



An EPR study of the vanadium species formed upon interaction of vanadyl N and C-capped tris(phenolate) complexes with AlEt₃ and AlEt₂Cl

Igor E. Soshnikov^{a,b}, Nina V. Semikolenova^a, Konstantin P. Bryliakov^{a,b}, Vladimir A. Zakharov^a, Carl Redshaw^{c,**}, Evgenii P. Talsi^{a,b,*}

^a G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

^b Novosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russian Federation

^c School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich NR4 7TJ, United Kingdom

ARTICLE INFO

Article history:

Received 1 November 2008

Received in revised form 17 December 2008

Accepted 18 December 2008

Available online 30 December 2008

Keywords:

Olefin polymerization

Vanadium

Active species

EPR

ABSTRACT

Reactions of vanadyl N and C-capped tris(phenolate) complexes **1** and **2** (Scheme 1) with AlEt₃ and AlEt₂Cl, in the absence and in the presence of ethyltrichloroacetate (ETA), were monitored by EPR. It was shown, that vanadium(IV) complexes with proposed structures L^NV^{IV}(Et)(AlEt₃) and L^NV^{IV}(Et)(AlEt₂Cl) are formed at the initial stage of interaction of **1** with AlEt₃ and AlEt₂Cl, respectively (L^N are unidentified products of interaction of the initial N-capped ligand and V=O moiety with aluminum alkyls). In the absence of re-activator (ETA), L^NV^{IV}(Et)(AlEt₃) and L^NV^{IV}(Et)(AlEt₂Cl) rapidly convert at room temperature to V(III) species, which relatively slowly transform to complexes L^NV^{III}Et₂ and L^NV^{III}(Et)Cl. Concentration of L^NV^{IV}(Et)(AlEt₂Cl) dramatically increases in the presence of ETA, that correlates with the increase of the polymerization activity of the catalyst system **1**/AlEt₂Cl. The complex L^NV^{IV}(Et)(AlEt₂Cl) can be precursor of the active species of polymerization. Similarly, ETA increases concentration of vanadium(IV) complex L^CV^{IV}(Et)(AlEt₂Cl) in the catalyst system **2**/AlEt₂Cl (L^C are unidentified products of interaction of the initial C-capped ligand and V=O moiety with aluminum alkyls). The complex L^CV^{IV}(Et)(AlEt₂Cl) can be precursor of the active species of polymerization.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The vanadium(V) complexes of N and C-capped tripodal ligands (complexes **1** and **2**, Scheme 1) serve as active, thermally robust pro-catalysts for ethylene homo- and ethylene/propylene copolymerization. The best results were obtained using dimethylaluminum chloride (AlMe₂Cl) or diethylaluminum chloride (AlEt₂Cl) as activator, and ethyltrichloroacetate (ETA) as re-activator. The nature of the cocatalyst used is crucial. Methylaluminoxane (MAO) gives far inferior activities, and AlMe₃ or AlEt₃ were inert as activator [1]. The nature of the active species formed upon activation of complexes **1** and **2** with AlMe₂Cl or AlEt₂Cl is unclear. This is common problem of vanadium based polymerization. Despite the ongoing interest in synthesis of new vanadium polymerization catalysts [2–19], little is known about the reaction mechanism.

In this work we have undertaken the EPR spectroscopic study of the paramagnetic vanadium species formed in the systems

1(**2**)/AlEt₃, **1**(**2**)/AlEt₂Cl, **1**(**2**)/AlEt₃/ETA, **1**(**2**)/AlEt₂Cl/ETA. The main goal was to ascertain species which can be the active intermediates of polymerization or their precursors.

2. Results and discussion

2.1. Reaction of **1** with AlEt₃

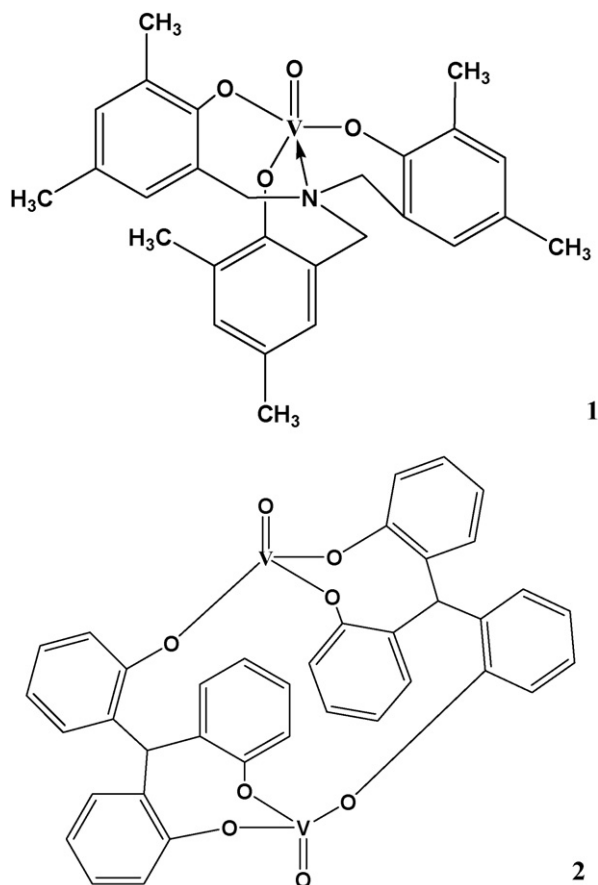
The vanadium(V) N-capped tris(phenolate) complex **1** is diamagnetic and displays sharp NMR peaks in d₈-toluene. These peaks immediately disappear after addition of AlEt₃ to the d₈-toluene solution of **1** at 20 °C ([AlEt₃]:[**1**] = 10:1, [**1**] = 10⁻² M). Thus, vanadium(V) complex **1** rapidly reduces to paramagnetic vanadium species at this temperature. The attempts to get some information on the structure of these paramagnetic species by ¹H NMR spectroscopy were unsuccessful because of the dramatic broadening of the corresponding resonances. The application of IR spectroscopy was also unfruitful due to the overlapping of the resonances of vanadium and aluminum compounds in the solution. The EPR spectroscopy gave the valuable information on the nature and stability of various vanadium species present in the systems studied.

The sample frozen immediately after the addition of AlEt₃ ([AlEt₃]:[**1**] = 10:1, [**1**] = 10⁻² M) to the solution of **1** in toluene at

* Corresponding author: Novosibirsk State University, Pirogova 2, 630090 Novosibirsk, Russian Federation. Fax: +7 383 3308056.

** Co-corresponding author: Tel.: +44 1603 593137.

E-mail addresses: Carl.Redshaw@uea.ac.uk (C. Redshaw), talsi@catalysis.ru (E.P. Talsi).



Scheme 1. Structures of **1** and **2**. In complex **2**, tert-butyl groups in positions 3, 5 of phenyl rings were omitted for clarity.

-30°C results in the appearance of the EPR signal of V(IV) complex **3_{Et}** (Fig. 1a). The EPR spectrum of **3_{Et}** is poorly resolved. Therefore, the only values of g_3 and A_3 can be precisely extracted from the EPR spectrum of **3_{Et}** (Table 1). Storing the sample of Fig. 1a during 10 min at -30°C , leads to the growth of the EPR spectrum of another vanadium(IV) complex **4_{Et}** at the expense of that of **3_{Et}** (Fig. 1b, Table 1). Concentration of complexes **3_{Et}** and **4_{Et}** does not exceed $(5 \pm 2)\%$ of the initial concentration of vanadium. The EPR signals of vanadium(IV) species rapidly disappear at 20°C (Fig. 1c).

Hence, upon the reaction of **1** with AlEt_3 at 20°C ($[\text{AlEt}_3]:[\mathbf{1}] = 10:1$), the rapid and quantitative reduction of V(V) to V(III) takes place. The reduction of V(III) to V(II) was not observed in the sample of Fig. 1. Complexes of V(II) display relatively sharp and highly characteristic EPR signals (see below).

To study the effect of $[\text{AlEt}_3]:[\mathbf{1}]$ ratio on the structure of vanadium species formed in the system **1**/ AlEt_3 , EPR spectra of the sample ($[\text{AlEt}_3]:[\mathbf{1}] = 100:1$, $[\mathbf{1}] = 10^{-2}\text{ M}$) were recorded (Fig. 2). As in the sample with the $[\text{AlEt}_3]:[\mathbf{1}]$ ratio of 10:1, complex **4_{Et}** was observed in the sample with $[\text{AlEt}_3]:[\mathbf{1}]$ ratio of 100:1, 10 min after mixing the reagents at -30°C (Fig. 2a). Concentration of **4_{Et}** does not exceed $(10 \pm 3)\%$ of the initial concentration of vanadium. **4_{Et}** rapidly disappears at 0°C due to the reduction of V(IV) into EPR

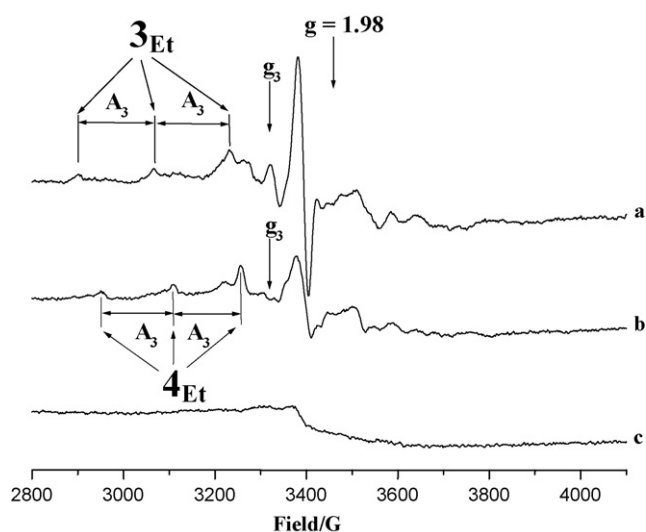


Fig. 1. EPR spectra (-196°C) of the sample **1**/ AlEt_3 in toluene ($[\text{AlEt}_3]:[\mathbf{1}] = 10:1$, $[\mathbf{1}] = 10^{-2}\text{ M}$) after various treatments: immediately after mixing of the reagents at -30°C (a); 10 min after storing sample in "a" at -30°C (b); 10 min after storing sample in "b" at 20°C (c).

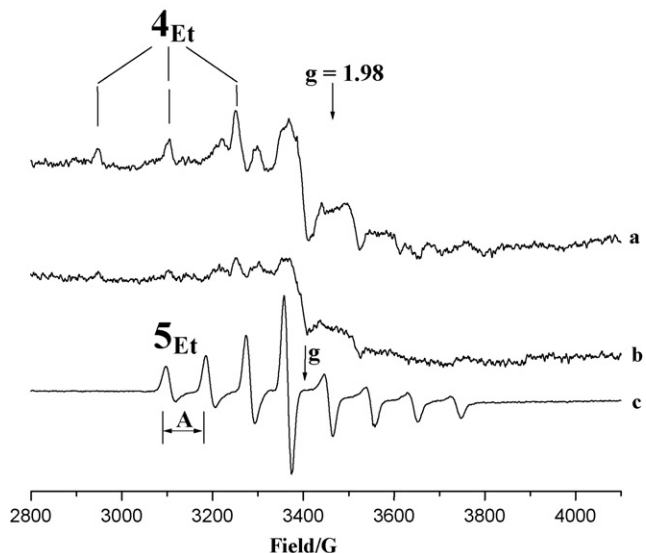


Fig. 2. EPR spectra (-196°C) of the sample **1**/ AlEt_3 in toluene ($[\text{AlEt}_3]:[\mathbf{1}] = 100:1$, $[\mathbf{1}] = 10^{-2}\text{ M}$) after various treatments: 10 min after mixing of the reagents at -30°C (a); 10 min after storing sample in "a" at 0°C (b); 3 h after storing sample in "b" at 20°C (c).

silent V(III) species (Fig. 2b). Further storing of the sample of Fig. 2b at 20°C results in the growth of the EPR signal of the stable V(II) complex **5_{Et}** (Fig. 2c, Table 1). The frozen-glass EPR spectrum of **5_{Et}** (Fig. 2c) resembles the EPR spectrum of the liquid solution, due to the low anisotropy of g and A tensors typical for V(II) species [20,21]. The liquid solution EPR spectrum of **5_{Et}** (Fig. 3) shows the additional 1:4:6:4:1 hyperfine splitting (ahfs) from four protons ($a_{\text{H}} = 3.3\text{ G}$) (Fig. 3, insert). This splitting is caused by CH_2 -protons of

Table 1
EPR spectroscopic data (g_3 and A_3) (-196°C) for vanadium(IV) species formed in the **1**(2)/ AlEt_3 and **1**(2)/ AlEt_2Cl systems in toluene.

	3_{Et}	3_{EtCl}	4_{Et}	4_{EtCl}	5_{Et}	7	8
$g_3 \pm 0.003$	1.949	~ 1.95	1.945	1.936	1.979 ^a	1.978 ^a	1.935
$A_3 \pm 2, \text{ G}$	164	~ 160	152	159	93 ^a	92 ^a	148

^a The almost isotropic EPR spectrum.

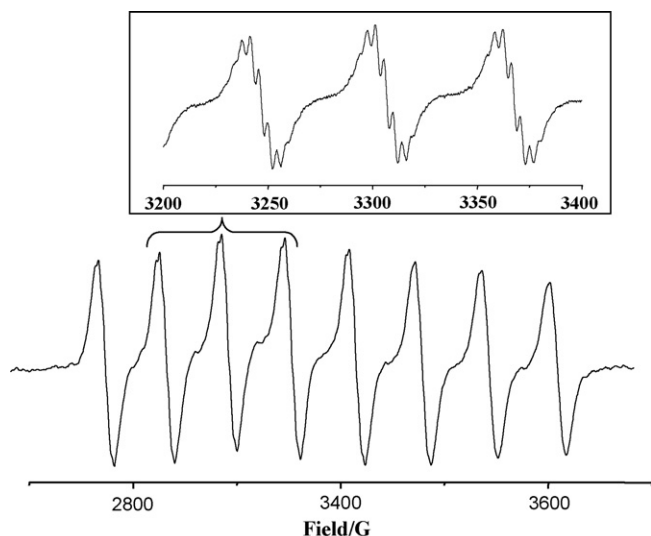


Fig. 3. EPR spectrum (20 °C) of complex 5_{Et} observed in the sample $1/AlEt_3$ in toluene 10 h after mixing the reagents at 20 °C ($[AlEt_3]:[1] = 100:1$, $[1] = 10^{-2}$ M). Insert shows additional hyperfine splitting 1:4:6:4:1 from four CH_2 -protons of two Et-groups.

two Et-groups. Therefore, 5_{Et} is V(II) complex of the type $L^N V^{II} Et_2$. We will use the symbol L^N for notation of all unidentified ligands of the vanadium species formed in the $1/AlEt_3$ and $1/AlEt_2Cl$ systems. These unidentified ligands can include the products of the interaction of the starting tris(phenolate) ligand and $V=O$ moiety with $AlEt_3$ or $AlEt_2Cl$.

The presented results show, that interaction of vanadium(V) complex **1** with the great excess of $AlEt_3$ ($[AlEt_3]:[1] = 100:1$) at 20 °C results in the very rapid reduction of V(V) to V(III), followed by relatively slow reduction of V(III) to V(II).

The EPR spectrum of the sample, containing re-activator (ETA) ($[AlEt_3]:[ETA]:[1] = 100:100:1$, $[1] = 10^{-2}$ M), recorded 10 min after mixing the reagents at -30 °C is the superposition of the EPR spectra of complexes 3_{Et} and 4_{Et} (Fig. 4a). This spectrum is at least by factor of 5 more intensive, than that in the absence of ETA (Fig. 2a) and can reach about 20% of the initial concentration of vanadium. Besides, high-field EPR resonances of 4_{Et} are better resolved, than in the spectrum of Fig. 2a. 3_{Et} and 4_{Et} disappear upon storing the sample at

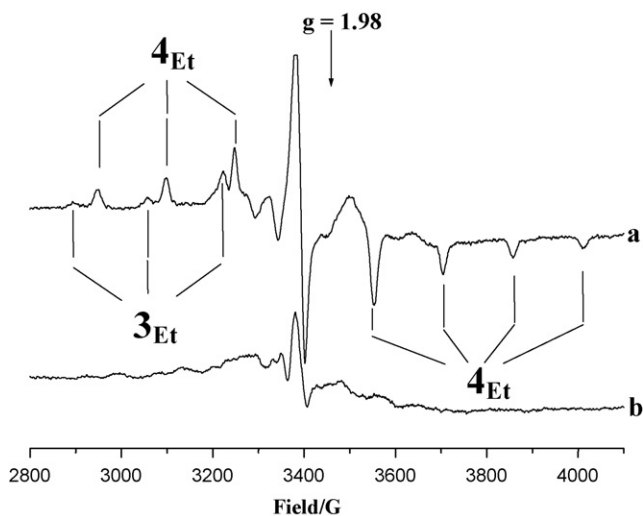


Fig. 4. EPR spectra (-196 °C) of the sample $1/AlEt_3/ETA$ in toluene ($[AlEt_3]:[ETA]:[1] = 100:100:1$, $[1] = 10^{-2}$ M) after various treatments: 10 min after mixing of the reagents at -30 °C (a); 10 h after storing sample in "a" at 20 °C (b).

20 °C, however formation of V(II) species was not observed (Fig. 4b). Hence, the maximum concentration of V(IV) species is much higher in the $1/AlEt_3/ETA$ system, than in the $1/AlEt_3$ counterpart. Besides, re-activator prevents the reduction of V(III) to V(II).

Our polymerization studies show that the system $1/AlEt_3/ETA$ is inert towards polymerization of ethylene, whereas the system $1/AlEt_2Cl/ETA$ is very active in this reaction (Table 2, runs 1–2). Therefore, it is interesting to compare vanadium species formed in these two systems.

2.2. Reaction of **1** with $AlEt_2Cl$

The sample frozen immediately after the addition of $AlEt_2Cl$ ($[AlEt_2Cl]:[1] = 10:1$, $[1] = 10^{-2}$ M) to the solution of **1** in toluene at -30 °C displays weak EPR spectrum of complex 3_{EtCl} (Fig. 5a). Storing this sample 10 min at -30 °C results in the conversion of 3_{EtCl} to 4_{EtCl} (Fig. 5b). EPR parameters of 3_{EtCl} coincide within the accuracy of our measurements with those for 3_{Et} , and EPR parameters of 4_{EtCl} are rather close to those for 4_{Et} (Table 1). Warming the sample of Fig. 5b to 20 °C results in the reduction of 4_{EtCl} into EPR silent V(III) species (Fig. 5c).

As in the case of $AlEt_3$, the increase of $[AlEt_2Cl]:[1]$ ratio up to 100:1 leads to further reduction of V(III) to V(II). The EPR spectrum of the sample ($[AlEt_2Cl]:[1] = 100:1$, $[1] = 10^{-2}$ M) recorded 20 min after mixing the reagents at -30 °C displays EPR spectrum of 4_{EtCl} (Fig. 6a). Warming the sample to 20 °C results in the immediate disappearance of V(IV) species (Fig. 6b). Storing this sample during 3 h at 20 °C gives the EPR signal, which is superposition of the EPR spectra of several complexes of V(II) (Fig. 6c). We will further denote these complexes as 5_{EtCl} . In contrast to 5_{Et} ($L^N V^{II} Et_2$), complexes 5_{EtCl} contain Cl-ligand (or ligands). Their structure can be schematically presented as $L^N V^{II}(Et)Cl$.

ETA dramatically increases (at least by factor of 5) the maximum concentration of V(IV) species in the reaction solution and prolongs their life. Fig. 7a shows EPR spectrum of the sample $1/AlEt_2Cl/ETA$ ($[AlEt_2Cl]:[ETA]:[1] = 100:100:1$), recorded 10 min after storing the sample at 20 °C. This spectrum is superposition of the EPR spectra of 4_{EtCl} and of the multiline spectrum of unknown vanadium(IV) species. Remind that in the absence of ETA, 4_{EtCl} immediately disappeared at 20 °C (Fig. 6b). Storing the sample of Fig. 7a during 10 h

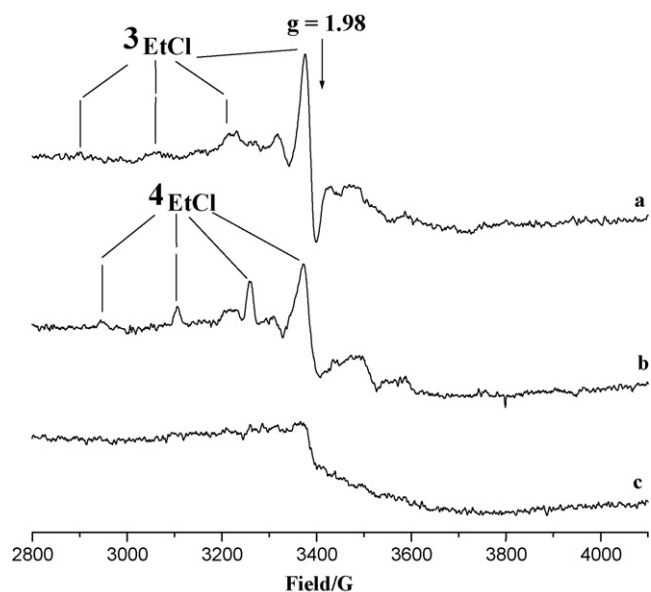


Fig. 5. EPR spectra (-196 °C) of the sample $1/AlEt_2Cl$ in toluene ($[AlEt_2Cl]:[1] = 10:1$, $[1] = 10^{-2}$ M) after various treatments: immediately after mixing of the reagents at -30 °C (a); 10 min after storing sample in "a" at -30 °C (b); 10 min after storing sample in "b" at 20 °C (c).

Table 2
Ethylene polymerization over vanadyl N and C-capped tris(phenolate) complexes^a.

Run	Pro-catalyst	[AlEt ₂ Cl]:[1(2)]	[ETA]:[1(2)]	T, °C	P(C ₂ H ₄), bar	PE yield, g	PE yield ^b	Activity ^c
1	N-capped (1)	5000	5000	80	5	12.6	1210	635
2	N-capped (1)	1000	1000	80	5	11.0	1100	425
3	N-capped (1)	1000	0	80	5	0.3	30	10
4 ^d	N-capped (1)	1000	1000	25	5	12.8	2560	200
5	C-capped (2)	5000	5000	80	2	11.7	1460	530
6	C-capped (2)	1000	1000	80	2	12.0	1500	640
7	C-capped (2)	1000	0	80	2	2.3	290	30
8 ^e	C-capped (2)	1000	1000	80	2	16.0	2000	590
9	C-capped (2)	1000	1000	25	2	20.2	2525	140

^a 150 ml toluene, 2 μmol of pro-catalyst, for 30 min.

^b ln kg PE mol V⁻¹ bar⁻¹.

^c ln kg PE mol V⁻¹ bar⁻¹ min⁻¹ (calculated according to the kinetic curve from the PE yield for 2 min).

^d 1 μmol of pro-catalyst.

^e AlMe₂Cl was used as activator.

at 20 °C leads to the decrease of the concentration of V(IV) species and very weak signals of V(II) complexes **5**_{EtCl} were observed (Fig. 7b).

We have found that the polymerization activity of the **1**/AlEt₂Cl/ETA system is c.a. 40 times higher than that of the **1**/AlEt₂Cl congener (Table 2, runs 2 and 3). The positive effect of ETA on the activity of the **1**/AlEt₂Cl systems is caused by the increase of the concentration of V(IV) alkylhalid species in the reaction solution. The alternative assumption, that V(III) species are active species of polymerization is improbable. According to our EPR data, in the presence of ETA, the formation of V(II) species is almost totally suppressed (Fig. 7b). Polymerization studies show, that high initial activity of the catalyst system **1**/AlEt₂Cl/ETA rapidly decreases even at 25 °C (Table 2, run 4). It is natural to attribute this deactivation to the reduction of V(IV) to V(III), than to the reduction of V(III) to V(II).

Thus, vanadium(IV) complex **4**_{EtCl}, observed in the catalyst system **1**/AlEt₂Cl can be precursor of the active species of polymerization. To be active, **4**_{EtCl} should contain V–Et bond. EPR parameters of **4**_{EtCl} only slightly differ from those of **4**_{Et}. Thus the structures of **4**_{Et} and **4**_{EtCl} are rather close. On the basis of these data, the proposed structures of **4**_{Et} and **4**_{EtCl} can be tentatively presented as L^NV^{IV}(Et)(AlEt₃) and L^NV^{IV}(Et)(AlEt₂Cl) (Scheme 2). The unknown ligands denoted as L^N, should include derivative of the

starting tris(phenolate) ligand, since the polymerization activity of the **1**/AlEt₂Cl/ETA system is sensitive to the nature of this ligand [1]. Unfortunately, we have not observed the additional hyperfine splitting from Et-ligand in the EPR spectra of **4**_{EtCl} and **4**_{Et} to confirm the incorporation of Et-ligand into their composition. The dramatic effect of chlorine atom on the polymerization activity (**4**_{EtCl} is active and **4**_{Et} is inert) can be caused by the weakening of V–Et bond under influence of the chlorine atom. Further studies are needed to verify this assumption.

Complexes **3**_{Et} and **3**_{EtCl}, detected at the early stages of interaction of **1** with AlEt₃ and AlEt₂Cl at low temperature can be assigned to the complexes L^NV^{IV}(AlEt₃) and L^NV^{IV}(AlEt₂Cl), respectively (Scheme 2). In these complexes the initial tripodal ligand or V=O moiety are modified by the interaction with aluminum alkyls. Besides, AlEt₃ and AlEt₂Cl molecules can be bound to the vanadium atom to form the corresponding adducts (Scheme 2). The unknown ligands denoted as L^N can be different in **3**_{Et}, **3**_{EtCl}, **4**_{Et} and **4**_{EtCl}.

To obtain additional support in favor of the key role of vanadium(IV) species in the polymerization of olefins by vanadium tris(phenolate) catalysts, we have studied systems based on C-capped complex **2** as a pro-catalyst.

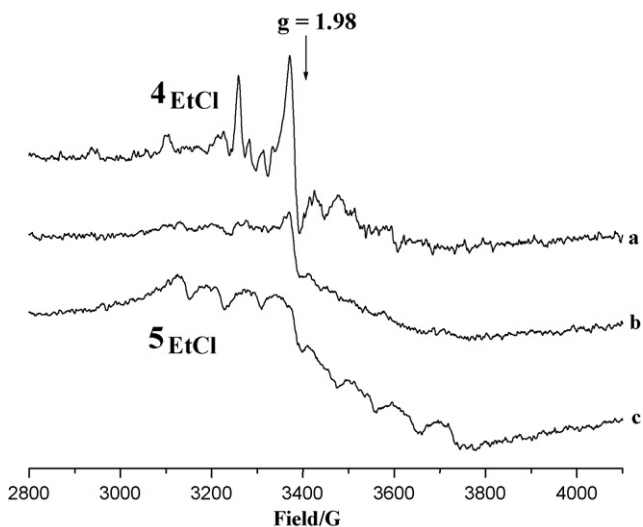


Fig. 6. EPR spectra (–196 °C) of the sample **1**/AlEt₂Cl in toluene ([AlEt₂Cl]:[**1**] = 100:1, [**1**] = 10⁻² M) after various treatments: 20 min after storing at –30 °C (a); 1 min after warming sample in “a” to 20 °C (b); 3 h after storing sample in “b” at 20 °C (c).

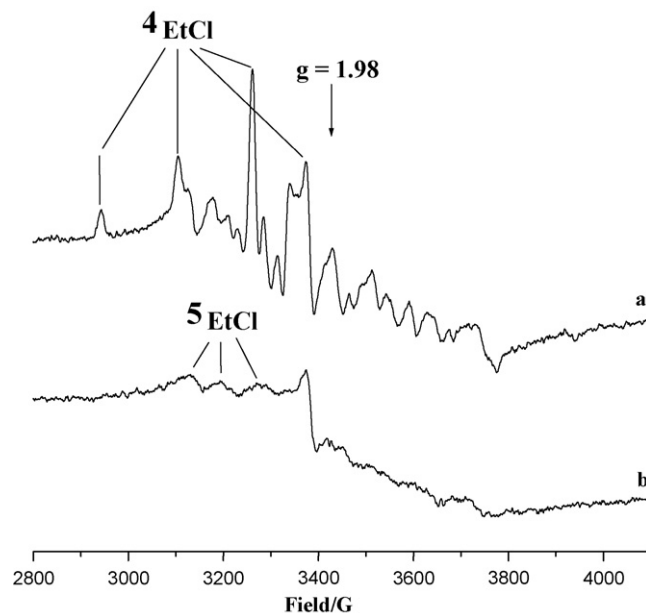
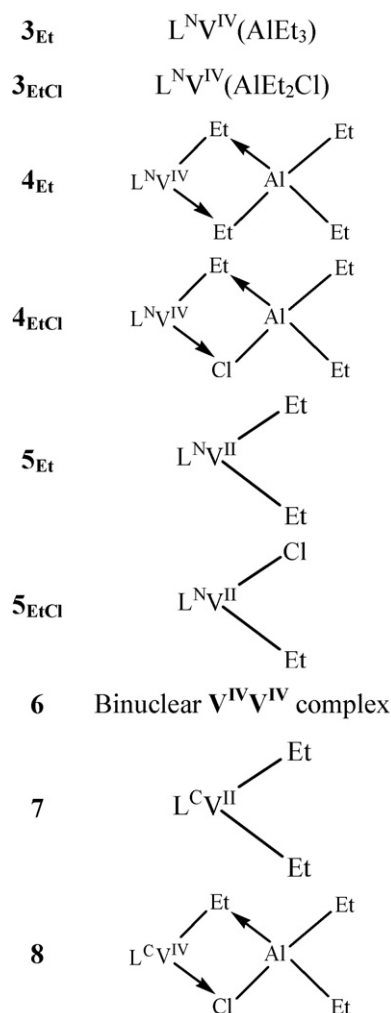


Fig. 7. EPR spectrum (–196 °C) of the sample **1**/AlEt₂Cl/ETA in toluene ([AlEt₂Cl]:[ETA]:[**1**] = 100:100:1, [**1**] = 10⁻² M) after various treatments: 10 min after mixing of the reagents at 20 °C (a); 10 h after storing sample in “a” at 20 °C (b).



Scheme 2. The proposed structures of the vanadium species formed in the systems **1**(**2**)/AlEt₃/ETA and **1**(**2**)/AlEt₂Cl/ETA.

2.3. Reaction of **2** with AlEt₃

The sample **2**/AlEt₃ ([AlEt₃]:[**2**] = 100:1, [**2**] = 10⁻² M) frozen 10 min after mixing the reagents at -30 °C shows EPR spectrum of new complex **6** (Fig. 8a). The multiline EPR spectrum of **6** is characteristic for V^{IV}V^{IV} binuclear species [22]. Apparently, the binuclear structure of **2** retains upon interaction with AlEt₃. Warming the sample of Fig. 8a to 20 °C results in the rapid disappearance of the EPR spectrum of **6**, due to the reduction of V(IV) to V(III) (Fig. 8b). Prolong storing of this sample at 20 °C leads to the growth of the signal of V(II) complex **7** (Fig. 8c). The *g* and *A* values of **7** are identical to those of **5**_{Et} (Table 1). The liquid solutions EPR spectrum of **7** displays the same hyperfine splitting from two Et-groups (*a*_H = 3.3 G), as complex **5**_{Et}. Thus, **7** is complex of the type L^CV^{II}Et₂. Symbol L^C will be used for notation of all unidentified ligands of vanadium species formed in the **2**/AlEt₃ and **2**/AlEt₂Cl systems.

In the presence of ETA ([AlEt₃]:[ETA]:[**2**] = 100:100:1, [**2**] = 10⁻² M), as in the case of the system **1**/AlEt₃/ETA, V(IV) species were observed in the reaction system even at 20 °C and formation of complexes of V(II) was suppressed.

2.4. Reaction of **2** with AlEt₂Cl

The EPR spectrum (-196 °C) of the sample **2**/AlEt₂Cl ([AlEt₂Cl]:[**2**] = 10:1, [**2**] = 10⁻² M) frozen 10 min after mixing the reagents at 0 °C belongs to the vanadium(IV) complex **8**. EPR parameters of **8** are

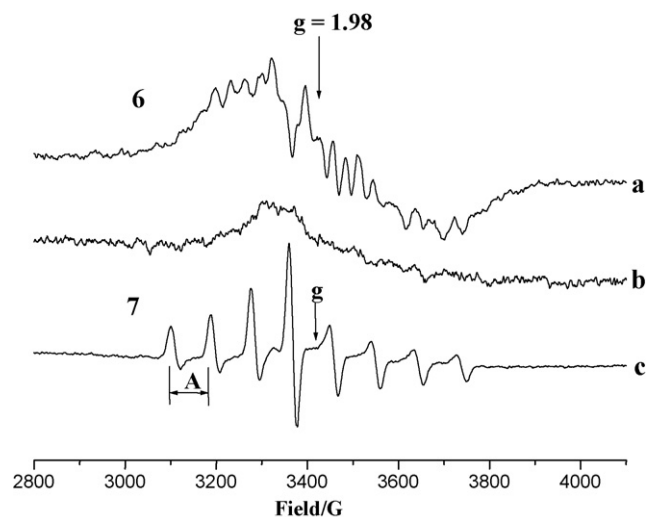


Fig. 8. EPR spectra (-196 °C) of the sample **2**/AlEt₃ in toluene ([AlEt₃]:[**2**] = 100:1, [**2**] = 10⁻² M) after various treatments: 10 min after mixing the reagents at -30 °C (a); 5 min after storing sample in "a" at 20 °C (b); 10 h after storing sample in "b" at 20 °C (c).

rather close to those of **4**_{EtCl} (Fig. 9, Table 1). By analogy with **4**_{EtCl}, the structure of **8** can be presented as L^CV^{IV}(Et)(AlEt₂Cl) (Scheme 2). Interestingly, the largest component of the EPR spectrum of **8** (the component of the perpendicular orientation) displays the 1:2:1 splitting (*a* = 10 G), which can be attributed to the ahfs from one Et-ligand in agreement with the proposed structure of **8**. Unfortunately, no splitting was observed on the components of the parallel orientation of the EPR spectrum of **8** (small signals in Fig. 9). Thus, the proposed assignment of ahfs in Fig. 9 is not such unambiguous as in the case of L^NV^{II}Et₂ or L^CV^{II}Et₂ species (Fig. 3).

EPR spectra of the sample **2**/AlEt₂Cl/ETA ([AlEt₂Cl]:[ETA]:[**2**] = 100:100:1, [**2**] = 10⁻² M) gradually warmed from -50 to 20 °C show, that concentration of **8** first decreases with the growth of temperature from -50 to -35 °C, then it starts to increase again at c.a. 0 °C and finally drops at 20 °C (Fig. 10). We have no precise explanation to this behavior. It can be connected with the decoupling of the starting binuclear complex into mononuclear units. However, it is important, that the unusual growth of the concentration of **8** upon warming the sample (Fig. 10) is paralleled by the unusual polymerization kinetics observed for the **2**/AlEt₂Cl/ETA system at

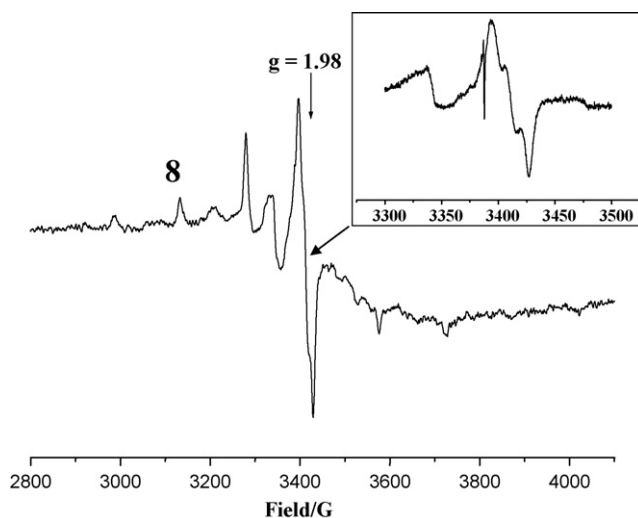


Fig. 9. EPR spectrum (-196 °C) of the sample **2**/AlEt₂Cl in toluene 10 min after mixing the reagents at 0 °C ([AlEt₂Cl]:[**2**] = 10:1, [**2**] = 10⁻² M).

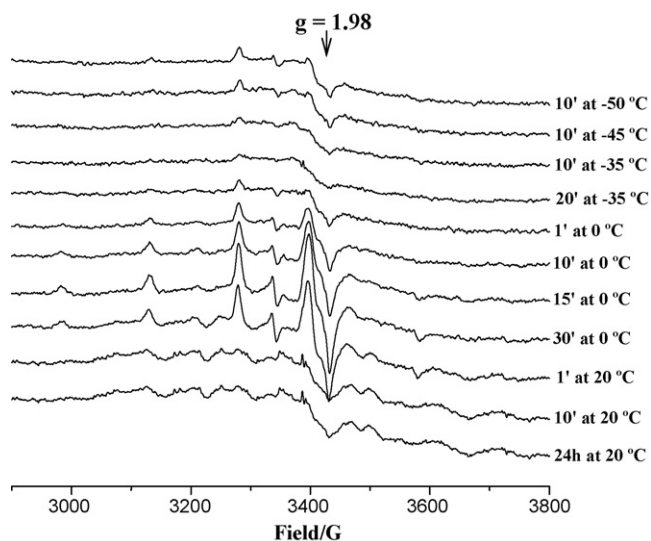


Fig. 10. EPR spectra (-196°C) of the sample **2**/AlEt₂Cl/ETA ([AlEt₂Cl]:[ETA]:[**2**] = 100:100:1, [**2**] = 10^{-2} M) recorded after successive warming.

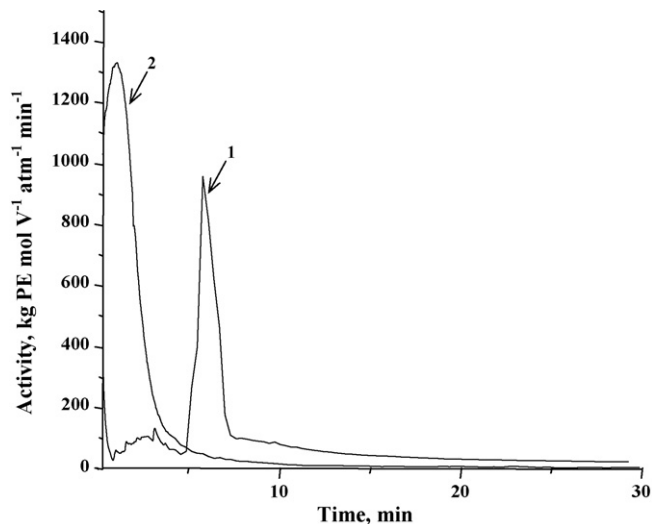


Fig. 11. Time dependence of ethylene polymerization activity over complex **2** activated with AlEt₂Cl ([AlEt₂Cl]:[ETA]:[**2**] = 1000:1000:1) at 25°C (curve 1) and 80°C (curve 2).

25°C (Fig. 11, curve 1, Table 2, run 9). At the beginning of the polymerization at 25°C , the system shows relatively low activity that sharply increases in 5 min of polymerization and then rapidly drops (Fig. 11, curve 1). The obtained data evidence in favor of the key role of the vanadium(IV) complex **8** in polymerization. At 80°C , the polymerization over **2**/AlEt₂Cl/ETA displays usual kinetic curve. It is characterized by high initial activity that rapidly falls and in 10 min of polymerization the catalyst became completely inactive (Fig. 11, curve 2).

3. Conclusions

EPR spectroscopic studies of the systems **1(2)**/AlEt₃, **1(2)**/AlEt₂Cl, **1(2)**/AlEt₃/ETA and **1(2)**/AlEt₂Cl/ETA show, that in all these systems vanadium is present in the reaction solution mainly in the form of complexes of V(III). Concentration of V(IV) species does not exceed 20% of the total concentration of vanadium. In the absence of ETA, V(IV) species very rapidly convert at room temperature into complexes of V(III). The latter

complexes relatively slowly transform at room temperature to V(II) complexes LV^{II}Et₂ or LV^{II}(Et)Cl, where L is unidentified ligand or ligands. In the presence of ETA, concentration of V(IV) species in the reaction solution dramatically increases. This correlates with the increase of the polymerization activity of the **1(2)**/AlEt₂Cl catalyst systems in the presence of ETA. Moreover, the rapid lost of polymerization activity of the **1(2)**/AlEt₂Cl systems correlates with the conversion of V(IV) to V(III), but not with the conversion of V(III) to V(II). Therefore, complexes of V(IV) seems to be active species of polymerization of the catalyst systems **1(2)**/AlEt₂Cl. These complexes can be tentatively presented as LV^{IV}(Et)(AlEt₂Cl).

4. Experimental

4.1. Materials

Toluene was dried over molecular sieves (4 Å), purified by refluxing over sodium metal and distilled under dry argon. Solids were transferred and stored in a glovebox. All experiments were carried out in sealed high vacuum systems using break-seal techniques. Complexes **1** and **2** were synthesized as described [1]. Commercial samples of triethylaluminum (AlEt₃), diethylaluminumchloride (AlEt₂Cl) and dimethylaluminumchloride (AlMe₂Cl) were used as 1 M solution in heptane/toluene mixture (1:1). Ethyltrichloroacetate was purchased from Aldrich.

4.2. Preparation of samples for EPR measurements

The weighed amount of complex **1(2)** (5×10^{-6} mol) was placed into the dried, argon filled EPR tube (length 200 mm, $d = 5$ mm), equipped with fine glass break-seals. The system with complex was evacuated to 2×10^{-2} Torr and sealed off from the vacuum line. 0.5 ml of heptane/toluene mixture with calculated quantities of AlEt₂Cl or AlEt₃ were transferred under vacuum into the EPR tube and immediately cooled to -196°C . For monitoring of the reaction of **1(2)** with AlEt₂Cl or AlEt₃, the EPR tube was sealed off from the system, warmed to -30°C by immersion in a thermostat (the Dewar with cooled ethanol and thermometer), the reagents were mixed by shaking the tube in the thermostat, and then the tube was stored for the appropriate interval of time at -30°C or other given temperature. To stop the reaction, the tube was immersed in liquid nitrogen and transferred to the quartz Dewar, and the EPR spectrum was recorded. All the EPR spectra if not specially noted were recorded at -196°C . The reaction can be continued by warming the tube again in the thermostat.

4.3. EPR measurements

EPR spectra were measured on a Bruker ER-200D spectrometer at 9.3 GHz, modulation frequency 100 kHz, modulation amplitude 4 G. Periclase crystal (MgO) with impurities of Mn²⁺ and Cr³⁺, which served as a side reference, was placed into the second compartment of the dual cavity. EPR spectra were quantified by double integration with 0.005 M VO(acac)₂ toluene solution as standard. The relative accuracy of the quantitative EPR measurements was $\pm 20\%$.

4.4. Ethylene polymerization

Ethylene polymerization was performed in a steel 0.3 l autoclave. Complex **1(2)** (2.0×10^{-6} mol) was introduced into the autoclave in an evacuated sealed glass ampoule. The autoclave was evacuated at 50°C , cooled down to 20°C and then charged with the freshly prepared solution of AlEt₂Cl and ETA in toluene (150 ml). After setting up the polymerization temperature and the ethylene pressure, the reaction was started by breaking of the ampoule of complex **1(2)**. During the polymerization (30 min), ethylene pressure,

temperature and stirring speed were maintained at constant levels. The experimental unit was equipped with an automatic computer-controlled system for the ethylene feed, maintaining the required pressure, recording the ethylene consumption and providing the kinetic curve output both in the form of a table and as a graph.

Acknowledgements

This work was supported by Russian Fund of Basic Research, grant 06-03-32700, K.P.B. and E.P.T. are grateful to the Royal Society (grant 2006/R4-IJP) for the financial support of this work.

References

- [1] C. Redshaw, M.A. Rowan, D.M. Homden, S.H. Dale, M.R.J. Elsegood, S. Matsui, S. Matsuura, *Chem. Commun.* (2006) 3329–3331.
- [2] H. Hagen, J. Boersma, G. van Koten, *Chem. Soc. Rev.* 31 (2002) 357–364.
- [3] S. Gambarotta, *Coord. Chem. Rev.* 237 (2003) 229–243.
- [4] Y. Nakayama, H. Bando, Y. Sonobe, Y. Suzuki, T. Fujita, *Chem. Lett.* 32 (2003) 766–767.
- [5] Y. Nakayama, H. Bando, Y. Sonobe, T. Fujita, *J. Mol. Catal. A: Chem.* 213 (2004) 141–150.
- [6] K. Nomura, A. Sagara, Y. Imanishi, *Macromolecules* 35 (2002) 1583–1590.
- [7] W. Wang, K. Nomura, *Macromolecules* 38 (2005) 5905–5913.
- [8] C. Redshaw, L. Warford, S.H. Dale, M.R.J. Elsegood, *Chem. Commun.* (2004) 1954–1955.
- [9] C. Redshaw, M.A. Rowan, L. Warford, D.M. Homden, A. Arbaoui, M.R.J. Elsegood, S.H. Dale, T. Yamato, C.P. Casas, S. Matsui, S. Matsuura, *Chem. Eur. J.* 13 (2007) 1090–1107.
- [10] V.V. Kotov, E.V. Avtomonov, J. Sundermeyer, E. Aitola, T. Repo, D.A. Lemenovskii, *J. Organomet. Chem.* 640 (2001) 21–28.
- [11] P. Mountford, H.R. Bigmore, M.A. Zuideveld, R.M. Kowalczyk, A.R. Cowley, M. Kranenburg, E.J.L. McInnes, *Inorg. Chem.* 45 (2006) 6411–6423.
- [12] J. Jaffart, C. Nayral, R. Choukroun, R. Mathien, M. Etienne, *Eur. J. Inorg. Chem.* (1998) 425–428.
- [13] K. Mashima, Y. Nakayama, N. Ikushima, M. Kaidzu, A.J. Nakamura, *J. Organomet. Chem.* 566 (1998) 111–116.
- [14] M.L.H. Green, C.T. Chen, L.H. Doerrer, V.C. Williams, *J. Chem. Soc. Dalton Trans.* (2000) 967–974.
- [15] V.C. Gibson, M.P. Coles, C.I. Dalby, I.R. Little, E.L. Marshall, M.H.R. da Costa, S. Mastroianni, *J. Organomet. Chem.* 591 (1999) 78–87.
- [16] A.C.A. Casagrande, P.S. dos Anjos, D. Gamba, O.L. Casagrande, J.H.Z. dos Santos, *J. Mol. Catal. A: Chem.* 255 (2006) 19–24.
- [17] R.B. Huang, N. Kukalyekar, C.E. Koning, J.C. Chadwick, *J. Mol. Catal. A: Chem.* 260 (2006) 135–143.
- [18] W. Wang, K. Nomura, *Adv. Synth. Catal.* 348 (2006) 743–750.
- [19] R.A. Henderson, D.L. Hughes, Z. Janas, R.L. Richards, P. Sobota, S. Szafert, *J. Organomet. Chem.* 554 (1998) 195–201.
- [20] J. Schneider, A. Räuber, *Phys. Lett.* 21 (1966) 380–381.
- [21] R.J. Morris, S.R. Wilson, G.S. Girolami, *J. Organomet. Chem.* 480 (1994) 1–9.
- [22] C.W. Hahn, P.G. Rasmussen, J.C. Bayón, *Inorg. Chem.* 31 (1992) 1963–1965.