

# ESR Studies on Vanadocene/Cocatalyst Systems for Ethylene Polymerization

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**ABSTRACT:** Three vanadocene–cocatalyst catalytic systems for ethylene polymerization— $\text{Cp}_2\text{ZrCl}_2/\text{Al}_2\text{Et}_3\text{Cl}_3$  [dichlorobis( $\eta$ -cyclopentadienyl)vanadium/ethylaluminumsesquichloride],  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  [dichlorobis( $\eta$ -cyclopentadienyl)vanadium/methylaluminoxane] and  $\text{Cp}_2\text{ZrCl}_2/\text{AlEt}_3$  [dichlorobis( $\eta$ -cyclopentadienyl)vanadium/triethylaluminum]—were monitored by electron spin resonance (ESR) spectroscopy. It was found that at least a certain kind of vanadium complex is formed after mixing dichlorobis( $\eta$ -cyclopentadienyl)vanadium with ethylaluminumsesquichloride. After introducing ethylene, a new kind of vanadium complex is detected by ESR. Ethylene can be polymerized by using a dichlorobis( $\eta$ -cyclopentadienyl)vanadium/ethylaluminumsesquichloride catalytic system. These results possibly indicate that the vanadium complex exists in the forms  $\text{ClCp}_2\text{VClEtAlCl}_2$  and  $\text{ClCp}_2\text{VClEtAlClEt}$ , which are responsible for forming active centers. The Dichlorobis( $\eta$ -cyclopentadienyl)vanadium/methylaluminoxane and dichlorobis( $\eta$ -cyclopentadienyl)vanadium/triethylaluminum systems also were monitored by ESR. Completely different spectra were recorded compared to those of the dichlorobis( $\eta$ -cyclopentadienyl)vanadium/ethylaluminumsesquichloride system. Ethylene almost cannot be polymerized by the dichlorobis( $\eta$ -cyclopentadienyl)vanadium/methylaluminoxane and dichlorobis( $\eta$ -cyclopentadienyl)vanadium/triethylaluminum catalytic systems, showing that resultant vanadium complexes of dichlorobis( $\eta$ -cyclopentadienyl)vanadium/methylaluminoxane and dichlorobis( $\eta$ -cyclopentadienyl)vanadium/triethylaluminum catalytic systems are different from that arising from the dichlorobis( $\eta$ -cyclopentadienyl)vanadium/ethylaluminumsesquichloride system. Plausible mechanisms are suggested for this. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1188–1194, 2001

**Key words:** ESR; vanadocene catalytic system; ethylene polymerization

## INTRODUCTION

Continued fundamental investigations of classic Ziegler–Natta catalysts for olefins polymerization

have led to a basic understanding of the polymerization active sites and the polymerization mechanism.<sup>1–2</sup> In recent years there have been a large number of studies of metallocene catalysts. A vast amount of information on catalytic mechanisms has been obtained for the olefin polymerization reactions catalyzed by these systems.<sup>3–5</sup> However, it is more difficult to investigate the coordination structure of the transition metal species

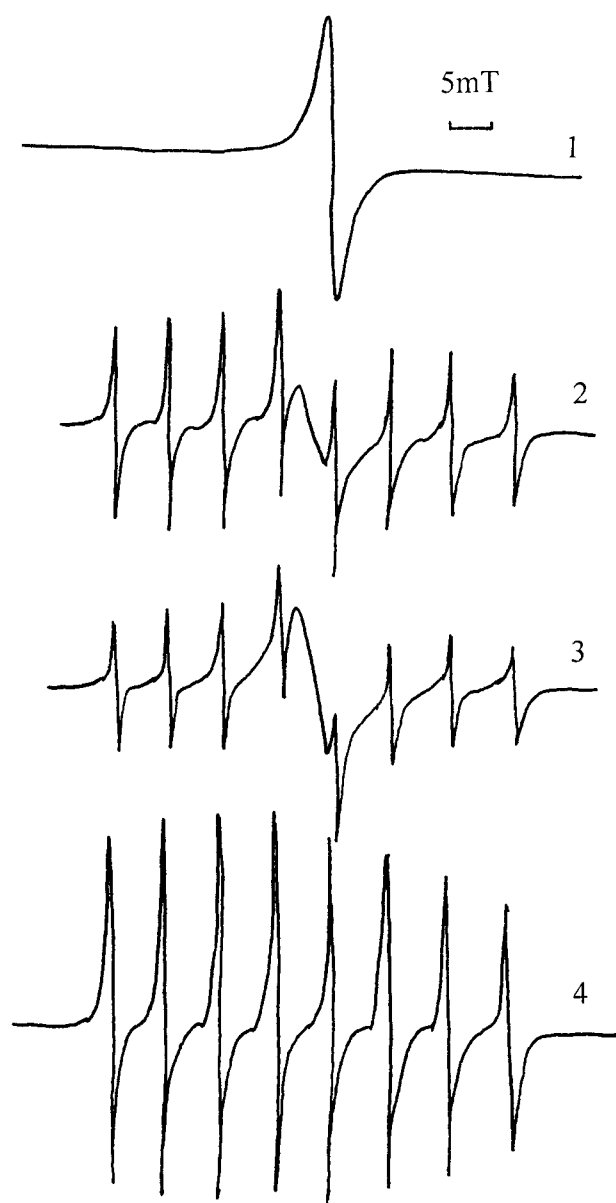
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**Table I Polymerization Conditions and Results**

Catalyst	Cocatalyst	V/Al (mol/mol)	T <sub>p</sub> (°C)	Activity (gPE/molV · h)
Cp <sub>2</sub> VCl <sub>2</sub>	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	1 : 1000	30	6.78 × 10 <sup>3</sup>
Cp <sub>2</sub> VCl <sub>2</sub>	MAO	1 : 1000	30	Trace
Cp <sub>2</sub> VCl <sub>2</sub>	MAO	1 : 1000	50	Trace
Cp <sub>2</sub> VCl <sub>2</sub>	AlEt <sub>3</sub>	1 : 1000	30	Trace
Cp <sub>2</sub> VCl <sub>2</sub>	AlEt <sub>3</sub>	1 : 1500	50	Trace

during olefin polymerization. Fortunately, if the transition metal in the catalytic system has an unpaired electron, the system can be monitored

**Figure 1** ESR spectra of Cp<sub>2</sub>VCl<sub>2</sub>.**Table II ESR Parameters of Cp<sub>2</sub>VCl<sub>2</sub>**

Entry	g <sup>1</sup>	g <sup>2</sup>	A <sup>2</sup> (mT)
1 (Cp <sub>2</sub> VCl <sub>2</sub> )	1.983	—	—
2 (0.002MCp <sub>2</sub> VCl <sub>2</sub> in toluene)	1.989	1.99	7.10
3 (0.01MCp <sub>2</sub> VCl <sub>2</sub> in toluene)	1.987	1.99	7.09
4 (0.01MCp <sub>2</sub> VCl <sub>2</sub> in CH <sub>2</sub> Cl <sub>2</sub> )	—	1.99	7.05

by electron spin resonance (ESR) technique, as indicated in several reports.<sup>1-2,6-9</sup> Cp<sub>2</sub>VCl<sub>2</sub> is one common metallocene in which V(IV) is ESR active. Although the active center of the vanadium catalytic system for olefin polymerization is generally believed to be trivalent and is ESR silent, indirect information of polymerization mechanism and coordination environment can be obtained through monitoring the change of ESR signals of the Cp<sub>2</sub>VCl<sub>2</sub>-cocatalyst system.<sup>10</sup> Usually, methylaluminoxane MAO, AlEt<sub>3</sub>, and Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> are used as cocatalysts for olefin polymerization, and MAO is most active in metallocene-cocatalyst catalytic systems because of its strong ionization function.

In the present work, Cp<sub>2</sub>VCl<sub>2</sub>-MAO, Cp<sub>2</sub>VCl<sub>2</sub>-AlEt<sub>3</sub>, and Cp<sub>2</sub>VCl<sub>2</sub>-Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> systems were used as catalytic systems for ethylene polymerization. Their ESR spectra were recorded and compared. Plausible polymerization mechanisms are suggested and explained below.

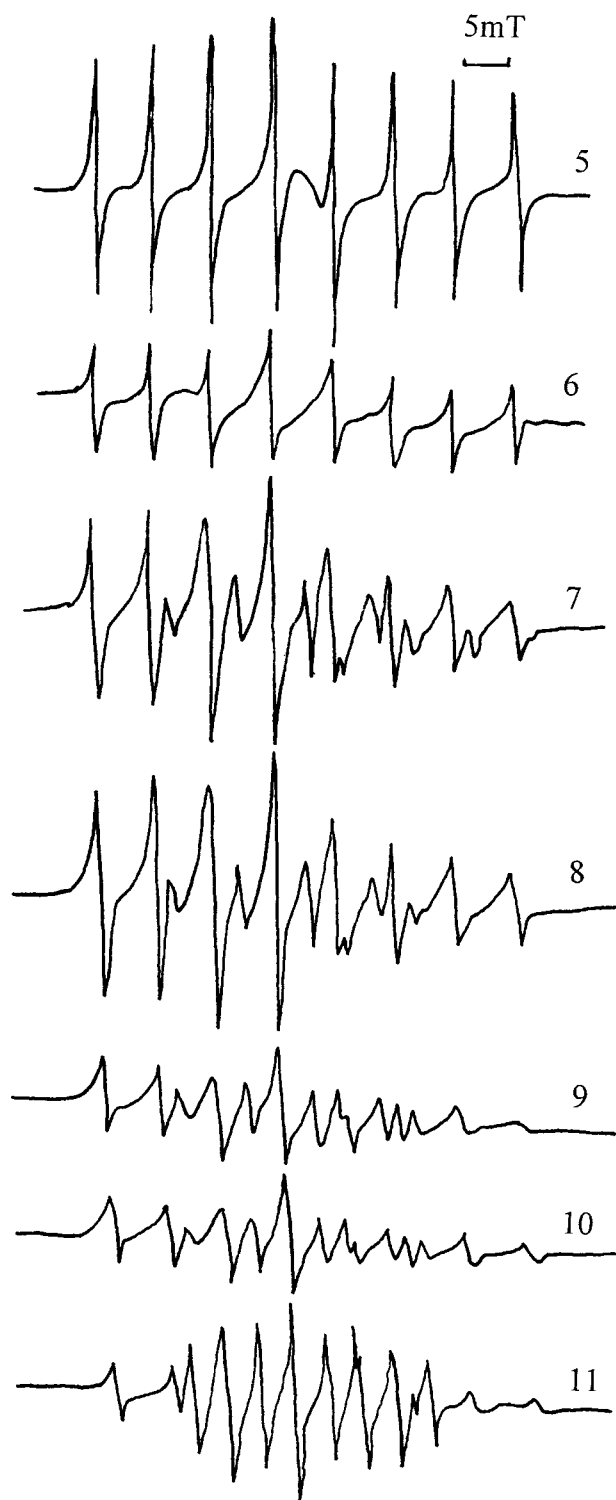
## EXPERIMENTAL

### Materials

MAO (Shering Co.), Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, AlEt<sub>3</sub>, and Cp<sub>2</sub>VCl<sub>2</sub> (Aldrich Co.) were used as received. Toluene was purified by refluxing over a Na-K alloy under a nitrogen atmosphere and distilled prior to use. Dichloromethane was heated under reflux over P<sub>2</sub>O<sub>5</sub> in a nitrogen atmosphere. Polymerization-grade ethylene was further purified by passing it over 4Å activated molecular sieves.

### Polymerization Procedure

The polymerization procedures used have been described elsewhere.<sup>11-13</sup> The polymerization was carried out in a 100-mL glass flask equipped with an ethylene inlet, magnetic stirrer, and vacuum line. The flask was filled with 50 mL of dry toluene and certain quantities of Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> or AlEt<sub>3</sub> or



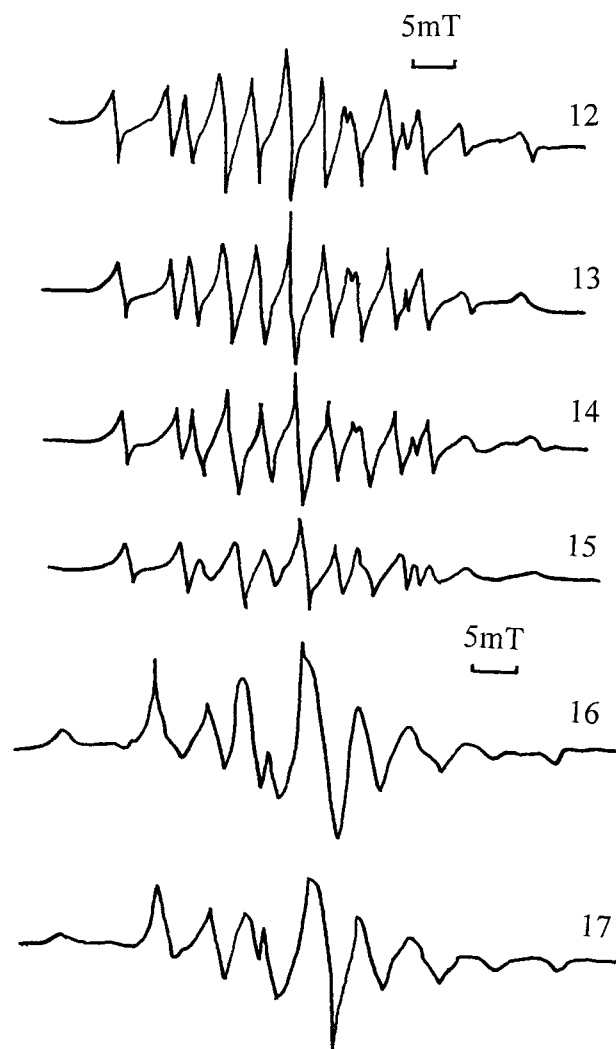
**Figure 2** ESR spectra of  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  system (measured at room temperature).

MAO. The mixture was stirred at  $30^\circ\text{C}$  or  $50^\circ\text{C}$  and then saturated with ethylene (1 atm). The reaction was initiated by adding the solution of

$\text{Cp}_2\text{VCl}_2$  in toluene. After 30 min the polymerization was terminated by the addition of acidified ethanol, and the polymer precipitated out from the solvent. The resultant polymer was separated by filtration and dried under vacuum until at a constant weight.

#### ESR Measurement

ESR spectra were recorded on a JEOL JES-FEIXG ESR spectrometer at room temperature or at a liquid-nitrogen temperature. The central magnetic field was 3250 G. The value of the  $g$  factor was determined by using a  $\text{Mn}^{2+}$  standard substance.



**Figure 3** ESR spectra of  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  system: samples 12, 13, 14, and 15 were measured at room temperature; samples 16 and 17 were measured at liquid nitrogen temperature.

**Table III** ESR Parameters of  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  System

Sample No.	V/Al	$g^1$	$g^2$	$A^2$ (mT)	$g^3$	$A^3$ (mT)
5 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 0.5	1.981	1.988	7.16	—	—
6 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 7	—	1.99	7.06	—	—
7 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 15	—	1.984	7.17	1.982	4.14
8 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 30	—	1.986	7.08	1.981	4.16
9 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 60	—	1.983	7.07	1.984	4.20
10 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 86	—	1.985	7.02	1.983	4.18
11 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 427	—	1.983	7.05	1.985	4.16
12 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 3000 <sup>a</sup>	—	1.99	7.09	1.986	4.17
13 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 3000 <sup>b</sup>	—	1.988	7.09	1.984	4.18
14 ( $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$ )	1 : 3000 <sup>c</sup>	—	1.987	7.10	1.987	4.13

<sup>a</sup> Measured after 10 min.<sup>b</sup> Measured after 20 min.<sup>c</sup> Measured after 30 min.

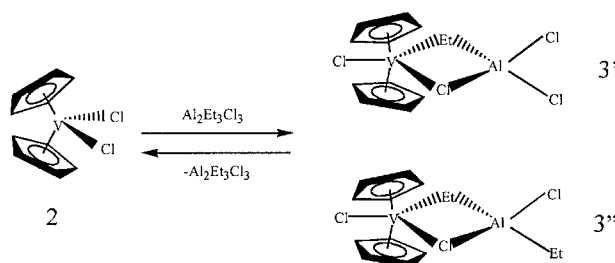
## RESULTS AND DISCUSSION

Typical results of ethylene polymerization catalyzed respectively by  $\text{Cp}_2\text{VCl}_2\text{-MAO}$ ,  $\text{Cp}_2\text{VCl}_2\text{-AlEt}_3$ , and  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  systems are summarized in Table I. A surprising result shown in Table I is that the  $\text{Cp}_2\text{VCl}_2\text{-MAO}$  system is almost inactive for ethylene polymerization. It is generally assumed that some of the Al centers in MAO have an exceptionally high propensity for abstracting a  $\text{CH}_3^-$  ion from the metallocene to sequester it in a weakly coordinating ion  $\text{CH}_3\text{-MAO}^-$ , which is an important coordinating ion for the formation of the polymerization center. The general formation mechanism  $\text{Cp}_2\text{MCl}_2 + \text{MAO} \rightarrow [\text{Cp}_2\text{M}(\text{CH}_3)]^+[\text{CH}_3\text{-MAO}]^-$  is considered. Moreover, it has been found that the  $\text{Cp}_2\text{VCl}_2\text{-AlEt}_3$  system is almost inactive and the  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  system has low activity. The results in Table I reveal that in addition to ionization function, the alkylation ability of a cocatalyst, for example  $\text{Cp}_2\text{MCl}_2 + \text{MAO} \rightarrow \text{Cp}_2\text{M}(\text{CH}_3)_2 + \text{MAO}$ , the reduction ability of the cocatalyst and the

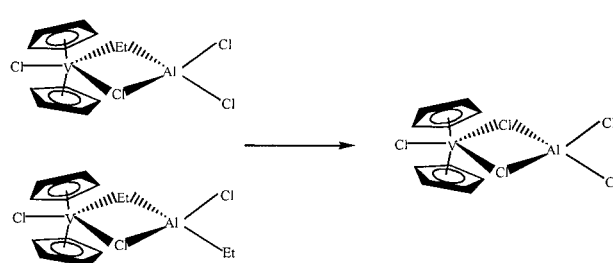
electronic structure of the transition metal also are important for ethylene polymerization.

The ESR signal usually is sensitive to the change of coordinating environment of paramagnetic species, especially the transition metal. Therefore, the ESR technique could be a logical research tool to aid in elucidating changes in the coordinating environment of paramagnetic species. It is known that more than 99% of the natural abundance of V is  $^{51}\text{V}$  and that its nuclear moment is 7/2. Thus, it is generally expected that the hyperfine structure of  $\text{V}^{+4}$  species may consist of 8 lines in its ESR spectrum.

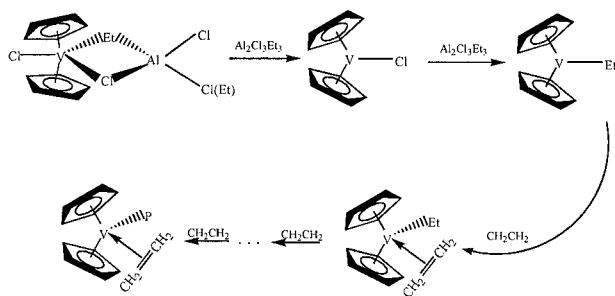
To distinguish the signals in the  $\text{Cp}_2\text{VCl}_2\text{-co-catalyst}$  systems, the ESR spectra of  $\text{Cp}_2\text{VCl}_2$  were recorded. The ESR spectra and ESR parameters of  $\text{Cp}_2\text{VCl}_2$  are summarized in Figure 1 and Table II, respectively. The ESR spectrum in Figure 1(1) shows a signal with a broad line width. Although there are various factors affecting the line width of the ESR spectrum, in this case the magnetic dipole-dipole interaction is reasonably assumed to be the major factor. Analysis of the



**Scheme 1** Plausible reaction between  $\text{Cp}_2\text{VCl}_2$  and  $\text{Al}_2\text{Et}_3\text{Cl}_3$ .



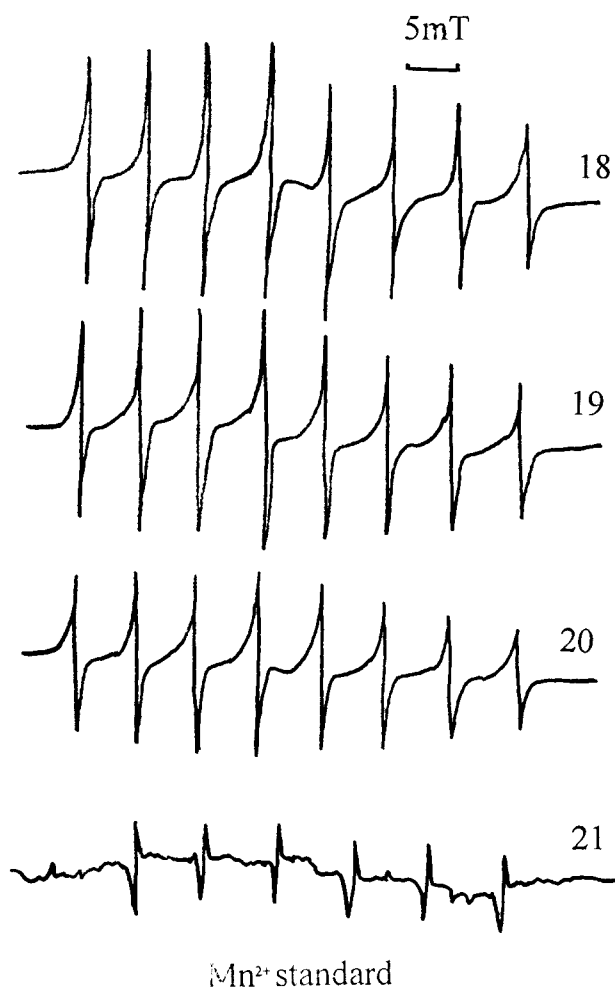
**Scheme 2** Transition from  $\text{ClCp}_2\text{VClEtAlClEt}(\text{Cl})$  to  $\text{ClCp}_2\text{VCl}_2\text{AlCl}_2$ .



**Scheme 3** Plausible mechanism of ethylene polymerization catalyzed by  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  system.

complicated spectrum was successfully accomplished by using the method developed by Hecht and Johnston.<sup>14</sup> The spectrum was analyzed using an axial symmetric spin Hamiltonian:<sup>15-17</sup>

$$H = \beta[g_{\parallel}H_zS_z + g_{\perp}H_xS_x + g_{\perp}H_yS_y] + A_{\parallel}S_zI_z + A_{\perp}S_xI_x + A_{\perp}S_yI_y$$



**Figure 4** ESR Spectra of  $\text{Cp}_2\text{VCl}_2/\text{AlEt}_3$  system (measured at room temperature).

**Table IV** ESR Parameters of  $\text{Cp}_2\text{VCl}_2\text{-AlEt}_3$  System

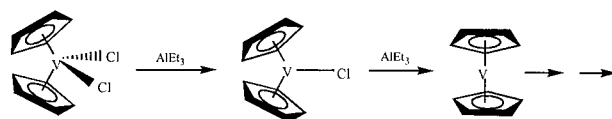
Entry	V/Al	$g^2$	$A^2$ (mT)
18 ( $\text{Cp}_2\text{VCl}_2/\text{AlEt}_3$ in toluene)	1 : 0.5	1.99	7.10
19 ( $\text{Cp}_2\text{VCl}_2/\text{AlEt}_3$ in toluene)	1 : 1	1.99	7.06
20 ( $\text{Cp}_2\text{VCl}_2/\text{AlEt}_3$ in toluene)	1 : 7	1.99	7.06
21 ( $\text{Cp}_2\text{VCl}_2/\text{AlEt}_3$ in toluene)	1 : 86	—	—

In a powder system ( $S = 1/2$ ), the intensity function is as follows:

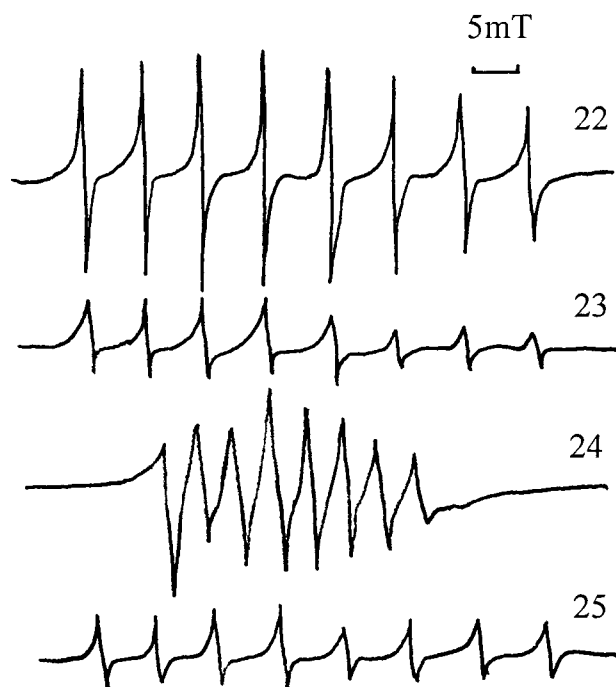
$$I(H) = \int_0^{2\pi} \int_0^{\pi} F(H, \theta, \phi) P(\theta, \phi) d\cos\theta d\phi$$

The simulation spectra can be obtained by treating the above equation on a computer.<sup>18</sup> The simulation spectrum is identical with that recorded in the experiment, which shows the above analysis is reasonable.<sup>6</sup> The dependence of  $\text{Cp}_2\text{VCl}_2$  solubility on solvent and concentration is demonstrated in Figure 1(1-4). Figure 1(2-3) indicates there are some small  $\text{Cp}_2\text{VCl}_2$  solid particles in the samples of entry 2 and entry 3. The result reveals the reason why  $\text{CH}_2\text{Cl}_2$  usually is used as a solvent when a catalytic system containing  $\text{Cp}_2\text{VCl}_2$  is used.<sup>19</sup>

The ESR spectra of the  $\text{Cp}_2\text{VCl}_2\text{-Al}_2\text{Et}_3\text{Cl}_3$  system are shown in Figures 2 and 3, and its ESR parameters are displayed in Table III. It was found that at a low Al:V ratio, such as in that in entry 5 (Table III), there are two paramagnetic species—with  $g^1 = 1.981$  and with  $g^2 = 1.988$  and  $A^2 \sim 7.1$  mT—which arise, respectively, from small  $\text{Cp}_2\text{VCl}_2$  solid particles and solvated  $\text{Cp}_2\text{VCl}_2$ . With increasing Al, going from V/Al = 1:15 to V/Al = 1:3000, a new signal, with  $g^3 \sim 1.983$  and  $A^3 \sim 4.16$  mT, appears. It is reasonable to assume the signal with  $g^3 \sim 1.983$  and  $A^3 \sim 41.6$  arises from species 3' and species 3'', shown in Scheme 1.<sup>13</sup> Because of their similar coordinating structures, it is impossible to distin-

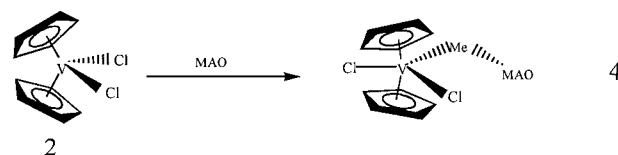


**Scheme 4** Plausible reaction between  $\text{Cp}_2\text{VCl}_2$  and  $\text{AlEt}_3$ .



**Figure 5** ESR spectra of  $\text{Cp}_2\text{VCl}_2$ -MAO system (measured at room temperature).

guish the ESR parameters of species 3' from species 3". However, these results indicate there is an equilibrium, as shown in Scheme 1. With reaction time increasing from 10 mins (entry 12) to 30 mins (entry 14) at  $\text{V/Al} = 3000$ , their ESR spectra are identical, showing that the coordination reaction in Scheme 1 is a fast and stable one. However, a transition (as shown at Scheme 2) from  $\text{ClCp}_2\text{VClEtAlClEt}(\text{Cl})$  to  $\text{ClCp}_2\text{VCl}_2\text{AlCl}_2$  can be observed after 2 weeks, and  $\text{ClCp}_2\text{VCl}_2\text{AlCl}_2$  is inactive for olefin polymerization.<sup>19</sup> After introducing ethylene, the ESR spectrum changes, as shown in Figure 3(15), which reveals a possible procedure for ethylene coordinating to vanadium. When the samples were frozen at liquid-nitrogen temperature, the spectra of samples in Figure 3(14) and Figure 3(15) changed to Figure 3(16)



**Scheme 5** Plausible reaction between  $\text{Cp}_2\text{VCl}_2$  and MAO system.

and Figure 3(17), respectively. The asymmetry of the resultant spectra demonstrates that the above analysis is possible.<sup>20</sup>

A plausible mechanism of ethylene polymerization catalyzed by  $\text{Cp}_2\text{VCl}_2$ - $\text{Al}_2\text{Et}_3\text{Cl}_3$  system is shown in Scheme 3. The mechanism indicates that the alkylation and the reduction ability of the cocatalyst also are important factors for the formation of a polymerization center.

The ESR spectra and parameters of the  $\text{Cp}_2\text{VCl}_2$ - $\text{AlEt}_3$  system are shown in Figure 4 and Table IV. As the  $\text{Al:V}$  ratio increases from  $\text{V/Al} = 1:0.5$  to  $\text{V/Al} = 1:86$ , species 2 with  $g^2 \sim 1.99$  and  $A^2 \sim 7.1\text{mT}$  quickly disappears, a development related to the strong reduction ability of  $\text{AlEt}_3$ . It is possible that  $\text{V(IV)}$  is reduced to an inactive species with a lower valence, as shown in Scheme 4.

The ESR spectra and parameters of the  $\text{Cp}_2\text{VCl}_2$ -MAO system are shown in Figure 5 and Table V. With an increasing  $\text{Al:V}$  ratio, from  $\text{V/Al} = 1:0.5$  to  $\text{V/Al} = 1:86$ , a new species with  $g^4 = 1.998$  and  $A^4 = 3.88\text{mT}$  was detected by the ESR spectrum. Comparing the ESR spectra of  $\text{Cp}_2\text{VCl}_2$ -MAO system with that of the  $\text{Cp}_2\text{VCl}_2$ - $\text{Al}_2\text{Et}_3\text{Cl}_3$  system, it is obvious that at  $\text{V/Al} = 1:86$ , the transition from species 2 to species 4 is complete, as shown in Scheme 5.

Possibly because of the weak reduction ability of MAO, it is more difficult to reduce  $\text{V(IV)}$  to  $\text{V(III)}$ . Therefore, the  $\text{Cp}_2\text{VCl}_2$ -MAO system is basically inactive for ethylene polymerization. In addition, it was found by a comparison of entry 22 to entry 25 that solvents do not affect the coordination environment of vanadium.

**Table V** ESR Parameters of  $\text{Cp}_2\text{VCl}_2$ -MAO System

Sample No.	V/Al	$g^2$	$A^2$ (mT)	$g^4$	$A^4$ (mT)
22 ( $\text{Cp}_2\text{VCl}_2$ -MAO in toluene)	1:0.5	1.99	7.01	—	—
23 ( $\text{Cp}_2\text{VCl}_2$ -MAO in toluene)	1:5	1.99	7.08	—	—
24 ( $\text{Cp}_2\text{VCl}_2$ -MAO in toluene)	1:86	—	—	1.998	3.88
25 ( $\text{Cp}_2\text{VCl}_2$ -MAO in $\text{CH}_2\text{Cl}_2$ )	1:0.5	1.99	7.05	—	—

However, the ESR results show that both the reaction between metallocene and the cocatalyst and the alkylation and reduction abilities of cocatalysts are influential in forming active species.

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