +1.09$ mT, $g_x = 2.001$, $g_y = 1.987$, $g_z = 2.000$ were obtained. The simulated spectrum using these parameters gave a good fit (Figure 2B). The parameters and simulation were derived as in part 2.[1] The fact that the parameters are so different from each other shows that the complex is of low symmetry, and the application of the method described in our previous paper[1] demonstrates that it has C_{2v} symmetry. The only possible structure for the complex with this symmetry is one in which the vanadium is in a trigonal bipyramidal structure (see Figure 3).

Reaction of this complex with pyridine or THF yielded a

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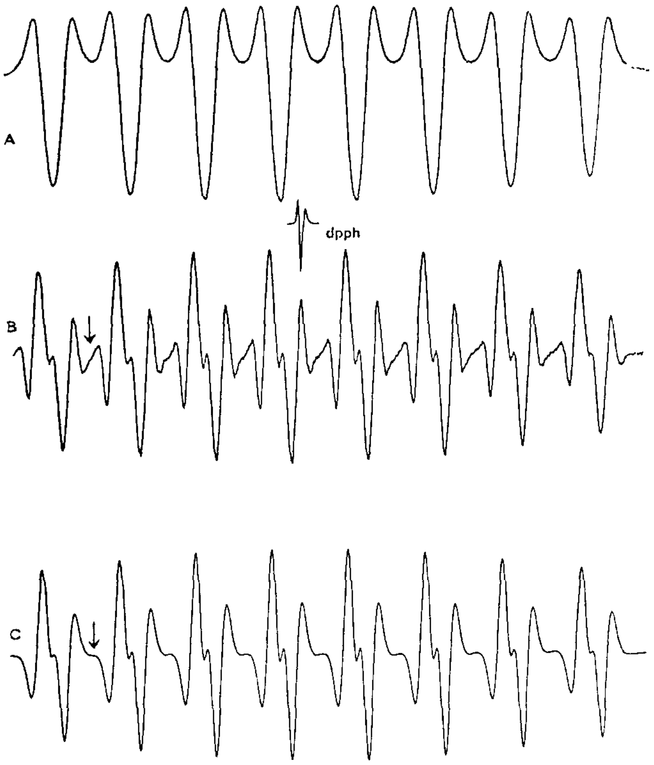

Figure 1. (A) Second derivative ESR spectrum of complex at room temperature. (B) Fifth derivative of ESR spectrum of complex at room temperature. (C) Computer simulation of Figure 1B.

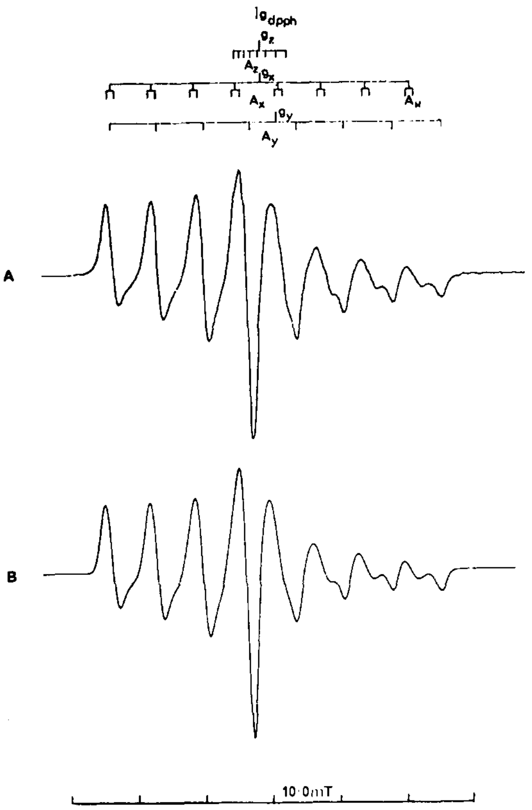

Figure 2. (A) Frozen solution spectrum of complex at 77 K with stick spectrum assignment. (B) Computer simulation of Figure 2A.

species having $A(^{51}V)_{iso}$ = 7.03 mT, g_{iso} = 1.988, and this on reaction (a) with HCl yielded a spectrum of Cp_2VCl_2, and (b) with Et_2AlCl yielded a spectrum of Cp_2VEt_2.[1] This indicates that the Cp groups from the starting material have remained on the vanadium in the complex. The fact that addition of pyridine or THF to our complex does not yield Cp_2VCl_2 immediately (as it does with the 1/1 complex of $Cp_2VCl_2/AlCl_3$[2]), but only after treatment of the first-formed product with HCl, suggests that pyridine first produces Cp_2VHCl, which is converted by HCl to Cp_2VCl_2 and by Et_2AlCl into Cp_2VEt_2. This experiment does not show conclusively whether the H atom is V–H or in the bridge. The fact that the complex has C_{2v} symmetry, however, shows definitely that the H is not in the bridge, and that the structure of the complex is as given in Figure 3. (Complexes between titanium biscyclopentadienyl compounds and group 3 Lewis acids through μ-chloro bridges are well-known.[10])

Application of the orbital rotation method[12] to orbitals in C_{2v} symmetry for a d^1 case indicates that all three g values should be below free spin. The fact that g_z is 2.000 (i.e., very close to the free spin value) can be explained in terms of considerable electron delocalization to the cyclopentadienyl rings which are π bonded above and below the vanadium along the z axis. This fact gives additional support to the structure given in Figure 3.

The magnitude of the H–Cp coupling constant in $Cp_2Ti(\mu\text{-}H)_2AlCl_2$ is 0.057 mT,[12] which is ten times smaller than in our complex, indicating far less metal orbital overlap with the Cp groups. This is because the Cp–Ti–Cp angle in the $Cp_2Ti(\mu\text{-}H)_2AlCl_2$ complex is more or less tetrahedral (as in Cp_2VCl_2), whereas in our complex (Figure 3) the Cp groups are located along the z axis (trigonal bipyramidal).

Aluminum hyperfine coupling is not observed in our complex, and this suggests that the aluminum is alkylated and bonded to the vanadium via μ-chloro bridging.[4]

In the normal course of complex formation between Cp_2VCl_2 and Et_2AlCl, we would expect the nonbridged group on the vanadium to be either Cl or Et. The fact that this group is an H atom means that the nonbridged Et group initially attached to the vanadium probably undergoes elimination of ethylene leaving the hydride.

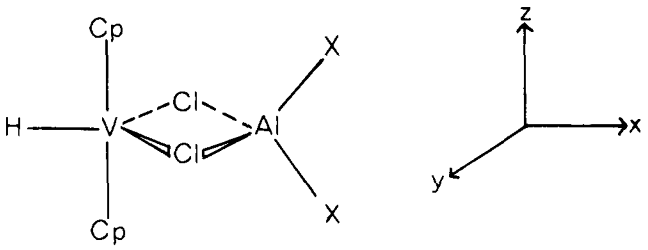

Figure 3. Proposed structure of complex.

The elimination of ethylene from the complex to yield a vanadium–hydride bond is not entirely surprising, since Brintzinger[13] has found that alkylation of Cp_2TiCl_2 with ethyl- or isopropyllithium or Grignard reagents leads to hydride formation, and Guggenberger and Tebbe[14] have characterized hydride complexes arising from complexing Cp_2TiCl_2 with triethylaluminum.

Theoretical Treatment

Using a crystal field treatment for C_{2v} symmetry, the unpaired electron is in an A_1 ground state, and the relative orbital character gives an electronic ground state

$$|\psi\rangle_0 = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$$

where

$$a^2 + b^2 = 1$$

The frozen solution spectral data can, therefore, be treated using the expressions derived from second-order perturbation theory by McGarvey.[15]

$$A_x = -K + P[\alpha_x - (g_0 - g_x)]$$

$$A_y = -K + P[\alpha_y - (g_0 - g_y)]$$

$$A_z = -K + P[\alpha_z - (g_0 - g_z)]$$

$$\alpha_x = \frac{-2}{7}(a^2 - b^2) - \frac{4}{7}\sqrt{3}ab\left(\frac{1 + (g_0 - g_z)}{8b^2}\right)\frac{-\sqrt{3}}{14} \times \frac{(a + b\sqrt{3})}{(a\sqrt{3} - b)}(g_0 - g_y)$$

$$\alpha_y = \frac{-2}{7}(a^2 - b^2) + \frac{4\sqrt{3}ab}{7}\left(\frac{1 + (g_0 - g_z)}{8b^2}\right)\frac{-\sqrt{3}}{14} \times \frac{(a - b\sqrt{3})}{(a\sqrt{3} + b)}(g_0 - g_x)$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{\sqrt{3}}{14}\left[\frac{(a + b\sqrt{3})}{(a\sqrt{3} - b)}(g_0 - g_y) + \frac{(a - b\sqrt{3})}{(a\sqrt{3} + b)}(g_0 - g_x)\right]$$

$$P = g_0 g_n{}^{51}\beta\beta_n\langle r^{-3}\rangle$$

$$K = -g_0 g_n{}^{51}\beta\beta_n\frac{2}{3}\chi$$

For the A and g values given above we obtain $a = -0.999$, $b = 0.031$, indicating that the unpaired electron on the vanadium is almost entirely d_{z^2} in character, which strongly supports the structure proposed, as we would expect strong delocalization through the π-bonded Cp groups. The above equations differ from those of part 2[1] in the matter of signs. This is due to the fact that we have chosen a different z axis in the present paper. In part 2 the z axis was chosen to be perpendicular to the plane containing the V and Cp groups. In this paper, it is chosen along the line of centers of the V and Cp groups. In both cases it lies along the line of maximum electron density.

The $\langle 1/r^3\rangle$ value obtained is 1.80 au compared with values of over 2 for Cp_2VL_2 compounds[9] (L is a ligand). Comparison of the calculated P values with those obtained from Hartree–Fock $\langle r^{-3}\rangle$ values[16] shows that the effective nuclear charge on the vanadium changes from ca. +1.0 for Cp_2VCl_2[1] to +0.2 for the complex $Cp_2VH(\mu\text{-}Cl)_2AlX_2$. This decrease in effective nuclear charge as the structure changes from tetrahedral to trigonal bipyramidal is probably due in the main to the greater orbital overlap which occurs between the Cp groups and the vanadium in the latter structure.

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Synthesis of Stable Chromium(V) Complexes of Tertiary Hydroxy Acids[1]

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Abstract: Stable, water-soluble chromium(V) complexes of the general formula $Na[OCr(O_2COCR_1R_2)_2]$ were prepared in 60–90% yields by the reaction of anhydrous sodium dichromate in acetone with tertiary α-hydroxy acids (2-hydroxy-2-methylpropionic, 2-hydroxy-2-methylbutyric, 2-ethyl-2-hydroxybutyric, 2-butyl-2-hydroxyhexanoic, 1-hydroxycyclopentanecarboxylic, 1-hydroxycyclohexanecarboxylic, and 2-hydroxy-2-phenylpropionic acids). The stoichiometry of the reaction is $Na_2Cr_2O_7 + 5R_1R_2C(OH)CO_2H = 2Na[OCr(O_2COCR_1R_2)_2] + R_1R_2CO + CO_2 + 5H_2O$.

We recently reported[2] the synthesis of the first stable water-soluble chromium(V) compound, potassium bis(2-hydroxy-2-methylbutyrato)oxochromate(V), prepared from 2-hydroxy-2-methylbutyric acid and chromium trioxide in an aqueous solution. Since chromium(V) is formed in an equimolar mixture (eq 1) with chromium(III), isolation of the complex involves its separation on ion exchange resins, removal of large quantities of water, and careful balancing between solubility of individual components and stability of the product. It is a tedious, low-yield (20%) synthesis of a limited potential which succeeded mainly due to the ability of 2-hydroxy-2-methylbutyric acid to sufficiently stabilize the pentavalent chromium in water. In order to avoid these disadvantages, we

$$2Cr(VI) + 2C_2H_5(CH_3)C(OH)COOH \rightarrow Cr(V) + Cr(III) + 2CH_3CH_2COCH_3 + 2CO_2 \quad (1)$$

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