

University of Groningen

## Vanadium complexes containing amido functionalized cyclopentadienyl ligands

Witte, Petrus Theodorus

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*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.].

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

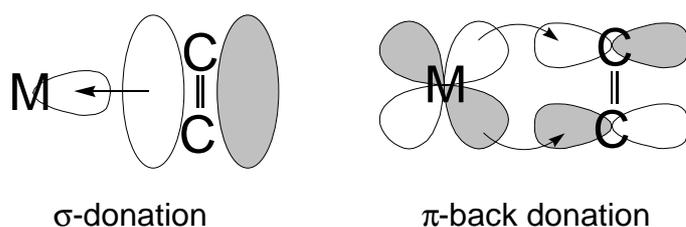
Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

## Chapter 4

# Olefin coordination towards cationic $d^0$ vanadium complexes

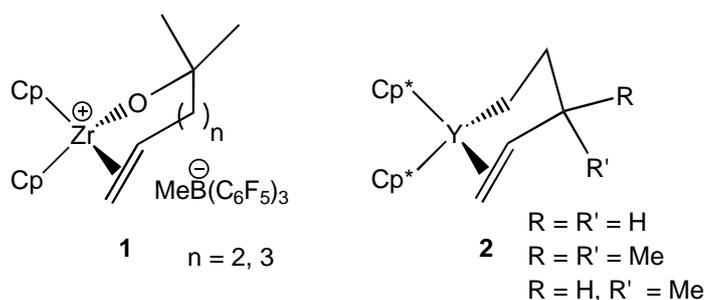
### 4.1 Introduction

Olefin coordination to a metal center consists of two contributions:  $\sigma$ -donation from a  $\pi$ -orbital of the olefin to an empty d-orbital of the metal, and  $\pi$ -back donation from a filled d-orbital on the metal to a  $\pi^*$ -orbital of the olefin (Figure 1).<sup>1</sup>



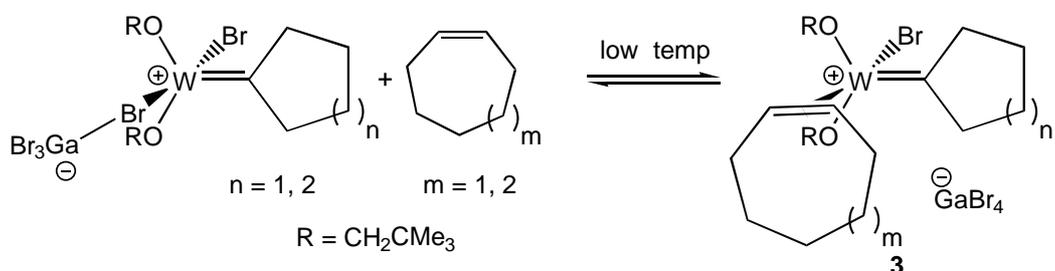
**Figure 1:** Olefin coordination to a metal center.

Since  $d^0$  metals have no filled d-orbitals, they lack the possibility for  $\pi$ -back donation and olefin coordination is expected to be relatively weak. Nevertheless, olefin coordination to a cationic  $d^0$  metal center has been proposed as one of the steps in the olefin polymerization catalyzed by cationic group 4 metallocene complexes.<sup>2</sup> Due to its high reactivity, the intermediate olefin adduct has never been observed. In fact, only few olefin adducts of  $d^0$  metal centers have been described in literature, and in most complexes the olefin is held in the proximity of the metal by a covalently bonded tether (Figure 2).<sup>3</sup>



**Figure 2:** Coordination of a tethered olefin to  $d^0$  metal centers.

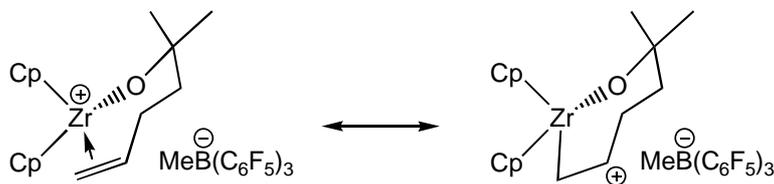
The above described compounds do not form stable adducts with olefins that are not tethered to the metal center. So far, only one  $d^0$  metal complex is reported that coordinates olefins that are not tethered to the metal center. The tungsten alkylidene  $[(Me_3CCH_2O)_2W(=C(CH_2)_n)Br][GaBr_4]$  ( $n = 1, 2$ ) reacted with cycloheptene or cyclooctene at low temperatures to generate the olefin adducts **3**, which were identified by  $^1H$  and  $^{13}C$  NMR (Scheme 1).<sup>4</sup> When the compounds were mixed at ambient temperatures, ring opening metathesis polymerization (ROMP) of the cyclic olefin took place.



**Scheme 1**

The cationic zirconium compound **1** ( $n = 2$ ) is the only isolated and structurally characterized  $d^0$  olefin adduct.<sup>3a</sup> The olefinic moiety of the alkoxy group coordinates in an asymmetric fashion ( $Zr-CH_2 = 2.68(2)$ ,  $Zr-CH = 2.89(2)$  Å). In the  $^{13}C$  NMR spectra of **1** the olefinic carbon atom closest to the metal center shows an upfield shift of 20 ppm compared to the free olefin, while the other olefinic carbon atom shows a downfield shift of 19 ppm. This can be

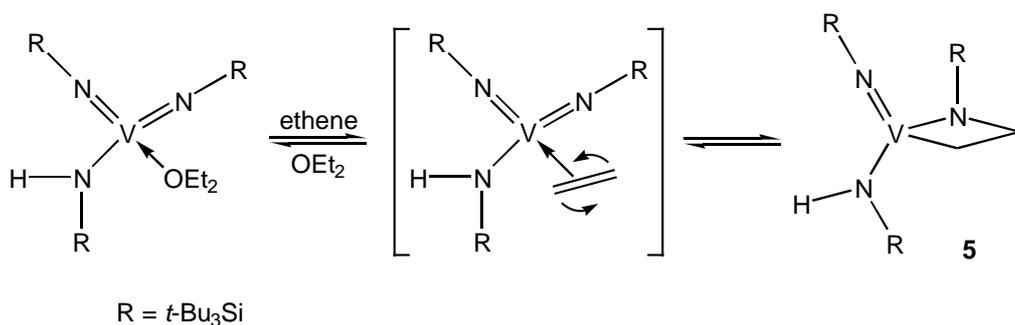
explained by a resonance structure in which the positive charge is on the substituted carbon atom (Scheme 2).



**Scheme 2**

It is possible that the observed polarization in **1** is influenced by the tether, which can force the olefinic moiety into an asymmetric coordination. Furthermore, the positive charge on the olefinic carbon atom will be stabilized by the substituent on this carbon atom. Nevertheless, in theoretical calculations on ethene coordination to cationic d<sup>0</sup> metal complexes, the ethene coordination is also asymmetric.<sup>5</sup> For example, in the model compounds for a ‘constrained geometry’ catalyst,  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{SiH}_2\text{NH})\text{M}(\eta^2\text{-ethene})\text{Me}]^+$  (**4**, M = Ti, Zr, Hf), Ti-C distances of 2.39 and 2.44 Å were calculated (no distances reported for M = Zr or Hf). Although the interaction of the ethene with the cationic d<sup>0</sup> metal centers is expected to be weak, calculations predict a high metal-olefin bond strength (**4**, M = Ti: 20.8 kcal·mol<sup>-1</sup>; M = Zr: 24.2 kcal·mol<sup>-1</sup>; M = Hf: 25.7 kcal·mol<sup>-1</sup>).

An ethene adduct of a d<sup>0</sup> vanadium(V) imido complex has been proposed as intermediate in the [2+2] cycloaddition of ethene over the vanadium-imido bond. In their work with vanadium(V) imido complexes, Horton *et al.* discovered that ethene reacts with one imido ligand of (*t*-Bu<sub>3</sub>SiN)<sub>2</sub>V(NHSi*t*-Bu<sub>3</sub>)(OEt<sub>2</sub>) to form the aza-metallacycle (*t*-Bu<sub>3</sub>SiN)V(NHSi*t*-Bu<sub>3</sub>)( $\eta^1, \eta^1\text{-CH}_2\text{CH}_2\text{NSi}t\text{-Bu}_3$ ) (**5**, identified by <sup>1</sup>H, <sup>13</sup>C and <sup>51</sup>V NMR, Scheme 3).<sup>6</sup> The CH<sub>2</sub>CH<sub>2</sub>-moiety of **5** is observed in <sup>1</sup>H and <sup>13</sup>C NMR as a singlet, which is explained by an equilibrium between the aza-metallacycle and an ethene adduct, in which the ethene is rapidly rotating. The intermediate d<sup>0</sup> vanadium ethene adduct is not observed.



Scheme 3

This chapter describes the reversible coordination of a series of olefins to the cationic  $d^0$  vanadium complexes described in Chapter 3. The effects of substituents on the olefin, amido, and imido ligands, on the coordination of the olefin is discussed, based on the various equilibrium constants of the adduct formation. Theoretical calculations on a model compound were performed to get an insight into the structure of the olefin adducts and the strength of the olefin coordination. For the coordination of cyclopentene to the solvated species of  $[(C_5H_4CH_2CH_2N*i*-Pr)V(N*t*-Bu)][MeB(C_6F_5)_3]$ , the thermodynamic parameters  $\Delta H^0$  and  $\Delta S^0$  were determined by variable temperature NMR.

## 4.2 Results and Discussion

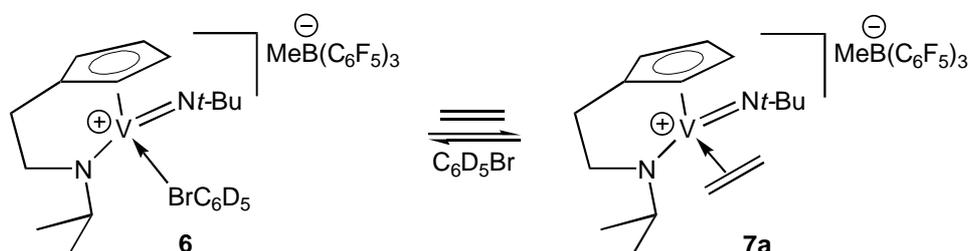
### 4.2.1 Reactivity of $[(\eta^5, \eta^1-C_5H_4CH_2CH_2N*i*-Pr)V(N*t*-Bu)]^+$ towards olefins

Addition of an excess of ethene to a  $C_6D_5Br$  solution of  $[(\eta^5, \eta^1-C_5H_4CH_2CH_2N*i*-Pr)V(N*t*-Bu)][MeB(C_6F_5)_3]$  (**6**, present as the solvent separated species, see Chapter 3), led to the generation of the ethene adduct  $[(\eta^5, \eta^1-C_5H_4CH_2CH_2N*i*-Pr)V(\eta^2-H_2C=CH_2)(N*t*-Bu)][MeB(C_6F_5)_3]$  (**7a**, Scheme 4). The olefin complexation is fully reversible, and **7a** reverted to the solvated species of **6** upon pumping off the ethene. Therefore we did not attempt to isolate the adduct, but instead identified it by its  $^1H$ ,  $^{13}C$  and  $^{51}V$  NMR spectra. In addition to the expected resonances for the Cp-amido and *t*-Bu-imido ligand, which have

shifted little compared to **6**, **7a** shows two multiplets in the  $^1\text{H}$  NMR spectrum (4.72 and 4.61 ppm, integral of  $2 \times 2\text{H}$ ) and one triplet in the  $^{13}\text{C}$  NMR spectrum (103.2 ppm,  $J_{\text{C-H}}$  164 Hz). These characteristics differ considerably from those of the vanadium aza-metallacyclic complex **5** reported by Horton (Scheme 2:  $^1\text{H}$ : 3.22 ppm;  $^{13}\text{C}$ : 48.3 ppm,  $J_{\text{C-H}}$  149 Hz),<sup>6</sup> and are much closer to the NMR data for free ethene ( $^1\text{H}$ : 5.29 ppm;  $^{13}\text{C}$ : 123.9 ppm,  $J_{\text{C-H}}$  160 Hz). From this we conclude that **7a** is an ethene adduct, the first one observed for a  $d^0$  metal center.

At room temperature the resonances of coordinated and free ethene are sharp, and only at high temperatures (80 °C) do the resonances of the coordinated ethene start to broaden. This is an indication that the exchange of coordinated ethene with the excess of free ethene is remarkably slow.

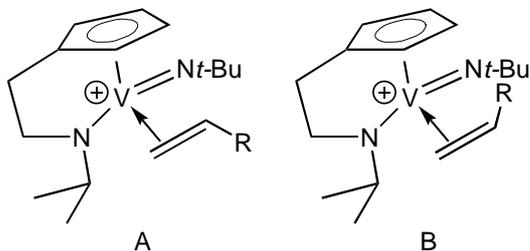
A clean sample of **7a** in  $\text{C}_6\text{D}_5\text{Br}$  is stable at room temperature for at least one week, however, it appears that small amounts of impurities can cause the ethene to polymerize, even at low temperatures.



**Scheme 4**

Complex **6** reacted reversibly with propene to form the propene adduct  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-H}_2\text{C}=\text{CHMe})(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7b**), which is observed in the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{51}\text{V}$  NMR spectra as a mixture of two diastereomers (ratio ~ 4:5), due to the two possible coordination modes of the propene (Figure 3). Upon coordination, the olefinic carbon atoms of the propene show  $^{13}\text{C}$  NMR chemical shift differences comparable to those in the zirconium adduct **1** (Scheme 2, Table 1).<sup>3a</sup> Therefore we propose that in **7b** the propene

coordinates asymmetrically with the substituted olefinic carbon atom further away from the metal center, comparable to the zirconium adduct **1**.



**Figure 3:** Two diastereomers of the propene adduct **7b**.

As expected, the isobutene adduct  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-H}_2\text{C}=\text{CMe}_2)(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7c**) appears as a single species in the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{51}\text{V}$  NMR spectra. The  $^{13}\text{C}$  NMR shifts of the olefinic moiety upon coordination (Table 1) are consistent with a polarization of the coordinated olefin as is described for **1**, and we again propose a structure with the substituted olefinic carbon atom further away from the metal than the unsubstituted carbon atom.

Table 1 shows the observed  $^{13}\text{C}$  NMR chemical shift differences ( $\Delta\delta$ ) for the olefinic carbon atoms upon olefin coordination. The larger downfield shift of the substituted carbon atom in the isobutene adduct **7c** compared to the propene adduct **7b** leads to the conclusion that the polarization in **7c** is more pronounced than in **7b**. This can be rationalized by two factors: the two methyl groups in the coordinating isobutene cause a larger steric interaction with other ligands on the vanadium metal, and they better stabilize the positive charge on the olefinic carbon atom.

**Table 1:**  $^{13}\text{C}$  NMR chemical shift differences ( $\Delta\delta$ ) for the olefinic moiety upon coordination.

Complex	$\Delta\delta(\text{CH}_2)$	$\Delta\delta(\text{CR})$
<b>1</b>	-20	+19
<b>7a</b>	-21	

<b>7b</b>	-24	+1
<b>7c</b>	-27	+35

Although the polarization of the coordinating olefin is clear when electron donating substituents are placed on one of the olefinic carbon atoms, it becomes unclear when olefins are used with electron withdrawing substituents, or with electron donating substituents on both olefinic carbon atoms. The cyclopentene adduct  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-C}_5\text{H}_8)(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7d**) and the styrene adduct  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-H}_2\text{C}=\text{CHPh})(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7e**) can be identified by <sup>1</sup>H, <sup>13</sup>C and <sup>51</sup>V NMR spectroscopy, and their <sup>13</sup>C NMR spectra show an upfield shift for both olefinic carbon atoms upon coordination.<sup>7</sup> It is unclear what causes this.

Just as the propene adduct **7b**, the styrene adduct **7e** is observed as a mixture of two diastereomers (ratio ~ 4:5). However, in **7e** interconversion of the two diastereomers is observed at room temperature. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the **7e** broad resonances are observed at ambient temperatures, which split up into two sets of resonances for the two diastereomers at lower temperatures. By determining the coalescence temperature ( $T_c$ ) of one set of two resonances, the free energy of activation ( $\Delta G^\ddagger$ ) for the interconversion of the two diastereomers can be calculated from Equation 1.<sup>8</sup> With  $T_c = 283 \pm 2$  K and  $\Delta\nu = 37 \pm 1$  Hz,  $\Delta G^\ddagger = 58.8 \pm 0.5$  kJ·mol<sup>-1</sup>.

$$\Delta G^\ddagger = 1.914 \cdot 10^{-2} \times T_c \times [9.972 + \log(T_c/\Delta\nu)] \quad (1)$$

For the olefin adducts **1** ( $n = 2$ ) and **2** ( $R = \text{H}$ ,  $R' = \text{Me}$ ) the interconversion of the two diastereomers has a  $\Delta G^\ddagger$  of 44.2 kJ·mol<sup>-1</sup> (no error reported) and  $40.6 \pm 0.2$  kJ·mol<sup>-1</sup> respectively,<sup>3a,3b</sup> however, it is uncertain if these processes proceed by the same mechanism as the interconversion in **7e**. The diastereomers of the adducts **1** and **2** can only interconvert by dissociation and subsequent recoordination of the olefin, however, the styrene in **7e** does not have to dissociate for interconversion. Instead, the coordinated styrene can change its coordination from the olefinic bond to the phenyl group, after which

the vinylic group can rotate and recoordinate with its other face. The cationic zirconium complex  $[\text{Cp}^*\text{ZrMe}_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$  is known to coordinate added styrene by its phenyl group, while no interaction with the vinylic group is observed.

#### 4.2.2 Comparison of the equilibrium constants

The coordination of olefins to  $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**6**) is reversible, and in the NMR spectra of the adducts **7** the starting compound **6** and an amount of free olefin is always observed. By careful integration of well-resolved resonances in the  $^1\text{H}$  NMR spectra, measured from samples with a known concentration, the  $K_{\text{eq}}$  for the reaction in Equation 2 was determined (Table 2). In these measurements we assume there is no influence from coordination of the  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  anion.



**Table 2:** Coordination of different olefins to **6**.

Olefin <sup>a</sup>	compound	$K_{\text{eq}}^{\text{b}}$
ethene	<b>7a</b>	$100 \pm 10$
propene	<b>7b</b>	$44 \pm 4$
isobutene	<b>7c</b>	$23 \pm 2$
cyclopentene	<b>7d</b>	$8 \pm 1$
styrene	<b>7e</b>	$10 \pm 1$

a) No reaction observed with 10 equivalents of 3,3-dimethyl-1-butene (*t*-Bu-ethene), 2,3-dimethyl-2-butene (tetramethyl-ethene). b)  $K_{\text{eq}}$  (at 25 °C) =  $[\mathbf{7}] \times [\text{C}_6\text{D}_5\text{Br}] \times [\mathbf{6}]^{-1} \times [\text{olefin}]^{-1}$ .

The interaction of an olefin with a  $d^0$  metal center consists only of  $\sigma$ -donation of the olefin to the metal. Therefore, olefins that are more electron rich are expected to interact more strongly with  $d^0$  metal centers. Although the olefinic moiety of propene is electron richer than that of ethene (because of electron donation of the methyl substituent) the  $K_{\text{eq}}$  of the formation of **7b** is much lower than that of **7a**. Apparently, the effect of the steric bulk of the

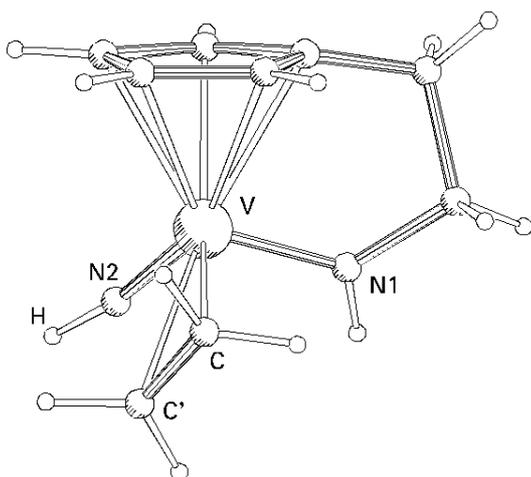
methyl substituent dominates the electronic effect. When the steric bulk is further increased (3,3-dimethyl-1-butene) or when four small substituents are introduced on the olefin (2,3-dimethyl-2-butene) no olefin adducts are observed. Di-substituted olefins (isobutene, cyclopentene) form adducts with complex **6**, but with a low  $K_{\text{eq}}$ . It appears that the steric hindrance of the 1,1-di-substituted olefin isobutene is less than that of the 1,2-di-substituted olefin cyclopentene. Because of the asymmetric coordination of the isobutene in **7c** (see section 4.2.1) the two methyl substituents are pointing away from the metal, which decreases the steric interactions with other ligands. In the cyclopentene adduct **7d** an asymmetric coordination will not help to decrease the steric interactions of the coordinating olefin.

Placing an electron withdrawing substituent on the olefin (styrene), lowers the  $K_{\text{eq}}$ , although this probably is a combination of the electron deficiency of the olefin in combination with a large substituent.

In order to investigate the influence of the steric and electronic properties of the vanadium center itself on the olefin coordination, the Cp-amido vanadium complexes  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe})\text{V}(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  and  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{Pr})\text{V}(\text{N}p\text{-Tol})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (see Chapter 3) were reacted with ethene and the  $K_{\text{eq}}$  was determined. The  $K_{\text{eq}}$  for the formation of the ethene adducts  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NR})\text{V}(\eta^2\text{-ethene})(\text{NR})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**8**: R = Me, R' = *t*-Bu; **9**: R = *i*-Pr, R' = *p*-Tol) is equal to the  $K_{\text{eq}}$  for the formation of **7a** (measured for **8**:  $K_{\text{eq}} = 99$ ; **9**:  $K_{\text{eq}} = 98$ ).<sup>10</sup> Apparently, the changes on the metal center influence the coordination of the olefin in the same way as they influence the stabilization by the solvent. These results compare well to the solvent coordination to the complexes  $[(\text{Cp-amido})\text{V}(\text{NR})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  as described in Chapter 3, sections 3.2.1 and 3.2.3, where the position of the equilibrium between the contact ion pair and the solvent separated ion pair depended on the coordinating properties of the solvent and not on the electronic or steric properties of the vanadium complex.

#### 4.2.3 Theoretical calculations on the ethene coordination

In order to get more information on the structure of the olefin adducts and the metal-olefin bond strength, theoretical calculations (DFT/B3LYP) on the model compound  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NH})\text{V}(\eta^2\text{-H}_2\text{C}=\text{CH}_2)(\text{NH})]^+$  (**7calc**) were performed.<sup>11</sup> These calculations were performed by Dr. P.H.M. Budzelaar of the University of Nijmegen.



**Figure 4:** Conformation of **7calc** with the lowest calculated energy.

In Figure 4 the conformation of **7calc** with the lowest calculated energy is shown, in which the ethene is coordinating parallel to the vanadium-imido bond. A second conformation with the ethene coordinating parallel to the vanadium-amido bond has a local energy minimum that is  $1.2 \text{ kcal}\cdot\text{mol}^{-1}$  higher in energy. However, the barrier for ethene rotation is low and the energy minima are shallow, so there appears to be no preference for a specific orientation of the ethene. This has also been found for the Cp-amido group 4 model complexes  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{SiH}_2\text{NH})\text{M}(\eta^2\text{-ethene})\text{Me}]^+$  (**4**, M = Ti, Zr, Hf).<sup>5</sup>

The ethene coordination in **7calc** is asymmetric ( $\text{V-C} = 2.43$ ;  $\text{V-C}' = 2.54 \text{ \AA}$ ). As observed in calculations on the group 4 complexes **4**, the C=C bond distance of the olefin has increased only slightly upon coordination ( $1.36 \text{ \AA}$  vs.  $1.33 \text{ \AA}$  for free ethene), indicating the lack of backbonding from the metal center. The calculated metal-ethene bond strength in **7calc** ( $31 \text{ kcal}\cdot\text{mol}^{-1}$ ) is

higher than in **4** (M = Ti: 20.8, M = Zr: 24.2, M = Hf: 25.7 kcal·mol<sup>-1</sup>), which may be caused by the following three factors.

*Charge on metal center:* Olefin coordination to a cationic metal center becomes stronger when the positive charge on the metal increases.<sup>12</sup> However, both the vanadium and the group 4 model complexes have a formal charge of +1, and in addition, the vanadium center (16 valence electrons) is less electron deficient than the group 4 metal centers (12 valence electrons). This would therefore predict a somewhat lower metal-olefin bond strength for **7calc**.

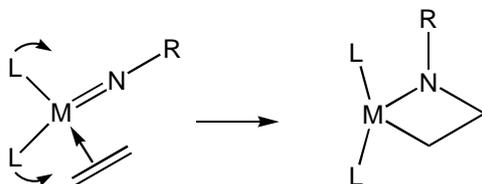
*Reorganization energy:* When olefin coordination to a metal center requires the metal center to change its structure, this will decrease the total metal-olefin bond strength. The bare cationic complexes [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>SiH<sub>2</sub>NH)TiMe]<sup>+</sup> and [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NH)V(NH)]<sup>+</sup> both have a pyramidal structure, with an inversion barrier of less than 3 kcal·mol<sup>-1</sup>,<sup>5</sup> therefore the reorganization energy of the olefin coordination will have no significant influence on the calculated metal-olefin bond strength.

*Steric interactions:* Ziegler *et al.* state that the main steric interaction of ethene in **4** will be with the methyl group.<sup>5</sup> The smaller steric interaction of the linear imido group in **7calc**, compared to the tetrahedral methyl group in **4**, can cause the stronger metal-olefin bond in **7calc**.

#### 4.2.4 Influence of the bridge between the Cp and amido functionality

In the introduction of this chapter (section 4.1, Scheme 3) the reaction of a neutral vanadium(V) imido complex with ethene is described, which generates a metallacyclic complex (**5**) by a [2+2] cycloaddition of the olefin over the V-N(imido) bond. Much to our surprise no reactivity of the cationic Cp-amido vanadium(V) complex **6** with olefins was observed. Our first assumption was that this is caused by the constrained geometry of the Cp-amido ligand.<sup>13</sup> A [2+2] cycloaddition of ethene over a vanadium-imido bond would generate an aza-metallacycle with a small N-V-C bite angle. In order to compensate for this small angle the other ligands can open up, as is shown in Scheme 5. We assumed that the bridge between the Cp and amido functionality in the adducts

**7** prevented opening of the Cp-V-amido bite angle, so that the aza-metallacycle could not be formed.



**Scheme 5**

Theoretical calculations predicted that the formation of an aza-metallacyclic product from an ethene adduct takes place without a significant energy barrier, and several structures with almost equal energies were calculated. From this we conclude that there is an equilibrium between the olefin adduct and the aza-metallacycle, which was also reported by Horton *et al.* (Scheme 3).<sup>6</sup> However, in Horton's case the equilibrium was shifted towards the aza-metallacycle, while we observe only the olefin adduct. To test if the equilibrium can be shifted to the aza-metallacycle, we investigated olefin coordination to Cp-amido vanadium complexes in which there is no bridge between the Cp and amido functionality.

The complexes [(RN)VCp(N*i*-Pr<sub>2</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (R = *t*-Bu, *p*-Tol, see Chapter 3) coordinated ethene to form the adducts [(RN)VCp(η<sup>2</sup>-ethene)(N*i*-Pr<sub>2</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**10**: R = *t*-Bu; **11**: R = *p*-Tol). However, in contrast to the coordination of ethene to **6** the ethene is quickly polymerized, even at -30°C and even if the methyl complexes used for the generation of the cation are analytically pure. It was therefore not possible to obtain good <sup>1</sup>H NMR spectra of the ethene adducts **10** and **11**. Nevertheless, resonances around 4.6 ppm are very comparable to the observed resonances for coordinating ethene in the ethene adducts **7a**, **8** and **9**.

We propose that in complexes **10** and **11** insertion of ethene in the vanadium amido bond generates a small amount of a cationic vanadium alkyl species which quickly polymerizes the ethene in the NMR tube. Although this

species is not observed, it is a reasonable assumption based on the reactivity of the Cp-amido complexes towards dimethyl-butadiene and 2-butyne as described in Chapter 3. No attempts have been made to identify the end groups of the polymer.

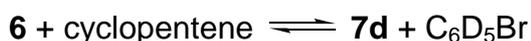
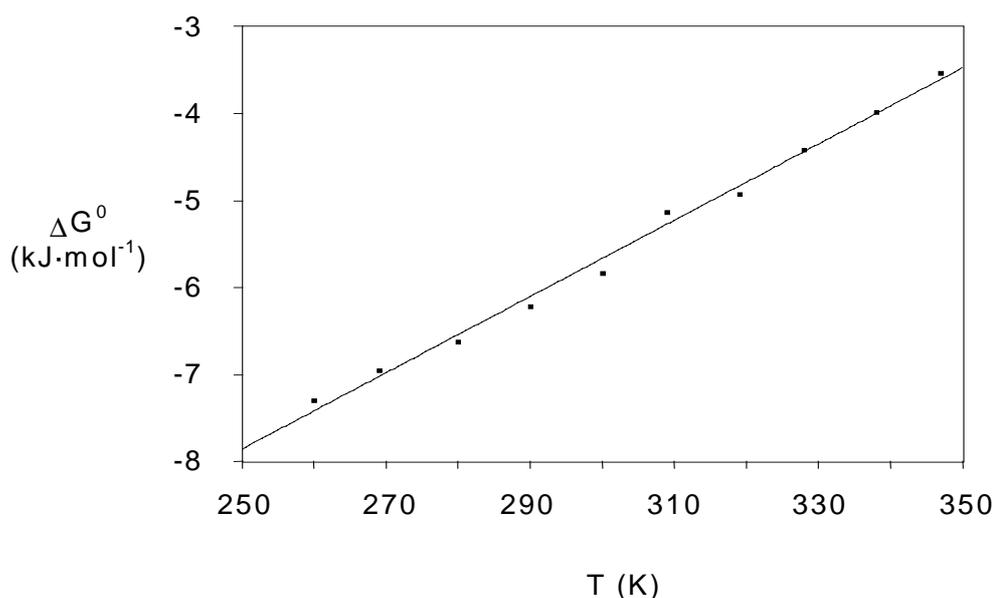
Since the polymerization of ethene is very fast, even at low temperatures, full characterization of the ethene adducts **10** and **11** was not possible. Instead, the cyclopentene adducts [(RN)VCp( $\eta^2$ -C<sub>5</sub>H<sub>8</sub>)(Ni-Pr<sub>2</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**12**: R = *t*-Bu; **13**: R = *p*-Tol) were fully characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>51</sup>V NMR spectroscopy. No significant differences between **12**, **13** and **7d** were observed.

#### 4.2.5 Thermodynamic measurements on the olefin coordination to **6**

From <sup>1</sup>H, <sup>13</sup>C and <sup>51</sup>V NMR measurements it is clear that the equilibrium of coordination of olefins to **6** can be shifted to the olefin adducts by lowering the temperature. After carefully measuring the K<sub>eq</sub> at different temperatures, the Gibbs free energy ( $\Delta G^0$ , in J·mol<sup>-1</sup>) could be calculated from Equation 3.<sup>14</sup> The parameters  $\Delta H^0$  and  $\Delta S^0$  could be calculated from Equation 4 after plotting  $\Delta G^0$  versus the temperature (T, in K, Figure 5).<sup>15</sup> For these measurements we investigated the coordination of cyclopentene, since the cyclopentene adduct **7d** exists as only one isomer. Furthermore cyclopentene is a liquid at room temperature, so olefin exchange between solution and the gas phase can be neglected and the total amount of olefin in solution can be assumed to be constant. In the measurements we assumed no influence of anion coordination.

$$\Delta G^0 = -R \times T \times \ln K_{eq} \quad (3)$$

$$\Delta G^0 = \Delta H^0 - \Delta S^0 \times T \quad (4)$$



$$\Delta S^0 = -0.04 \pm 0.01 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

$$\Delta H^0 = -19 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$$

**Figure 5:** Plot of  $\Delta G^0$  versus T for the formation of **7d**.

The  $\Delta S^0$  value for the formation of **7d** ( $-0.04 \pm 0.01 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ) is smaller than the value for the displacement of the  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  anion by  $\text{PMe}_3$  in the zirconium complex  $[\text{Cp}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  ( $-0.08 \pm 0.01 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),<sup>16</sup> and the displacement of the  $[\text{GaBr}_4]^-$  anion in the tungsten complex **3** ( $n = 1$ ) by cycloheptene ( $-0.23 \pm 0.01 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ).<sup>4</sup> All three  $\Delta S^0$  values are small, since there is no change in the number of particles during the reactions. However, in the reported literature examples an anionic particle ( $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$  or  $[\text{GaBr}_4]^-$ ) is replaced by a neutral particle ( $\text{PMe}_3$  or cycloheptene). It is possible that the observed differences in the  $\Delta S^0$  values reflect the cation-anion interactions that are still present after the anion displacements, and that will further decrease the entropy.

The  $\Delta H^0$  of  $-19 \pm 1 \text{ kJ}\cdot\text{mol}^{-1}$  shows that cyclopentene coordination to **6** is slightly exothermic, although the value is much lower than the above mentioned displacements ( $-41 \text{ kJ}\cdot\text{mol}^{-1}$  for  $[\text{Cp}_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]/\text{PMe}_3$ ;<sup>16</sup>  $-57 \pm 2 \text{ kJ}\cdot\text{mol}^{-1}$

for **3**,  $n = 1$ ).<sup>4</sup> From the measurements on the equilibrium constants of the formation of the olefin adducts **7** (Tabel 2) it is clear that the bonding of cyclopentene to the vanadium center is weak, compared to the bonding of ethene. It is therefore expected that the formation of the ethene adduct **7a** is more exothermic than the cyclopentene adduct **7e**, and will be more in the range of the above mentioned displacements.

### 4.3 Conclusion

The cationic d<sup>0</sup> vanadium(V) complexes described in Chapter 3 reacted reversibly with a range of olefins to generate the corresponding olefin adducts. This is only the second example of olefin adduct formation with a d<sup>0</sup> metal complex in which the olefin is free and not also connected to the metal by a covalently bonded tether, and the first example where simple olefins such as ethene and propene coordinate to the d<sup>0</sup> metal center.

Theoretical calculations predict an unusually high vanadium-ethene bond strength. Measurement of the equilibrium constants of the formation of adducts with several olefins shows that the strength of the interaction of the olefin with the metal center decreases when the steric bulk of the coordinating olefin increases. Although the bonding of the olefin to the vanadium center is only established by  $\sigma$ -donation, even electron donating substituents on the olefin decrease the tendency to form adducts, probably because of increased steric interactions. Steric interactions probably also decrease the tendency of the vanadium center to form adducts with the solvent, which is abundant in much larger quantities than the olefins.

The exchange of coordinated ethene with free ethene, as well as the stabilization of the equilibrium of olefin adduct formation is slow. An associative displacement of a coordinated ligand is difficult, because of the steric crowding around the metal center, while dissociative displacement requires a lot of energy, because of the high vanadium-ligand bond strength.

We have determined the  $\Delta S^0$  and  $\Delta H^0$  values for the coordination of cyclopentene to the solvated species of [(C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(N*t*-

Bu)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]. The  $\Delta S^0$  value of the displacement of a solvent molecule by an olefin is small since there is no change in the number of particles in this reaction. The formation of the cyclopentene adduct is an exothermic process, although the  $\Delta H^0$  value for the coordination of cyclopentene to the cationic vanadium Cp-amido complex is smaller than for other reported adduct formations. Since ethene binds stronger to the metal center than cyclopentene, a larger  $\Delta H^0$  value is expected for ethene coordination.

#### 4.4 Experimental

##### General considerations

All reactions were carried out under N<sub>2</sub>, using standard glove-box and vacuum line techniques. C<sub>6</sub>D<sub>5</sub>Br was degassed and stored on mol. sieves under nitrogen. NMR spectra were recorded on a Varian Unity 500 spectrometer, all spectra were recorded in C<sub>6</sub>D<sub>5</sub>Br at -30°C. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm relative to TMS, using residual solvent resonances as internal reference. <sup>51</sup>V NMR chemical shifts are reported in ppm relative to VOCl<sub>3</sub>, which is used as an external reference. Coupling constants (J) and line widths at half height ( $\Delta v_{1/2}$ ) are reported in Hz. The density of C<sub>6</sub>D<sub>5</sub>Br was measured in the region of 5 to 35°C on an Anton Paar DMA 35n portable density meter. [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(N*t*-Bu)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**6**), [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe)V(N*t*-Bu)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>], [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(N*p*-Tol)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>], [(*t*-BuN)VCp(N*i*-Pr<sub>2</sub>)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] and [(*p*-ToIN)VCp(N*i*-Pr<sub>2</sub>)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] are described in the previous chapter. Ethene (99.9%, Hoekloos), propene (99.9%, Hoekloos) and isobutene (99%, Aldrich) were used as received. Cyclopentene (Acros) and styrene (Aldrich) were stored under nitrogen and used as received. The 1D-<sup>1</sup>H NMR spectra of the styrene adduct **7e** and the cyclopentene adducts **7d**, **12** and **13** contained too much of the starting vanadium complex and free olefin to perform an integration of the resonances (product resonances were small compared to other resonances and many resonances overlap). Therefore these NMR spectra were interpreted based on the 2D-<sup>1</sup>H, <sup>1</sup>H and 2D-<sup>1</sup>H, <sup>13</sup>C NMR spectra.

##### Generation of [( $\eta^5, \eta^1$ -C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V( $\eta^2$ -ethene)(N*t*-Bu)]][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**7a**)

An NMR tube equipped with a Teflon (Young) valve was filled with 0.874 g of a 66 mM solution of **6** in C<sub>6</sub>D<sub>5</sub>Br. The tube was connected to a high vacuum line, frozen and evacuated. Subsequently, a calibrated volume of ethene was condensed into the NMR tube, so that a pressure of approximately 1 bar was reached after the NMR tube was closed and thawed out. The NMR tube was kept at room temperature for one hour before measuring, to let the equilibrium stabilize. The exact amount of ethene in solution was determined by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, 25°C): *free olefin*: δ 5.29 (s); **7a**: δ 5.71 (br, 1H, Cp), 5.61 (br, 1H, Cp), 5.34 (sept, J<sub>H-H</sub> = 6, 1H, CH of *i*-Pr), 5.27 (br, 1H, Cp), 5.02 (br, 1H, Cp), 4.72 (m, 2H, =CHH), 4.61 (m, 1H, NCHH), 4.33 (m, 2H, =CHH), 3.26 (dd, J<sub>H-H</sub> = 15 / 7, 1H, NCHH), 2.70 (dd, J<sub>H-H</sub> = 13 / 7, 1H, CpCHH), 1.91 (m, 1H, CpCHH), 0.94 (s, 9H, *t*-Bu), 0.82, 0.59 (d, J<sub>H-H</sub> = 6, 7, 3H, 2 CH<sub>3</sub> of *i*-Pr). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>, -30°C): *free olefin*: δ 123.9 (t, J<sub>C-H</sub> = 160); **7a**: δ 141.9 (C<sub>ipso</sub> of Cp), 109.6, 109.2, 103.1, 101.3 (d, J<sub>C-H</sub> = 173, 173, 179 and 181 respectively, 4 CH of Cp), 103.2 (d, J<sub>C-H</sub> = 164, =CH<sub>2</sub>), 76.3 (d, J<sub>C-H</sub> = 143, CH of *i*-Pr), 73.3 (t, J<sub>C-H</sub> = 138, NCH<sub>2</sub>), 29.5 (t, partial overlap, CpCH<sub>2</sub>), 31.1 (q, J<sub>C-H</sub> = 132, CH<sub>3</sub> of *t*-Bu), 22.6, 20.7 (q, J<sub>C-H</sub> = 127 and 127 respectively, 2 CH<sub>3</sub> of *i*-Pr), C<sub>q</sub> of *t*-Bu not observed. <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, 25°C): δ -707 (Δν<sub>1/2</sub> = 750).

Generation of [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(η<sup>2</sup>-propene)(N*t*-Bu)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**7b**)

The same procedure was used as for **7a**, only now the propene pressure after thawing out the NMR tube was approximately 2 bars. The exact amount of propene in solution was determined by <sup>1</sup>H NMR. Two isomers were formed (A:B ~ 4:5).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): *free olefin*: 5.71 δ (m, 1H, =CHCH<sub>3</sub>), 5.00 (d, J<sub>H-H</sub> = 17, 1H, =CHH cis to CH<sub>3</sub>), 4.94 (d, J<sub>H-H</sub> = 10, 1H, =CHH trans to CH<sub>3</sub>), 1.58 (d, J<sub>H-H</sub> = 6, 3H, =CHCH<sub>3</sub>); **7b**: δ 6.26<sup>B</sup>, 6.01<sup>A</sup> (m, =CHCH<sub>3</sub>), 5.98, 5.93, 5.55, 5.43, 5.40, 5.34, 5.30, 5.08 (m, Cp), 5.66, 5.42 (CH of *i*-Pr), 4.65, 4.39 (m, NCHH), 4.33<sup>B</sup>, 4.01<sup>A</sup> (d, J<sub>H-H</sub> = 17<sup>B</sup>, 17<sup>A</sup>, =CHH cis to CH<sub>3</sub>), 4.15<sup>A</sup>, 3.65<sup>B</sup> (d, J<sub>H-H</sub> = 9<sup>A</sup>, 8<sup>B</sup>, =CHH trans to CH<sub>3</sub>), 3.31, 3.16 (m, NCHH), 2.58, 2.54 (m, CpCHH), 1.99, 1.88 (m, CpCHH), 1.32<sup>A</sup>, 1.28<sup>B</sup> (d, J<sub>H-H</sub> = 5<sup>A</sup>, 5<sup>B</sup>, =CHMe), 0.98, 0.95 (s, *t*-Bu), 0.80, 0.72, 0.66, 0.56 (d, J<sub>H-H</sub> = 6, Me of *i*-Pr). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>, -30°C): *free olefin*: 134.4 (d, J<sub>C-H</sub> = 155, =CHCH<sub>3</sub>), 116.8 (t, J<sub>C-H</sub> = 153, =CH<sub>2</sub>), 20.5 (q, overlap, CH<sub>3</sub>); **7b**: δ 142.2, 141.8 (s, 2 C<sub>ipso</sub> of Cp), 137.7, 135.4 (d, J<sub>C-H</sub> = 157, 159, 2 =CHCH<sub>3</sub>), 111.2, 110.3, 109.6, 109.2, 102.4, 102.3, 101.3, 101.2 (d, J<sub>C-H</sub> = 182, 177, 175, 173, 174, 174, 177 and 177 respectively, 8 CH of Cp), 92.7, 92.5 (t, J<sub>C-H</sub> = 160, 159, 2 =CH<sub>2</sub>), 77.0, 76.4 (t, 2 NCH<sub>2</sub>), 73.4, 72.7 (d, 2 CH of *i*-Pr), 31.2, 30.9 (q, J<sub>C-H</sub> = 127 and 128 respectively, 2 CH<sub>3</sub> of *t*-Bu), 29.7, 29.5 (2 CpCH<sub>2</sub>), 23.4, 22.9, 22.8, 22.6 (4 CH<sub>3</sub> of *i*-Pr), 20.2, 20.1 (2 =CHCH<sub>3</sub>), C<sub>q</sub> of *t*-Bu not observed. <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, 25°C): δ -646, -650 (partial overlap).

Generation of [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(η<sup>2</sup>-isobutene)(N*t*-Bu)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**7c**)

The same procedure was used as for **7a**, only now the isobutene pressure after thawing out the NMR tube was approximately 2 bars. The exact amount of isobutene in solution was determined by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): *free olefin*: δ 4.70 (s, 2H, =CH<sub>2</sub>), 1.59 (s, 6H, =CCH<sub>3</sub>); **7c**: δ 5.79 (br, 1H, Cp), 5.60 (m, 2H, CH of *i*-Pr and Cp), 5.26 (br, 1H, Cp), 4.99 (br, 1H, Cp), 4.54 (m, 1H, NCHH), 3.76 (s, 1H, =CHH), 3.69 (s, 1H, =CHH), 3.24 (m, 1H, NCHH), 2.60 (m, 1H, CpCHH), 1.82 (m, 1H, CpCHH), 1.72 (s, 3H, =CCH<sub>3</sub>), 0.96 (s, 3H, =CCH<sub>3</sub>), 0.94 (s, 9H,

*t*-Bu), 0.87 (d,  $J_{\text{H-H}} = 7$ , 3H,  $\text{CH}_3$  of *i*-Pr), 0.64 (d,  $J_{\text{H-H}} = 7$ , 3H,  $\text{CH}_3$  of *i*-Pr).  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $-30^\circ\text{C}$ ): *free olefin*:  $\delta$  142.6 (s,  $=\text{CCH}_3$ ), 112.0 (t,  $J_{\text{C-H}} = 154$ ,  $=\text{CH}_2$ ), 25.1 (q,  $J_{\text{C-H}} = 125$ ,  $=\text{CCH}_3$ ); **7c**:  $\delta$  177.5 (s,  $=\text{CCH}_3$ ), 142.3 ( $\text{C}_{\text{ipso}}$  of Cp), 112.0, 110.7, 101.0, 101.4 (4 CH of Cp), 84.8 (t,  $J_{\text{C-H}} = 156$ ,  $=\text{CH}_2$ ), 76.5 (CH of *i*-Pr), 72.7 (NCH<sub>2</sub>), 30.9 ( $\text{CH}_3$  of *t*-Bu), 29.9 (CpCH<sub>2</sub>), 29.1, 29.0, 23.9, 19.2 (2  $\text{CH}_3$  of *i*-Pr and 2  $=\text{CCH}_3$ ),  $\text{C}_q$  of *t*-Bu not observed.  $^{51}\text{V}$  NMR (131.4 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $25^\circ\text{C}$ ):  $\delta$  -577 ( $\Delta\nu_{1/2} = 860$ ).

Generation of  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-cyclopentene})(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7d**)

An NMR tube equipped with a Teflon (Young) valve was filled with 0.687 g of a 111 mM solution of **6** in  $\text{C}_6\text{D}_5\text{Br}$ . The tube was connected to a high vacuum line, frozen and evacuated. Subsequently, 0.197 mmol of cyclopentene was condensed into the NMR tube, after which the NMR tube was closed and thawed out.

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $-30^\circ\text{C}$ ): *free olefin*:  $\delta$  5.65 (s, 2H,  $=\text{CH}$ ), 2.20 (t,  $J_{\text{H-H}} = 8$ ,  $=\text{CH-CH}_2$ ), 1.68 (q,  $J_{\text{H-H}} = 8$ ,  $=\text{CH-CH}_2\text{-CH}_2$ ); **7d**:  $\delta$  5.83 (Cp), 5.79, 5.78 (2  $=\text{CH}$ ), 5.77 (CH of *i*-Pr), 5.65, 5.15, 5.09 (3 Cp), 4.62 (NCHH), 3.40 (NCHH), 2.67 (CpCHH), 2.00 ( $=\text{CH-CH}_2$ ), 1.94 (CpCHH), 1.00 (*t*-Bu), 0.91 ( $\text{CH}_3$  of *i*-Pr), 0.79 ( $=\text{CH-CH}_2\text{-CH}_2$ ), 0.70 ( $\text{CH}_3$  of *i*-Pr).  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{C}_6\text{D}_6$ ,  $-30^\circ\text{C}$ ): *free olefin*:  $\delta$  131.3 (d,  $J_{\text{C-H}} = 159$ ,  $=\text{CH}$ ), 33.3 (t,  $J_{\text{C-H}} = 128$ ,  $=\text{CH-CH}_2$ ), 23.7 (t,  $J_{\text{C-H}} = 127$ ,  $=\text{CH-CH}_2\text{-CH}_2$ ); **7d**:  $\delta$  142.4 (s,  $\text{C}_{\text{ipso}}$  of Cp), 125.7, 124.4 (d,  $J_{\text{C-H}} = 156$ , 160, 2  $=\text{CH}$ ), 111.4, 111.3, 102.7, 102.1 (d,  $J_{\text{C-H}} = \text{overlap}$ , overlap, 179 and 174 respectively, 4 CH of Cp), 77.1 (d,  $J_{\text{C-H}} = 143$ , CH of *i*-Pr), 73.3 (t,  $J_{\text{C-H}} = 139$ , NCH<sub>2</sub>), 35.1, 34.9 (t,  $J_{\text{C-H}} = 133$  and 133 respectively, 2  $=\text{CH-CH}_2$ ), 30.9 (q,  $J_{\text{C-H}} = 130$ ,  $\text{CH}_3$  of *t*-Bu), 29.7 (t,  $J_{\text{C-H}} = 130$ , CpCH<sub>2</sub>), 23.2 (q, overlap,  $\text{CH}_3$  of *i*-Pr), 22.1 (t,  $J_{\text{C-H}} = 130$ ,  $=\text{CH-CH}_2\text{-CH}_2$ ), 19.8 (q,  $J_{\text{C-H}} = 126$ ,  $\text{CH}_3$  of *i*-Pr),  $\text{C}_q$  of *t*-Bu not observed.  $^{51}\text{V}$  NMR (131.4 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $25^\circ\text{C}$ ):  $\delta$  -521 ( $\Delta\nu_{1/2} = 4300$ ).

Generation of  $[(\eta^5, \eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}i\text{-Pr})\text{V}(\eta^2\text{-styrene})(\text{N}t\text{-Bu})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**7e**)

To 0.929 g of a 0.223 mM solution of **6** in  $\text{C}_6\text{D}_5\text{Br}$  was added 78.4 mg (0.75 mmol) of styrene. Compound **7e** had to be measured immediately in order to prevent polymerization, which takes place even at low temperatures. Two isomers are formed (A:B ~ 4:5).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_5\text{Br}$ ,  $-30^\circ\text{C}$ ): *free olefin*:  $\delta$  7.25 (d,  $J_{\text{H-H}} = 8$ , 2H, CH of Ph), 7.17 (t,  $J_{\text{H-H}} = 8$ , 2H, CH of Ph), 7.12 (t,  $J_{\text{H-H}} = 7$ , 1H, CH of Ph), 6.61 (dd,  $J_{\text{H-H}} = 18 / 11$ , 1H,  $=\text{CH}$ ), 5.64 (d,  $J_{\text{H-H}} = 18$ , 1H,  $=\text{CHH}$  cis to Ph), **xxx** (d,  $J_{\text{H-H}} = 11$ , 1H,  $=\text{CHH}$  trans to Ph); **7e**:  $\delta$  6.81<sup>A</sup> (dd,  $J_{\text{H-H}} = 17 / 10$ ,  $=\text{CH}$ ), 6.73<sup>B</sup> (dd,  $J_{\text{H-H}} = 18 / 10$ ,  $=\text{CH}$ ), 5.89, 5.74 (br, 2 Cp), 5.62 (shoulder of solvent, CH of *i*-Pr), 5.31 (overlap, Cp), 5.24 (m, CH of *i*-Pr), ~5.1<sup>A</sup> (overlap with styrene,  $=\text{CHH}$  cis to Ph), 5.04 (overlap, 2 Cp), 5.01, 4.93, 4.78 (br, 3 Cp), 4.53<sup>B</sup> (d,  $J_{\text{H-H}} = 17$ ,  $=\text{CHH}$  cis to Ph), 4.48<sup>B</sup> (d,  $J_{\text{H-H}} = 10$ ,  $=\text{CHH}$  trans to Ph), 4.36, 4.16 (m, 2 NCHH), 3.79<sup>A</sup> (d,  $J_{\text{H-H}} = 9$ ,  $=\text{CHH}$  trans to Ph), 3.16 (dd,  $J_{\text{H-H}} = 14 / 7$ , NCHH), 3.09 (dd,  $J_{\text{H-H}} = 14 / 8$ , NCHH), 2.62 (dd,  $J_{\text{H-H}} = 13 / 7$ , CpCHH), 2.28 (dd,  $J_{\text{H-H}} = 13 / 7$ , CpCHH), 1.88, 1.73 (m, 2 CpCHH), 0.94 (s, *t*-Bu), 0.93 (shoulder, *t*-Bu), 0.88, 0.76, 0.68, -0.09 (d,  $J_{\text{H-H}} = 6$ , 6, 6 and 6 respectively, 4  $\text{CH}_3$  of *i*-Pr).  $^{13}\text{C}$  NMR: *free olefin*

(125.7 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 138.8 (s, C<sub>ipso</sub> of styrene), 137.7 (d, J<sub>C-H</sub> = 150, =CH), 129.3 (d, J<sub>C-H</sub> = 159, CH of Ph), 128.6 (d, J<sub>C-H</sub> = 160, CH of Ph), 127.0 (d, J<sub>C-H</sub> = 158, CH of Ph), 114.4 (t, J<sub>C-H</sub> = 158, =CH<sub>2</sub>); **7e**: δ 142.2, 141.5 (s, 2 C<sub>ipso</sub> of Cp), 135.8, 133.6, 133.3, 133.2, 132.9, 129.2, 129.1, 129.0, 128.4, 128.1 (2 =CH, 2 C<sub>ipso</sub> of Ph and 6 CH of Ph), 113.5, 112.6, 111.7, 111.1, 102.2, 101.8, 101.7, 101.3 (8 CH of Cp), 86.0, 83.8 (t, J<sub>C-H</sub> = 162 and 159 respectively, 2 =CH<sub>2</sub>), 77.0, 76.0 (2 CH of *i*-Pr), 73.3, 72.6 (2 NCH<sub>2</sub>), 30.9, 30.8 (2 CH<sub>3</sub> of *t*-Bu), 29.7, 29.6 (2 CpCH<sub>2</sub>), 24.2, 24.1, 22.5, 20.6 (4 CH<sub>3</sub> of *i*-Pr), C<sub>q</sub> of *t*-Bu not observed. <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ -614 (Δv<sub>½</sub> = 2200).

Generation of [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>Me)V(η<sup>2</sup>-ethene)(N*t*-Bu)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**8**)

The same procedure was used as for **7a**, starting from [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>NMe)V(N*t*-Bu)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]. The exact amount of ethene in solution was determined by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 5.74 (br, 1H, Cp), 5.52 (br, 1H, Cp), 5.22 (br, 1H, Cp), 4.96 (br, 1H, Cp), 4.71 (m, 2H, =CH<sub>2</sub>), 4.54 (m, 1H, NCHH), 4.29 (m, 2H, =CH<sub>2</sub>), 3.79 (s, 3H, NCH<sub>3</sub>), 3.63 (m, 1H, NCHH), 2.48 (m, 1H, CpCHH), 2.25 (m, 1H, CpCHH), 0.91 (s, 9H, *t*-Bu). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 140.8 (C<sub>ipso</sub> of Cp), 109.0, 103.3, 101.5, 100.1 (4 CH of Cp), 101.3 (t, J<sub>C-H</sub> = 165, =CH<sub>2</sub>), 84.9 (NCH<sub>3</sub>), 64.4 (NCH<sub>2</sub>), 30.8 (CH<sub>3</sub> of *t*-Bu), 28.0 (CpCH<sub>2</sub>), C<sub>q</sub> of *t*-Bu not observed. <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ -734 (Δv<sub>½</sub> = 3500).

Generation of [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(η<sup>2</sup>-ethene)(N*p*-Tol)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**9**)

The same procedure was used as for **7a**, starting from [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>N*i*-Pr)V(N*p*-Tol)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]. The exact amount of ethene in solution was determined by <sup>1</sup>H NMR.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 6.89 (br, 4H, CH of *p*-Tol), 5.85 (br, 1H, Cp), 5.49 (br, 1H, Cp), 5.31 (overlap with free ethene, CH of *i*-Pr), 5.25 (br, 1H, Cp), 5.12 (m, 1H, Cp), 4.79 (m, 2H, =CH<sub>2</sub>), 4.68 (m, 1H, NCHH), 4.22 (m, 2H, =CH<sub>2</sub>), 3.50 (m, 1H, NCHH), 2.68 (m, 1H, CpCHH), 2.17 (s, 4H, CH<sub>3</sub> of *p*-Tol and shoulder of CpCHH), 0.99 (d, J<sub>H-H</sub> = 7, 3H, CH<sub>3</sub> of *i*-Pr), 0.65 (d, J<sub>H-H</sub> = 7, 3H, CH<sub>3</sub> of *i*-Pr). <sup>13</sup>C {<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 159.3, 142.0, 141.1 (2 C<sub>q</sub> of *p*-Tol and C<sub>ipso</sub> of Cp), 123.8 (CH of *p*-Tol), 109.7, 109.3, 105.1, 104.4 (4 CH of Cp), 104.9 (=CH<sub>2</sub>), 75.2 (NCH<sub>2</sub>), 74.1 (CH of *i*-Pr), 29.2 (CpCH<sub>2</sub>), 23.0 (CH<sub>3</sub> of *i*-Pr), 22.2 (CH<sub>3</sub> of *p*-Tol), 21.3 (CH<sub>3</sub> of *i*-Pr), 1 CH of *p*-Tol not observed (probably due to overlap with solvent resonances). <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ -600 (Δv<sub>½</sub> = 6500).

Generation of [(*t*-BuN)VCp(η<sup>2</sup>-cyclopentene)(N*i*-Pr<sub>2</sub>)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**10**)

The same procedure was used as for **7d**, starting from [(*t*-BuN)VCp(N*i*-Pr<sub>2</sub>)][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>].

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C): δ 6.43 (br, 1H, =CH), 5.44 (s, 5H, Cp), 4.95 (br, 1H, =CH), 4.41 (sept, J<sub>H-H</sub> = 6, 1H, CH of *i*-Pr), 3.16 (br, 1H, CH of *i*-Pr), 1.47 (d, J<sub>H-H</sub> = 6, 3H, CH<sub>3</sub> of *i*-Pr), 0.99 (s, 9H, *t*-Bu), 0.84 (d, J<sub>H-H</sub> = 7, 3H, CH<sub>3</sub> of *i*-Pr), 0.70 (d, J<sub>H-H</sub> = 6, 3H, CH<sub>3</sub> of *i*-Pr), 0.54 (d, J<sub>H-H</sub> = 7, 3H, CH<sub>3</sub> of *i*-Pr), =CH-CH<sub>2</sub> and =CH-CH<sub>2</sub>-CH<sub>2</sub> not observed. <sup>13</sup>C {<sup>1</sup>H} NMR (125.7

MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C):  $\delta$  128.7, 120.3 (2 =CH), 108.5 (Cp), 80.9 (C<sub>q</sub> of *t*-Bu), 70.6, 60.4 (2 CH of *i*-Pr), 35.0, 34.8 (2 =CH-CH<sub>2</sub>), 33.2 (CH<sub>3</sub> of *i*-Pr), 31.6 (CH<sub>3</sub> of *t*-Bu), 26.9 (CH<sub>3</sub> of *i*-Pr), 23.3 (=CH-CH<sub>2</sub>-CH<sub>2</sub>), 22.3, 19.4 (2 CH<sub>3</sub> of *i*-Pr). <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, 25°C):  $\delta$  -555 ( $\Delta\nu_{1/2}$  = 700).

Generation of [(*p*-TolN)VCp( $\eta^2$ -cyclopentene)(N*i*-Pr<sub>2</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (13)

The same procedure was used as for **7d**, starting from [(*p*-TolN)VCp(N*i*-Pr<sub>2</sub>)] [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>].

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C):  $\delta$  6.90 (s, CH of *p*-Tol), 6.32 (s, =CH), 5.42 (s, Cp), 4.74 (s, =CH), 4.38 (br, CH of *i*-Pr), 3.22 (br, CH of *i*-Pr), 2.18 (s, CH<sub>3</sub> of *p*-Tol), 1.81 (=CH-CH<sub>2</sub>), ~1.6 (overlap with free olefin, CH<sub>3</sub> of *i*-Pr), 1.02 (CH<sub>3</sub> of *i*-Pr), 0.75 (CH<sub>3</sub> of *i*-Pr), 0.57 (CH<sub>3</sub> of *i*-Pr), =CH-CH<sub>2</sub>-CH<sub>2</sub> not observed. <sup>13</sup>C {<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>5</sub>Br, -30°C):  $\delta$  160.0, 141.4 (2 C<sub>ipso</sub> of *p*-Tol), 127.7, 125.8 (2 CH of *p*-Tol), 129.9, 115.6 (2 =CH), 109.4 (Cp), 69.2, 61.2 (2 CH of *i*-Pr), 35.0, 26.4 (2 CH<sub>3</sub> of *i*-Pr), 35.0, 33.2 (2 =CH-CH<sub>2</sub>), 22.2 (CH<sub>3</sub> of *p*-Tol), 22.1 (=CH-CH<sub>2</sub>-CH<sub>2</sub>), 20.2, 19.5 (2 CH<sub>3</sub> of *i*-Pr). <sup>51</sup>V NMR (131.4 MHz, C<sub>6</sub>D<sub>5</sub>Br, 25°C):  $\delta$  -397 ( $\Delta\nu_{1/2}$  = 2500).

Determination of K<sub>eq</sub>

The K<sub>eq</sub> was determined from the <sup>1</sup>H NMR spectra of the reaction mixtures at 25°C. The ratio olefin adduct: solvent separated ion pair was determined by integrating well separated resonances of both complexes (mostly resonances of the Cp moiety or of the ethylene bridge). In order to have reliable data, a relaxation time (d1) of 25 seconds was used during the measurement, and an average integral value of several resonances was calculated. When gaseous olefins were used, the amount of olefin in the reaction mixture was calculated from its integral.

The K<sub>eq</sub> of the formation of **7a** was determined at 25°C from 4 samples with different vanadium and olefin concentrations (values: 89, 94, 105, 108). From this K<sub>eq</sub> = 100 ± 10 was calculated.

The results of the variable temperature <sup>1</sup>H NMR measurements on the coordination of cyclopentene to **6** (Table 3), were corrected for errors in the temperature by calibration with 100% methanol (temperatures < 0°C) or 100% ethylene glycol (temperatures > 0°C). In order to compensate for the variable density of the solvent at different temperatures, the density of C<sub>6</sub>D<sub>5</sub>Br was determined in the range of 5 to 39 °C (measuring range of the density meter is 0 to 40 °C) and extrapolated to -10 °C and +70 °C. The equation for the solvent density is: density = 1.57 - 1.41 × 10<sup>-3</sup> × T (r<sup>2</sup> = 0.996, density in g/mL, T in °C). When the temperature was decreased (starting at 30°C in steps of -10°C), the solution was kept at the new temperature for 45 minutes before the <sup>1</sup>H NMR measurement was started, so that the equilibrium could stabilize. In the temperature range of 30°C to 80°C (steps of +10°C) a waiting time of 30 minutes was

used. Below -10°C the  $K_{eq}$  values did no longer respond to temperature changes, and these results have not been used in the calculations.

**Table 3:** <sup>1</sup>H NMR measurements on the coordination of cyclopentene to **6**.

Temp (K)	Fraction Adduct	$K_{eq}$	$\Delta G^0$ (kJ·mol <sup>-1</sup> )
260	0.557	29.4	-7.30
269	0.495	22.5	-6.96
280	0.436	17.3	-6.63
290	0.374	13.2	-6.22
300	0.323	10.4	-5.84
309	0.257	7.39	-5.14
319	0.232	6.41	-4.93
328	0.194	5.05	-4.42
338	0.165	4.14	-3.99
347	0.141	3.41	-3.54

Calculation of  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$

For every value of  $K_{eq}$ , the  $\Delta G^0$  was calculated using Equation 3 (Table 3). By plotting  $\Delta G^0$  vs. T,  $\Delta H^0$  and  $\Delta S^0$  were calculated using Equation 4. The equation for  $\Delta G^0$  is:  $\Delta G^0 = 0.0437 \cdot T - 18.8$  ( $r^2 = 0.993$ ,  $\Delta G^0$  in kJ·mol<sup>-1</sup>, T in K). This resulted in values of -19 kJ·mol<sup>-1</sup> for  $\Delta H^0$  and -0.04 kJ·mol<sup>-1</sup>·K<sup>-1</sup> for  $\Delta S^0$ . The error in the calculations was estimated by repeating the calculations using  $K_{eq}$  values 10% higher and lower than the observed values. This resulted in errors of  $\pm 1$  kJ·mol<sup>-1</sup> for  $\Delta H^0$  and  $\pm 0.01$  kJ·mol<sup>-1</sup>·K<sup>-1</sup> for  $\Delta S^0$ .

#### 4.5 References

- (1) Shriver, D.F.; Atkins, P.W.; Langford, C.H., *Inorganic Chemistry*, 2<sup>nd</sup> edition, Oxford University Press, Oxford, **1994**, 685-686.
- (2) (a) Arlman, E.J.; Cossee, P., *J. Catal.*, **1964**, 3, 99. (B) Cossee, P., *J. Catal.*, **1964**, 3, 80.
- (3) Zirconium alkoxide complex (a) Wu, Z.; Jordan, R.F.; Petersen, J.L., *J. Am. Chem. Soc.*, **1995**, 117, 5867.  
Yttrium alkyl complex (b) Casey, C.P.; Hallenbeck, S.L.; Pollock, D.W.; Landis, C.R., *J. Am. Chem. Soc.*, **1995**, 117, 9770. (c) Casey, C.P.; Hallenbeck, S.L.; Wright, J.M.; Landis, C.R., *J. Am. Chem. Soc.*, **1997**, 119, 9680. (d) Casey, C.P.; Fagan, M.A.; Hallenbeck, S.L., *Organometallics*, **1998**, 17, 287.  
Other d<sup>0</sup> metal olefin adducts (e) Temme, B.; Karl, J.; Erker, G., *Chem. Eur. J.*, **1996**, 919. (f) Karl, J.; Erker, G., *Chem. Ber. / Recueil.*, **1997**, 130, 12619. (g) Karl, J.; Dahlmann, M.; Erker, G.; Bergander, K., *J. Am. Chem. Soc.*, **1998**, 120, 5643.
- (4) Kress, J.; Osborn, J.A., *Angew. Chem. Int. Ed. Eng.*, **1992**, 31, 1585.

- (5) Bis-Cp complexes (a) Woo, T.K.; Fan, L.; Ziegler, T., *Organometallics*, **1994**, *13*, 432.  
(b) Woo, T.K.; Fan, L.; Ziegler, T., *Organometallics*, **1994**, *13*, 2252.  
Constrained geometry complexes: (c) Fan, L.; Harrison, D.; Woo, T.K.; Ziegler, T., *Organometallics*, **1995**, *14*, 2018.
- (6) de With, J.; Horton, A.D., *Organometallics*, **1993**, *12*, 1493.
- (7) The  $^{13}\text{C}$  NMR resonance of the  $\text{H}_2\text{C}=\text{CHPh}$  carbon of the coordinated styrene in **7e** could not be observed, and we expect it overlaps with resonances of the free styrene and the solvent. This means that it appears 2 - 10 ppm upfield from the corresponding resonance of the free styrene.
- (8) Sandström, J., *Dynamic NMR spectroscopy*; Academic Press, London, **1982**, 96.
- (9) Gillis, D.J.; Tudoret, M.-J.; Baird, M.C., *J. Am. Chem. Soc.*, **1993**, *115*, 2543.
- (10) Since the neutral methyl complexes used for the generation of the adducts **8** and **9** are oils, they could not be purified completely. The small amounts of impurities probably cause the slow observed polymerization of the ethene, which can influence the determination of  $K_{\text{eq}}$ . No polymer formation was observed after the  $K_{\text{eq}}$  measurement of **8** and **9**, however, after one night at room temperature the  $^1\text{H}$  NMR spectrum shows that all ethene is polymerized. Furthermore, the equilibrium reaction of **6** with ethene stabilizes slowly, which means that leaking of ethene from the reaction mixture by polymerization may influence the determination of  $K_{\text{eq}}$ .
- (11) All calculations performed using the Gaussian 94 package (Gaussian 94, Revision E.1; Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Gill, P.M.W.; Johnson, B.G.; Robb, M.A.; Cheeseman, J.R.; Keith, T.A.; Peterson, G.A.; Montgomery, J.A.; Raghavachari, K.; Al-Lahan, M.A.; Zakrewski, V.G.; Ortiz, J.V.; Foresman, J.B.; Cioslowski, J.; Stefanov, B.B.; Nanayakkara, A.; Challacombe, M.; Peng, C.Y.; Ayala, P.Y.; Chen, W.; Wong, M.W.; Andres, J.L.; Replogle, E.S.; Gomperts, R.; Martin, R.L.; Fox, D.J.; Binkley, J.S.; DeFrees, D.J.; Baker, J.; Stewart, J.P.; Head-Gordon, M.; Gonzalez, C.; Pople, J.A. Gaussian, Inc.: Pittsburgh, PA, 1995) using the B3LYP functional (Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648). The small split-valence 3-216 basis (ref. a) was used for C, H and N, and the small core LANL 202 basis (ref. b) was used for V. (a) Binkley, S.; Pople, J.A.; Hehre, W.J., *J. Am. Chem. Soc.*, **1980**, *102*, 939. (b) Hay, P.J.; Wadt, W.R., *J. Chem. Phys.*, **1985**, *82*, 299.
- (12) Margl, P.; Deng, L.; Ziegler, T., *Organometallics*, **1998**, *17*, 933.
- (13) Witte, P.T.; Meetsma, A.; Hessen, B.; Budzelaar, P.H.M., *J. Am. Chem. Soc.*, **1997**, *119*, 10561.
- (14) Klotz, I.M.; Rosenberg, R.M., *Chemical Thermodynamics: basic theory and methods*, 5<sup>th</sup> edition, Wiley & Sons, New York, **1994**, 162.
- (15) Atkins, P.W., *Physical Chemistry*, 3th edition, Oxford University Press, Oxford, **1986**, 221-222.

- (16) Beck, S.; Prosenc, M-H.; Brintzinger, H.H., *J. Mol. Catal. A. Chem.*, **1998**, *128*, 41.