Vanadium complexes containing amido functionalized cyclopentadienyl ligands

Witte, Petrus Theodorus

Chapter 3

Generation of cationic vanadium(V) complexes

3.1 Introduction

Cationic alkyl species are presumed to be the active species in the catalytic olefin polymerization (see Chapter 1).[1] MAO (MethylAluminOxane) is often used as a cocatalyst for the generation of these cationic species, but since MAO is an ill-defined system,[2] and a large excess of the cocatalyst is needed, the reaction mixtures are difficult to study. Well-defined cationic complexes can be generated by alkyl abstraction from a metal alkyl compound with a strong Lewis acid such as $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$, or by protonation with a Brønsted acid, for instance $[PhNHMe_2][B(C_6F_5)_4]$ (see Chapter 1).[3] Most of this work has been performed on group 4 metal complexes, and the number of cationic vanadium catalysts generated with these cocatalysts is limited to only a few examples.[4]

This chapter describes the generation and characterization of cationic Cp-amido vanadium(V) complexes from neutral vanadium methyl complexes described (see Chapter 2). Alkyl abstraction by $B(C_6F_5)_3$ generated the expected $[(Cp\text{-}amido)V(NR)][MeB(C_6F_5)_3]$ complexes, which exists as a mixture of the solvent separated and contact ion pair in solution. The ratio between these two species depends on the solvent. Alkyl abstraction by $[Ph_3C][B(C_6F_5)_4]$ generated $[(Cp\text{-}amido)V(NR)][B(C_6F_5)_4]$, which is only present as the solvent separated ion pair in solution. The attempted generation of $[(Cp\text{-}amido)V(NR)][B(C_6F_5)_4]$ by protonation with $[PhNHMe_2][B(C_6F_5)_4]$ resulted in activation of the substituent on the amido functionality of the Cp-amido ligand.

The cationic complexes described in this chapter are unsuitable for olefin polymerization, since they lack a V-C(alkyl) bond. However, this allows for a study of the reactivity of the V-N(amido) and V-N(imido) bonds towards unsaturated substrates. In the cationic complex $[(CpCH_2CH_2N$*i*-Pr)V(N*t*-

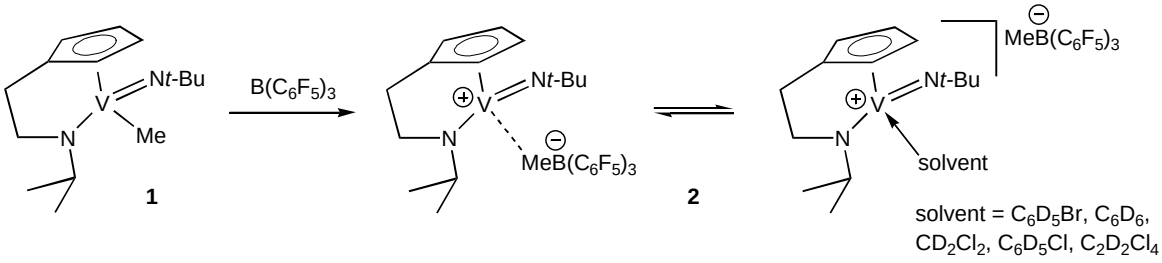
Bu)][MeB(C_6F_5)$_3$], insertion of 2,3-dimethyl-butadiene and 2-butyne into the V-N(amido) bond was observed, generating aza-metallacyclic complexes. No reactivity of the V-N(imido) bond was observed.

Isolation of the cationic complexes described in this chapter as crystalline solids proved difficult. Therefore, many of the complexes were generated *in situ* and studied by different NMR techniques.

3.2 Results and Discussion

3.2.1 Methyl abstraction from (η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*t*-Bu)

A frequently employed method to generate cationic complexes is alkyl (methyl or benzyl) abstraction by the Lewis acid B(C_6F_5)$_3$. The anion [RB(C_6F_5)$_3$]$^-$ (R = Me, CH_2Ph) thus formed can remain coordinated to the metal center or dissociate, depending on the circumstances (see Chapter 1, section 1.3). Methyl abstraction from (η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*t*-Bu) (**1**) by B(C_6F_5)$_3$ in pentane formed [(η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)V(N*t*-Bu)][MeB(C_6F_5)$_3$] (**2**, Scheme 1) as an analytically pure orange precipitate, in an 81% isolated yield.



Scheme 1

The ^{19}F NMR chemical shift difference between the *p*-F and *m*-F resonances of the C_6F_5 groups of the anion ($\Delta\delta_{m-p}$) is very sensitive to anion coordination.[5] In C_6D_5Br solution **2** is predominantly present as the solvent separated ion pair, as indicated by a $\Delta\delta_{m-p}$ of 2.4 ppm (contact ion pair: $\Delta\delta_{m-p}$ > 3 ppm). Small resonances in the ^{19}F NMR spectrum of **2** ($\Delta\delta_{m-p}$ = 4.3 ppm)

indicate that the contact ion pair is also present in C_6D_5Br, although in a small amount (< 10%, Scheme 1).

There is a significant difference in the ^1H NMR methyl resonance between **1** and **2**. For the methyl complex **1** this resonance appears at 0.7 ppm ($\Delta\nu_{½}$ 7 Hz), for **2** it appears at 1.13 ppm ($\Delta\nu_{½}$ 25 Hz) in C_6D_5Br, and an additional small resonance at -0.2 ppm can be assigned to the contact ion pair. This is confirmed by NMR measurements of **2** in the apolar solvent C_6D_6, where the ^{19}F NMR indicates that **2** is predominantly present as the contact ion pair ($\Delta\delta_{m\text{-}p}$ = 4.4 ppm), and the methyl resonance appears at -0.2 ppm ($\Delta\nu_{½}$ 24 Hz) in the ^1H NMR spectrum. In chlorinated solvents (CD_2Cl_2, C_6D_5Cl and $C_2D_2Cl_4$) ^1H NMR spectra show a mixture of solvent separated and contact ion pair. From the ^{19}F NMR spectra the ratios of the two species is determined (ratio solvent separated: contact ion pair; CD_2Cl_2 4:1; C_6D_5Cl 2:1; $C_2D_2Cl_4$ 1:2).

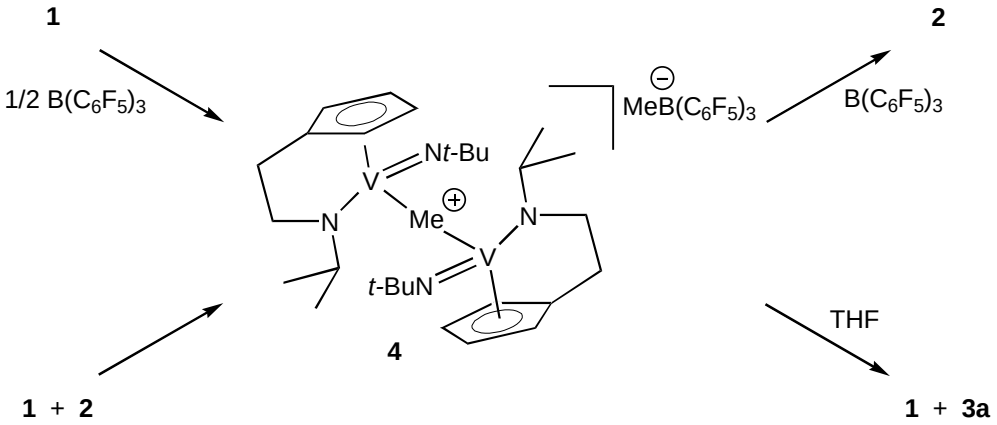
Methyl abstraction from **1** by the Lewis acidic trityl reagent $[Ph_3C][B(C_6F_5)_4]$ in C_6D_5Br generated Ph_3CMe and $[(\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(N\textit{t}\text{-}Bu)][B(C_6F_5)_4]$ (**2**'), which has an identical ^1H NMR spectrum as the solvated cation **2** in C_6D_5Br. In the ^{19}F NMR spectrum the $[B(C_6F_5)_4]^-$ anion is observed.

Although solvent coordination to **2** has not been observed directly by spectroscopic methods, it is a reasonable assumption.[6] Theoretical calculations, that will be presented in Chapter 4, predict a very low inversion barrier (< 2 kJ·mol^{-1}) for the pyramidal vanadium metal center in the unsolvated cation $[(Cp\text{-amido})V(N\textit{t}\text{-}Bu)]^+$. However, in the ^1H and ^{13}C NMR spectra the cationic complex **2** is observed as an asymmetric complex, indicating that inversion of the metal center does not occur (on NMR time scale), probably because of solvent stabilization.

Addition of Lewis bases to a C_6D_5Br solution of **2** cleanly generated the corresponding adducts $[(\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(L)(N\textit{t}\text{-}Bu)][MeB(C_6F_5)_3]$ (**3a**: L = THF; **3b**: L = PMe_3; **3c**: L = $PhNMe_2$). In the ^1H and ^{13}C NMR spectra, resonances of the Lewis bases shift slightly upon coordination. In the ^{31}P NMR spectrum of **3b** a broad plateau-shaped resonance is observed for the coordinated PMe_3 ligand, because of unresolved coupling with the quadrupolar

vanadium nucleus. Complex **3a** showed no exchange (on the NMR time scale) with an excess (~3 eq.) of THF. The Lewis base adducts **3** are insoluble in C_6D_6.

Reaction of **1** with 0.5 equivalent of $B(C_6F_5)_3$ in C_6D_5Br did not generate an equimolar mixture of **1** and **2**, but a new complex, which was identified as the methyl bridged bimetallic Cp-amido vanadium(V) complex [{(η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)V(N*t*-Bu)}$_2$(μ-Me)][$MeB(C_6F_5)_3$] (**4**, Scheme 2). Since **4** has two asymmetric vanadium centers it can consist of two diastereomers, as previously observed in methyl bridged bimetallic *ansa*-zirconocenes.[7] Resonances of the Cp-amido and imido ligand of **4** in the ^{1}H and ^{13}C NMR are comparable to those of **1** and **2**; only in the ^{13}C NMR spectrum are some of the resonances for the two diastereomers resolved. Unlike the ^{1}H NMR resonances for the methyl group of the neutral Cp-amido methyl complexes, which are all broadened due to unresolved coupling with the quadrupolar vanadium nucleus ($\Delta\nu_{1/2}$ 7 - 18 Hz), the resonance of the bridging methyl group in **4** is relatively sharp ($\Delta\nu_{1/2}$ 2 Hz).



Scheme 2

The bimetallic complex **4** could also be generated by mixing equimolar amounts of **1** and **2**, and reacted with additional $B(C_6F_5)_3$ to form **2**. Addition of THF to a solution of **4** resulted in the formation of an equimolar mixture of the neutral methyl complex **1** and the cationic THF adduct **3a** (Scheme 2).

3.2.2 Thermolysis of $[(\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(N\textit{t}\text{-}Bu)][MeB(C_6F_5)_3]$

Although the cationic complex **2** was stable as a solid at room temperature for several months, decomposition was observed in solution. In C_6D_5Br an unidentified solid was formed (two days at room temperature); in C_6D_6 slow and clean decomposition to a new complex was observed when a sealed NMR tube was kept at room temperature for about one year (at 60°C the decomposition was faster, but unidentified side products were formed as well). From the ^1H and ^{13}C NMR spectra it can be concluded that the η^5,η^1-$C_5H_4CH_2CH_2N\textit{i}$-Pr structure is retained in the decomposition product. The ^{19}F NMR spectrum showed the formation of $MeB(C_6F_5)_2$,[3d] and a new complex which is probably $(\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(C_6F_5)(N\textit{t}\text{-}Bu)$ (**5**, Equation 1).

$$[(\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(N\textit{t}\text{-}Bu)][MeB(C_6F_5)_3] \longrightarrow (\eta^5,\eta^1\text{-}C_5H_4CH_2CH_2N\textit{i}\text{-}Pr)V(C_6F_5)(N\textit{t}\text{-}Bu) + MeB(C_6F_5)_2 \quad (1)$$

The transfer of a C_6F_5 group from a borate anion to a cationic metal center has been observed before,[3d] and is indicated by a downfield shift of the *o*-F resonance of the newly formed M-C_6F_5 group in the ^{19}F NMR. For example, the cationic zirconium complex $[\{1,2\text{-}(Me_3Si)C_5H_3\}_2ZrMe][MeB(C_6F_5)_3]$ decomposes in one day at room temperature to generate $MeB(C_6F_5)_2$ and $\{1,2\text{-}(Me_3Si)C_5H_3\}_2Zr(Me)(C_6F_5)$, which displays two *o*-F resonances at -109 and -110 ppm.[3d] In the vanadium complex **5** rapid rotation of the C_6F_5 ligand occurs and only one *o*-F resonance is found (-109 ppm).

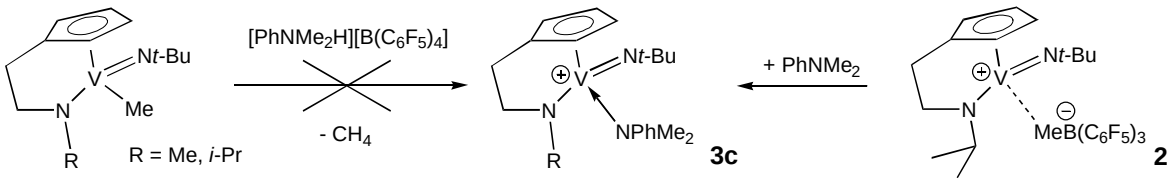
3.2.3 Methyl abstraction from other vanadium(V) methyl complexes

Methyl abstractions from other vanadium(V) methyl complexes containing the Cp-amido ligand or unbridged Cp and amido ligands (see Chapter 2) were performed *in situ* in C_6D_5Br using $B(C_6F_5)_3$. The cationic

complexes [(η^5,η^1-$C_5H_4CH_2CH_2NMe$)V(N*t*-Bu)][$MeB(C_6F_5)_3$] (**6**), [(η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)V(N*p*-Tol)][$MeB(C_6F_5)_3$] (**7**), [(*t*-BuN)VCp(N*i*-Pr_2)][$MeB(C_6F_5)_3$] (**8**) and [(*p*-TolN)VCp(N*i*-Pr_2)][$MeB(C_6F_5)_3$] (**9**) were identified by ^{1}H, ^{13}C, ^{51}V and ^{19}F NMR. In all four complexes the ^{19}F NMR spectrum shows that a mixture of the solvent separated and the contact ion pair is present in solution; no significant differences in the ratio between the two species was observed. Just as for the cationic Cp-amido vanadium(V) complex **2** described above, the solvent separated ion pair is the predominant species in C_6D_5Br (> 90%).

3.2.4 Cationic complexes through protonation

As mentioned in the introduction of this chapter, another way to generate cationic complexes is by protonation with a Brønsted acid. A reagent frequently used for this reaction is [$PhNMe_2H$][$B(C_6F_5)_4$], which upon reaction with a metal alkyl species liberates the alkyl group as the alkane and generates the conjugate base $PhNMe_2$. Thus, protonation of the Cp-amido vanadium methyl complex **1** with [$PhNMe_2H$][$B(C_6F_5)_4$] was expected to generate methane and [(η^5,η^1-$C_5H_4CH_2CH_2N$*i*-Pr)V($NPhMe_2$)(N*t*-Bu)][$B(C_6F_5)_4$] (Scheme 3). The cationic part of this complex was generated previously by reaction of the cationic complex **2** with $PhNMe_2$ (complex **3c**, section 3.2.1).



Scheme 3

In the protonation of (η^5,η^1-$C_5H_4CH_2CH_2NR$)VMe(N*t*-Bu) (R = Me, *i*-Pr; in C_6D_5Br or THF-d_8) gas evolution was observed, but the expected aniline adducts were not formed. Instead, the substituent on the amido functionality of the Cp-amido ligand was activated. In the ^{1}H NMR spectra of the protonation

products, the former NMe group appears as two doublets (J_{H-H} = 9 Hz , integral 2 x 1H), and the former N*i*-Pr group as two singlets (integral 2 x 3H), indicating that the amido substituents have been deprotonated. In the ^{13}C NMR spectra the NC resonances appear at 65 ppm (t, 163 Hz) and 78 ppm (s) respectively. These resonances compare well to those of the tantalum complex Cp*Ta(H_2CNMe)Me_2 (N*C*: 65 ppm, t, 155 Hz), formed by thermal decomposition of the amido complex Cp*Ta(NMe_2)Me_3.[8] Based on the ^1H and ^{13}C NMR spectra, the tantalum complex is described as a metallacyclic structure (Figure 1A). In contrast, deprotonation of one of the *i*-Pr groups of the hafnium di-aza-butadiene complex Cp*Hf(σ^2,π-(*i*-Pr)$_2$-DAB)Cl, yields an imine adduct (Figure 1B),[9] of which the NC resonance (157 ppm, s) compares better to free the imine MeN=*C*H_2 (N*C*: 155 ppm, no J_{C-H} reported).[10]

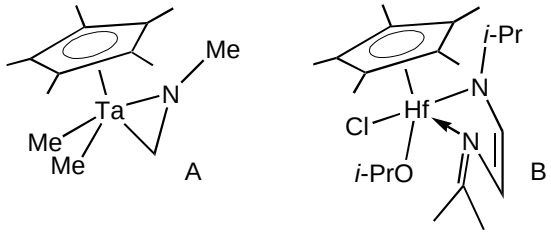
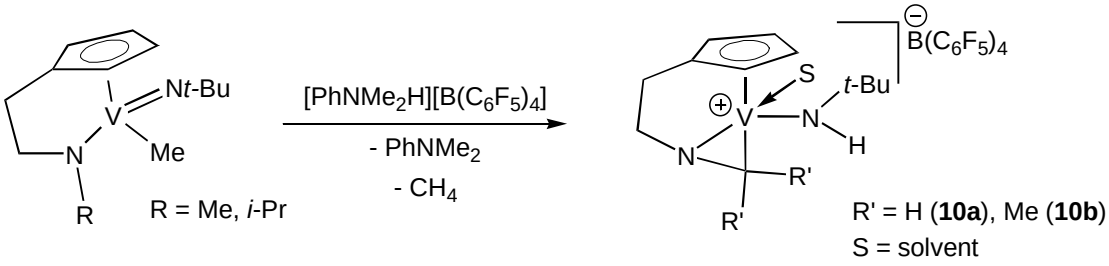


Figure 1: Other imine species

After the protonation of the vanadium complexes with [PhNMe_2H][B(C_6F_5)$_4$] a new resonance appears (integral 1H) with a solvent dependent chemical shift (5.5 ppm in THF-d_8, 3.7 in C_6D_5Br). The (unresolved) coupling pattern that is observed for this resonance does not arise from coupling with other protons, as was shown in a 2D-^1H,^1H COSY NMR experiment. Instead, it probably arises from coupling with a nitrogen atom, therefore this resonance is ascribed to a N-H group. No resonances are observed for the V-Me group.

We propose that protonation of the imido ligand has taken place, after which the amido substituent is deprotonated by the V-Me group to generate methane and a vanadium complex of the type [($C_5H_4CH_2CH_2NCR_2$)V(NH*t*-

Bu)][B(C_6F_5)$_4$] (**10a**: R = H; **10b**: R = Me, Scheme 4). Based on the ^{13}C NMR data complexes **10** are described as metallacyclic compounds.



Scheme 4

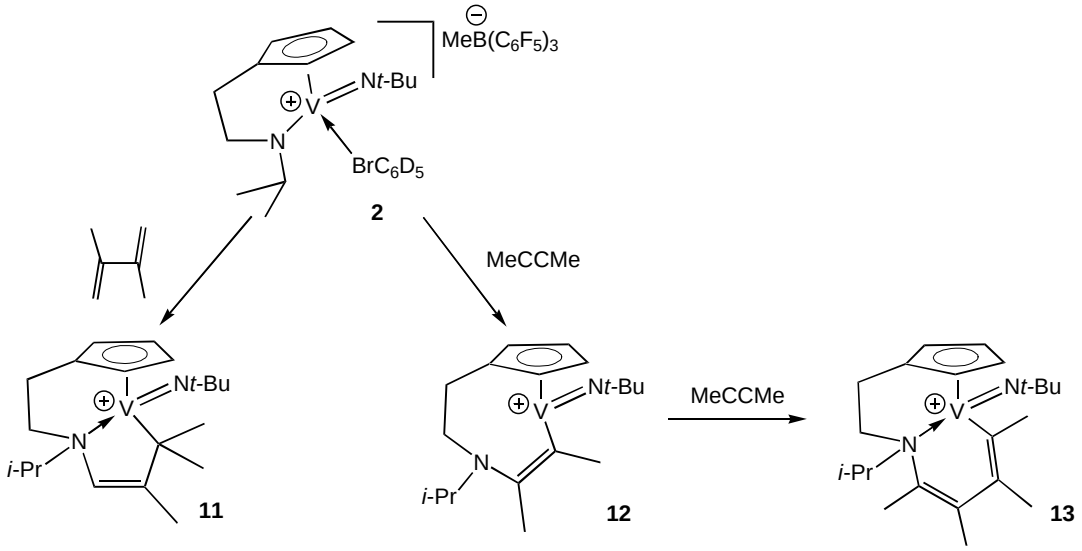
When complex **10b** was generated in C_6D_5Br, the formed $PhNMe_2$ did not coordinate to the vanadium center, and could be washed out by precipitating the cationic complex in pentane. When **10b** was generated in THF-d_8 and subsequently precipitated in pentane, the $PhNMe_2$ was also washed out. However, the ^{1}H NMR spectrum of this precipitated complex in C_6D_5Br was slightly different from the spectrum of **10b** in C_6D_5Br, probably because of coordination of THF-d_8 to the cationic vanadium center (no resonances of coordinated THF-d_8 could be observed in the ^{1}H or ^{13}C NMR spectra). Although no further experiments were performed to prove this, we believe that complexes **10** are stabilized in solution by solvent coordination, and that the aniline that is formed in the generation of **10** is too sterically hindered to coordinate to the vanadium center. This could also explain the results obtained in the generation of the sterically less hindered species **10a** in C_6D_5Br, where a mixture of compounds is formed, which are probably the solvated species and the aniline adduct.

3.2.5 Reactivity of [($C_5H_4CH_2CH_2N$*i*-Pr)V(N*t*-Bu)]$^+$ towards unsaturated substrates

The cationic complexes described in this chapter lack a metal-alkyl bond, and it is therefore unlikely that they will catalyze the polymerization of olefins.

However, they do give the opportunity to study the interaction of a cationic d^0 metal center with different substrates, and to study the relative reactivity of the V-N(amido) and V-N(imido) bonds in these complexes. The cationic Cp-amido complex **2** reacted with simple olefins like ethene and propene to form the corresponding olefin adducts. These d^0 metal olefin adducts will be extensively described in Chapter 4.

The reactivity of 2,3-dimethyl-butadiene or 2-butyne with **2**, described here, is very different from that of mono-olefins. The NMR data suggest that these substrates insert into the V-N(amido) bond to generate the complexes [{η^5,η^1,η^1-$C_5H_4CH_2CH_2N$(*i*-Pr)CH=C(Me)CMe_2}V(N*t*-Bu)][$MeB(C_6F_5)_3$] (**11**), [{η^5,η^1-$C_5H_4CH_2CH_2N$(*i*-Pr)$(CMe)_2$}V(N*t*-Bu)][$MeB(C_6F_5)_3$] (**12**) and [{η^5,η^1,η^1-$C_5H_4CH_2CH_2N$(*i*-Pr)$(CMe)_4$}V(N*t*-Bu)][$MeB(C_6F_5)_3$] (**13**, Scheme 5).



Scheme 5

The involvement of the V-N(amido) bond in the insertions is clearly indicated by the strong upfield shift of the CH resonance of the *i*-Pr substituent in the ^{1}H NMR spectrum. In all previously described (Cp-amido)V(NR)X complexes this proton points towards the metal center (Chapter 2, section 2.2.6) and experiences an anisotropic effect of the metal, resulting in a downfield shift in the ^{1}H NMR. After the insertion into the V-N(amido) bond, the

sp^3 hybridization of the nitrogen atom in the newly formed amine functionality moves the *i*-Pr group away from the metal, thereby eliminating the anisotropic effect. This is indicated in the ^{1}H NMR spectrum by an upfield shift of the methine proton (**2**: δ 5.7 ppm; **11**: δ 3.3 ppm; **12**: δ 2.2 ppm; **13**: δ 2.8 ppm; ligand precursor $C_5H_5(CH_2)_2NH$*i*-Pr: δ 2.6 ppm).

In the ^{1}H and ^{13}C NMR spectra of **12** and **13**, insertion of 2-butyne leads to respectively two and four new resonances for CH_3 groups. In the ^{13}C NMR spectra the carbon atom bonded directly to the vanadium is probably too broad to observe, and respectively one and three new quaternary carbons are found. In the ^{1}H and ^{13}C NMR spectra of **11**, three new CH_3 and one new CH group are observed, indicating that the diene did not insert into the V-N(amido) bond in the expected 1,2 or 1,4 fashion. The resonance of the CH group shows a large downfield shift (^{1}H: 7.55 ppm; ^{13}C: 183 ppm), and in the ^{1}H NMR NOE interactions with both methyls of the N*i*-Pr group and with the NCH_2 moiety of the ethylene bridge are observed (Figure 2). This clearly indicates that the reaction has taken place with the V-N(amido) bond, and not with the V-N(imido) bond. The N*t*-Bu group only has NOE interactions with two of the Cp protons.

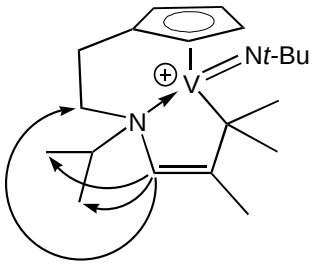
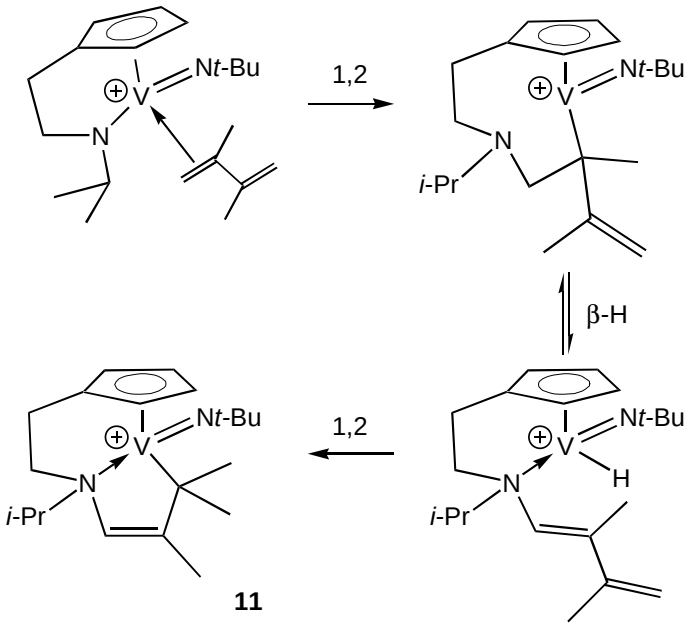


Figure 2: Selected NOE interactions in **11**

In the ^{51}V NMR spectra, complexes **11** and **13** appear at a comparable chemical shift (**11**: -492 ppm; **13**: -441 ppm), while **12** appears at -186 ppm. We propose that this large chemical shift difference is caused by amine decoordination in **12**, probably because of ring strain in the small four-membered ring.



Scheme 6

Complexes **12** and **13** are formed by insertion of 2-butyne in the V-N(amido) bond and subsequent insertion of a second molecule of 2-butyne in the newly formed V-C bond. Formation of **11** is less straight forward. A possible mechanism for the formation of **11** is shown in Scheme 6; a 1,2 insertion of one of the double bonds of the diene into the V-N(amido) bond takes place, followed by β-H elimination and subsequent insertion of the other double bond of the diene in the newly formed vanadium-hydride. The formation of **11** is not clean, and impurities may arise from a 2,1-insertion of one of the double bonds, or decomposition of one of the intermediates. Complex **11** is thermally stable in solution at room temperature for one week, unlike complexes **12** and **13** which decompose even at 0^{o}C.

Insertion of an unsaturated substrate into a metal-amido bond is not uncommon,[11] but has so far only been observed for polar substrates (for instance CO_2, SO_2), or for alkynes with strongly electron-withdrawing substituents (for instance CO_2Me). It is possible that coordination of the non-polar diene and alkyne substrates to the cationic vanadium center polarizes the

unsaturated carbon-carbon bond, thus making it susceptible for nucleophilic attack by the amido ligand.

In contrast to the high reactivity of the V-N(amido) bond, the V-N(imido) bond appears to be inert. Metal imido complexes are known to react with non-activated substrates with unsaturated carbon-carbon bonds (for instance 2-butyne, ethene) by a [2+2] cycloaddition, to form aza-metallacyclic products.[12] The cationic vanadium complex **2** can react with dimethyl-butadiene either by a [2+2] cycloaddition over the V-N(imido) bond or insertion into the V-N(amido) bond. The geometry of the complex only allows a subsequent β-H elimination to take place if the nitrogen atom decoordinates from the metal center (Scheme 6). Since this is only possible when the diene has reacted with the V-N(amido) bond, it can explain why no reaction of dimethyl-butadiene with the V-N(imido) bond is observed. Reaction of 2-butyne with the mixed amido imido vanadium complex $(RN)_2V(NHR)(OEt_2)$ (R = *t*-Bu_3Si) takes place exclusively with the imido ligand,[12a] and, as other examples,[12b] it is irreversible. It is therefore unclear why no reaction of 2-butyne with the V-N(imido) bond of **2** is observed.

3.3 Conclusions

Cationic vanadium(V) Cp-amido complexes could be obtained by methyl abstraction by the Lewis acid $B(C_6F_5)_3$ from the neutral metal methyl complexes, described in Chapter 2. In solution the complexes exist as a mixture of the solvent separated and the contact ion pair, and both species are observed in all used solvents. There appears to be no ligand influence in the ratio between solvent separated and contact ion pair, instead, this ratio is determined by the coordinating properties of the solvent. In chlorinated solvents (CD_2Cl_2, C_6D_5Cl, $C_2D_2Cl_4$) approximately the same amount of solvent separated and contact ion pair is observed. However, in C_6D_5Br, which has a similar dielectric constant as C_6D_5Cl, the major species is the solvent separated complex. Apparently, the bromine atom of bromobenzene is more Lewis basic than the chlorine atom of chlorobenzene.

Attempts to generate [(Cp-amido)V(N*t*-Bu)]$^+$ complexes by protonation with [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] led to the unexpected protonation of the imido ligand, and a subsequent deprotonation of the substituent on the amido functionality by the V-Me group. Such a deprotonation has not been observed in the neutral methyl precursors.

In the cationic complex [(C$_5$H$_4$CH$_2$CH$_2$N*i*-Pr)V(N*t*-Bu)][MeB(C$_6$F$_5$)$_3$], the imido functionality appeared to be inert towards C-C unsaturated substrates. Instead, insertion into the V-N(amido) bond was observed for 2,3-dimethyl-butadiene and 2-butyne. This is the first example known to us where insertion of an olefin or an apolar alkyne into a metal-amido bond was observed. It is possible that the C-C unsaturated bond is polarized by coordination to the cationic metal center, making it susceptible for a nucleophilic attack by the amido ligand.

3.4 Experimental

General considerations

All experiments were performed under nitrogen atmosphere using standard glove-box, Schlenk and vacuum line techniques. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use (C$_6$D$_6$, THF-d$_8$), or degassed and stored on mol. sieves under nitrogen (C$_6$D$_5$Br, C$_6$D$_5$Cl, CD$_2$Cl$_2$, C$_2$D$_2$Cl$_4$). Pentane and THF were distilled from Na/K alloy before use. PMe$_3$ was prepared according to literature procedures, using MeMgI in stead of MeMgBr.[13] B(C$_6$F$_5$)$_3$[14] was prepared according to literature procedures. [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] were kindly provided by Dr. H.J.G. Luttikhedde from Åbo Akademi University, Finland. (η^5,η^1-C$_5$H$_4$CH$_2$CH$_2$N*i*-Pr)VMe(N*t*-Bu) (**1**), (η^5,η^1-C$_5$H$_4$CH$_2$CH$_2$NMe)VMe(N*t*-Bu), (η^5,η^1-C$_5$H$_4$CH$_2$CH$_2$N*i*-Pr)VMe(N*p*-Tol), (*t*-BuN)VCp(N*i*-Pr$_2$)Me and (*p*-TolN)VCp(N*i*-Pr$_2$)Me are described in the previous chapter. 2,3-dimethyl-1,3-butadiene (Aldrich) was degassed, dried over MgSO$_4$ and distilled before use. 2-butyne was degassed and stored under nitrogen. NMR spectra were run on Varian Gemini 200, VXR-300 and VXR-500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to TMS, using residual solvent resonances as internal reference. ^{19}F NMR chemical shifts are reported in ppm relative to CFCl$_3$, which is used as an external reference. ^{19}F NMR shifts are only reported for **2** and **2**', and are the same for all other complexes. ^{51}V NMR chemical shifts are reported in ppm relative to VOCl$_3$, which is used as an external reference. Coupling constants (J) and line widths at half height ($\Delta\nu_{1/2}$) are reported in Hz. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Synthesis of $[(C_5H_4CH_2CH_2N\textit{i}\text{-Pr})V(N\textit{t}\text{-Bu})][MeB(C_6F_5)_3]$ (**2**)

In 2 mL of pentane 43 mg (0.15 mmol) of **1** was dissolved and slowly added to a stirred solution of 100 mg (0.19 mmol) of $B(C_6F_5)_3$ in 10 mL of pentane, and the resulting suspension was stirred for 5 more minutes. After 10 minutes an orange precipitate had settled and the solution was decanted. The orange powder was washed three times with 5 mL of pentane and dried *in vacuo*. This yielded 97 mg (0.12 mmol = 81%) of analytically pure **2** as an orange powder.

^{1}H NMR (500 MHz, C_6D_6, 25^{o}C): δ 5.86 (br, 1H, Cp), 5.80 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 5.59 (br, 1H, Cp), 5.46 (br, 1H, Cp), 4.74 (m, 1H, NC*H*H), 4.52 (br, 1H, Cp), 2.98 (dd, J_{H-H} = 7 / 13, 1H, NCH*H*), 2.28 (dd, J_{H-H} = 7 / 13, 1H, CpC*H*H), 1.44 (m, 1H, CpCH*H*), 0.84 (s, 9H, *t*-Bu), 0.63 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.47 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), -0.20 (br, $\Delta\nu_{½}$ = 24, 3H, BCH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_6, 25^{o}C): δ 148.9 (d, J_{C-F} = 242, C_6F_5), 142.9 (C_{ipso} of Cp), 139.3 (d, J_{C-F} = 240, C_6F_5), 137.6 (d, J_{C-F} = 245, C_6F_5), 112.6, 112.3, 102.1, 100.9 (4 CH of Cp), 75.5 (CH of *i*-Pr), 72.8 (NCH_2), 29.3 ($CpCH_2$), 30.5 (CH_3 of *t*-Bu), 21.3, 20.2 (2 CH_3 of *i*-Pr), C_q of *t*-Bu and B-Me not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25^{o}C): δ -514 ($\Delta\nu_{½}$ = 1600). *^{19}F NMR* (188.2 MHz, C_6D_6, 25^{o}C): δ -133.6, -134.9* (*o*-F), -162.2*, -166.2 (*p*-F), -166.8*, -168.7 (*m*-F). Resonances marked with an asterisk are from the contact ion pair (>90%).

^{1}H NMR (200 MHz, C_6D_5Br, 25^{o}C): δ 6.06 (br, 1H, Cp), 5.73 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 5.52 (br, 1H, Cp), 5.37 (br, 1H, Cp), 5.13 (br, 1H, Cp), 4.70 (m, 1H, NC*H*H), 3.56 (dd, J_{H-H} = 7 / 13, 1H, NCH*H*), 2.70 (dd, J_{H-H} = 6 / 13, 1H, CpC*H*H), 2.09 (m, 1H, CpCH*H*), 1.13 (br, $\Delta\nu_{½}$ = 25, 3H, BCH_3), 1.01 (s, 9H, *t*-Bu), 0.99 (shoulder, *i*-Pr), 0.76 (d, J_{H-H} = 6, 3H, *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, 25^{o}C): δ 148.9 (d, J_{C-F} = 239, C_6F_5), 143.2 (C_{ipso} of Cp), 138.0 (d, J_{C-F} = 241, C_6F_5), 136.0 (d, J_{C-F} = 248, C_6F_5), 112.8, 110.8, 103.4, 103.0 (4 CH of Cp), 75.8 (CH of *i*-Pr), 73.9 (NCH_2), 29.2 ($CpCH_2$), 30.7 (CH_3 of *t*-Bu), 22.3, 20.7 (2 CH_3 of *i*-Pr), 11.5 (br, $\Delta\nu_{½}$ ~ 100 Hz, BCH_3), C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25^{o}C): δ -544 ($\Delta\nu_{½}$ = 1300). *^{19}F NMR* (188.2 MHz, C_6D_5Br, 25^{o}C): δ -133.4, -134.5* (*o*-F), -162.0*, -165.7 (*p*-F), -166.3*, -168.1 (*m*-F). Resonances marked with an asterisk are from the contact ion pair (<10%).

^{19}F NMR (188.2 MHz, CD_2Cl_2, 25^{o}C): δ -135.3*, -135.8 (*o*-F), -163.3*, -165.7 (*p*-F), -167.5*, -168.5 (*m*-F). Resonances marked with an asterisk are of the contact ion pair (20%). *^{19}F NMR* (188.2 MHz, C_6D_5Cl, 25^{o}C): δ -134.4 (overlap of solvent separated and contact ion pair) (*o*-F), -161.9*, -164.9 (*p*-F), -166.2*, -167.4 (*m*-F). Resonances marked with an asterisk are of the contact ion pair (33%). *^{19}F NMR* (188.2 MHz, $C_2D_2Cl_4$, 25^{o}C): δ -134.9, -135.3* (*o*-F), -162.4*, -165.8 (*p*-F), -166.8*, -168.4 (*m*-F). Resonances marked with an asterisk are of the contact ion pair (66%). *Anal. calcd (%) for $C_{33}H_{27}BF_{15}N_2V$*: C: 49.65, H: 3.41, N: 3.51, V: 6.38, found: C: 49.78, H: 3.28, N: 3.40, V: 6.31.

Generation of $[(C_5H_4CH_2CH_2N\textit{i}\text{-Pr})V(N\textit{t}\text{-Bu})][B(C_6F_5)_4]$ (**2'**)

A solution of 10.5 mg (37 μmol) of **1** in 0.1 mL of C_6D_5Br was added to a suspension of 39 mg (42 μmol) of $[Ph_3C][B(C_6F_5)_4]$ in 0.4 mL of C_6D_5Br. ^1H NMR showed clean conversion to **2'** and Ph_3CMe.

^1H NMR (300 MHz, C_6D_5Br, 25°C): *Ph_3CMe* δ 7.08 (m, 15H, Ph), 2.02 (s, 3H, Me); chemical shifts for **2'** identical to those of **2** in C_6D_5Br. *^{19}F NMR* (188.2 MHz, C_6D_5Br, 25°C): δ -133.5 (*o*-F), -163.9 (*p*-F), -167.7 (*m*-F).

Generation of $[(C_5H_4CH_2CH_2N$*i*-Pr)V(THF)(N*t*-Bu)$][MeB(C_6F_5)_3]$ (**3a**)

A solution of 20 mg (0.07 mmol) of **1** in 0.1 mL of C_6D_5Br was added to a solution of 10 mg (0.08 mmol) of $B(C_6F_5)_3$ in 0.4 mL of C_6D_5Br and 6 μl (0.07 mmol) of THF was added subsequently by microsyringe. NMR showed clean conversion to **3a**.

^1H NMR (500 MHz, C_6D_5Br, 25°C): δ 6.12 (m, 1H, Cp), 5.89 (m, 1H, Cp), 5.64 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.37 (m, 1H, Cp), 5.02 (m, 1H, Cp), 4.93 (m, 1H, NC*H*H), 3.48 (m, 1H, NCH*H*), 3.42 (m, 2H, α-H of THF), 3.32 (m, 2H, α-H of THF), 2.75 (m, 1H, CpC*H*H), 2.01 (m, 1H, CpCH*H*), 1.52 (m, 4H, β-H of THF), 1.02 (s, 9H, *t*-Bu), 0.93 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.73 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *$^{13}C\{^1H\}$ NMR* (125.7 MHz, C_6D_5Br, 25°C): δ 143.2 (C_{ipso} of Cp), 112.4, 111.8 (2 CH of Cp), 102.7 (br, 2 CH of Cp), 80.8 (α-C of THF), 75.0 (CH of *i*-Pr), 73.2 (NCH_2), 31.6 (CH_3 of *t*-Bu), 30.1 ($CpCH_2$), 26.5 (β-C of THF), 22.2, 22.0 (2 CH_3 of *I*-Pr), C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -567 ($\Delta\nu_{½}$ = 940).

Generation of $[(C_5H_4CH_2CH_2N$*i*-Pr)V(PMe_3)(N*t*-Bu)$][MeB(C_6F_5)_3]$ (**3b**)

A solution of 20 mg (0.07 mmol) of **1** in 0.1 mL of C_6D_5Br was added to a solution of 10 mg (0.08 mmol) of $B(C_6F_5)_3$ in 0.4 mL of C_6D_5Br. This solution was transferred into an NMR tube equipped with a Teflon Young valve. The tube was connected to a high vacuum line, frozen in liquid nitrogen and evacuated. Subsequently, one equivalent of PMe_3 was condensed into the NMR tube, which was then closed and thawed out. NMR showed clean conversion to **3b**.

^1H NMR (500 MHz, C_6D_5Br, 25°C): δ 5.58 (br, 1H, Cp), 5.52 (br, 1H, Cp), 5.50 (br, 1H, Cp), 5.33 (sept, J_{H-H} = 7, 1H, CH of *i*-Pr), 5.01 (br, 1H, Cp), 4.11 (m, 1H, NC*H*H), 3.36 (m, 1H, NCH*H*), 2.42 (m, 1H, CpC*H*H), 2.09 (m, 1H, CpCH*H*), 0.98 (d, J_{P-H} = 10, 9H, $P(CH_3)_3$), 0.91 (s, 9H, *t*-Bu), 0.93 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.62 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *$^{13}C\{^1H\}$ NMR* (125.7 MHz, C_6D_5Br, 25°C): δ 137.2 (C_{ipso} of Cp), 108.6, 106.2, 104.7, 100.3 (4 CH of Cp), 73.1 (CH of *i*-Pr), 70.7(NCH_2), 31.8 (CH_3 of *t*-Bu), 29.1 ($CpCH_2$), 23.5, 21.4 (2 CH_3 of *i*-Pr), 17.3 (d, J_{P-C} = 28, $P(CH_3)_3$), C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -832 (d, J_{P-V} = 280). *^{31}P NMR* (202 MHz, C_6D_5Br, 25°C): δ 7 (plateau, $\Delta\nu_{top}$ = 2225).

Generation of $[(C_5H_4CH_2CH_2N$*i*-Pr)V($NPhMe_2$)(N*t*-Bu)$][MeB(C_6F_5)_3]$ (**3c**)

Complex **3c** was generated similarly to **3a**, using $PhNMe_2$ in stead of THF. ^1H NMR showed clean conversion to **3c** and additional resonances for the excess of $PhNMe_2$ (~ 3 eq.)

^{1}H NMR (500 MHz, C_6D_5Br, 25°C): δ 7.22 (partial overlap, *o*-CH of Ph), 7.04 (t, J_{H-H} = 7, 2H, *m*-CH of Ph), 5.88 (m, 2H, Cp and CH of *i*-Pr), 4.96 (m, 2H, Cp and NC*H*H), 4.65 (m, 1H, Cp), 3.93 (m, 1H, Cp), 3.38 (m, 1H, NCH*H*), 2.82 (s, 3H, NCH_3), 2.59 (s, 3H, NCH_3), 2.50 (m, 1H, CpC*H*H), 1.84 (m, 1H, CpCH*H*), 1.08 (s, 9H, *t*-Bu), 0.96 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.87 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), *p*-CH of Ph not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -551 ($\Delta\nu_{½}$ = 830).

Generation of $[\{(C_5H_4CH_2CH_2N$*i*$-Pr)V(N$*t*$-Bu)\}_2(\mu\text{-Me})][MeB(C_6F_5)_3]$ (**4**)

A solution of 5 mg (17 μmol) of **1** in 0.1 mL of C_6D_5Br was added to a solution of 5 mg (9.7 μmol) of $B(C_6F_5)_3$ in 0.4 mL of C_6D_5Br. NMR showed formation of **4** (additional small resonances probably arose from **2** since a small excess of borane was used). The resonances marked with an asterisk are well-resolved resonances for the two diastereomers that appeared with almost equal chemical shift.

^{1}H NMR (500 MHz, C_6D_5Br, 25°C): δ 5.80 (m, 2H, Cp), 5.53 (sept, J_{H-H} = 7, 1H, *i*-Pr), 5.39 (m, 1H, Cp), 5.32 (m, 1H, Cp), 4.61 (m, 1H, NC*H*H), 3.43 (m, 1H, NCH*H*), 2.66 (m, 1H, CpC*H*H), 2.06 (m, 1H, CpCH*H*), 1.09 (s, 9H, *t*-Bu), 1.02 (m, 3H, *i*-Pr), 0.79 (m, 3H, *i*-Pr), -0.57, -0.58 (2 x s, $\Delta\nu_{½}$ = 2, total 3H, μ-CH_3). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, 25°C): δ 140.2* (C_{ipso} of Cp), 111.9*, 109.9, 102.6*, 101.1 (4 CH of Cp), 73.2* (CH of *i*-Pr), 71.6 (NCH_2), 30.1 ($CpCH_2$), 31.7 (CH_3 of *t*-Bu), 22.2*, 21.8* (2 CH_3 of *i*-Pr), C_q of *t*-Bu and μ-Me not observed. *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -628 ($\Delta\nu_{½}$ = 1184).

Generation of $(C_5H_4CH_2CH_2N$*i*$-Pr)V(C_6F_5)(N$*t*$-Bu)$ (**5**)

Approximately 20 mg (0.07 mmol) of **2** was dissolved in 0.5 mL of C_6D_6 and kept at room temperature for one year in a sealed NMR tube. NMR showed the clean conversion to **5** and $MeB(C_6F_5)_2$.

^{1}H NMR (500 MHz, C_6D_6, 25°C): $MeB(C_6F_5)_2$: δ 1.34 (m, CH_3); **5**: δ 5.64 (m, 1H, Cp), 5.62 (m, 1H, *i*-Pr), 5.60 (m, 1H, Cp), 5.46 (m, 1H, Cp), 5.29 (m, 1H, Cp), 4.77 (m, 1H, NC*H*H), 3.29 (m, 1H, NCH*H*), 2.48 (m, 1H, CpC*H*H), 1.96 (m, 1H, CpCH*H*), 1.18 (s, 9H, *t*-Bu), 1.01 (d, J_{H-H} = 7, 3H, *i*-Pr), 0.88 (d, J_{H-H} = 7, 3H, *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_6, 25°C, due to overlap in the region of 135 to 150 ppm resonances for the C_6F_5 moieties of $MeB(C_6F_5)_2$ and **5** could not be assigned): $MeB(C_6F_5)_2$: δ 1.34 (s, CH_3); **5** δ 131.0 (C_{ipso} of Cp), 105.4, 103.5, 96.3, 93.9 (4 CH of Cp), 66.4 (CH of Pr), 63.6 (NCH_2), 24.3 ($CpCH_2$), 26.4 (CH_3 of *t*-Bu), 17.0, 16.6 (2 CH_3 of *i*-Pr), C_q of *t*-Bu not observed. *^{51}V NMR* (131.4 MHz, C_6D_6, 25°C): δ -827 ($\Delta\nu_{½}$ = 390). *^{19}F NMR* (470.3 MHz, C_6D_6, 25°C): $MeB(C_6F_5)_2$: δ -131.6 (*o*-F), -148.7 (*p*-F), -163.2 (*m*-F).

Generation of $[(C_5H_4CH_2CH_2NMe)V(N$*t*$-Bu)][MeB(C_6F_5)_3]$ (**6**)

A solution of 17 mg (67 μmol) of $(C_5H_4CH_2CH_2NMe)VMe(N$*t*$-Bu)$ in 0.1 mL of C_6D_5Br was added to a solution of 40 mg (78 μmol) of $B(C_6F_5)_3$ in 0.4 mL of C_6D_5Br. NMR showed the

complete conversion to **6**, without observed side products. ^{19}F NMR showed a small amount of contact ion pair (<10%).

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): δ 6.04 (br, 1H, Cp), 5.44 (br, 1H, Cp), 5.33 (br, 1H, Cp), 5.08 (br, 1H, Cp), 4.44 (m, 1H, NC*H*H), 3.87 (s, 3H, NCH_3), 3.61 (m, 1H, NCH*H*), 2.48 (m, 1H, CpC*H*H), 2.28 (m, 1H, CpCH*H*), 0.92 (s, 9H, *t*-Bu). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, -30°C): δ 143.0 (C_{ipso} of Cp), 114.7, 108.1, 104.8, 104.1 (4 CH of Cp), 84.9 (NCH_3), 79.2 (C_q of *t*-Bu), 64.5 (NCH_2), 30.9 (CH_3 of *t*-Bu), 28.3 ($CpCH_2$). *^{51}V NMR* (131.4 MHz, C_6D_5Br, -30°C): δ -565 ($\Delta\nu_{½}$ = 7000).

Generation of $[(C_5H_4CH_2CH_2N$*i*-Pr)V(N*p*-Tol)][$MeB(C_6F_5)_3$] (**7**)

Complex **7** was generated similarly to **6**, starting from $(C_5H_4CH_2CH_2N$*i*-Pr)VMe(N*p*-Tol). NMR showed the complete conversion to **7**, without observed side products. ^{19}F NMR showed a small amount of contact ion pair (<10%).

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): δ 6.83 (br, 4H, CH of *p*-Tol), 5.85 (br, 1H, Cp), 5.74 (br, 1H, Cp), 5.45 (br, 2H, Cp and CH of *i*-Pr), 5.05 (m, 1H, Cp), 4.69 (m, 1H, NC*H*H), 3.63 (m, 1H, NCH*H*), 2.72 (m, 1H, CpC*H*H), 2.16 (s, 4H, CH_3 of *p*-Tol and shoulder of CpCH*H*), 1.09 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.71 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, -30°C): δ 160.7, 143.5, 142.3 (2 C_q of *p*-Tol and C_{ipso} of Cp), 137.9 (CH of *p*-Tol), 113.4, 110.8, 106.2, 105.5 (4 CH of Cp), 75.2 (NCH_2), 73.6 (CH of *i*-Pr), 29.3 ($CpCH_2$), 23.1 (CH_3 of *i*-Pr), 22.1 (CH_3 of *p*-Tol), 21.6 (CH_3 of *i*-Pr), 1 CH of *p*-Tol not observed (probably due to overlap with solvent resonances). *^{51}V NMR* (131.4 MHz, C_6D_5Br, -30°C): δ -430 ($\Delta\nu_{½}$ = 10500).

Generation of [(*t*-BuN)VCp(N*i*-Pr_2)][$MeB(C_6F_5)_3$] (**8**)

Complex **8** was generated similarly to **6**, starting from (*t*-BuN)VCp(Ni-Pr_2)Me. NMR showed the complete conversion to **8**, without observed side products. ^{19}F NMR showed a small amount of contact ion pair (<10%).

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): δ 5.60 (s, 5H, Cp), 5.00 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 3.31 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 1.41 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.03 (s, 9H, *t*-Bu), 0.98 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.78 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.75 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, -30°C): δ 109.7 (Cp), 81.0 (C_q of *t*-Bu), 71.6, 61.3 (2 CH of *i*-Pr), 33.1 (CH_3 of *i*-Pr), 31.7 (CH_3 of *t*-Bu), 27.6, 21.0, 20.8 (3 CH_3 of *i*-Pr). *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -492 ($\Delta\nu_{½}$ = 1400).

Generation of [(*p*-TolN)VCp(N*i*-Pr_2)][$MeB(C_6F_5)_3$] (**9**)

Complex **9** was generated similarly to **6**, starting from (*p*-TolN)VCp(Ni-Pr_2)Me. NMR showed the complete conversion to **9**, without observed side products. ^{19}F NMR showed a small amount of contact ion pair (<10%).

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): δ 6.91 (s, 4H, CH of *p*-Tol), 5.65 (s, 5H, Cp), 5.04 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 3.36 (sept, J_{H-H} = 6, 1H, CH of *i*-Pr), 2.18 (s, 3H, CH_3 of *p*-Tol), 1.40 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 1.05 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr), 0.84 (d, J_{H-H} = 6, 3H, CH_3 of *i*-Pr), 0.78 (d, J_{H-H} = 7, 3H, CH_3 of *i*-Pr). *$^{13}C\{^{1}H\}$ NMR* (125.7 MHz, C_6D_5Br, -30°C): δ 161.3, 140.6 (2 C_{ipso} of *p*-Tol), 130.4, 126.2 (2 CH of *p*-Tol), 110.7 (Cp), 70.9, 62.7 (2 CH of *i*-Pr), 33.0, 27.3 (2 CH_3 of *i*-Pr), 22.2 (CH_3 of *p*-Tol), 20.9, 20.8 (2 CH_3 of *i*-Pr). *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): δ -397 ($\Delta\nu_{½}$ = 2500).

Generation of $[(C_5H_4CH_2CH_2N{=}CMe_2)V(NH\textit{t}\text{-Bu})][MeB(C_6F_5)_3]$ (**10b**)

A solution of 30 mg (105 μmol) of **1** in 0.5 mL of THF-d_8 was added to 84 mg (105 μmol) of $[PhNHMe_2][B(C_6F_5)_4]$. Gas evolution was observed immediately and the color of the solution changed from brown to red-brown while the $[PhNMe_2H][B(C_6F_5)_4]$ dissolved (~ 30 seconds). NMR showed clean conversion to **10b** and free $PhNMe_2$.

^{1}H NMR (300 MHz, THF-d_8, 25°C): *free $PhNMe_2$:* δ 7.11 (t, J_{H-H} = 7, 2H, *m*-CH of Ph), 6.68 (d, J_{H-H} = 8, 2H, *o*-CH of Ph), 6.59 (t, J_{H-H} = 7, 1H, *p*-CH of Ph), 2.89 (s, 6H, CH_3); **10b** δ 6.20 (m, 2H, Cp), 5.88 (m, 1H, Cp), 5.69 (m, 1H, Cp), 5.50 (br, 1H, NH), 4.04 (m, 2H, NCH_2), 2.78 (m, 1H, CpC*H*H), 2.69 (m, 1H, CpCH*H*), 1.99 (s, 3H, $=CCH_3$), 1.91 (s, 3H, $=CCH_3$), 1.38 (s, 9H, *t*-Bu). *^{1}H NMR* (300 MHz, C_6D_5Br, 25°C): δ 5.47 (br, 1H, Cp), 5.37 (br, 1H, Cp), 5.27 (br, 1H, Cp), 5.17 (br, 1H, Cp), 3.71 (br, NH), 3.59 (m, 1H, NC*H*H), 3.44 (m, 1H, NCH*H*), 2.21 (m, 2H, $CpCH_2$), 1.72 (s, 3H, $=CCH_3$), 1.42 (s, 3H, $=CCH_3$), 0.98 (s, 9H, *t*-Bu). *^{13}C NMR* (125.7 MHz, THF-d_8, -50°C): *free $PhNMe_2$:* δ 151.8 (s, C_{ipso} of Ph), 130.7 (dd, J_{C-H} = 156 / 8, CH of Ph), 114.5 (d, J_{C-H} = 158, CH of Ph), 42.0 (q, J_{C-H} = 136, $N(CH_3)_2$); **10b** δ 140.0 (s, C_{ipso} of Cp), 119.0, 107.6, 102.8, 98.7 (d, J_{C-H} = 173, 176, 175, 173, 4 CH of Cp), 79.1 (br, $\Delta\nu_{½}$ = 21, C_q of *t*-Bu), 78.2 (s, $=C(CH_3)_2$), 60.0 (t, J_{C-H} = 140, NCH_2), 34.7 (q, J_{C-H} = 127, $=C(CH_3)_2$), 32.3 (q, J_{C-H} = 127, CH_3 of *t*-Bu), 31.4 (t, J_{C-H} = 129, $CpCH_2$), 25.6 (q, J_{C-H} = 125, $=C(CH_3)_2$). *^{51}V NMR* (131.4 MHz, THF-d_8, 25°C): δ -354 ($\Delta\nu_{½}$ = 1900).

Generation of $[(C_5H_4CH_2CH_2N{=}CH_2)V(NH\textit{t}\text{-Bu})][MeB(C_6F_5)_3]$ (**10a**)

Complex **10a** was generated similarly to **10b**, starting from (η^5,η^1-$C_5H_4CH_2CH_2NMe$)VMe(N*t*-Bu). NMR showed clean conversion to **10a** and $PhNMe_2$.

^{1}H NMR (500 MHz, THF-d_8, 25°C): δ 6.47 (br, 1H, Cp), 6.29 (br, 1H, Cp), 6.18 (br, 1H, NH), 5.88 (br, 1H, Cp), 5.75 (br, 1H, Cp), 4.08 (m, 1H, NC*H*H), 3.62 (m, 1H, NCH*H*), 3.20 (d, J_{H-H} = 9, 1H, =C*H*H), 2.65 (m, 3H, $CpCH_2$ and =CH*H*), 1.33 (s, 9H, *t*-Bu). *^{13}C NMR* (125.7 MHz, THF-d_8, -90°C): δ 139.6 (C_{ipso} of Cp), 118.1, 106.8, 105.0, 98.7 (4 CH of Cp), 79.0 (br, $\Delta\nu_{½}$ = 39, C_q of *t*-Bu), 65.2 (t, J_{C-H} = 142, NCH_2), 64.4 (t, J_{C-H} = 163, $=CH_2$), 32.0 (CH_3 of *t*-Bu), 29.0 ($CpCH_2$). *^{51}V NMR* (131.4 MHz, THF-d_8, 25°C): δ -563 ($\Delta\nu_{½}$ = 470).

Generation of $[(C_5H_4CH_2CH_2N(\textit{i}\text{-Pr})CH{=}CMeCMe_2)V(N\textit{t}\text{-Bu})][MeB(C_6F_5)_3]$ (**11**)

To a solution of 45 mg (56 μmol) of **2** in C_6D_5Br, 8 μl (70 μmol) of 2,3-dimethyl-butadiene was added by microsyringe, after which the color of the solution changed from brown to red-brown. ^{1}H NMR showed complete conversion to **11**, additional resonances for the excess of the diene and small impurities in the region of 0 - 7 ppm.

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): 7.55 (s, 1H, =CH), 5.60 (br, 1H, Cp), 5.32 (br, 1H, Cp), 5.13 (br, 1H, Cp), 5.02 (br, 1H, Cp), 3.33 (m, 1H, CH of *i*-Pr), 3.2 - 2.7 (m, 4H, NCH_2 and $CpCH_2$), 1.64 (s, 3H, CCH_3), 1.51 (s, 3H, CCH_3), 1.64 (s, 3H, CCH_3), 1.00 (br, CH_3 of *i*-Pr with shoulder of CCH_3), 0.86 (s, 9H, CH_3 of *t*-Bu), 0.82 (br, 3H, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, -30°C): 182.9 (=CH), 157.3 (=*C*CH_3), 143.9 (C_q of Cp), 114.0, 107.6, 101.9, 96.5 (4 CH of Cp), 77.8 (C_q of *t*-Bu), 72.7 (NCH_2), 62.2 (CH of *i*-Pr), 36.6 ($CpCH_2$), 30.8 (CH_3 of *t*-Bu), 27.3, 26.9, 25.6 (=CCH_3 and VC(*C*H_3)$_2$), 24.5, 23.1 (2 CH_3 of *i*-Pr). *^{51}V NMR* (131.4 MHz, C_6D_5Br, 25°C): -492 ($\Delta\nu_{½}$ = 1000).

Generation of [{$C_5H_4CH_2CH_2N$(*i*-Pr)$(CMe)_2$}V(Nt-Bu)][$MeB(C_6F_5)_3$] (**12**)

A solution of 10 mg (35 μmol) of **1** in 0.1 mL of C_6D_5Br was added to a solution of 23 mg (45 μmol) of $B(C_6F_5)_3$ in 0.4 mL of C_6D_5Br. This solution was transferred into an NMR tube equipped with a Teflon Young valve. The tube was connected to a high vacuum line, frozen in liquid nitrogen and evacuated. Subsequently, 1.2 equivalents of 2-butyne were condensed into the NMR tube, which was then closed, thawed out and kept at 0°C for 10 minutes. ^{1}H NMR showed complete conversion to **12**, small amounts of **13**, 2-butyne and impurities in the region of 0 - 7 ppm.

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): 6.53 (br, Cp), 5.71 (br, Cp), 5.27 (br, Cp), 4.99 (br, Cp), 2.86 (m, NC*H*H), 2.65 (m, NCH*H*), 2.37 (m, CpC*H*H), 2.21 (m, CH of *i*-Pr), 2.00 (m, CpCH*H*), 1.84 (s, CCH_3), 1.16 (s, CCH_3), 1.03 (s, CH_3 of *t*-Bu), 0.63 (br, CH_3 of *i*-Pr), 0.23 (br, CH_3 of *i*-Pr). *^{13}C {^{1}H} NMR* (125.7 MHz, C_6D_5Br, -30°C): 132.9 (C_q of Cp), 122.3 (*C*CH_3), 120.6, 110.2, 104.0, 95.1 (4 CH of Cp), 78.9 (C_q of *t*-Bu), 58.7, 56.6 (CH of *i*-Pr and NCH_2), 31.5 (CH_3 of *t*-Bu), 26.3, 24.2, 23.0, 21.3, 5.0 (2 CH_3 of *i*-Pr, 2 C*C*H_3 and $CpCH_2$). *^{51}V NMR* (131.4 MHz, C_6D_5Br, -30°C): -181 ($\Delta\nu_{½}$ = 8900).

Generation of [{$C_5H_4CH_2CH_2N$(*i*-Pr)$(CMe)_4$}V(Nt-Bu)][$MeB(C_6F_5)_3$] (**13**)

The NMR tube in which **12** was generated was connected to a high vacuum line, frozen in liquid nitrogen and evacuated. Subsequently, 2 equivalents of 2-butyne were condensed into the NMR tube, which was then closed, thawed out and kept at room temperature for 30 minutes. NMR showed complete conversion to **13**, 2-butyne and small amounts of impurities in the region of 0 - 7 ppm.

^{1}H NMR (500 MHz, C_6D_5Br, -30°C): 5.56 (br, Cp), 5.1 (br, Cp), 5.27 (br, Cp), 5.09 (br, Cp), 2.83 (CH of *i*-Pr and NC*H*H), 2.37 (m, NCH*H*), 2.16 (m, CpC*H*H), 1.96 (m, CpCH*H*), 2.16 (s, CCH_3), 1.39 (s, CCH_3), 1.35 (s, CCH_3), 1.31 (s, CCH_3), 1.03 (s, CH_3 of *t*-Bu), 0.75 (br, CH_3 of

i-Pr), 0.60 (br, CH_3 of *i*-Pr). *^{13}C {^1H} NMR* (125.7 MHz, C_6D_5Br, -30°C): 135.1, 133.0, 129.2, 114.0 (C_q of Cp and 3 CCH_3), 113.8, 108.5, 105.4, 97.4 (CH of Cp), 77.5 (br, C_q of *t*-Bu), 66.6 (CH of *i*-Pr), 59.0 (NCH_2), 31.1 (CH_3 of *t*-Bu), 26.0 ($CpCH_2$), 30.6, 22.1, 20.8, 20.1, 18.9, 18.4 (2 CH_3 of *i*-Pr, 4 CCH_3). *^{51}V NMR* (131.4 MHz, C_6D_5Br, -30°C): -436 ($\Delta\nu_{1/2}$ = 8100).

3.5 References

(1) See for instance: Jordan, J.F., *Adv. Organometall. Chem*., **1991**, *32*, 325.

(2) Sinn, H., *Macromol. Symp*., **1995**, *97*, 27.

(3) (a) Jia, L.; Yang, X.; Stern, C.L.; Marks, T.J., *Organometallics*, **1997**, *16*, 842. (b) Bochmann, M.; Lancaster, S.J., *J. Organometallic Chem*., **1992**, *434*, C1. (c) Chien, J.C.W.; Tsai, W-M.; Rausch, M.D., *J. Am. Chem. Soc*., **1991**, *113*, 8570. (d) Yang, X.; Stern, C.L.; Marks, T.J., *J. Am. Chem. Soc*., **1994**, *116*, 10015.

(4) (a) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P., *Organometallics*, **1995**, *14*, 4471. (b) Budzelaar, P.H.M.; van Oort, A.B.; Orpen, A.G., *Eur. J. Inorg. Chem*., **1998**, 1485. (c) Kim, W-K.; Fevola, M.J.; Liable-Sands, L.M.; Rheingold, A.L.; Theopold, K.H., *Organometallics*, **1998**, *17*, 4541.

(5) Horton, A.D.; de With, J.; van der Linden, A.J.; van de Weg, H., *Organometallics*, **1996**, *15*, 2672.

(6) Reaction of Cp^*TiMe_3 with $B(C_6F_5)_3$ in aromatic solvents yields the arene complexes $[Cp^*Ti(\eta^6\text{-arene})Me_2][MeB(C_6F_5)_3]$ (ref. 6a), but other arene coordination modes have also been proposed (ref. 6b). Halogenated solvents can coordinate by its halogen atom (ref. 6c), although this is most frequently observed for late transition metal complexes (ref. 6d). (a) Gillis, D.J.; Tudoret, M-J.; Baird, M.C., *J. Am. Chem. Soc*., **1993**, *115*, 2543. (b) Eisch, J.J.; Pombrik, S.I.; Zheng, G-X., *Organometallics*, **1993**, *12*, 3856. (c) Plenio, H., *Chem. Rev*., **1997**, *97*, 3363, and ref. 125 herein. (d) Kulawiec, R.J.; Crabtree, R.H., *Coord. Chem. Rev*., **1990**, *99*, 89.

(7) (a) Bochmann, M.; Lancaster, S.J., *Angew. Chem. Int. Ed. Eng*., **1994**, *33*, 1634. (b) Chen, Y-X.; Stern, C.L.; Yang, S.; Marks, T.J., *J. Am. Chem. Soc*., **1996**, *118*, 12451.

(8) Mayer, J.M.; Curtis, C.J.; Bercaw, J.E., *J. Am. Chem. Soc*., **1983**, *105*, 2651.

(9) Bol, J.E.; Hessen, B.; Teuben, J.H.; Smeets, W.J.J.; Spek, A.L., *Organometallics*, **1992**, *11*, 1981.

(10) Guillemin, J-C.; Denis, J-M., *Tetrahedron*, **1988**, *4*, 4431.

(11) Chisholm, M.H.; Rothwell, I.P., *Comp. Coord. Chem*., **1987**, *2*, 161.

(12) (a) de With, J.; Horton, A.D.; Orpen, A.G., *Organometallics*, **1993**, *12*, 1493. (b) Bennet, J.L.; Wolczanski, P.T., *J. Am. Chem. Soc*., **1994**, *116*, 2179.

(13) Luetkens Jr., M.L.; Sattelberger, A.P.; Murray, H.H.; Basil, J.D.; Fackler Jr., J.P.; Jones, R.A.; Heaton, D.E., *Inorg. Synth*., **1989**, *26*, 7.

(14) Tjaden, A.B.; Swenson, D.C.; Jordan, R.F.; Petersen, J.L., *Organometallics*, **1995**, *14*, 371.