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Vanadium-based Ziegler–Natta: challenges, promises, problems

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Contents

Abstract

The chemistry of vanadium is reviewed in the view of the ability of this metal to act as a catalyst for olefin homo- and copolymerization. The unique ability of some vanadium catalysts to perform random and super-random copolymerization makes these species particularly desirable for elastomer manufacture in spite of their rather chronic low activity. In order to assess the factors that affect the activity, we have synthesized a number of vanadium complexes of mono- and polydentate ligands based on different donor atoms and attempted the isolation of catalytically active intermediates. In this review, several ligand features have been examined and their ability to affect the metal oxidation state has been related to the stability of the vanadium–carbon bond and catalytic activity.

Keywords: Catalyst; Ziegler–Natta; Vanandium

1. Introduction

The original discovery, independently made in the 1950s by Ziegler and Natta, concerning the ability of a mixture of an early transition metal salt mixed with alkyl aluminum to perform olefin homo- and copolymerization [1] marked a milestone in the history of catalysis and revolutionized our modern lifestyle. After almost 50 years since their discovery, Ziegler–Natta olefin polymerization is still today a target of continuous research in both the academic and industrial sector. The current level of knowledge can be roughly summarized in terms of the formation of M–R functions that, in the presence of a Lewis acid (a large excess of Al cocatalyst is commonly employed), gain a substantial localization of positive charge on the metal center. The discovery made in the 1980s that ‘cationization’ of the metal center may enhance the ability of the M–C bond to perform olefin insertion [2] gave birth to what is today commonly known as ‘cationic Ziegler–Natta’. As usual the design of the ligand systems has played a particularly important role in the growth of this field enabling the development of a remarkable wealth of technology.

Before the recent discovery by Gibson, [3] Brookhart, [4] and Bennet [5] of the potent catalytic activity of electron-rich late metals which revolutionized our way of thinking in this field, the paradigm requiring highly acidic metals for a performing catalyst has traditionally dominated the scene of Ziegler–Natta catalysis. For this

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reason, with only some exceptions research has been traditionally focused on high-valent Group 3 and 4 metals and lanthanides [6]. Since the early stages of his studies, Natta established the ability of simple tri- and tetravalent vanadium salts to perform random and superandom olefin copolymerization [7]. In spite of the fact that the catalytic activity is a few orders of magnitude smaller than that displayed by Group IV based catalysts, the unique quality of the polymers produced by vanadium catalysts makes them irreplaceable for the manufacture of synthetic rubber and elastomers (EPDM) [8]. As a matter of fact, vanadium-based Ziegler–Natta technology is today very well established and widely used in the industrialized world.

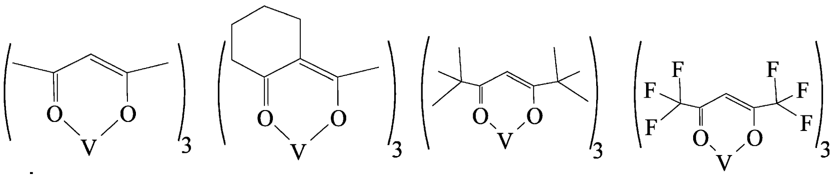
While considering trivalent vanadium from the coordination chemistry point of view, the ability of a d^2 trivalent vanadium complex to perform as a Ziegler–Natta catalyst indeed is puzzling. The coordination chemistry of these species is characterized by a carbene-like type of reactivity capable of performing one- or two-electron oxidative addition reactions and providing anchoring moieties for a variety of functions including dinitrogen and cumulenes [9]. By contrast, trivalent vanadium alkyls are relatively rare and aside from the π-bonded systems less than a handful of examples of stable trivalent trialkyl derivatives have been reported in the literature [9,10]. Obviously, the stability of the vanadium–carbon bond towards reductive elimination plays a critical role in the behavior of vanadium complexes as Ziegler–Natta catalysts. The paucity of vanadium alkyl species in the literature possibly speaks for an intrinsic instability of the V–C bond and has led workers in the field to ascribe the poor activity of vanadium catalysts to the tendency to perform reductive elimination towards inactive divalent species [11]. For this very reason the use of mild oxidizing agents capable of restoring the trivalent state is a must in vanadium catalyzed EPDM technology [8r].

In summary, medium-valent vanadium catalysts show irreplaceable features in terms of polymer quality, but also exhibits chronic deficiencies arising from the poor stability of the catalytically active species towards reductive elimination to divalent vanadium compounds. In the patent literature there are other catalytic systems based on different oxidation states of vanadium [8]. The most popular certainly are the pentavalent vanadyl halides and alkoxides [12]. While tetravalent vanadium catalysts are rare, information about trivalent complexes till recently was restricted to the commercially used $V(acac)_3$ [8r]. Nevertheless, it is reasonable to state that all the vanadium catalysts presently known display a common trend in terms of loss of activity. Given the strong oxidizing power of pentavalent vanadium it also seems reasonable to conclude that these different catalysts simply might provide different ways to feed the same catalytically active vanadium species to the system.

The starting point of our research in this field was a study on the catalytic activity of the commercially used $V(acac)_3$ system [13]. The aim was to understand the role of the oxidation state in sustaining the activity, and those factors, which control the catalyst stability. In other words, the search for a potent and competitive vanadium catalyst may start from the understanding of the factors governing the stability and reactivity of the V–C bond. For this purpose we synthesized a series of $V(R\text{-}acac)_3$ bearing rather diversified substituents. While the *Cy*-*acac* system was expected to substantially improve the solubility of the catalytically active species (always an issue in this particular catalytic system), the *t*-Bu-*acac* system was expected to increase the steric hindrance without substantially modifying the electronic factors. The *F*-*acac* ligand was deliberately selected to increase the Lewis acidity of the metal while keeping the steric hindrance comparable with the *t*-Bu ligand. The results of the polymerization experiments carried out with these catalysts were rather informative (Table 1). Basically, the modifications introduced in the ligand system do not have a significant impact on the activity, polymer quality or composition. This clearly indicates that in the catalytically active system the ligands have been completely abstracted from vanadium thus implying that the primary role of the Al catalyst is that of abstracting ligand molecules and providing in return alkyl functions and halide atoms. The trivalent vanadium alkyl can reasonably be expected to be both highly reactive toward olefins and very unstable towards reductive elimination. Accordingly, attempts to isolate and structurally characterize the catalyst or even the deactivated catalysts afforded only a form of 'VCl_2' thus conclusively demonstrating that formation of inactive V(II) derivative is indeed responsible for the sudden drop of catalytic activity. Furthermore, the isolation and characterization of $[Al(acac)_2]^+$ confirmed that the ligand system has migrated from vanadium to Al (Scheme 1).

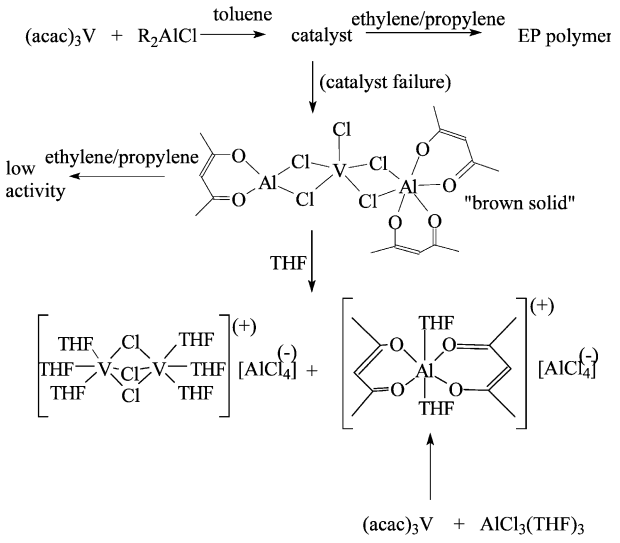
Having produced evidence that reduction to the divalent state, indeed, is responsible for the drop of catalytic activity of the trivalent complex, the next step was an attempt to understand the role of the so-called reactivating substances. As mentioned briefly above, the role of these mild oxidizing agents is thought to be that of restoring the trivalent state [8r]. Unfortunately, finding a suitable divalent vanadium complex that could model the deactivated species proved impossible due to the lack of precise information about the nature of the catalytically active species. Nevertheless, it was possible to synthesize and characterize the divalent $V(acac)_2$(TMEDA). Although the presence of TMEDA was not desirable, treatment with reactivating substances allowed us at least to gain some hint about the possible

Table 1



	V(*acac*)$_3$ (**1**)		V(*Cy-acac*)$_3$ (**2**)		V(*t*-Bu-*acac*)$_3$ (**3**)		V(*F-acac*)$_3$ (**4**)	
	DEAC	EASC	DEAC	EASC	DEAC	EASC	DEAC	EASC
Activity [a]	994	980	1168	990	746	622	762	800
$M_w \times 10^3$	219	702	218	716	290	1265	277	801
Mw/Mn	2.3	2.5	2.3	2.2	2.2	2.4	2.2	2.3
% ethylene	62	52	59	53	65	57	63	54

[a] kg of copolymer per mol catalyst h^{-1}.

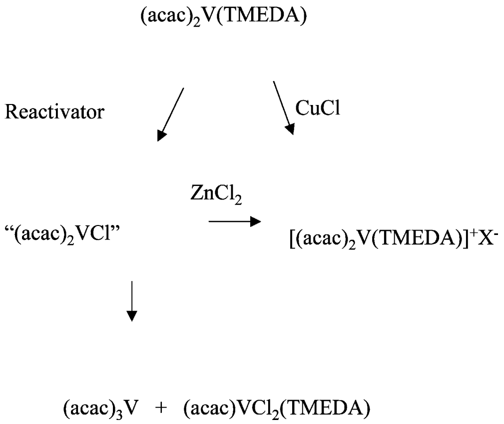


Scheme 1.

mechanism of action of these species. As outlined in Scheme 2, the reaction of V(*acac*)$_2$TMEDA afforded both trivalent V(*acac*)$_3$ and V(*acac*)Cl$_2$(TMEDA). While this second species displayed only marginal activity, the original catalyst (or catalyst precursor) was thus regenerated via a convoluted series of reactions.

During our search for clues about the nature of the catalytically active species we also kept in consideration that the inactive V(II) might in fact be generated not by a V–C reductive elimination process but instead by a disproportionation reaction. In agreement with this hypothesis the tetravalent V(*acac*)$_2$Cl$_2$ displayed higher activity than the corresponding V(*acac*)$_3$.

Having clarified the problems and challenges provided by these vanadium catalysts, we have embarked into a more systematic study aimed to understand: (1) the stability of the V–C bond; (2) the mobility of the ligand (transmetallation or ligand leaching) and (3) the role of the ligand donor atom in stabilizing the V–C bond.



Scheme 2.

We will now review the behavior of some vanadium complexes of different ligand systems based on O and N donor atoms.

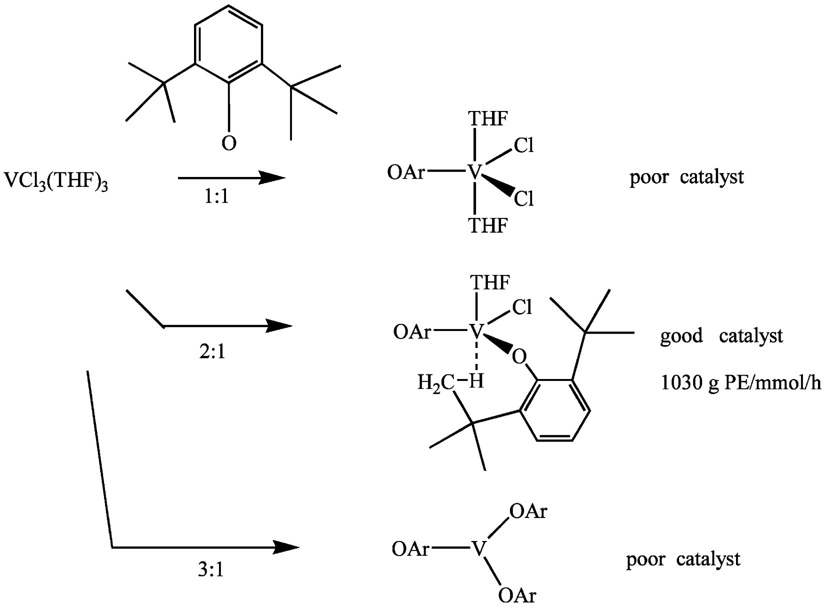
2. Oxygen-based ligands (aryloxides)

Vanadium aryloxides are an interesting variation of the *acac* ligand system. In the past, we have prepared and fully characterized the first homoleptic and trivalent vanadium aryloxides finding that the presence of weak Lewis bases such as THF may disrupt dinuclear aggregation generating monomeric species [14]. On the same line and with the help of the sterically demanding phenoxides [2,6-(*t*-Bu)$_2$PhO]$^-$ we have now prepared a series of mono, di- and tri-substituted trivalent vanadium species (Scheme 3). The three complexes can be easily synthesized by simply controlling the reaction stoichiometry. The structures of these species were as expected, with the exception of the 2:1 complex. This complex displays a trigonal bipyramidal arrangement, where one coordination site is occupied by the hydrogen atom of one the two *t*-Bu substituents, forming a fairly short agostic interaction. While the other vanadium aryloxides show only marginal activity as olefin polymerization catalyst, this particular complex displays a very respectable level of activity, producing unimodal polymer with rather high Mw and a fairly narrow distribution. The remarkable disparity of behavior between the three complexes indicated that unlike the *acac* ligand system, there is no complete ligand abstraction by the Al cocatalyst in this present case. In an attempt to understand how this system works, we have investigated the reactivity with several alkylating agents including AlR_3 derivatives. As outlined in Scheme 4 the reaction of $V(ArO)_2Cl(THF)$ with $AlMe_3$ afforded a mixture of two compounds. The vanadium residue is basically the tetravalent $V(ArO)_2Me_2$ while the Al moiety is $Al(ArO)Me_2(THF)$. Together, these two species well illustrate the ligand migration as occurring during the reaction. However, the increase in the vanadium oxidation state can only be explained assuming a disproportionation reaction, with a possible parallel formation of an unidentified 'V(ArO)Cl' species. Of the several Al alkyl derivatives used to scan the reactivity of $V(ArO)Cl_2(THF)$, Me_4AlLi provided a second piece of the puzzle. The species isolated and crystallized from the reaction mixture (Scheme 5) is a divalent and cationic form of 'VCl_2' with a $AlMe_3(OAr)$ counteranion. Particularly interesting was the result of the reaction of $V(ArO)_3$ with $AlEtCl_2$, which allowed the isolation of an attractive V_2Al_4 cluster (Scheme 6) featuring complete migration of the alkoxide ligands onto the Al moieties.

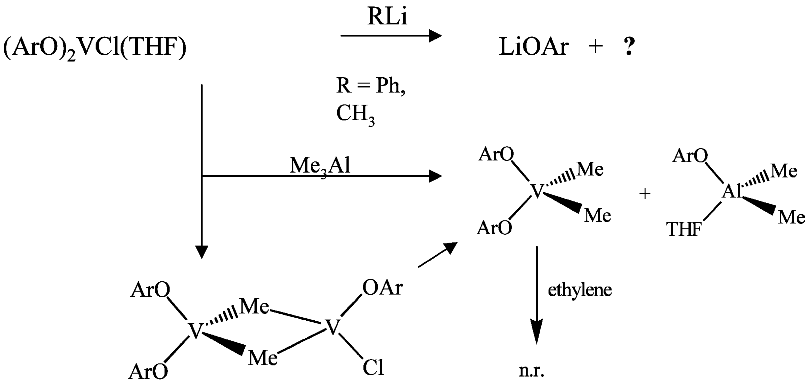
We can summarize the above results as follows. The vanadium atom again undergoes reduction, although this process is most likely to occur via a disproportionation mechanism rather than direct alkyl reductive elimination. As it was anticipated, the ligand system was leached out of the vanadium but apparently not to the extent observed in the chemistry of V(*acac*)$_3$. The catalytically active species is probably a large cluster where both V and Al share the ligand system, the alkyl and the halide.

The large steric hindrance of the aryloxide residue probably plays an important role in determining the type of aggregation and ultimately the stability of the C–C bond which, in turn, is directly linked to catalyst activity. For this purpose we have synthesized the $V(2,6\text{-}Me_2PhO)_2Cl(THF)_2$ derivative finding good activity in spite of the quenching by the two residual molecules of THF (Scheme 7). Removal of THF as in the homoleptic dimer $[V(ArO)_2]_2(\mu\text{-}OAr)_2$ enabled substantially higher activity in terms of ethylene polymerization, but minimal in terms of copolymerization (Scheme 8), thus indicating that propylene might deactivate these vanadium aryloxide catalysts.

In summary, oxygen based ligands such as aryloxides support a very high level of catalytic activity. However, ligand abstraction, tendency to disproportionate and to form inactive divalent species constitute the main obstacle for the development of a competitive vanadium catalyst.



Scheme 3.



Scheme 4.

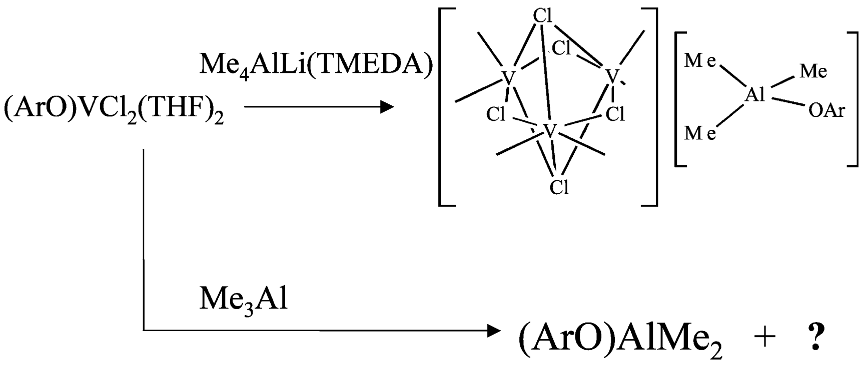
3. Nitrogen-based ligands

Anionic organic amides are the next class of ligands that will be examined. Among the several advantages offered by these ligands (ready accessibility, large variety of substituents, electronic flexibility, etc.) the increased stability of the ligand–vanadium bond and a decreased stability of the Al–N bond, with a consequent lower possibility of ligand leaching, was particularly attractive.

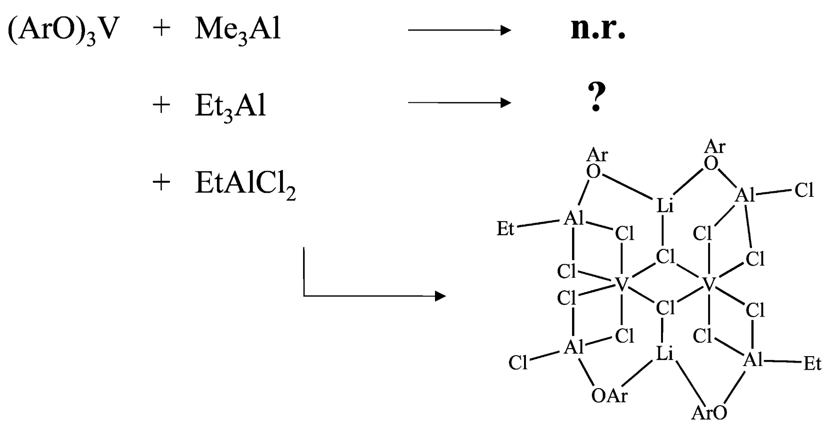
The simple reaction of $VCl_3(THF)_3$ with $LiNR_2$ takes considerably different pathways depending on reaction stoichiometry. The result of the reaction with a stoichiometric ratio of two amide per one vanadium is straightforward, affording the corresponding di-substituted divalent complex. In contrast, the reaction with the ratio 1:1 afforded a mixture of the tetravalent $V(R_2N)_2Cl_2$ and 'VCl_2' [15]. This once more reiterates the ability of vanadium complexes to move through several oxidation states via simple disproportionation reactions. Alkylation of both complexes afforded the corresponding stable alkyl derivatives that could be activated towards polymerization by treatment with $AlCl_3$. Particularly informative was the observation that the tetravalent species displays higher activity and produces copolymers of excellent quality (Scheme 9) [16]. Nevertheless, the catalyst was also rapidly deactivated, possibly suggesting that the formation of inactive divalent species is still occurring in spite of the stability of the $V(amide)_2R_2$ complexes. These observations indicated that: (a) the tetravalent state is probably the most promising in terms of catalytic activity, and (b) that disproportionation is always possible and responsible for the reduction of the vanadium center.

In order to decrease the possibility of disproportionation, we have used a tridentate diamide ligand. The preparation of $[V(SiN_3)]_2(\mu\text{-}Cl)_2]$ $[SiN_3 = (Me_3Si)N[CH_2CH_2N(SiMe_3)]_2]$ as a red–violet crystalline material was carried out according to the procedure described by Cloke [17] via room temperature reaction of $Li_2[SiN_3]$ with $VCl_3(THF)_3$ in THF (Scheme 10). When activated by 60 equivalents of $AlMe_2Cl$, $AlMe_3$ or PMAO-IP, the vanadium complex displayed substantial activity as an ethylene polymerization catalyst. The catalytic activity recorded for polymerization experiments carried out with $AlMe_2Cl$ at 50 °C and under 300 psig of ethylene was 660 kg of PE mol^{-1} per h. The polyethylene showed catalyst unimodality with average molecular weight of 721 000 and polydispersity of 2.3.

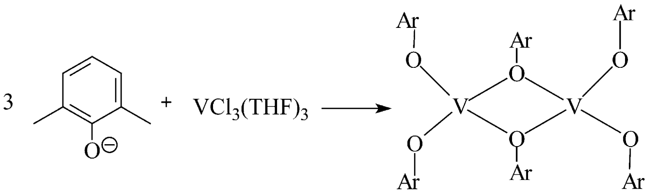
In common with other vanadium catalysts, this catalyst is short lived at either 35 or 140 °C, typically not remaining active for more than 20–30 min. Such deactivation is usually attributed to reduction of the vanadium center to the inactive divalent state. However, we have shown that amide ligands may stabilize tetra-



Scheme 5.



Scheme 6.



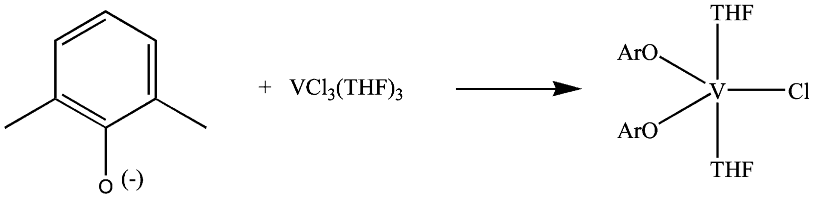
- 730 kg PE/mol/h
- minimal EP activity

Scheme 8.

valent vanadium alkyls [15,16] while, by using the silylamino(disilylamido) ligand, Cloke has isolated a mononuclear trimethylsilylmethyl derivative and successfully hydrogenolyzed it to produce the corresponding dinuclear and trivalent vanadium hydride [18]. In all these reactions there was no indication of reduction of the vanadium center suggesting that amide ligands indeed provide sufficient stabilization to the V–C function.

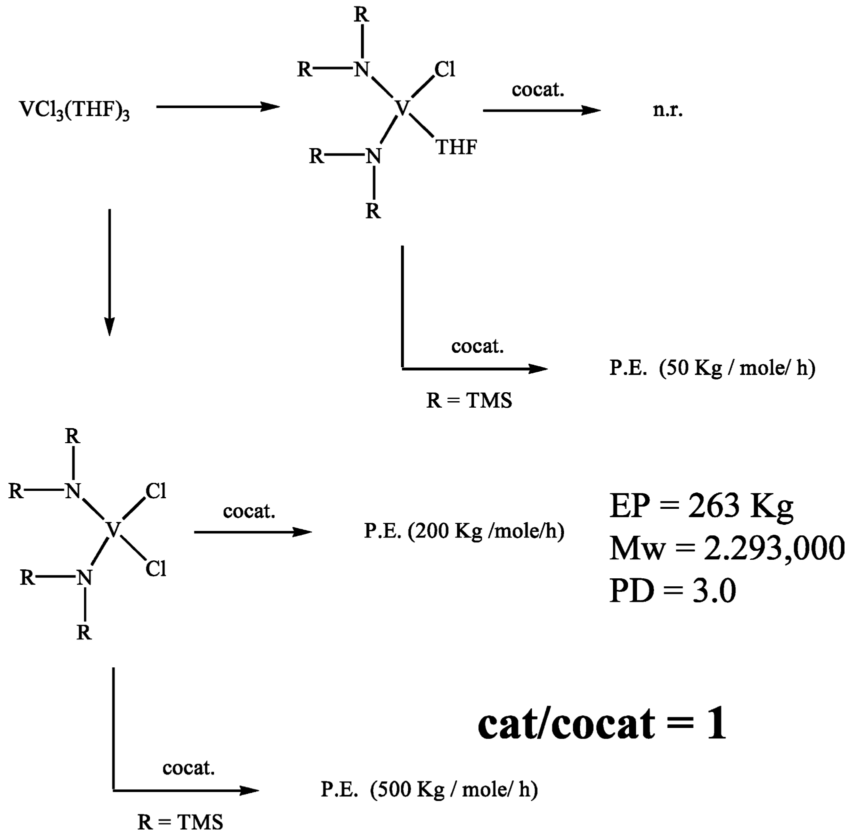
The ability of this versatile ligand system to support more standard vanadium-alkyls was verified by reacting the halide complex reported above with MeLi in hexane resulting in the formation of a methyl-bridged dimer $[V(SiN_3)]_2(\mu\text{-Me})_2$. Treatment of the reaction solution with $AlCl_3$ reformed the starting material $[V(SiN_3]_2(\mu\text{-Cl})_2$ in good yield indicating that rapid scrambling of alkyl groups occurs with Al but no ligand leaching. Simple addition of pyridine gave red crystals of $V[SiN_3]_2(Me)(Py)]$ in good yield. The versatility of the silylamino silyldiamide ligand to stabilize the vanadium carbon bond reiterates questions about the factors determining the catalyst failure. One possibility, although unlikely, is still that the ligand might be leached out of the metal center by the aluminum cocatalyst with a consequent decrease of the stability of the V–C bond. To rule out this possibility, we have studied the interaction of the starting halide mentioned above with the aluminum cocatalyst in the hope of trapping some vanadium–aluminum species.

The reaction with either PMAO-IP, $AlMe_3$ or $AlMe_2Cl$ in hexane initially gave a red solution which afforded, after a few days, emerald-green crystals of the tetrametallic $[V(SiN_3]_2(\mu\text{-Cl})_2$ (Scheme 11). As expected, the best yield was obtained with Me_3Al. The X-ray crystal structure clearly showed that the ligand remains triply bound to the vanadium center. The main frame of the complex is virtually the same as in the starting chloride with the two $V(SiN_3)$ moieties held together by two bridging chlorines. However, there are two major differences. Firstly, two Me_2Al residues are now co-

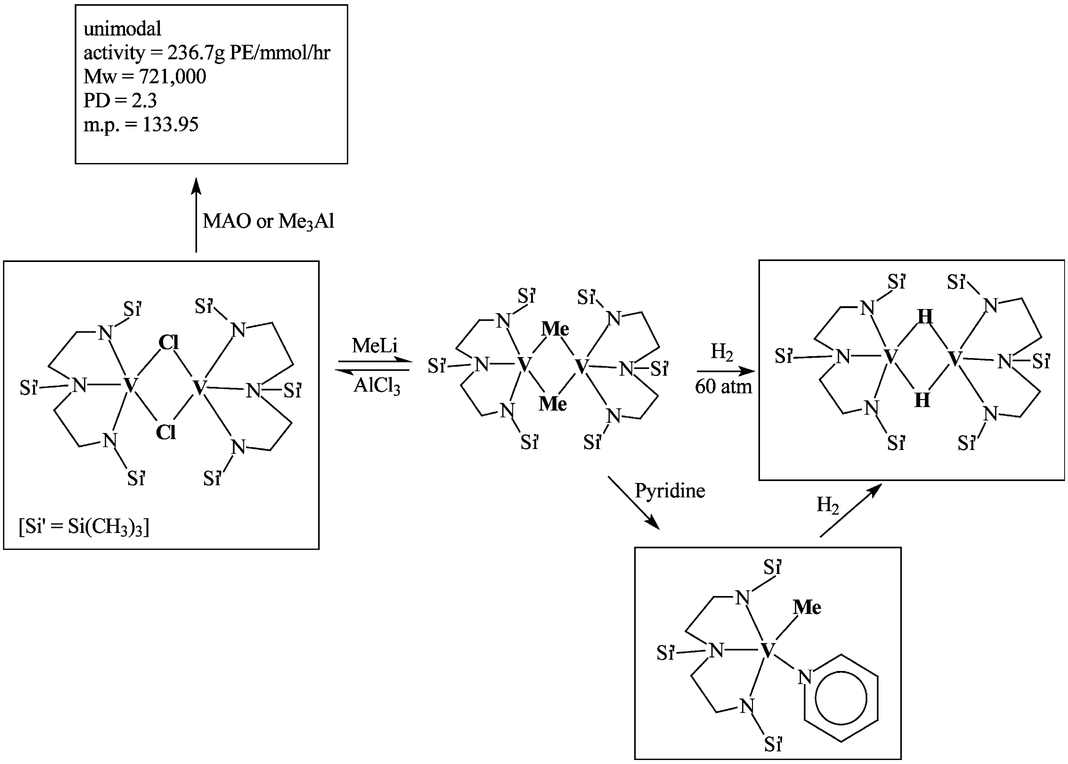


- good catalyst,
(~500 kg PE/mol/h
- deactivated by
propylene

Scheme 7.



Scheme 9.



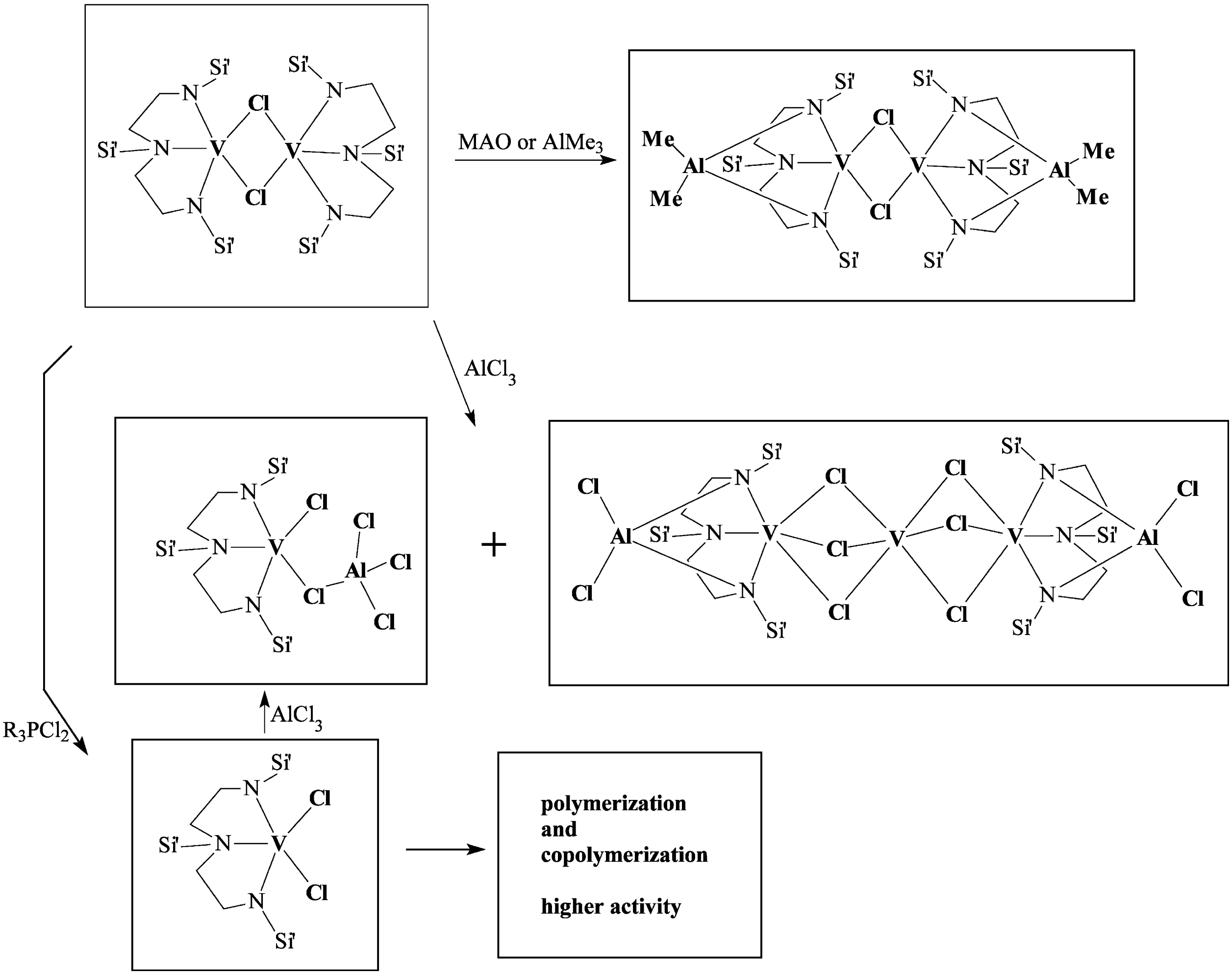
Scheme 10.

ordinated each to one ligand's amide nitrogen atoms. Secondly, the vanadium center has been reduced to the inactive divalent state thus accounting for the catalyst failure.

The isolation and characterization of this species indicates that no ligand leaching occurs in the present catalytic system but instead aggregation with the cocatalyst. Yet, the vanadium center was reduced to the inactive divalent state. Thus, questions arise about how the reduction occurred given that simple chorine replacement by Me groups afforded thermally stable trivalent methyl derivatives.

In Ziegler–Natta catalysis, PMAO or AlR_3 in general play a dual role as both alkylating agent and a Lewis acid. In order to separately analyze these two different aspects of the aluminum derivatives, we also reacted the starting chloride complex with $AlCl_3$, a pure Lewis acid, with no possibility of functioning as a reducing agent. The reaction afforded two different compounds (Scheme 11). The major component is the hetero-bimetallic and tetravalent $(SiN_3)V(Cl)(\mu\text{-}Cl)AlCl_3$ which is basically the result of the coordination of $AlCl_3$ to the tetravalent $(SiN_3)VCl_2$ via sharing of one of the two vanadium chlorine atoms. The second component of the reaction mixture is particularly intriguing. The complex is a mixed valence V(II)/V(III) hetero-bimetallic pentamer $[\{[(SiMe_3)(AlCl_2)NCH_2CH_2]_2(Me_3Si)NV\}(\mu\text{-}Cl)_3V(\mu\text{-}Cl)_3[(SiMe_3)(AlCl_2)NCH_2CH_2]_2(Me_3Si)NV\}]$ in which there are two vanadium atoms formally in the +3 oxidation state and one in the +2.

The simultaneous formation of these two species clearly indicates that $AlCl_3$ triggers a disproportionation reaction through which V(II) and V(IV) species are formed. The fact the central vanadium atom in one of the two complexes has been stripped of the ligand system clearly indicates that ligand leaching still occurred in spite of the tridenticity of the ligand and the higher affinity of vanadium for nitrogen donor atoms. However, the fact that two $AlCl_2$ residues are connected to the periphery of the trimetallic cluster in a fashion which is identical to the coordination of the $AlMe_2$ residues indicates that the ligand leaching is only partial and probably governed by equilibrium. Thus, the isolation of both tetra and divalent vanadium species

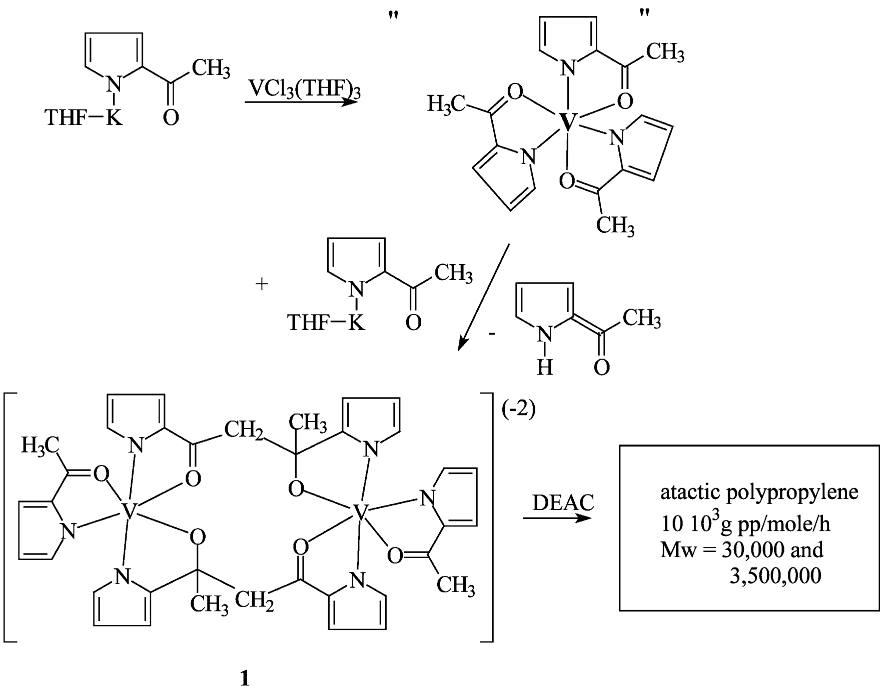


Scheme 11.

in the reaction with $AlCl_3$ clearly indicates that a disproprotionation is at the basis of the reduction of the vanadium center. However, the fact that a vanadium atom has retained its ligand system and yet has been reduced, strongly suggests that no ligand leaching occurred during the reaction of the starting complex with $AlMe_3$ as can be expected given its lower Lewis acidity. Thus, the only possibility to explain the reduction of the metal center in this case is to assume that the addition intermediate $(Me_2Al)(SiN_3)VClMe$, which is also likely to be the catalytically active species, has an intrinsic instability of the V–C bond. Thus, the search for a long-lasting vanadium catalyst remains determined by the understanding of the factors affecting the stability of the V–C bond.

4. N–O based ligands (acetylpyrrole)

Given the performance of the O- and N-based ligand systems, it might be desirable to combine the ability of both donor atoms within the same ligand system. The anion of acetylpyrrole has some attractive features. Particularly intriguing is the vague reminiscence with the single-site constrained-geometry Cp ligands in case the anion will adopt the π-bonding mode with the metal. The potassium salt K(AcPyrr)(THF) [AcPyrr = α-$(CH_3CO)C_4H_3N$] reacted with $VCl_3(THF)_3$ in THF at room temperature affording the $[VK(AcPyrr)(THF)]_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ complex (Scheme 12). The two bridging 1,3-di-(α-pyrrolyl)-3-hydroxy-butan-1-one trianionic ligands bridging the two vanadium centers arise from the aldol condensation of two acetylpyrrole units. Although this type of process typically requires the intervention of a base, we found no sign for this transformation during the initial deprotonation of acetylpyrrole by KH thus suggesting that vanadium acts as a templating agent by triggering the aldol condensation of two of the three acetylpyrrolide anions. This complex is a versatile catalyst for ethylene homo-, co- and terpolymerization. For this study the investigation was limited to propylene, norbornene and 1-hexene as comonomers. The activity of the catalyst activated by either DEAC or DMAC and calculated on the basis of the amount of isolated polymer places this complex amongst the most active vanadium catalysts reported so far. For example, the activity for the formation of ethylene–propylene copolymer is substantially higher than that reported for the commercially used V(*acac*)$_3$ [994 Kg EP mol^{-1} per 30 min]. In addition, the average molecular weight of the polymer was substantially higher while the polydispersity and composition remained comparable. As expected the polyethylene samples were unexciting displaying rather low molecular weight and broad polydispersity. The diagram of the ethylene uptake as a function of time recorded for an ethylene homopolymerization experiment clearly indicated that the catalyst was active only in the first 16–17 min after which activity was no longer present. By assuming that even in this case the deactivation was the result of the reduction of the vanadium center to the divalent state, attempts to extend catalyst life were done by carrying out polymerization experiments in the presence of ethyl trichloroacetate (ETA) as

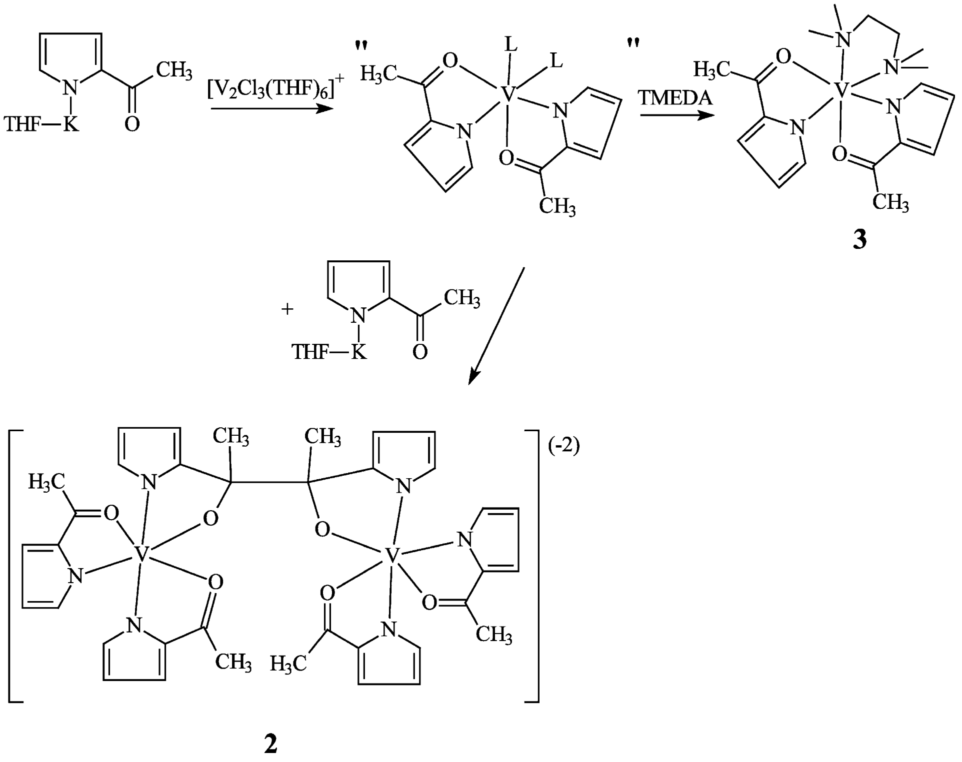


Scheme 12.

a reactivating substance. The role of this particular compound in the chemistry of V(*acac*)$_3$ is believed to be that of reoxidizing intermediate V(II) species to trivalent state capable of re-entering the catalytic cycle 8r. To our surprise, the activity was substantially decreased indeed indicating that a complete and irreversible catalyst deactivation occurred after only 8 min. Accordingly, the amount of polymer produced was also substantially lower. The detrimental effect of ETA suggests that (a) the divalent species resulting from the deactivation process is either not reoxidized by ETA or produces an inactive species upon oxidation and (b) the striking difference of behavior with the V(*acac*)$_3$ catalyst (where the employment of ETA is necessary to optimize catalyst performance) can only be ascribed to the presence of the acetylpyrrolide ligand which, therefore, is likely to remain connected to the vanadium center. Finally, the nature of the aluminum alkyl co-catalyst (DMAC vs. DEAC) has a rather strong influence on the activity which could be ascribed to the stability of the corresponding intermediate vanadium alkyl initiators (i.e. a V–Me function is likely to have a longer life-time than the corresponding V–Et).

In an attempt to verify that the rapid drop in catalytic activity once again may be ascribed to a reduction process, we have attempted the synthesis of novel divalent vanadium complexes of the acetylpyrrolide ligand system. The aim was two-fold: (a) to verify the inability of the divalent state to promote olefin polymerization under Ziegler–Natta conditions; (b) to understand the anomalous behavior with respect to the oxidation by ETA.

The reaction of $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ with K(AcPyrr)(THF) proceeded in two different manners depending on the reaction stoichiometry. Reactions carried out with an excess of ligand afforded the dinuclear trivalent vanadium complex $[(AcPyrr)_2\ VK(THF)]_2[(C_4H_3N)(CH_3)(O)C{-}C(O)(CH_3)(C_4H_3N)]$ (Scheme 13). The $[(C_4H_3N)(CH_3)\ (O)C{-}C(O)(CH_3)(C_4H_3N)]^{4-}$ tetra anion which bridges the two vanadium centers is the result of the pinacolic condensation of two acetylpyrrolide ligands. Given the strength of divalent vanadium as reductant, the reduction of one acetylpyrrolide ligand to the corresponding pinacol is not particularly surprising [19]. Thus, it is conceivable that a divalent species produced by the normal deactivation process may undergo an internal reoxidation reaction at the expenses of the acetylpyrrolide ligand reforming a trivalent complex ready to re-enter the catalytic cycle. As a fascinating possibility, the high catalytic activity of the first complex might be a direct consequence of this behavior. Accordingly, the second complex also is an active catalyst for ethylene homo- and copolymerization although slightly less active. However, the kinetic profile of the ethylene polymerization reaction showed that the catalyst is active only during the first 3 min after which the activity suddenly comes to an end. Furthermore, when the polymerization reaction was carried out in the



Scheme 13.

presence of ETA as a reactivating substance, the catalyst remained active for up to 45–46 min and the production of polyethylene was the highest ever observed for a vanadium catalyst (8.5 kg mol^{-1} per 20 min).

When the preparation of the second complex was carried out with a stoichiometric ratio ligand–V of 2:1 a blue solution was obtained possibly indicating that the vanadium atom was present in the divalent state. Unfortunately, attempts to grow crystals of suitable size only afforded microcrystalline material which analyzed as $V(AcPyrr)_2(THF)_2$. The complex was derivatized via treatment with TMEDA affording the mononuclear and divalent $V(AcPyrr)_2(TMEDA)$ (Scheme 13). The isolation of a divalent compound in significant yield clearly indicates that in the absence of excess acetylpyrrolide no reductive coupling to form a pinacol may occur and that Lewis bases such as THF or TMEDA are necessary to stabilize the divalent species.

To our surprise, complex $V(AcPyrr)_2(TMEDA)$ displayed in spite of the divalent state a non-negligible catalytic activity in terms of ethylene polymerization thus breaking the paradigm that divalent complexes should be inactive. However, the activity (0.550 kg mol^{-1} per 20 min) was indeed substantially lower than that of complexes $[(AcPyrr)VK(THF)]_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ and $(AcPyrr)_2VK(THF)\}_2$ $[(C_4H_3N)(CH_3)(O)C{-}C(O)(CH_3)(C_4H_3N)]$ whereas higher activity (1.5 kg mol^{-1} per 20 min) was obtained via previous treatment of $V(AcPyrr)_2(TMEDA)$ with ETA.

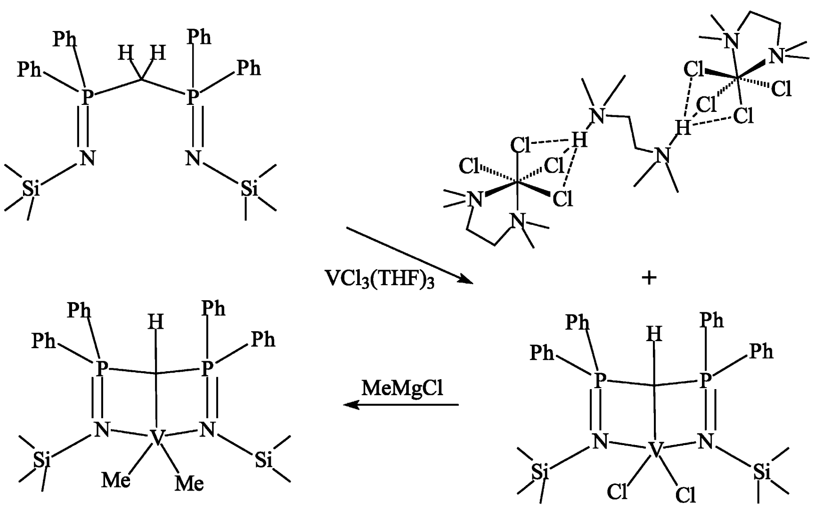
Unfortunately, repeated attempts to isolate intermediate complexes deriving from the direct interaction between the three complexes reported in this paper and a variety of alkyl aluminum derivatives and even $AlCl_3$ as a model only afforded non-crystalline materials. Therefore, we can only speculate about the identity of the intermediate species and the factors responsible for the high activity of $[(AcPyrr)VK(THF)\}_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ and $[(AcPyrr)_2VK(THF)]_2[(C_4H_3N)(CH_3)(O)C{-}C(O)(CH_3)(C_4H_3N)]$. At this stage we can only conclude that complexes $\{(AcPyrr)VK(THF)\}_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ and $[(C_4H_3N)(CH_3)(O)C{-}C(O)(CH_3)(C_4H_3N)][(AcPyrr)_2VK(THF)]_2$ are not part of the same catalytic cycle and that the unusually high catalytic activity displayed by $[(AcPyrr)_2VK(THF)]_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ and $[(C_4H_3N)(CH_3)(O){-}C{-}C(O)(CH_3)(C_4H_3N)][(AcPyrr)_2VK(THF)]_2$ is the result of ligand resistance to leaching with consequent improved stability of the V–C bond. It is also tempting to speculate that the dinuclear nature of these complexes may also play an important role in improving the activity of the catalyst. The reduction of $[(AcPyrr)_2VK(THF)]_2[(C_4H_3N)C(O)CH_2CO(CH_3)(C_4H_3N)]_2$ to the divalent state, which usually occurs during the olefin polymerization reaction promoted by vanadium, cannot be responsible in the present case for the observed complete deactivation. In fact, a simple pinacolic type of reaction will regenerate another active catalyst that, by being more robust and more resistant to oxidizing agents, may last even longer.

5. C–N ligands (the 'pincer' phosphinimido)

Organometallic vanadium species do not display particular stability unless in the presence of appropriate supporting ligands and for this reason an organometallic based ligand system might provide information about the stability of V–C bond and catalytic activity. One of the ligand systems selected for this work was the pincer-type bis-phosphinimide P_2N_2 anion $[P_2N_2 = (Me_3Si)N{=}P(Ph)_2CHP(Ph)_2{=}N(SiMe_3)]$ [20] because of its tridentate and tripodal-like bonding mode and the electronic flexibility provided by the delocalization of the negative charge between the deprotonated carbon and the two nitrogen atoms. Also desirable was the presence of the P=N function, which is well known to support both a very high level of catalytic activity [21] and to stabilize a large variety of metal complexes and oxidation states [22].

Reaction of $VCl_3(THF)_3$ with the diphosphinediimine ligand $[(Me_3Si)N{=}P(Ph)_2\,C(H)_2P(Ph)_2{=}N(SiMe_3)]$ in its neutral form and in the presence of TMEDA afforded the violet $V(P_2N_2)Cl_2$ and the red–purple $[(TMEDA)VCl_4]_2[H_2(TMEDA)]$ (Scheme 14). Metal complexes of the deprotonated phosphinoimine derivatives are organometallic species only from the formal point ofview, given that resonance structures with the negative charge localized on the nitrogen rather than on the carbon atom are likely to be the most important. On the other hand, the ammonium acidic protons are tightly coordinated in the second complex between TMEDA and two $VCl_3(TMEDA)$ units bridging the TMEDA nitrogen atom and one of the four chlorine atoms bound to the vanadium center. The strong hydrogen bonding may well be responsible for quenching the acidity of the ammonium cation.

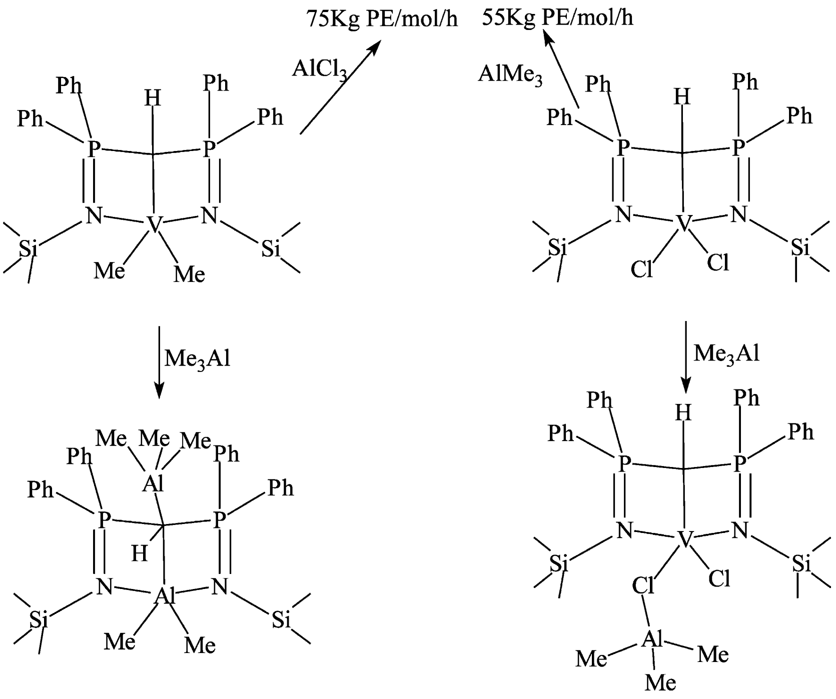
The first complex was converted into the corresponding isostructural dimethyl derivative $V(P_2N_2)Me_2$ via simple treatment with MeLi (Scheme 15) followed by crystallization from ether. Both the dichloro and dimethyl derivative display minimal catalytic activity in terms of ethylene polymerization and no activity in terms of EP copolymerization. The dimethyl derivative displayed slightly higher activity upon activation with $AlCl_3$, a pure Lewis acid. Unexpectedly, the treatment of the dialkyl with Me_3Al afforded complete ligand demetallation with formation of an unusual zwitterionic type of structure where two Al atoms are connected to the ligand. This strange result possibly explains the failure of these vanadium complexes as catalysts. Therefore, in



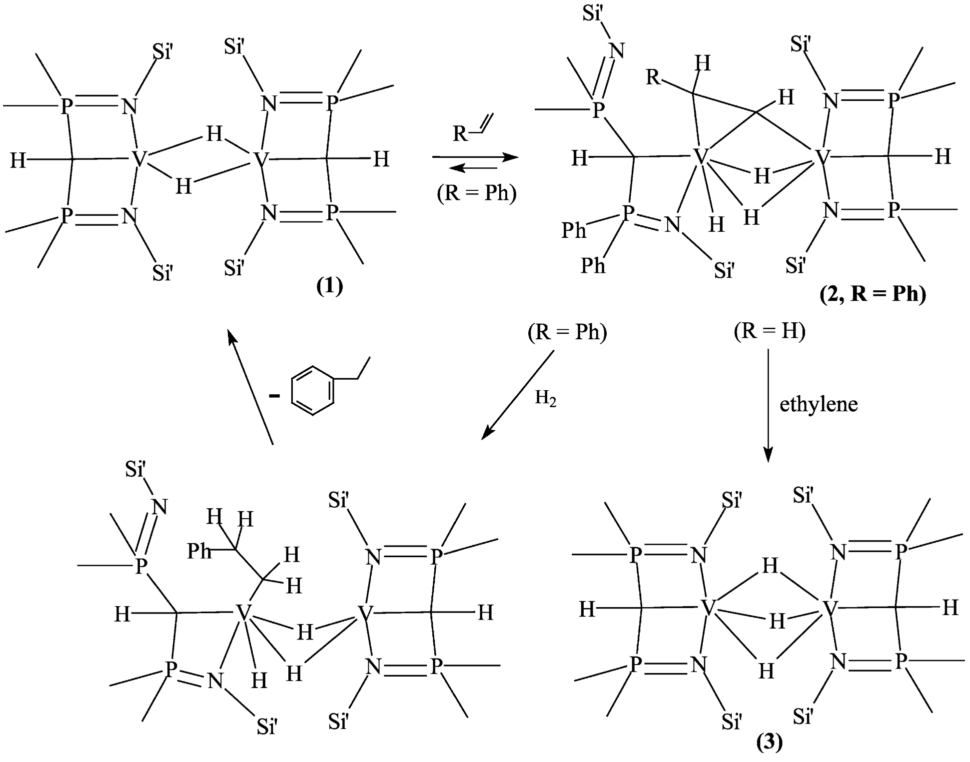
Scheme 14.

order to understand the interaction of reactive organometallic species with olefins we have taken a slightly different approach.

Hydrogenolysis of the dialkyl species under pressure and at room temperature afforded a divalent hydride bridged complex $[V(P_2N_2)]_2(\mu\text{-}H)_2$ (Scheme 16) [23]. Treatment of this species with styrene results in a rapid color change to brown–green from which dark-brown crystals of a new paramagnetic compound complex $[(P_2N_2)V]_2(H)(\mu\text{-}H)_2$ (μ, η^1:η^2-CHCHPh) were isolated. The complex consists of two vanadium atoms each differently bonded to a phosphinimide P_2N_2 anion. The first vanadium is surrounded by the ligand, which uses the central bridgehead carbon and the two nitrogen as donors. The second vanadium uses instead the carbon atom for bonding and only one of the two nitrogen atoms. The second nitrogen atom remains uncoordinated and points away from the vanadium atom. This particular vanadium atom is also side-on coordinated to a bridging styryl unit forming two comparable V–C distances. The hexa-coordination of the vanadium π-bonded to the styryl moiety is severely flattened and strongly suggests that another hydride, probably terminally bonded, might be present in what otherwise



Scheme 15.



Scheme 16.

appears to be an empty coordination site. Also the strange partial dissociation of one of the two nitrogen atoms of the pincer ligand substantiates this proposal. The IR spectrum showed one medium intensity resonance at 1786 cm^{-1}, which is likely to the attributed to the terminally bonded hydride.

The long C–C bond distance of the styryl moiety indicates that a substantial reduction of the C–C double bond has occurred. Since $[(P_2N_2)V\}_2(\mu\text{-}H)_2$ was readily formed by reductive hydrogenolysis of a trivalent alkyl under pressure and at room temperature, it is conceivable to expect that the styryl derivative could also undergo hydrogenolysis forming ethylbenzene and a vanadium hydride ready for another cycle of hydrogenation. Accordingly, the catalytic hydrogenation of styrene (Figure 20) proceeds slowly at room temperature and atmospheric pressure but considerably faster under H_2 pressure. In a standard experiment under H_2 pressure (60 atm), a solution of $[(P_2N_2)V]_2(\mu\text{-}H)_2$ (10 mg) in toluene (100 ml) completed the conversion of 1 g of styrene to ethylbenzene in 15 h corresponding to about 10 turnovers per min. Although, the overall catalytic activity is rather modest comparing with the well-established late-metal hydrogenation catalysts, nevertheless, this is the first time that catalytic styrene hydrogenation is observed for vanadium.

The divalent dihydride $[(P_2N_2)V]_2(\mu\text{-}H)_2$ also reacts with ethylene under atmospheric pressure and at room temperature to form the dinuclear and mixed valence V(II)/V(III) Tris–hydride derivative $[(P_2N_2)V]_2(\mu\text{-}H)_3$. Other than for the presence of the three bridging hydrides, this complex does not display any particular feature. The GC-MS of the reaction mother liquor clearly showed the presence of larger than stoichiometric amounts of 2-butene and a smaller amount of 3-methyl-1,4-pentadiene. No other products were detected in the chromatogram. The presence of these two products indicates that $[(P_2N_2)V]_2(\mu\text{-}H)_2$ promotes ethylene di- and trimerization. However, while the dimerization of ethylene to 2-butene does not require acquisition or loss of hydrogen atoms and, therefore, can be achieved in a catalytic fashion, the formation of the diene does require the formal elimination of one molecule of hydrogen. At this stage, we are unsure whether 2-butene is formed as such or if it stems from isomerization of initially formed 1-butene. Since no H_2 gas was detected in the reaction mixture, the formation of the mixed-valence tris-hydride is most likely resulting from the formation of the pentadiene. Given that the hydride is unreactive towards olefins, its formation may well poison the catalytic formation of 2-butene.

6. Conclusions

In conclusion, with this presentation we offered a series of results about the behavior of vanadium complexes as Ziegler–Natta catalysts. Vanadium complexes have a promising potential as catalysts and for some applications in particular. The main problem and challenge provided by these catalysts lie in the ability of vanadium to move around several oxidation states via disproportionation reactions. Among the several redox states available to vanadium the tetravalent one seems to be the most promising in terms of catalyst performance and for providing the appropriate stability to the V–C bond. The characteristic of the vanadium center to undergo rather easily transmetallation reactions with the aluminum cocatalyst (leaching) is probably at the basis of the deactivation systematically observed with the vanadium catalysts. The search for new long-lasting catalytic system based on vanadium and capable of maintaining the most desirable characteristics should, therefore, be oriented towards design of new ligand systems.

Acknowledgements

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