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Vanadium complexes containing amido functionalized cyclopentadienyl ligands

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2000

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Witte, P. T. (2000). *Vanadium complexes containing amido functionalized cyclopentadienyl ligands*. [s.n.].

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Chapter 5

Synthesis of di-, tri- and tetravalent vanadium complexes

5.1 Introduction

Since the initial reports of the use of Cp-amido ligands on the group 3 metal scandium,¹ most research has focused on the use of this type of ligand in catalytic olefin polymerization by group 4 metal complexes (Cp-amido)MCl₂.^{2,3} Despite numerous reported ligand variations and their influence on the catalyst performance, studies on the effect of the electronic configuration of the metal center have not been performed. Only in theoretical calculations on the insertion barrier of ethene in the M-Me bond, the cationic d⁰ [(Cp-amido)M(IV)Me]⁺ complex is compared to the neutral d¹ (Cp-amido)M(III)Me complex (M = Ti, Zr, Hf).^{4a} Just before this thesis was completed, a theoretical study was published in which the potential of complexes of the first row metals Ti, V, Cr and Mn with a d-electron count of 1-4 as olefin polymerization catalysts was discussed. Based on the study of elementary steps as ethylene binding, chain propagation, and chain termination, systems with a high oxidation state and a d-electron count up to three (for instance a d¹ vanadium(IV) complex) were considered to have the best catalytic properties.^{4b} The synthesis of d¹ (Cp-amido)VCl₂ complexes makes experimental comparison with the known d⁰ (Cp-amido)TiCl₂ complexes possible.⁵

In this chapter we describe the synthesis of the first Cp-amido vanadium(IV) di-chloro complex and initial results on its performance as an ethene polymerization catalyst precursor. This is compared to the performance of the isostructural d⁰ titanium analogue.

Since attempts to introduce the Cp-amido ligand directly on a vanadium(IV) precursor failed, the ligand was introduced on vanadium(III). After

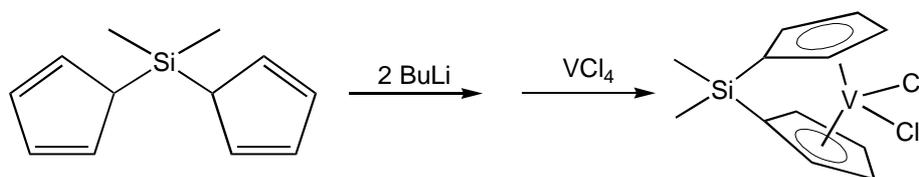
a one-electron reduction a Cp-amido vanadium(II) complex was obtained, which could be oxidized by PhICl_2 to the desired Cp-amido vanadium(IV) dichloride.

5.2 Results and discussion

5.2.1 Attempted ligand introduction on vanadium(IV) precursors

Introduction of a Cp-amido ligand on a group 4 metal center is generally performed by either salt metathesis, HCl elimination or amine elimination (see Chapter 2), starting from metal(IV) chloro or amido complexes. However, these three methods proved unsuccessful in the synthesis of Cp-amido vanadium(IV) complexes.

Salt metathesis: The *ansa*-vanadocene dichloride $\{\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\}\text{VCl}_2$ was synthesized in a salt metathesis reaction of the di-lithium salt of the ligand with VCl_4 in a very low yield (7%, Scheme 1).⁶ We attempted the synthesis of $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{VCl}_2$ in a similar way, by addition of a THF solution of the di-lithium salt of the Cp-amido ligand, $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr}]\text{Li}_2$ (see Chapter 2), to a pentane solution of VCl_4 at 0°C . This led to the immediate formation of a dark precipitate which was insoluble in pentane, toluene and THF, and which could not be characterized.

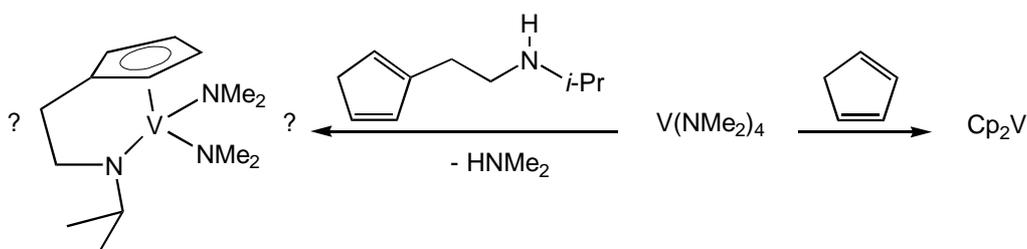


Scheme 1

HCl elimination: Introduction of the Cp-amido ligand on titanium(IV) by HCl elimination has been performed by reacting the neutral ligand precursor with TiCl_4 in the presence of a base (NEt_3).^{5a} However, VCl_4 is known to react

with tertiary amines; the reduced vanadium complex $\text{VCl}_3(\text{NMe}_3)$ is one of the complexes that has been isolated from the reaction of NMe_3 with VCl_4 .⁷ For this reason, the HCl elimination route was not attempted.

Amine elimination: The Cp-amido ligand can be introduced on vanadium(V) by amine elimination (Chapter 2, section 2.2.2). For introducing the ligand on vanadium(IV) we studied the reaction of the ligand precursor $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{N}(\text{H})i\text{-Pr}$ with $\text{V}(\text{NMe}_2)_4$ (in C_6D_6), which could generate $(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\text{NMe}_2)_2$ by amine elimination. After heating the reaction mixture for half an hour at 80°C in an NMR tube, resonances for the (diamagnetic) ligand precursor had disappeared and resonances for HNMe_2 had appeared; the color of the solution had changed from green to red. When the reaction of $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{N}(\text{H})i\text{-Pr}$ with $\text{V}(\text{NMe}_2)_4$ was performed on preparative scale, a red paramagnetic oil was obtained and no products could be crystallized. Addition of Me_3SiCl to convert the supposedly generated di-amido complex to the di-chloro complex⁸ also did not yield crystalline products. The vanadium amido complex $\text{V}(\text{NMe}_2)_4$ has been used before in an amine elimination reaction. However, in the reaction with C_5H_6 (CpH) reduction occurs and the vanadium(II) complex Cp_2V was isolated (Scheme 2).⁹



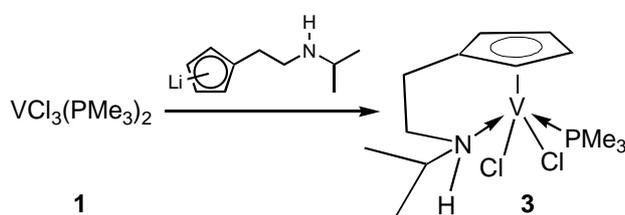
Scheme 2

5.2.2 Synthesis of vanadium(III) Cp-amido complexes

An alternative route for the synthesis of (Cp-amido)M(IV) complexes is ligand introduction on a M(III) precursor, and subsequent oxidation to the desired M(IV) dichloride. This route is used for the synthesis of $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{-Bu})\text{M}(\text{Cl})_2$.

Bu)TiCl₂, where the magnesium salt of the ligand [C₅Me₄SiMe₂N*t*-Bu]Mg₂Cl₂ is reacted with TiCl₃(THF)₃, and the Ti(III) intermediate oxidized *in situ* with PbCl₂ to the Cp-amido titanium(IV) dichloride.¹⁰ In order to investigate if such a route is possible for vanadium, we synthesized a Cp-amido vanadium(III) complex. However, attempts to synthesize this complex directly from VCl₃(PMe₃)₂ by reaction with the di-lithium salt [C₅H₄CH₂CH₂N(H)*i*-Pr]Li₂ failed. Therefore a step-wise introduction of the Cp-amido ligand was performed, starting with the attachment of the Cp moiety to the vanadium center.

Introduction of a single unsubstituted cyclopentadienyl ligand on vanadium(III) is possible by reaction of CpNa with VCl₃(PMe₃)₂ (**1**), yielding the purple paramagnetic complex CpVCl₂(PMe₃)₂ (**2**).¹¹ From the reaction of the mono-lithium salt [C₅H₄CH₂CH₂N(H)*i*-Pr]Li with **1** the Cp-amine complex (η⁵,η¹-C₅H₄CH₂CH₂N(H)*i*-Pr)VCl₂(PMe₃) (**3**) was isolated as a purple paramagnetic complex in a reasonable yield (59%, Scheme 3). The complex is well soluble in THF, but only sparingly in toluene; in both solvents slow decomposition is observed at room temperature. Single crystals were obtained by diffusion of pentane vapor into a THF solution of the complex. The crystal structure of complex **3** (Figure 1, Table 1) shows that the amine functionality of the ligand is coordinating to the vanadium center, which implies that the chelating effect of the amine functionality is strong enough to drive out one of the PMe₃ ligands. Even when the synthesis was performed in the presence of an excess of PMe₃ (5 equivalents), **3** was isolated and no evidence was found for the formation of a complex where the amine functionality is not coordinating.



Scheme 3

The Cp-amine complex **3** is essentially isostructural to the Cp complex **2**.¹¹ Both complexes have a four-legged piano stool conformation with the chlorine ligands in a trans configuration; in **3** the amine has replaced one of the phosphine ligands of **2**. This last feature has no significant effect on the V-Cl bond lengths (**2**: 2.401(1) and 2.405(1) Å), or on the V-Cg bond length (**2**: 1.973 Å; Cg = centroid of the Cp ring). Also the angles Cl(1)-V-Cl(2) (**2**: 126.1(0)°) and Cl-V-Cg (**2**: 116.0 and 117.9°) are very similar for both complexes. The coordinating amine in **3** has no effect on the V-P bond length (**2**: 2.507(1) and 2.510(1) Å), but the P-V-N angle in **3** is significantly larger than the P-V-P angle in **2** (**2**: 132.6(0)°). The V-N bond length in **3** (2.290(2) Å) is similar to that of other vanadium(III) amine complexes (average: 2.24 Å).¹²

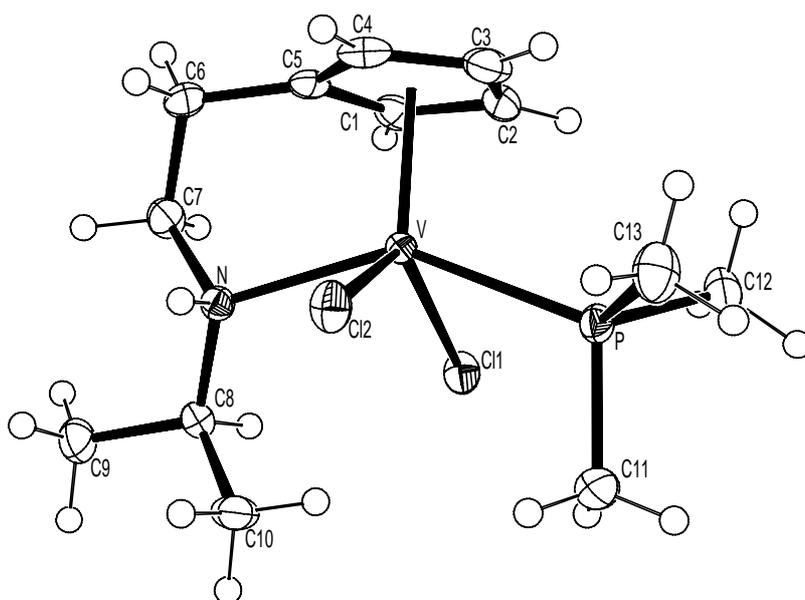


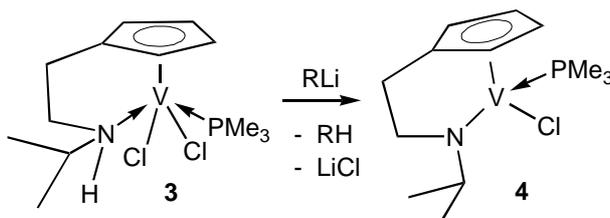
Figure 1: Crystal structure of **3**.

Table 1: Selected bond distances and angles in **3**.

V-N	2.290(2)	Cg-V-N	106.33(6)
V-Cl(1)	2.3904(8)	Cg-V-Cl(1)	116.35(3)
V-Cl(2)	2.4134(9)	Cg-V-Cl(2)	118.04(3)
V-P	2.5140(8)	Cg-V-P	111.13(3)
V-Cg	1.9662(13)	P-V-N	142.45(6)
H...Cl	2.82(3)	Cl(1)-V-Cl(2)	125.53(3)
		Cl(1)-V-P	79.08(3)
		Cl(2)-V-P	79.17(3)
		Cl(1)-V-N	86.87(6)

In the solid state **3** is associated to form a dimer, by hydrogen bridging of the N-H with a chloride ligand of a neighboring molecule (2.82(3) Å). This is probably the reason why the N-H vibration is not observed in the IR spectrum (solid **3** in nujol mull), and it can also explain the low solubility of **3** compared to **2**.

The Cp-amine rhenium complex (C₅H₄CH₂CH₂N(H)Me)Re(CO)₂, which is described in literature,^{3c} can be converted to a Cp-amido rhenium complex by deprotonation with butyl lithium, yielding [(C₅H₄CH₂CH₂NMe)Re(CO)₂]Li and generating butane. In a comparable reaction, the Cp-amine complex **3** is converted into a Cp-amido complex by reaction with an alkyl lithium reagent, generating the alkane and lithium chloride (Scheme 4).



Scheme 4

When the purple complex **3** was treated with one equivalent of Me₃SiCH₂Li, a color change to green was observed. When MeLi was used, gas evolution (probably methane) was observed together with this color change. The product of this reaction, the Cp-amido vanadium(III) complex (η^5, η^1 -C₅H₄CH₂CH₂N \dot{i} Pr)VCl(PMe₃) (**4**, Scheme 4), is paramagnetic and was identified by its crystal structure.

The structure of **4** (Figure 2, Table 2) shows slightly shorter V-Cl (2.3597(6) Å) and V-P (2.4791(6) Å) bond lengths compared to **3**, as can be expected for a complex with a lower coordination number. The V-Cg (1.9537(10) Å) distance is similar to that of **3**. As expected, the V-N(amido) bond in **4** (1.8728(17) Å) is much shorter than the V-N(amine) bond in **3**

(2.290(2) Å), caused by strong π -donation of the nitrogen atom; the V-N(amido) bond in **4** is one of the shortest found for vanadium(III) (1.83 - 1.96 Å).^{12b,13} The Cp-V-N bite angle of the Cp-amido ligand in **4** (114.07(6)°) is larger than that of the Cp-amine ligand in **3** (106.33(6)°).

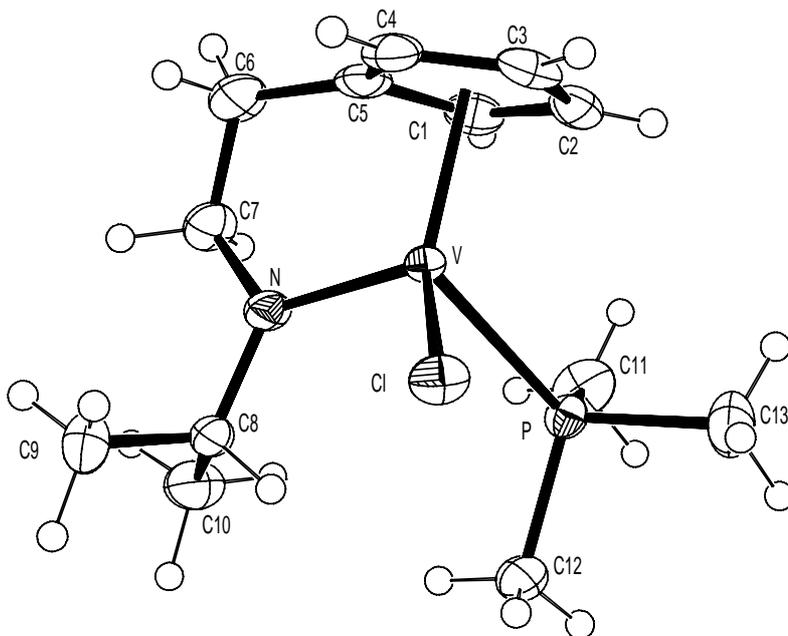


Figure 2: Crystal structure of **4**.

Table 2: Selected bond distances and angles in **4**.

V-N	1.8728(17)	Cg-V-N	114.07(6)
V-Cl	2.3597(6)	Cg-V-P	116.71(2)
V-P	2.4791(6)	Cg-V-Cl	124.54(2)
V-Cg	1.9537(10)	N-V-Cl	103.86(6)
		N-V-P	102.63(6)
		Cl-V-P	90.99(2)

5.2.3 Attempted oxidation of **4** to a Cp-amido vanadium(IV) complex

The reagent used in titanium chemistry for the oxidation of a Ti(III) complex to the desired Ti(IV) dichloride, PbCl_2 , is not suitable to oxidize the Cp-amido vanadium(III) complex **4** to a vanadium(IV) di-chloro species. Although PbCl_2 has been used in vanadium chemistry to oxidize vanadium(II) complexes to vanadium(III), subsequent oxidation to vanadium(IV) did not occur.¹⁴ Two

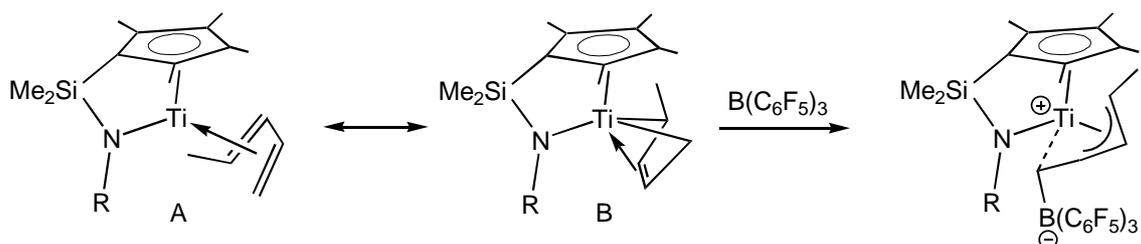
reported methods to oxidize vanadium(III) complexes to vanadium(IV) chlorides are reaction with one equivalent CuCl ¹⁵ or PCl_3 .¹⁶ We attempted both methods for the oxidation of **4** to the (Cp-amido) VCl_2 , but without success. Although both reagents react with **4**, as was seen by the formation of metallic copper in the reaction of **4** with CuCl and the change of the color of the solution from green to brown in both reactions, no Cp-amido vanadium complexes could be isolated from the reaction mixtures. It is possible that the PMe_3 ligand interferes with the oxidation of the vanadium center, since the phosphine ligand itself can also be oxidized. Therefore we attempted the synthesis of Cp-amido vanadium(III) complexes without a coordinated phosphine ligand.

Neither the reaction of $\text{VCl}_3(\text{THF})_3$ with the di-lithium salt $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{H})i\text{-Pr}]_2\text{Li}_2$, or a step-wise ligand introduction yielded a Cp-amido vanadium(III) complex. This is not surprising, since reaction of CpNa with $\text{VCl}_3(\text{THF})_3$ also failed to yield well-defined mono-Cp complexes.¹¹

A phosphine-free vanadium(III) Cp-amido complex was obtained when the phosphine complex **4** was reacted with an allyl-Grignard (THF, -30°C). The IR spectrum of the brown-red crystals (obtained after extraction with pentane at 0°C , and crystallization at -60°C), probably $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^3\text{-C}_3\text{H}_5)$, clearly shows a vibration for an η^3 -allyl group (1501 cm^{-1}) while the phosphine ligand is no longer observed. However, since the allyl complex is extremely soluble and possibly thermally labile, it could not be obtained analytically pure.

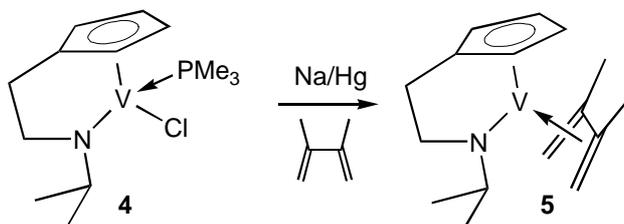
5.2.4 Synthesis of a vanadium(II) Cp-amido complex

In Chapter 3 (sections 3.2.1 and 3.2.3) the generation of cationic complexes by methyl abstraction with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ is described. This cocatalyst has also been used in the group 4 chemistry to convert M(II) diene adducts into M(IV) cationic complexes. The Cp-amido titanium(II) diene adduct $(\text{C}_5\text{Me}_4\text{SiMe}_2\text{N}t\text{-Bu})\text{Ti}(1,3\text{-pentadiene})$ reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to generate a cationic titanium(IV) allyl complex, which is an active olefin polymerization catalyst (Scheme 5).¹⁷


Scheme 5

Since oxidation of the Cp-amido vanadium(III) complex **4** to a Cp-amido vanadium(IV) complex was not successful, we synthesized a Cp-amido vanadium(II) diene adduct, which could act as a precursor for a Cp-amido vanadium(IV) olefin polymerization catalyst. Furthermore, this method yields a phosphine free Cp-amido vanadium complex, thus opening the possibility for selective oxidation of the vanadium center to the desired vanadium(IV) dichloride.

One-electron reduction of the vanadium(III) complex **4** with sodium amalgam in the presence of 2,3-dimethyl-butadiene (Scheme 6) led to the formation of a dark green complex, which could be crystallized from pentane.¹⁸ The IR spectrum of this paramagnetic complex reveals the absence of a phosphine ligand.


Scheme 6

Despite conformational disorder in the ethylene bridge around a crystallographic mirror plane, crystal structure determination showed that this complex is the vanadium(II) diene adduct $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^4\text{-C}_6\text{H}_{10})$

(**5**, Figure 3, Table 3). The diene ligand in **5** coordinates in a prone fashion, with C(8)-C(9) only 0.015 Å longer than C(9)-C(19) and V-C(9) 0.054 Å longer than V-C(8). This is in agreement with the Cp-amido titanium diene complexes (C₅Me₄SiMe₂NR)Ti(diene) (R = *t*-Bu, Ph, Scheme 5),^{17b} where the prone isomer (A) has mainly a Ti(II) diene character and the supine isomer (B) mainly a Ti(IV) metallacyclopentene character.

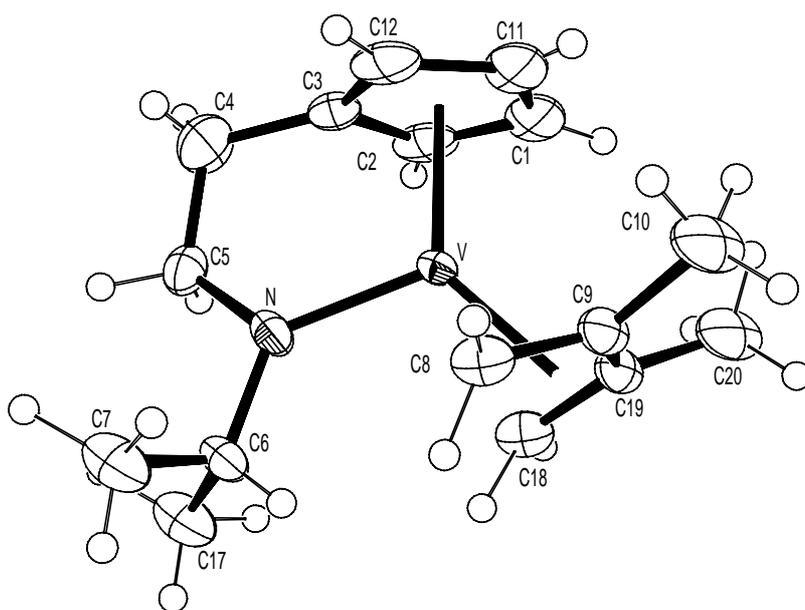


Figure 3: Crystal structure of **5**.

Table 3: Selected bond distances and angles in **5**.

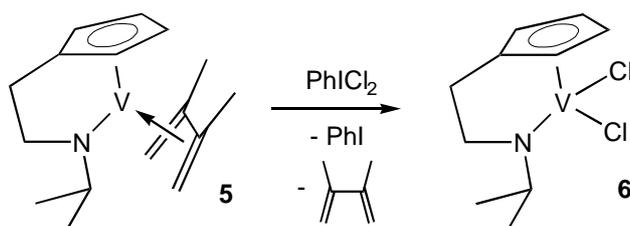
V-N	1.924(4)	Cg-V-N	110.17(6)
V-C(8)	2.192(4)	Cg-V-C(8)	133.66(11)
V-C(9)	2.246(3)	Cg-V-C(9)	117.55(10)
V-Cg	1.952(2)	N-V-C(8)	94.44(14)
C(8)-C(9)	1.412(5)	N-V-C(9)	128.30(14)
C(9)-C(19)	1.397(5)		

The vanadium(II) diene adduct **5** reacted with B(C₆F₅)₃ in pentane to form an unstable microcrystalline complex. The poor solubility of the product suggests that a zwitterionic complex vanadium(IV) allyl complex may have been formed, however, attempts to redissolve this complex in toluene only led to decomposition. The reaction of **5** with B(C₆F₅)₃ in toluene under ethene

pressure did not lead to ethene polymerization. It is possible that the expected vanadium(IV) allyl species that is generated in this reaction is too unstable (probably because of the strong oxidizing power of vanadium(IV) in combination with the stability of allyl radicals) and decomposes even in the presence of ethene. In general, vanadium(IV) allyl complexes are much less stable than their group 4 analogues, and non have been reported so far.

5.2.5 Synthesis of a vanadium(IV) Cp-amido complex

Oxidation of vanadium(II) complexes to vanadium(III) species has been reported for a variety of reagents,^{14,19} however, a possible subsequent oxidation to vanadium(IV) seems to be dependent on the ligand system. For example, decamethyl-vanadocene (Cp^*_2V) can be oxidized to the vanadium(IV) complex Cp^*_2Vl_2 using one equivalent of I_2 , whereas oxidation of vanadocene (Cp_2V) with I_2 does not go beyond the vanadium(III) complex Cp_2Vl , even with an excess of I_2 .¹⁹ The vanadium(I) complex $\text{Cp}^*\text{V}(\text{CO})_4$ can be oxidized by Cl_2 to the vanadium(IV) complex Cp^*VCl_3 .²⁰ For the synthesis of a Cp-amido vanadium(IV) dichloride from the Cp-amido vanadium(II) complex **5**, Cl_2 should be a suitable oxidizing reagent; to facilitate the addition of the correct stoichiometry, we used the crystalline PhlCl_2 as a source of Cl_2 .²¹



Scheme 7

The oxidation of **5** by PhlCl_2 is exothermic, and in order to control the reaction temperature the solvent (THF) was condensed onto a mixture of solid **5** and PhlCl_2 (liquid nitrogen temperature). After melting of the THF, the green

color of the solution changed to brown in a few seconds. In the reaction the diene and PhI are liberated (Scheme 7), as indicated by GC/MS analysis. Crystallization of the organometallic product from toluene²² yielded dark crystals of $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{Ni-Pr})\text{VCl}_2$ (**6**) in a 57% yield.

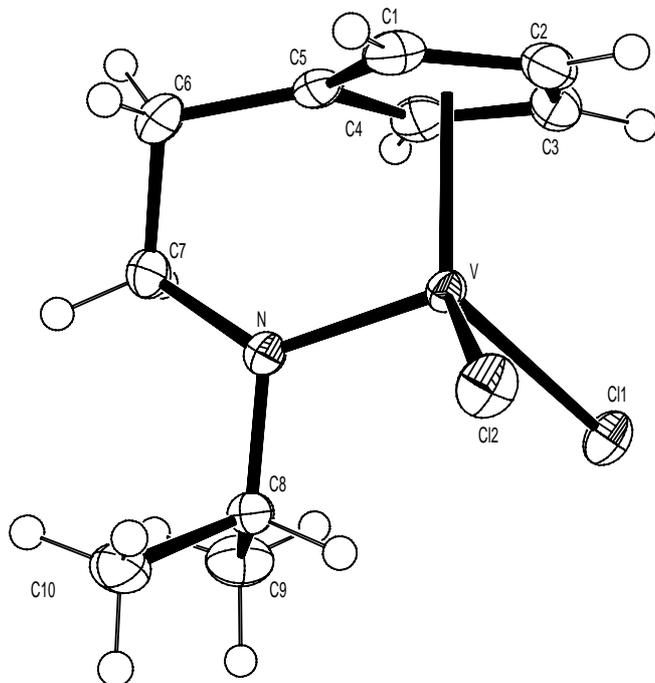


Figure 4: Crystal structure of **6**.

Table 4: Selected bond distances and angles in **6** (M = V) and **7** (M = Ti).⁵

	6	7		6	7
M-N	1.8308(13)	1.864(2)	Cg-M-N	105.11(4)	104.4(1)
M-Cl(1)	2.2879(5)	2.2752(11)	Cg-M-Cl(1)	119.90(2)	118.3(1)
M-Cl(2)	2.2958(4)	2.2996(12)	Cg-M-Cl(2)	122.09(2)	118.5(1)
M-Cg	1.9336(8)	2.008(4)	Cl(1)-M-Cl(2)	95.61(2)	103.01(2)
			N-M-Cl(1)	107.45(4)	104.98(8)
			N-M-Cl(2)	105.33(4)	106.53(7)

When the structure of the vanadium(IV) di-chloride **6** (Figure 4, Table 4) is compared to that of its d^0 titanium analogue $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{Ni-Pr})\text{TiCl}_2$ (**7**),⁵ the observed differences are small. The M-Cg and M-N distances are smaller for **6**, which can be explained by the smaller ionic radius of the V^{4+} ion. In contrast, the M-Cl distances are slightly longer for **6** (average 2.292 Å for **6**,

2.287 Å for **7**); the Cl(1)-M-Cl(2) angle in **6** ($95.61(2)^\circ$) is significantly smaller than in **7** ($103.01(2)^\circ$). These features are also observed when the crystal structures of the isostructural vanadium and titanium di-chloro complexes $(\text{MeCp})_2\text{VCl}_2$ (**8**) and $(\text{MeCp})_2\text{TiCl}_2$ (**9**) are compared.²³ EPR studies reveal that the extra electron in the d^1 complex **8** occupies an orbital in plane with the two chlorides and the metal, but perpendicular to the plane of the two Cp-centroids and the metal. The d^1 electron forces the two chlorides closer together, resulting in a more acute Cl-V-Cl angle. In order to minimize steric hindrance the V-Cl bonds are elongated. Since the structural features of the Cp-amido complexes **6** and **7** are comparable to those of the bis-Cp complexes **8** and **9**, we assume that the d^1 electron in **6** occupies an orbital with a similar orientation as described for **8** (Figure 5).

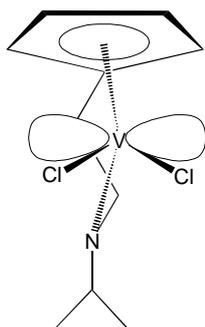


Figure 5: Orbital accomodating the d^1 electron in **8**.

5.2.6 Ethene polymerization by Cp-amido vanadium complexes

The synthesis of the Cp-amido vanadium(IV) di-chloro complex **6**, makes it possible to compare isostructural d^0 and d^1 metal complexes $(\text{Cp-amido})\text{MCl}_2$ ($\text{M} = \text{Ti}, \text{V}$) as catalyst precursors for olefin polymerization. The Cp-amido titanium(IV) di-chloro complex $(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{TiCl}_2$ (**7**) is active in the catalytic polymerization of ethene, after activation with MAO. In order to minimize deactivation of the catalyst by reduction, the complex was injected into the autoclave after this was charged with the MAO and put under ethene

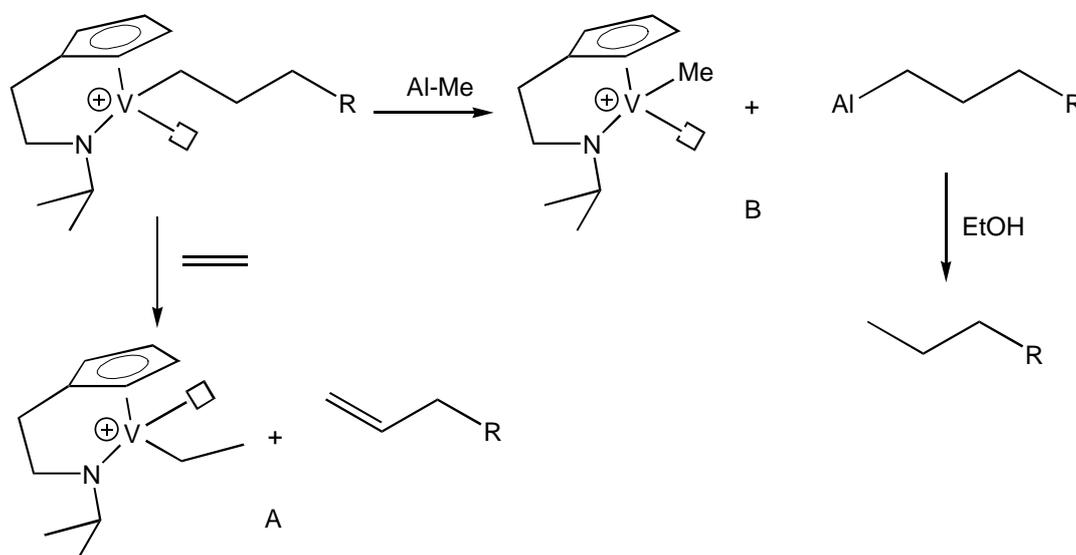
pressure.^{5b} The Cp-amido vanadium(IV) complex **6** was tested under identical conditions for comparison (Table 5).

Table 5: Ethene polymerization data for **6** and **7**.

complex	yield (g)	activity (kg·mol ⁻¹ ·h ⁻¹ ·bar ⁻¹)	M _w (g·mol ⁻¹)	M _n (g·mol ⁻¹)	M _w /M _n	melting point (°C)
6	4.7	209	14900	4900	3.0	129
7	12.0	534	139000	59500	2.3	134

15 μmol catalyst, 500 eq. MAO, 3 bar ethene, 50°C, 250 mL toluene, 30 minutes.

These first results show that the vanadium complex **6** is active in ethene polymerization after activation with MAO, although the activity is somewhat lower than that of the isostructural titanium complex **7**, and molecular weight of the produced polymer is much lower. Both catalysts are still active when the reaction is quenched after 30 minutes.



Scheme 8

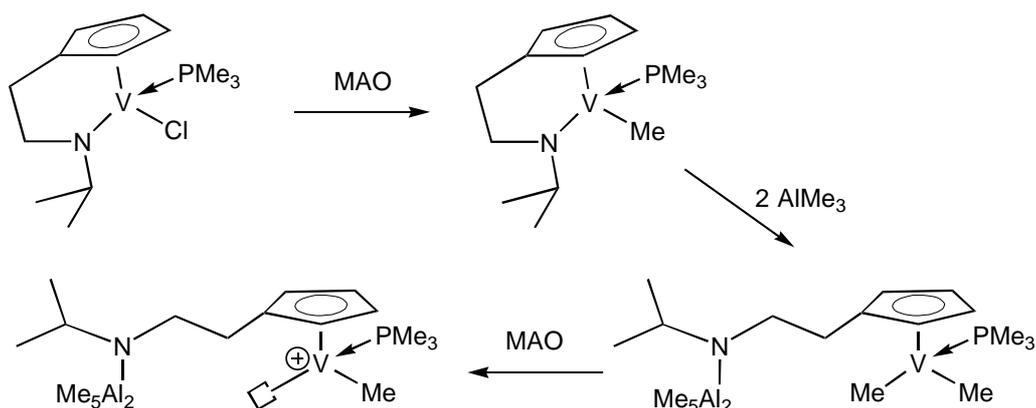
The short chain length of the polymers produced by the vanadium based catalyst allows for end group determination by ¹H NMR. The polymer has mainly vinylic end groups, indicative of termination by β-H transfer to monomer

(Scheme 8, route A). Integration of saturated and unsaturated end groups shows that about 13% of the polymer chains are fully saturated, indicative for termination by chain transfer to aluminum (Scheme 8, route B).²⁴

It is tempting to assume that the above described differences between the titanium and vanadium based catalyst are due to the effect of the extra d-electron in the $[(\text{Cp-amido})\text{VR}]^+$ cationic species, which is presumed to be the active species in the polymerization. However, from ethene polymerization experiments with Cp-amido vanadium(III) complexes activated by MAO it appears that the Cp-amido ligand is not inert towards the MAO cocatalyst.

When we tested the Cp-amido vanadium(III) complex **4** as catalyst precursor under identical conditions as used for **6** and **7**, this complex proved active in the ethene polymerization, producing polymer with remarkably similar properties as those of the polymer produced by **6**/MAO (**4**/MAO M_w : 15100; M_n : 7970; M_w/M_n : 1.9, activity of **4**/MAO is in the same range as that of **6**/MAO, but since the runs were performed with a different batch of MAO activities can not be compared). Activation of the di-chloro complexes **6** and **7** is presumed to proceed by methylation and subsequent methyl abstraction to generate the cationic $[(\text{Cp-amido})\text{MMe}]^+$ species (see Chapter 1, Scheme 1). However, when these two steps take place with the mono-chloro vanadium(III) complex **4**, the cationic $[(\text{Cp-amido})\text{V}(\text{PMe}_3)]^+$ species is generated, which will be inactive as a catalyst since it lacks a metal-alkyl bond.

A possible activation pathway is shown in Scheme 9: AlMe_3 , which is always present in MAO,²⁵ is known to react with metal-amido bonds to generate metal-methyl species;²⁶ subsequent methyl abstraction could now generate a cationic vanadium(III) methyl species.



Scheme 9

5.3 Conclusions

Vanadium(IV) Cp-amido complexes are not directly available from vanadium(IV) precursors. Instead, ligand introduction on vanadium(III) is performed, followed by one electron reduction and subsequent two electron oxidation. This route not only gives entry to vanadium(IV) Cp-amido complexes, but also opens the field of vanadium(III) and (II) chemistry.

The Cp-amido vanadium(IV) complex catalyzes the polymerization of ethene after activation with MAO, although the activity is lower than that of the isostructural titanium based catalyst. The much lower molecular weight of the polymer formed by the vanadium based catalyst compared to the titanium based catalyst, is a result of faster β -H elimination by the vanadium based catalysts. Chain transfer to aluminum is a minor termination pathway. However, polymerization experiments with a Cp-amido vanadium(III) complex yield polymer with very similar properties as the polymer produced with the vanadium(IV) based catalyst. It is therefore unclear what the actual active species is in these polymerizations. More experiments on these systems, preferably polymerization reactions by well-defined cationic vanadium(IV) species, for instance $[(\text{Cp-amido})\text{VMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$, are necessary.

5.4 Experimental

General considerations

All experiments were performed under nitrogen atmosphere using standard glove-box, Schlenk, and vacuum line techniques. Deuterated solvents (Aldrich) were either dried over Na/K alloy and vacuum transferred before use (C_6D_6 , THF- d_6) or degassed, flushed with nitrogen and stored over mol. sieves ($C_2D_2Cl_4$). Toluene, THF, diethyl ether and pentane were distilled from Na or Na/K alloy before use. The following were prepared according to literature procedures: $C_5H_5(CH_2)_2NH*i*-Pr$,²⁷ (η^5, η^1 - $C_5H_4(CH_2)_2N*i*-Pr$) $TiCl_2$ (**7**),^{5a} $PhCl_2$,²¹ PMe_3 using $MeMgI$ instead of $MeMgBr$,²⁸ $VCl_3(THF)_3$,²⁹ $MeLi$ /diethyl ether (Aldrich) was used as purchased, 2,3-dimethyl-1,3-butadiene (Aldrich) was degassed, dried over $MgSO_4$ and distilled before use. Ethene (AGA 99.5%) was passed over a supported copper scavenger (BASF R 3-11) and mol. sieves (3\AA) before being passed to the reactor. NMR spectra were run on a Varian Unity-500 spectrometer. IR spectra were recorded from nujol mulls between KBr discs on a Mattson Galaxy 4020 FT-IR spectrophotometer. GC analyses were performed on a HP 6890 instrument equipped with a HP-1 dimethylpolysiloxane column (19095 Z-123). GC/MS spectra were recorded at 70 eV using a HP 5973 mass-selective detector attached to a HP 6890 GC as described above. DSC was performed on a Perkin-Elmer DSC 7 calorimeter; melting points were determined from the second heating run. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations. GPC measurements were carried out at the University of Groningen by high temperature GPC ($150^\circ C$), using 1,2,4-trichlorobenzene as solvent and narrow MWD polystyrene standard samples as references. The measurements were performed on a LC-1000 system (Spectra Physics) equipped with 2 PL-Gel mixed-C columns, RALLS light scattering detector, H502 viscometer (Viscotek), refractive index detector and DM400 data manager (Viscotek).

Synthesis of (η^5, η^1 - $C_5H_4CH_2CH_2N(H)*i*-Pr$) $VCl_2(PMe_3)$ (**3**)

To a suspension of 0.61 g $VCl_3(THF)_3$ (1.6 mmol) in 25 mL of THF, 0.4 mL of PMe_3 (3.8 mmol) was added. The resulting brown solution was stirred for an hour at ambient temperature, and then cooled to $-80^\circ C$. A solution of 0.15 g Me_3SiCH_2Li (1.6 mmol) in 5 mL THF was slowly added by syringe to a solution of 0.25 g $C_5H_5CH_2CH_2N(H)*i*-Pr$ (1.6 mmol) in 3 mL of THF (cooled in an ice bath) and subsequently stirred for 30 min. The solution containing the lithiated ligand was added drop wise to the cold VCl_3 -solution, after which the mixture was allowed to warm up. At $-40^\circ C$ the color of the solution changed from brown to purple. The solution was brought to room temperature and stirred overnight. The volatiles were removed *in vacuo*, and the resulting purple solid was stripped of residual THF by stirring with 20 mL of pentane which was subsequently pumped off. After extraction with warm toluene, the solvent was removed from the extract *in vacuo* and the resulting solid was redissolved in 15 mL of THF. Crystallization was achieved by slow diffusion of pentane vapor into the solution. Yield: 0.33 g (0.94 mmol, 59%) of purple crystalline **3**. These crystals were suitable for X-ray structure determination.

$^1\text{H NMR}$ (500 MHz, THF- d_8 , 25°C): δ 6.5 ($\Delta\nu_{1/2} = 820$ Hz, 6H, CH_3 of *i*-Pr), 4.0 (br, overlaps solvent), -17.8 ($\Delta\nu_{1/2} = 2150$ Hz, 9H, PMe_3). *IR*: 635 (w), 669 (m, PMe_3), 735 (s, PMe_3), 816 (s), 849 (w), 866 (w), 880 (m), 945 (s, PMe_3), 990 (s), 1040 (s), 1051 (s), 1119 (m), 1140 (m), 1157 (m), 1221 (m), 1256 (m), 1275 (m, PMe_3), 1298 (m, PMe_3), 1319 (w), 1341 (w), 1360 (sh), 1422 (m, PMe_3), 3082 (w), 3214 (m) cm^{-1} . *Anal. calcd for* $\text{C}_{13}\text{H}_{25}\text{VNPCl}_2$: C, 44.85; H, 7.24; N, 4.06; V, 14.63; Cl, 20.37. Found: C, 44.77; H, 7.30; N, 4.04; V, 14.55; Cl, 20.50.

Synthesis of (η^5, η^1 - $\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr}$) $\text{VCl}(\text{PMe}_3)$ (**4**)

From 3: To a solution of 0.71 g of **3** (2.0 mmol) in 15 mL THF, at 0°C, a cooled solution of 0.19 g $\text{Me}_3\text{SiCH}_2\text{Li}$ (2.0 mmol) in 5 mL THF was added drop wise. The color of the solution immediately changed from purple to green. After stirring for one more hour at room temperature, the volatiles were removed *in vacuo* and the green oil was stripped of residual THF by twice stirring with 10 mL pentane which was subsequently pumped off. The resulting green solid was extracted with a mixture of 2 mL pentane and 10 mL ether. Cooling this solution to -25 °C yielded 0.36 g (1.2 mmol, 58%) green crystalline **4** in two crops.

From $\text{VCl}_3(\text{THF})_3$: To a solution of 0.75 g $\text{VCl}_3(\text{THF})_3$ (2.0 mmol) in 30 mL THF, 0.45 mL of PMe_3 (4.3 mmol) was added. The solution was stirred for an hour after which it was cooled to -50 °C. A solution of 0.19 g $\text{Me}_3\text{SiCH}_2\text{Li}$ (2.0 mmol) in 5 mL THF was slowly added to an solution of 0.32 g $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{N}(\text{H})i\text{-Pr}$ (2.0 mmol) in 5 mL THF, cooled in an ice bath, and stirred for half an hour. This solution was slowly added to the VCl_3 -solution at -50°C, and the color of the solution changed from brown to purple in a minute. The solution was brought to room temperature, and stirred overnight. The mixture was then cooled to 0°C and a cold solution of 0.19 g $\text{Me}_3\text{SiCH}_2\text{Li}$ (2.0 mmol) in 5 mL THF was slowly added. The color of the solution changed from purple to green. The solution was brought to room temperature and stirred for an additional hour. The volatiles were then removed *in vacuo* and the green solid was stripped of residual THF by stirring with 15 mL of pentane which was subsequently pumped off. The solid was extracted with a mixture of 5 mL pentane and 5 mL ether and cooled to -70 °C, from which **4** was obtained as green crystals in two crops, yielding 0.18 g (0.62 mmol, 31%). Recrystallization by slow cooling of a pentane/ether solution of **4** produced crystals suitable for an X-ray structure determination.

$^1\text{H NMR}$ (500 MHz, C_6D_6 , 25°C): δ 14.0 ($\Delta\nu_{1/2} = 240$ Hz, 3H, *i*-Pr Me), 7.6 ($\Delta\nu_{1/2} = 210$ Hz, 3H, *i*-Pr Me), -0.6 ($\Delta\nu_{1/2} = 260$ Hz, 9H, PMe_3). *IR*: 635 (w), 665 (s, PMe_3), 733 (s, PMe_3), 783 (m), 804 (m), 814 (s), 841 (w), 945 (s, PMe_3), 990 (m), 1038 (m), 1119 (m), 1140 (m), 1150 (m), 1171 (m), 1283 (m, PMe_3), 1298 (w, PMe_3), 1308 (w), 1319 (w), 1341 (m), 1424 (w, PMe_3), 3082 (w), 3214 (m) cm^{-1} . *Anal. calcd for* $\text{C}_{13}\text{H}_{24}\text{VNPCl}$: C, 50.09; H, 7.76; N, 4.49; V, 16.34; Cl, 11.37. Found: C, 49.95; H, 7.91; N, 4.29; V, 16.27; Cl, 11.80.

Synthesis of (η^5, η^1 - $\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr}$) $\text{V}(\eta^4\text{-C}_6\text{H}_{10})$ (**5**)

From 4: To a solution of 0.67 g of **4** (2.1 mmol) in 20 mL of THF, 2,3-dimethyl-1,3-butadiene (0.75 mL, 6.3 mmol) was added to the green solution. 49 mg of Na-sand (2.1 mmol) was added to 50 g of frozen Hg and carefully dissolved by thawing out the Hg. When the Na/Hg was at room temperature it was added to the vanadium solution, and the solution was stirred for two hours. The dark green THF solution was transferred into a new Schlenk and the residual Hg was washed twice with 5 mL THF. All THF solutions were combined, the volatiles removed *in vacuo*, and the resulting dark solid stripped twice with 10 mL pentane. The solid was then extracted twice with 30 mL pentane and crystallized by cooling to -25 °C. **5** was obtained as dark green crystals, 0.14 g (0.50 mmol, 24%).

From $VCl_3(THF)_3$: 6.59 g $VCl_3(THF)_3$ (17.6 mmol) was dissolved in 150 mL THF and 4.0 mL PMe_3 (38.6 mmol) was added. The solution was stirred for an hour after which it was cooled with an alcohol bath (bath temperature -50 °C). 20 mL 0.88 M MeLi solution in ether (17.6 mmol) was slowly added (5 minutes) to an ice-cooled solution of 2.71 g $C_5H_5CH_2CH_2N(H) i-Pr$ (17.6 mmol) in 20 mL THF and stirred for half an hour. The cooled ligand solution was slowly added to the cooled vanadium solution, and stirred at low temperature for one hour. The solution was then heated to room temperature, stirred for one night, and cooled with an alcohol bath (bath temperature -30 °C). 20 mL 0.88 M MeLi solution in ether (17.6 mmol) was slowly added (5 minutes). The solution was stirred at low temperature for half an hour, and at room temperature for two more hours, after which 2.5 mL 2,3-di-methyl-butadiene (22.1 mmol) was added. 0.40 g Na-sand (17.6 mmol) was added to 140 g of frozen Hg and carefully dissolved by thawing out the Hg. When the Na/Hg was at room temperature it was added to the vanadium solution, and the solution was stirred for four hours. The dark green THF solution was concentrated and transferred into a new Schlenk and the residual Hg was washed twice with 20 mL THF. All THF solutions were combined, the volatiles removed *in vacuo*, and the resulting dark solid stripped twice with 15 mL pentane. The solid was then extracted twice with 30 mL pentane and crystallized by cooling to -60 °C. **5** was obtained as dark green crystals in four portions, total 3.15 g (11.2 mmol, 63%). These crystals were suitable for single crystal X-ray structure determination.

1H NMR (C_6D_6 , 25 °C): δ 21.6 ($\Delta\nu_{1/2} = 900$ Hz), 4.9 ($\Delta\nu_{1/2} = 300$ Hz), -3.6 ($\Delta\nu_{1/2} = 240$ Hz). IR: 851(w), 864(w), 897(m), 955(m), 1026(s), 1053(s), 1121(m), 1146(m), 1165(m), 1230(m), 1262(m), 1379(w), 3040(w), 3090(w) cm^{-1} . Anal. calcd for $C_{16}H_{25}VN$: C: 68.07, H: 8.93, N: 4.96, V: 18.04; found: C: 65.92, H: 8.75, N: 4.95, V: 17.68. Carbon analyses, determined on several independently prepared samples of this compound, were consistently found to be too low, whereas the H, N and V values were as expected. This may be related to explosive decomposition of the compound in the analyzer.

Synthesis of (η^5, η^1 - $C_5H_4CH_2CH_2N i-Pr$) VCl_2 (**6**)

Onto a solid mixture of 0.30 g of **5** (1.1 mmol) and 0.30 g of $PhCl_2$ (1.1 mmol), 20 mL THF was condensed at liquid nitrogen temperature. Subsequently the mixture was thawed out.

Upon melting of the THF, a green solution formed which then quickly changed to brown. After reaching room temperature, the solution was stirred for an additional hour. The volatiles were removed *in vacuo* and the solid was stripped of remaining volatiles by stirring with 15 mL of toluene which was subsequently pumped off. The formation of 2,3-dimethyl-1,3-butadiene and iodobenzene as main organic reaction products was observed by GC/MS analysis of the volatiles. The solid was extracted with hot toluene. Cooling the extract to -25°C yielded 0.17 g (0.63 mmol, 57%) of **6** as red-brown crystals. Recrystallization by diffusion of pentane vapor into a THF solution yielded crystals suitable for X-ray structure determination.

$^1\text{H NMR}$ (THF- d_8 , 25°C): δ -0.8 ($\Delta\nu_{1/2} = 170$ Hz, *i*-Pr Me). IR: 629 (w), 685 (w), 723 (m), 781 (w), 810 (s), 826 (m), 845 (m), 866 (m), 945 (w), 959 (w), 974 (m), 1003 (w), 1017 (w), 1034 (w), 1053 (w), 1071 (w), 1111 (w), 1146 (m), 1163 (w), 1173 (w), 1231 (w), 1254 (m), 1314 (w), 1327 (w), 1339 (w), 3081 (w), 3177 (w) cm^{-1} . Anal. calcd for $\text{C}_{10}\text{H}_{15}\text{VNCl}_2$: C: 44.31, H: 5.58, N: 5.17, V: 18.79, Cl: 26.16; found: C: 44.36, H: 5.50, N: 5.23, V: 18.72, Cl: 25.69.

Ethene polymerization experiments

Polymerization reactions were carried out in a thermostated (electrical heating, water cooling), pressure-controlled Medimex 1l stainless steel autoclave, under batch conditions. For each run, the autoclave was charged with 250 mL toluene and 5.5 mL of a 1.4 M MAO (7.7 mmol) solution in toluene. The autoclave was heated to 50 °C and pressurized with ethene (3 bar). A catalyst precursor solution was made by dissolving 15 μmol of either **4**, **6** or **7** in 10 mL of toluene and polymerization was started by injecting this solution into the autoclave, ethene was continuously fed to the reactor. After 30 min. the runs were interrupted by the injection of 10 mL of methanol. The reactor was then vented and opened to the atmosphere. The polyethene was stirred in a mixture of 300 mL of methanol and 100 mL 0.5 M HCl in H_2O for several hours, collected on a glass frit and rinsed four times with 100 mL of methanol. The products were then dried *in vacuo* at 80 °C.

4/MAO: yield: 7.0 g; M_w : 15100; M_n : 7970; M_w/M_n : 1.9.

6/MAO: yield: 4.7 g; M_w : 14900; M_n : 4900; M_w/M_n : 3.0; melting point: 129 °C; $^1\text{H NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_2$, 125°C): δ 5.97 (m, R- $\text{CH}_2\text{-CH=CH}_2$), 5.04 (d, $J = 17.1$ Hz, R- $\text{CH}_2\text{-CH=CHH}$), 4.98 (d, $J = 10.3$ Hz, R- $\text{CH}_2\text{-CH=CHH}$), 2.10 (q, $J = 7.1$ Hz, R- $\text{CH}_2\text{-CH=CH}_2$), 0.94 (t, $J = 6.9$ Hz, CH_3).

7/MAO: yield: 12.0 g; M_w : 139000; M_n : 59500; M_w/M_n : 2.3; melting point: 134 °C.

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