Vanadium(III) and -(IV) Complexes with *O,N*-Chelating Aminophenolate Ligands: Synthesis, Characterization and Activity in Ethene/Propene Copolymerization

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Monoanionic, potentially bi- or terdentate aminophenolates, ([OC$_6$H$_3$(CH$_2$NMe$_2$)-2-R-4)]$^-$, R = H (**a**), Me (**b**), *t*Bu (**c**), Cl (**d**), N=NPh (**e**), MeO (**f**) and [OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$^-$ (**g**)), have been used in the synthesis of well-defined vanadium-based catalysts for the polymerization of α-olefins. The reaction of [Cp$_2$V] with the parent phenol of **g** resulted in oxidation of the vanadium(II) nucleus to obtain the vanadium(III) (tris)phenolate [V(OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)$_3$] (**1**). Vanadium(III) aminophenolates could not be obtained by reaction of [VCl$_3$(THF)$_3$] with the sodium phenolates because of incorporation of NaCl. However, use of the corresponding silyl ether Me$_3$SiOC$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-4 (**2**) resulted in the formation of the chlorovanadium (bis)phenolate [VCl(OC$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-4)$_2$] (**3**). Attempts to oxidize **3** to the corresponding dichlorovanadium(IV) (bis)phenolate were not successful. No reaction was observed with CuCl,

AgCl and PbCl$_2$. A dark blue compound **4** was obtained with CuCl$_2$, which was tentatively assigned as a V^{III}/Cu^{II} dinuclear species. Treatment of the vanadium(IV) oxo (bis)phenolates **5a**–**5f** with SOCl$_2$ in benzene at room temperature or in toluene at reflux temperature resulted in the formation of dark blue compounds **6a**–**6f**, whose stoichiometries indicated excess chloride. Only when **5a** and **5d** were reacted with SOCl$_2$ at –70 °C could the desired dichlorovanadium (bis)phenolates [VCl$_2$(OC$_6$H$_4$(CH$_2$NMe$_2$)-2)$_2$] (**7a**) and [VCl$_2$(OC$_6$H$_3$(CH$_2$NMe$_2$)-2-Cl-4)$_2$] (**7d**) be obtained. X-ray crystal structure determination of **1** and **3** showed that both compounds have a trigonal bipyramidal geometry with two aminophenolate ligands bound in a bidentate η^2-*O,N* fashion to the vanadium center in similar ways. The compounds **1**, **3**, **6** and **7** were tested for ethene/propene copolymerization.

Introduction

Although the activity of vanadium-based catalysts is often inferior to that of other systems, their use has several advantages, such as (1) the preparation of high molecular weight polymers with narrow molecular weight distributions, (2) the preparation of ethene/α-olefin copolymers with high α-olefin incorporation, and (3) the preparation of syndiotactic polypropene.[1] One of the reasons for the reduced activity of vanadium-based catalysts is their deactivation during the polymerization process due to the reduction of catalytically active vanadium species to less active or even inactive low-valent species. One way to overcome this problem would be the stabilization of the higher oxidation states of the vanadium center by ancillary ligands. To this end, we recently set out to study the use of mono-anionic, potentially bidentate aminophenolate ligands (see Figure 1). These ligands have been chosen since vanadium systems with oxygen-containing ligands are known to give polymers with narrow molecular weight distributions,[2]

while the nitrogen donor atom can help in stabilizing the high oxidation state of the vanadium center by V–N coordination. In addition to the latter effect, an *ortho*-amino functionality itself represents a substituent with considerable bulk, which can prevent bimolecular deactivation pathways of the vanadium catalyst.[1,3] Finally, the electronic properties of the vanadium center can be considerably influenced by varying the *meta* and *para* substituents on the phenolate ring, as we have recently shown for vanadium(IV) oxo (bis)phenolate complexes.[4] It turns out that these ligands cannot be employed in vanadium(V) chemistry, since the *ortho*-amino function causes reduction of the vanadium(V) center to vanadium(IV).[5] Therefore, in our further studies we have focused on employing these *ortho*-aminophenolate ligands in systems with the vanadium center in the formal 3$^+$ or 4$^+$ oxidation state.

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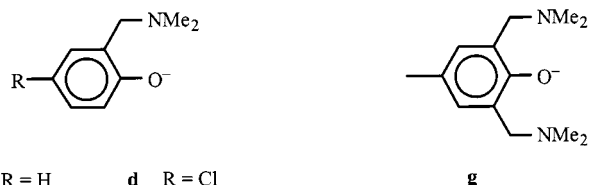
a R = H	**d** R = Cl	**g**
b R = Me	**e** R = N=NPh	
c R = *t*Bu	**f** R = MeO	

Figure 1. Selected *ortho*-aminophenolate ligands

Results and Discussion

In the course of our attempts to synthesize vanadium(II) phenolates, we have treated [Cp$_2$V] with the bis(amino)-phenol HOC$_6$H$_2$(CH$_2$NMe$_2$)$_2$–2,6-Me-4 (see Scheme 1). Instead of the expected vanadium(II) (bis)phenolate, this reaction gave a bright orange compound, which was identified by X-ray crystallography (vide infra) as the vanadium(III) (tris)phenolate [V(OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)$_3$] (1). The formal 3$^+$ oxidation state of vanadium in 1 was confirmed by its magnetic susceptibility (μ_{eff} = 2.52 μ_b), which is characteristic of a d^2 high-spin complex.[6] Oxidation of low-valent vanadium(II) to vanadium(III) by phenols with the concomitant formation of molecular hydrogen is not uncommon. The formation of vanadium(III) species can be avoided only when phenols with larger *ortho*-substituents like *i*Pr, *t*Bu or Ph are used.[7] This oxidation is not restricted to phenols themselves, but also occurs when sodium phenolates are used. In the latter case, however, a disproportionation reaction occurs with the formation of the vanadium(III) phenolate and metallic vanadium.[8]
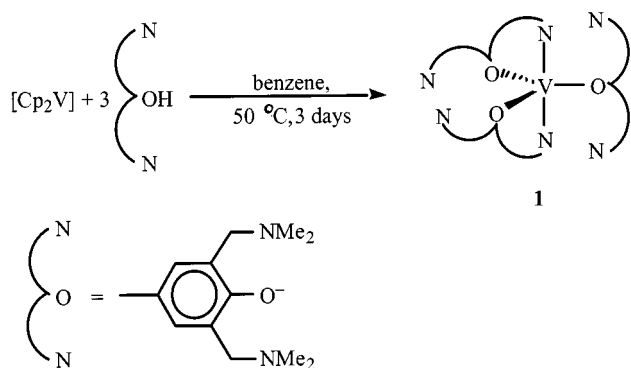

Scheme 1. Synthesis of the vanadium(III) (tris)phenolate 1

In our further studies [VCl$_3$(THF)$_3$] was used as the starting material for the synthesis of vanadium(III) aminophenolate complexes. It must be noted that a salt metathesis reaction with the corresponding sodium phenolate gave non-reproducible results. Depending on the temperature and the solvent used, none or only part of the expected amount of NaCl precipitated from the reaction mixture, indicating the formation of hetero di- or tri-nuclear complexes. The exact nature of these complexes was not determined but examples of such compounds are known in lanthanide chemistry.[9] In this kind of complex the aminophenolate ligands form bridges between different metal atoms via the oxygen atoms while the amino nitrogen atoms coordinate to either the metal or sodium. To overcome the problem of NaCl incorporation the corresponding silyl ether, Me$_3$Si-OC$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-4 (2), was used. Treatment of [VCl$_3$(THF)$_3$] with two equivalents of the silyl ether 2 in refluxing THF (see Scheme 2) resulted in the formation of the chlorovanadium (bis)phenolate [VCl(OC$_6$H$_3$(CH$_2$-

NMe$_2$)-2-Me-4)$_2$] (3), which was isolated as a moderately air-sensitive, crystalline orange solid.
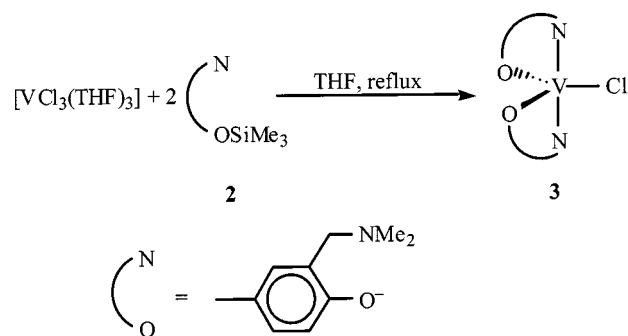
Scheme 2. Synthesis of the chlorovanadium (bis)phenolate 3

Synthesis of Vanadium(IV) Phenolates

Rather than using VCl$_4$, which is an inconvenient starting material because of its volatility and oxidative nature, we attempted to use the chlorovanadium (bis)phenolate 3 as starting material for the synthesis of the corresponding dichlorovanadium(IV) (bis)phenolate. Attempts to oxidize 3 with CuCl, AgCl or PbCl$_2$ were in vain, as no reaction was observed. However, when CuCl$_2$ was used a dark blue complex (4) was almost immediately formed (Scheme 3). Although the exact nature of 4 remains unclear, elemental analysis indicated the isolation of a complex with a V(OR)$_2$CuCl$_3$·CH$_2$Cl$_2$ stoichiometry (OR = OC$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-4). Complex 4 is insoluble in alkanes, aromatic solvents like benzene and toluene, and Et$_2$O. It is poorly soluble in chloroform and reasonably soluble in CH$_2$Cl$_2$ and THF. The severe line-broadening in the ^{1}H NMR spectrum of 4 in CD$_2$Cl$_2$ indicates that it is a paramagnetic species.
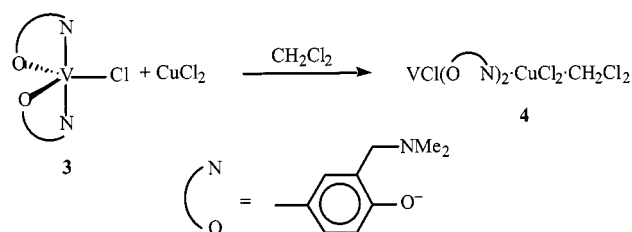
Scheme 3. Synthesis of the dinuclear vanadium/copper compound 4

For a complex with the observed V:Cu:anion stoichiometry, three combinations of V/Cu oxidation states are conceivable, viz. V^{III}/Cu^{II}, V^{IV}/Cu^I or V^V/Cu^0. In view of the V^{IV}/V^V oxidation potential, the V^V/Cu^0 combination is not likely. Oxidation of the vanadium nucleus in 4 by CuCl$_2$ to vanadium(IV) would result in the formation of a complex with a paramagnetic, EPR active vanadium center and a diamagnetic copper(I) center. EPR analysis of a 2 mM solution of 4 in CH$_2$Cl$_2$ showed the characteristic octet of a vanadium(IV) compound. Since the signal was very weak, it is most likely caused by an impurity. This would mean that the vanadium nucleus has not been oxidized in the re-

action with $CuCl_2$ and we believe that **4** is best described as a V^{III}/Cu^{II} dinuclear species.

In view of these results, another route to dichlorovanadium(IV) (bis)phenolate complexes was studied, i.e. the reaction of vanadyl complexes, $[VO(OR)_2]$ (**5a**−**5f**),[4] with thionyl chloride. In this reaction the $[V=O]^{2+}$ unit is transformed into a $[VCl_2]^{2+}$ unit with the liberation of SO_2.[10] Treatment of compounds **5** with excess $SOCl_2$ in benzene at room temperature or in toluene at reflux temperature gave dark blue/green compounds (**6a**−**6f**), which are insoluble in alkanes, aromatics like benzene and toluene, and Et_2O. They are slightly to very soluble in THF, CH_2Cl_2 and MeCN.

None of the elemental analyses of compounds **6**[11] agreed with the formula $VCl_2(OR)_2$, but they all had stoichiometries containing various amounts of excess chlorine. The amount of additional chlorine appears to be independent of both reaction time and reaction temperature. Also the presence of approximately half an equivalent of sulfur is remarkable. Attempts to grow crystals suitable for a crystal structure determination failed and so far this has hampered the identification of these complexes.

When exactly one equivalent of thionyl chloride was added to **5a** at −70 °C the desired dichlorovanadium (bis)-phenolate, $[VCl_2(OC_6H_4(CH_2NMe_2)-2)_2]$ (**7a**) was obtained in a 76% yield (see Scheme 4). During this reaction a toluene-insoluble solid with a Cl:V ratio greater than two was also formed, as is also the case when the reaction is carried out at room temperature (vide supra).[12] Treatment of the vanadyl (bis)phenolates **5c** and **5d** with thionyl chloride at −70 °C resulted in the formation of the desired dichloro compound $[VCl_2(OC_6H_3(CH_2NMe_2)-2-Cl-4)_2]$ (**7d**) in the case of **5d**, whereas for **5c** a compound (**7c**) with a Cl:V ratio of 3.5 was found.[13] Compounds **7a**, **7c** and **7d** are dark blue, insoluble in alkanes, sparingly soluble in aromatics like benzene and toluene, but very soluble in polar solvents like CH_2Cl_2, THF and MeCN.
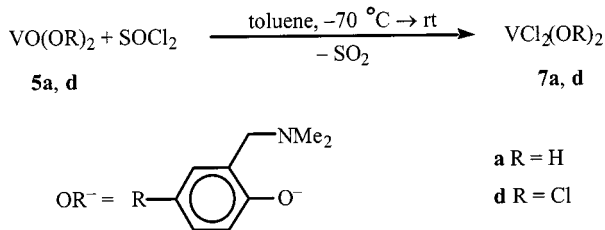
Scheme 4. Synthesis of the vanadium dichloro (bis)phenolates **7a** and **7d**

The difference in reactivity between compounds **5** and a large number of vanadyl Schiff base complexes, $[VOL_2]$, is remarkable. The latter all give the corresponding dichloro-vanadium complexes in high yields.[14] The only difference between the present $[VO(OR)_2]$ complexes and the Schiff base containing $[VOL_2]$ complexes is the presence of an sp^3 amine nitrogen in the former vs. an sp^2 imine nitrogen atom in the latter. Unfortunately, the mechanism of the reaction of $[VOL_2]$ with thionyl chloride is not known. If, however, a vanadium(V) species is formed in a side reaction, then

this could be an explanation for the different results in the reactions of compounds **5**. It is known that vanadium(V) compounds can be reduced by trialkylamines. Moreover, when the vanadium(V) species contains a halogen, this amine will be recovered as the trialkylammonium halide.[15] The source of the proton in this reaction is not known. Recently we reported that the use of *ortho*-aminophenolates in vanadium(V) chemistry gave rise to the formation of vanadium(IV) compounds.[5] Consequently, the formation of a vanadium(V) chloride in the reaction of **5** with $SOCl_2$ would immediately result in the reduction of the vanadium(V) nucleus to yield a vanadium(IV) vanadate species and a quaternary ammonium substituent (see Scheme 5). As two amine functionalities are present in the molecule, the reaction sequence can occur twice. The results we obtained in the synthesis of compounds **7** led us to believe that indeed a change in oxidation state is responsible for this behavior. The oxidation potential of the *t*Bu-substituted vanadyl complex is lower than those of the H- and Cl-substituted complexes (ΔE_{ox} = 60 and 130 mV, respectively).[4] A complex with a lower oxidation potential would easily lead to the formation of an unstable vanadium(V) complex, and from there to a vanadium(IV) complex with ammonium substituents and excess chlorine. The reason that this behavior is not observed for the Schiff base complexes could be twofold. Firstly, the side-reaction involving the oxidation to vanadium(V) does not occur because of their higher oxidation potentials. Secondly, the side reaction is an equilibrium. If the oxidation to vanadium(V) would occur, no chlorovanadate species would be formed as the vanadium(V) center is not reduced by an imine function. Instead it may react to return to the starting vanadium(IV) compound and subsequently react with $SOCl_2$ to form the dichlorovanadium compound.
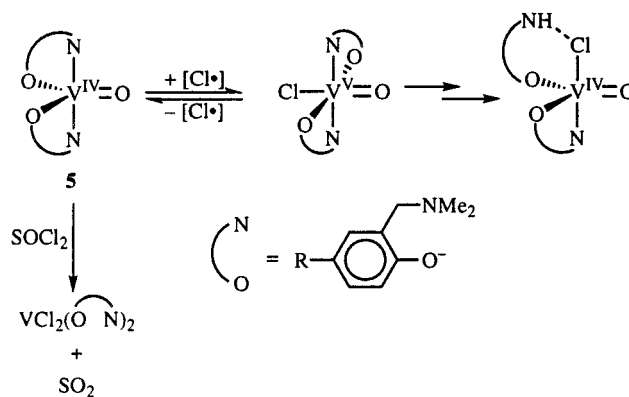
Scheme 5. Postulated reaction mechanism for the formation of an ammonium vanadate(IV) species

IR analysis corroborated the suggestion that **6** are ammonium chlorovanadate complexes. Comparison of the IR spectrum of **6b**[16] with the one of the ammonium chloro-vanadate complex $[VOCl_2(OC_6H_2(CH_2NMe_2)-2-Me-4-(CH_2NHMe_2)-6)]$,[4] revealed that the 2900−2800 cm^{-1} regions (i.e., the region in which the complex resonance pattern for the intramolecular hydrogen bond is found) are very similar.

Solid-State Structures of 1 and 3

The ^{1}H NMR spectra of the vanadium(III) complexes display broad peaks with no substructure due to the paramagnetism of these d^2 compounds. This means little or no structural information can be obtained with NMR. The high-spin state of these compounds makes them also inaccessible to conventional X-band EPR analysis.[17] Consequently, in order to get information about the structure, a single crystal X-ray structure determination is of great importance. Crystallization of **1** from hexane gave single crystals suitable for X-ray crystal structure analysis. The molecular structure of **1** is depicted in Figure 2. Selected bond lengths and angles are given in Table 1. The geometry around the vanadium center is a distorted trigonal bipyramid (21% on the Berry pseudorotation path between D_{3h} and C_{4v} [18]). The three oxygen atoms are in the equatorial plane ($\Sigma(O-V-O) = 359.82°$) while the two coordinating nitrogen atoms are in the apical positions (N1–V–N3 = 171.74(8)°); i.e., two bis(amino)phenolate ligands are bonded in a bidentate η^2-O,N fashion to the vanadium center in a similar way. The third phenolate ligand is bonded in an η^1-O monodentate fashion. The V-O and O-C bond lengths and the V-O-C bond angles fall within the range reported for vanadium(III) phenolates (1.818-1.927 Å, 1.315-1.378 Å and 132.2-158.3, respectively).[19] The V–O–C angle of the monodentate bonded ligand is considerably larger than those in the chelate rings. This allows more π-bonding to the vanadium center, which is reflected in a slight shortening of the V–O bond.

Table 1. Selected bond lengths and bond angles for **1**

Bond lengths (Å)

V1−O1	1.876(2)	V1−N3	2.189(2)
V1−O2	1.866(2)	O1−C1	1.350(3)
V1−O3	1.853(2)	O2−C14	1.350(3)
V1−N1	2.195(2)	O3−C27	1.345(3)

Bond angles (deg)

O1−V1−O2	126.31(8)	V1−O3−C27	148.1(2)
O1−V1−O3	116.83(8)	N1−V1−N3	171.74(8)
O2−V1−O3	116.68(8)	O1−V1−N1	88.61(7)
V1−O1−C1	133.48(18)	O2−V1−N3	88.56(8)
V1−O2−C14	134.2(2)		

1. It has crystallographic C_2 symmetry with the symmetry axis along the V−Cl bond. The equatorial plane is formed by the two oxygen atoms of the phenolate ligands and the chlorine atom. The apical positions are occupied by the coordinating nitrogen atoms (N1−V−N1′ = 175.65(18)°). The V−Cl bond length (2.2923(16) Å) lies in the range reported for vanadium(III) chlorides (2.277−2.418 Å).[20a,20c] The bond lengths and bond angles involving the bidentate η^2-O,N bonded ligand are comparable to those in **1**. Compound **3** cocrystallizes with one equivalent of toluene.
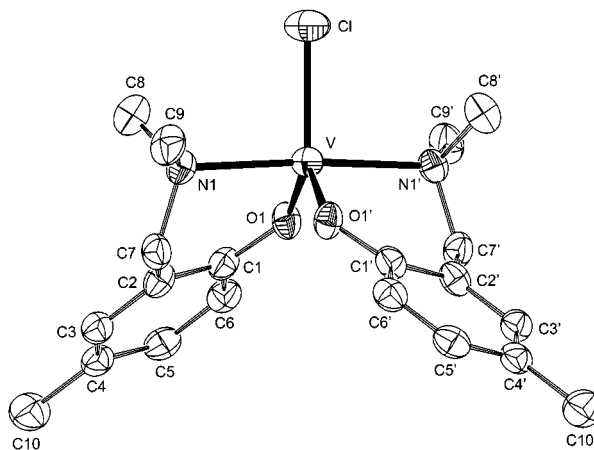
Figure 3. Displacement ellipsoid plot of **3**, drawn at 50% probability; hydrogen atoms are omitted for clarity; symmetry operation ′: −x, y, 0.5−z
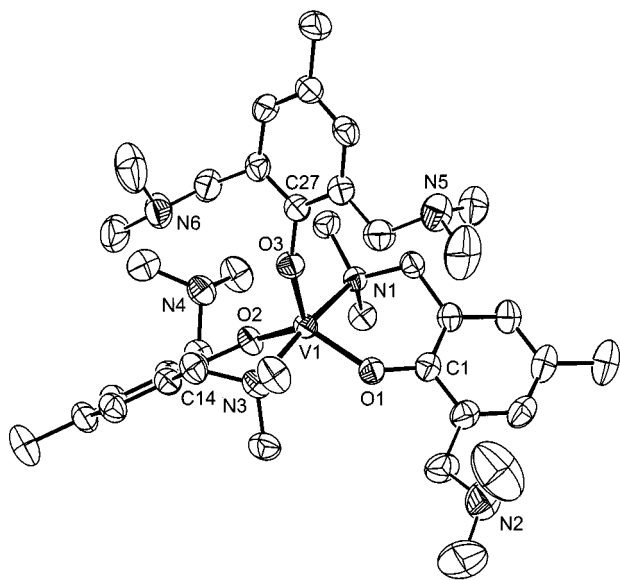

Figure 2. Displacement ellipsoid plot of **1**, drawn at 50% probability; hydrogen atoms are omitted for clarity; only one conformation of the disordered aminobenzyl groups is shown

Table 2. Selected bond lengths and bond angles for **3**

Bond lengths (Å)

V − Cl	2.2923(16)	V−O1	1.854(3)
V − N1	2.187(3)	O1−C1	1.345(4)

Bond angles (deg)

Cl − V − O1	122.38(8)	O1−V−N1	88.71(11)
Cl − V − O1′	122.38(8)	N1−V−N1′	175.65(18)
O1 − V − O1′	115.23(16)	V−O1−C1	133.4(2)

Polymerization Tests

Crystallization of **3** from toluene gave single crystals suitable for an X-ray crystal structure determination. The molecular structure is depicted in Figure 3 and pertinent bond lengths and bond angles are given in Table 2. The geometry around the vanadium center is trigonal bipyramidal as in

The vanadium(III) and -(IV) compounds obtained in this work were tested for ethene/propene copolymerization. The

polymerization tests were carried out in pentamethylheptane (PMH) at 30̊ C for a period of 10 minutes. The ethene/propene pressure was 8 bar and the ethene/propene molar ratio was kept constant at 1:2. $Et_{1.5}AlCl_{1.5}$ was used as cocatalyst. The reaction vessel was loaded with 500 mL of PMH, 20 equivalents of cocatalyst and the monomers. The catalysts ($\pm$ 25 µmol), dissolved or suspended in toluene, were injected into the reaction vessel without premixing of the cocatalyst. The results of these preliminary tests are listed in Table 3.

Table 3. Ethene/propene copolymerization results with vanadium aminophenolate complexes

Complex [a]	Yield (g)	Activity[b]	C_3 (mass%)	η[c] (dL/g)	Mw[d]
1	0.9	27	n.d.	n.d.	–
3	5.3	159	37.5	5.86	6.7
6a	0.7	21	n.d.	n.d.	–
6c	2.6	78	38.2	8.15	10.5
6e	4.6	138	39.1	7.29	9.0
6f	0.7	21	n.d.	n.d.	–
7c	7.4	222	32.3	4.95	5.0
7d	6.3	189	29.5	5.95	6.3

[a] Polymerization conditions: 25 µmol [V], 20 equiv. $Et_{1.5}AlCl_{1.5}$, 500 mL PMH, 30 °C, 8 bar ethene/propene ratio 1:2, 10 min. reaction time. – [b] Activity in kg/mol[V]·h·bar. – [c] Intrinsic viscosity measured in decalin at 135 °C. – [d] Molecular weight in g/mol $\times 10^{-5}$.

The activities found vary over one order of magnitude, with the activities of complexes **6** significantly lower than those of **7**. The reason for these lower activities is probably the poor solubility of the former complexes, as only **6e** is slightly soluble in toluene whereas **6a**, **6c** and **6f** are completely insoluble in toluene. The activity of **1** is low in comparison with **3**. The reason for this difference is probably the rate of formation of the catalytically active species. The steric bulk of the pendant amino substituents probably hinders the approach of an aluminium species, which is necessary for ligand exchange with subsequent formation of a vanadium alkyl compound.

IR analysis of the polymers shows that the incorporation of propene varied between approximately 30 and 40%. The molecular weights of the polymers were calculated based on their intrinsic viscosities (in decalin at 135°). The molecular weights varied between 5.0×10^5 and 10.5×10^5 g/mol. When these results are compared to those reported by Gambarotta and co-workers for tetravalent $(R_2N)_2VCl_2$ (R = *i*Pr, Cy) complexes[21] some differences can be noted. The activities are of the same order of magnitude (430 and 165 kg EP/mol[V]·h·bar, respectively). The molecular weight (Mw = 2293000 for R = *i*Pr) is much higher, but the propene incorporation is slightly lower (27%). Unfortunately, it is difficult, if not impossible, to make a fair comparison with the results reported in the literature. Often the conditions are different or details of the polymerization reactions are not mentioned.

Experimental Section

General: All reactions were performed in an atmosphere of dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents

were carefully dried and distilled prior to use. $[Cp_2V]$,[22] $[VCl_3(THF)_3]$,[23] the phenols **b** and **g**,[24] and the vanadium oxo (bis)phenolates **5a–5f** were prepared according to literature procedures. $SOCl_2$ was distilled from quinoline. Et_3N was distilled from CaH_2. All other chemicals were obtained from commercial sources and used as received. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim, Germany. ^1H NMR spectra were recorded on a Bruker AC300 spectrometer or a Varian Unity Inova 300 spectrometer. EPR spectra were recorded on a Bruker ESP 300 spectrometer.

Synthesis of $[V(OC_6H_2(CH_2NMe_2)_2–2,6-Me-4)_3]$ (1): A mixture of $[Cp_2V]$ (0.44 g, 2.42 mmol) and $HOC_6H_2(CH_2NMe_2)_2–2,6-Me-4$ (1.96 g, 8.82 mmol) in benzene (40 mL) was stirred for 50 hours at 70 °C during which time the color slowly changed from purple to green. After removal of the solvent in vacuo a green oil was obtained. Leaving the oil to stand yielded two crops of a red solid (1.04 g; 60%). Recrystallization from hexane at 4 °C gave bright orange crystals. Mp: 129 °C. – $C_{39}H_{63}N_6O_3V$: calcd. C 65.52, H 8.88, N 11.76; found C 65.33, H 8.89, N 11.80. – IR (KBr, cm^{-1}): 2998(m), 2972(s), 2941(s), 2903(s), 2851(s), 2828(s), 2909(s), 2758(s), 2728(m), 2714(m), 1780(w), 1609(w), 1576(w), 1468(s), 1362(m), 1300(s), 1283(s), 1256(s), 1172(m), 1146(m), 1042(m), 1005(m), 984(m), 872(s), 845(s), 826(m), 638(m), 600(m), 557(m). – Magnetic susceptibility: $\mu_{eff} = 2.52\mu_b$.

Synthesis of $Me_3SiOC_6H_3(CH_2NMe_2)-2-Me-4$ (2): A solution of $HOC_6H_4(CH_2NMe_2)-2-Me-4$ (**b**) (11.41 g, 68.63 mmol) in Et_2O (25 mL) was added dropwise to a stirred solution of Me_3SiCl (11.3 mL, 89.3 mmol) and Et_3N (12.4 mL, 89.3 mmol) in Et_2O (300 mL). A white precipitate was immediately formed and the resulting mixture was stirred for 16 hours. The precipitate was subsequently removed by filtration. The filtrate was concentrated in vacuo to give a yellowish oil. This oil was flash-distilled to give **2** as a colorless oil (13.13 g; 80%). – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.27 (s, 9 H, $SiMe_3$), 2.25 (s, 6 H, NMe_2), 2.28 (s, 3 H, Me), 3.37 (s, 2 H, CH_2), 6.69 (d, 1 H, $^3J_{H,H}$ = 8 Hz, Ar-H^6), 6.92 (dd, 1 H, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, Ar–H^5), 7.13 (d, 1 H, $^4J_{H,H}$ = 2 Hz, Ar–H^3).

Synthesis of $[VCl(OC_6H_3(CH_2NMe_2)-2-Me-4)_2]$ (3): A solution of $Me_3SiOC_6H_3(CH_2NMe_2)-2-Me-4$ (**2**) (4.44 g, 18.70 mmol) in THF (20 mL) was added dropwise to a stirred suspension of $[VCl_3(THF)_3]$ (3.52 g, 9.42 mmol) in THF (50 mL). A dark red solution was immediately obtained, which was then heated at reflux for one hour. After removal of the solvent in vacuo the residue was extracted with toluene (80 mL) and the resulting solution was left to stand for several days, yielding bright orange crystals (0.74 g; 16%). Cooling the supernatant solution to −20 °C gave a second crop (0.98 g; 21%). M.p.: 122 °C. – $C_{20}H_{28}N_2O_2VCl·C_7H_8$: calcd. C 63.97, H 7.16, N 5.53; found C, 63.29, H 6.83, N 5.50.

Synthesis of $[VCl(OC_6H_3(CH_2NMe_2)-2-Me-4)_2CuCl_2]$ (4): $CuCl_2$ (0.39 g, 2.90 mmol) was added as solid to a stirred solution of $[VCl(OC_6H_3(CH_2NMe_2)-2-Me-4)_2·C_7H_8]$ (**3**) (0.9 g, 1.7 mmol) in CH_2Cl_2 (50 mL). The color changed to dark blue within a few minutes. The mixture was stirred for two days after which it was filtered. The volume of the solution was reduced to 30 mL in vacuo. The solution was layered with Et_2O (30 mL) and left to stand for three days. A dark blue oil was formed which upon drying in vacuo yielded a dark blue solid (0.94 g; 87%). – $C_{21}H_{30}N_2O_2VCuCl_3·CH_2Cl_2$: calcd. C 39.77, H 4.77, N 4.42; Cl, 27.95; found C, 39.73, H 5.38, N 4.39; Cl, 27.60.

Synthesis of $[VCl_2(OC_6H_4(CH_2NMe_2)-2)_2]$ (7a): $SOCl_2$ (1.5 mL, 2.1 M in toluene, 3.2 mmol) was added to a stirred suspension of

$[VO(OC_6H_4(CH_2NMe_2)-2)_2]$ **(5a)** (1.14 g, 3.10 mmol) in toluene (40 mL) at −70 °C. The solution was allowed to slowly warm to room temperature, during which it turned dark green and a dark colored precipitate was formed. After stirring for an additional 16 hours the solution was separated from the precipitate by centrifugation/decantation and the residue was extracted twice with toluene (40/20 mL). The volume of the combined toluene fractions was reduced to 15 mL in vacuo after which pentane (40 mL) was added. The solvent was removed by centrifugation/decantation and the residue was washed with pentane (2 × 25 mL). Compound **7a** was obtained as a dark blue powder after drying in vacuo (0.99 g, 76). − $C_{18}H_{24}N_2O_2VCl_2$: calcd. C 51.20, H 5.73, N 6.63; V, 12.06; Cl, 16.79; found C, 50.99, H 5.75, N 6.49; V, 11.83; Cl, 16.65. − EPR (toluene): A_{iso} = 84.1 Gauss; g_{iso} = 1.955.

Synthesis of $[VCl_2(OC_6H_3(CH_2NMe_2)-2-Cl-4)_2]$ (7d): Compound **7d** was prepared in a similar way to **7a** starting from $[VO(OC_6H_3(CH_2NMe_2)-2-Cl-4)_2]$ **(5d)** (0.53 g, 1.22 mmol) and $SOCl_2$ (0.6 mL, 2.1 M in toluene, 1.2 mmol) and was obtained as a dark blue powder (0.32 g, 54). − $C_{18}H_{22}N_2O_2VCl_4$: calcd. C 44.02, H 4.52, N 5.70; Cl, 28.87; found C, 43.88, H 4.50, N 5.67; Cl, 28.84. − EPR (toluene): A_{iso} = 84.00; g_{iso} = 1.953.

X-ray Crystallographic Structure Determination and Refinements. Orange crystals of **1** suitable for X-ray diffraction were grown by cooling a saturated hexane solution to 4 °C while orange crystals of $3 \cdot C_7H_8$ were grown from toluene at room temperature. X-ray intensities were measured on an Enraf−Nonius CAD4T diffractometer with rotating anode and graphite monochromator (Mo−$K\alpha$, λ = 0.71073 Å).

Crystal structure of **1**: Yellow block, 0.25 × 0.25 × 0.25 mm³. The structure was solved with direct methods (SHELXS86[25]) and refined with the program SHELXL93[26] against F^2 for all reflections up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å⁻¹. An ab-

sorption correction was not considered necessary. Non-hydrogen atoms were refined freely with anisotropic displacement parameters; hydrogen atoms were refined as rigid groups. Three of the uncoordinated aminobenzyl groups were refined with disorder models.

Crystal structure of **3**: Yellow plate, 0.38 × 0.30 × 0.05 mm³. The structure was solved with Patterson methods (DIRDIF97[27]) and refined with the program SHELXL97[28] against F^2 of all reflections up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.59 Å⁻¹. An absorption correction based on Psi-scans was applied (0.87−0.97 transmission). Non-hydrogen atoms were refined freely with anisotropic displacement parameters; hydrogen atoms were refined as rigid groups. The crystal structure contains large voids (670 Å³) filled with disordered toluene molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON,[29] CALC SQUEEZE, 196 e/unit cell)

Both structures were checked for higher symmetry with the program PLATON.[29] Crystal data and details of the data collection are shown in Table 4. Geometrical calculations and illustrations were performed with PLATON.[29]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-139534 (**1**) and -139535 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Table 4. Crystallographic data for **1** and **3**.

	1	3
Empirical formula	$C_{39}H_{63}N_6O_3V$	$C_{20}H_{28}N_2O_2VCl \cdot C_7H_8$
Formula weight	714.91	506.995
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (No. 2)	$Pbcn$ (No. 60)
a, Å	9.2793(7)	11.712(2)
b, Å	13.9788(10)	16.4182(16)
c, Å	17.4615(12)	13.5356(16)
α, deg	110.474(5)	90
β, deg	99.989(6)	90
γ, deg	96.252(6)	90
V, Å³	2054.1(3)	2602.8(6)
Z	2	4
D_{calc}, g cm⁻³	1.156	1.294
μ (Mo $K\alpha$), mm⁻¹	0.28	0.496
$F(000)$	772	1072
T, K	225	150
θ range	1.28−27.46	2.14−25.00
hkl range	−11 → 12,	−13 → 1,
	−16 → 18,	−19 → 19,
	−22 →15	−16 → 0
Measured reflections	12616	4488
Unique reflections	9388	2289
Observed refl. [$I > 2\sigma(I)$]	6519	1300
Parameters/restraints	510/0	119/0
Final $R1$[a]	0.061	0.0563
Final $wR2$[b]	0.165	0.1339
Goodness of fit	1.019	0.96
Residual electron density	−0.34 → 0.73	−0.18 → 0.43

[a] $R1 = \Sigma\|F_c| - |F_c\|/\Sigma|F_c|$ based on observed reflections. − [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ based on all reflections.

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[11] **6a**: Anal. found C 42.58, H 4.84, N 4.63, Cl 26.12, V 8.60, S 2.30. Based on nitrogen analysis 4.63 ≈ 2 N: MW = 605; stoichiometry: 21.4 C; 29.0 H; 4.5 Cl; 1.0 V; 0.4 S. Based on residual mass: 4.1 O. **6c**: Anal. found C 46.05, H 5.81, N 3.80; Cl, 26.97. Based on nitrogen analysis 3.80 ≈ 2 N: MW = 737; stoichiometry: 28.3 C; 42.5 H; 5.6 Cl. **6d**: Anal. found C 38.03, H 3.86, N 4.43, Cl 34.29. Based on nitrogen analysis 4.43 ≈ 2 N: MW = 632; stoichiometry: 20.0 C; 24.2 H; 6.1 Cl. **6e**: Anal. found C 56.34, H 4.83, N 12.33; Cl, 13.51. Based on nitrogen analysis 12.33 ≈ 6 N: MW = 682; stoichiometry: 32.0 C; 32.6 H; 2.6 Cl. **6f**: Anal. found C 43.98, H 5.02, N 4.17; Cl, 23.49; V, 8.43, S 3.51. Based on nitrogen analysis 4.17 ≈ 2 N: MW = 672; stoichiometry: 24.6 C; 33.7 H; 4.5 Cl; 1.1 V; 0.7 S. Based on residual mass: 4.8 O.

[12] The residue in the case of **7a** contained three equivalents of chlorine. Anal. found C 47.44, H 5.38, N 5.90, Cl 22.35. Based on nitrogen analysis 5.90 ≈ 2 N: MW = 475; stoichiometry: 18.8 C; 25.3 H; 3.0 Cl.

[13] **7c**: Anal. found C 53.85, H 7.01, N 4.67; Cl, 20.59. Based on nitrogen analysis 4.67 ≈ 2 N: MW = 600; stoichiometry: 26.9 C; 41.7 H; 3.5 Cl.

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