

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 1

General Introduction

1.1 Ziegler-Natta catalysts for olefin polymerization

In the 1950's Ziegler *et al.* investigated the reaction of tri-ethyl aluminum with ethene. They found that traces of colloidal nickel change the course of the reaction to ethene dimerization, and almost exclusive formation of 1-butene.¹ This led to a systematic search of the use of other metal salts as possible catalysts in this reaction. The investigators found that traces of metal salts of the group 4, 5 and 6 metals in combination with aluminum alkyls catalyzed the polymerization of ethene to linear HDPE (High Density PolyEthylene), even at low pressures and temperatures,¹ while at that time industrial processes were only able to make branched LDPE (Low Density PolyEthylene).^{1,2} Shortly after Ziegler's discovery, Natta reported the stereospecific polymerization of propene to isotactic polypropene, using Ziegler's $\text{TiCl}_4/\text{AlEt}_3$ catalyst.³ Before this discovery polypropylene was of low molecular weight, had uninteresting properties and no commercial value.⁴

Nowadays, most commercial processes still use TiCl_4 based catalysts with aluminum alkyl cocatalysts, but with the current technology polymer yields exceed 20 kg of polymer per gram of catalyst, with an isotactic index of 95%.⁴ World wide, millions of tons of polyolefins are nowadays produced using Ziegler-type catalysts.⁵

1.2 Vanadium based catalysts

There are several differences between vanadium and titanium based Ziegler-Natta catalysts. Most importantly, vanadium based Ziegler catalysts are unique in their ability to incorporate comonomers in a random order, an important characteristic to produce an amorphous, elastomeric product.⁵ In

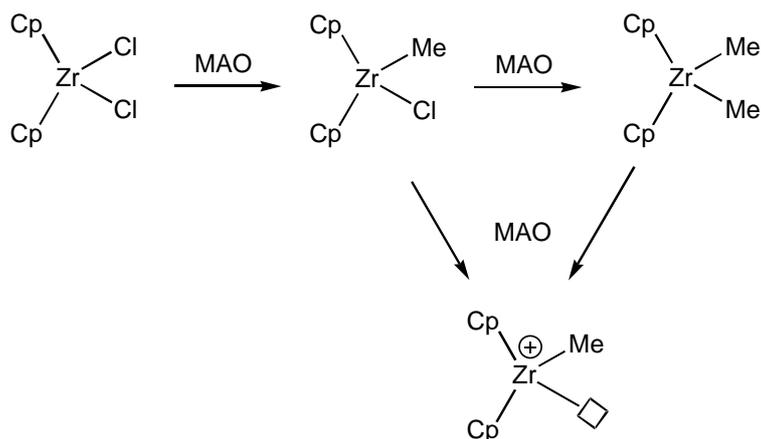
industry, vanadium based catalysts are generally used in the production of Ethylene-Propylene copolymers (EPM; M stands for saturated back-bone) and Ethylene-Propylene-Diene terpolymers (EPDM).⁵

Titanium based Ziegler catalysts form heterogeneous systems, which contain multiple active sites and therefore produce a polymer with a broad molecular weight distribution⁶ ($M_w/M_n = 3 - 7$).^{7,8} In contrast, vanadium based Ziegler systems are soluble and single-site, as indicated by the narrow molecular weight distribution of the produced polymer ($M_w/M_n < 3$).^{8,9}

A long standing question in the chemistry of vanadium based Ziegler catalysts is the oxidation state of the active species. Early studies already indicated that vanadium(0) and vanadium(I) species were inactive, but it was unclear whether the active species was in an oxidation state of +2, +3 or +4.¹⁰ Nowadays, the generally accepted idea is that the active species is formed by reduction of the vanadium(IV) or vanadium(V) catalyst precursor by the aluminum cocatalyst, to form a vanadium(III) alkyl species. However, since the vanadium appears to be further reduced to inactive vanadium(II) species, organic halides (for instance butyl-perchloro-crotonate ester) are added to the reaction mixtures to reoxidize the vanadium to the +3 oxidation state.¹¹

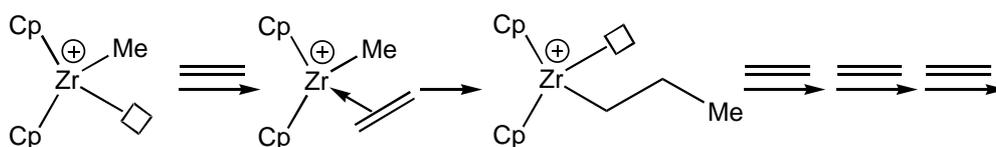
1.3 Single-site catalysts

Soluble catalysts based on group 4 metallocenes were initially used as simple model compounds for the heterogeneous Ziegler catalysts, but became an important and independent class of catalysts after the discovery of MAO (MethylAluminOxane, formally $[AlMeO]_n$) as a powerful cocatalyst. The narrow molecular weight distribution of the produced polymer ($M_w/M_n < 3$) indicates that these soluble catalysts, just as the soluble vanadium catalysts, are single site catalysts.¹²



Scheme 1

Studies on the activation of metallocenes by MAO reveal that high MAO/metallocene ratios are necessary to generate an active species. When the catalyst precursor Cp_2ZrCl_2 is treated with MAO, the metal is alkylated to generate Cp_2ZrMeCl and, when an excess of MAO is used, Cp_2ZrMe_2 . When the ratio Al/Zr exceeds 200, methyl or chloride abstraction generates the cationic species $[\text{Cp}_2\text{ZrMe}]^+$ (Scheme 1).¹³ This cationic species is now recognized as the active species in olefin polymerization.¹⁴ The polymerization is believed to take place by coordination of the olefin to the vacant side of the cationic metal center, and subsequent insertion into the metal-alkyl bond, as previously described for Ziegler-type catalysts (Scheme 2).¹⁵



Scheme 2

An advantage of the metallocene derived catalysts is that their properties can be tuned by rational ligand modifications. By connecting the two Cp moieties of the achiral metallocenes the ligand system becomes rigid (*ansa*-metallocenes, Figure 1A);¹⁶ after introduction of substituents on the Cp rings

stereoselective polymerization of propene is possible. When one Cp moiety is replaced by an amido group, the metal becomes more open and electron deficient (constrained geometry catalysts, Figure 1B);¹⁷ this catalyst shows a random incorporation of α -olefins in copolymerizations. Additional advantages of the constrained geometry catalysts over the *ansa*-metallocenes are the higher stability towards MAO, the higher thermal stability, and the higher molecular weight of the produced polymer. Recently, new catalysts have been developed based on late transition metals (Figure 1C);¹⁸ in general late transition metals are more tolerant towards functional groups.

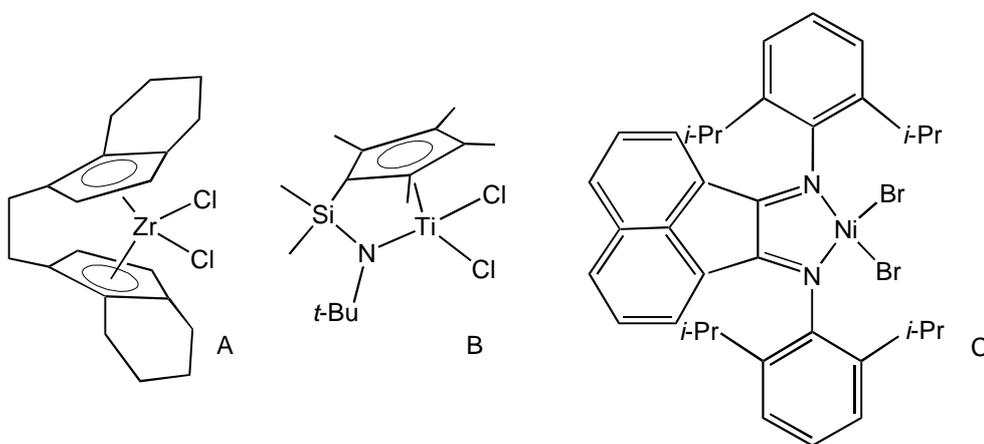
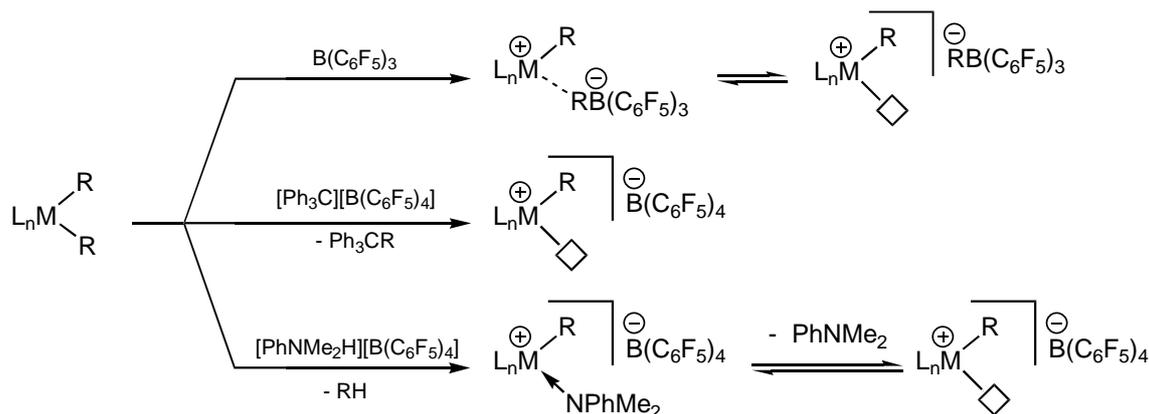


Figure 1: Examples of soluble catalyst precursors.

1.4 Well defined cationic complexes

Although the role of MAO in generating catalytically active cationic species is now reasonably well understood, the exact composition of MAO is still unknown.¹⁹ Furthermore, a large excess of the cocatalyst is necessary to generate the active species, which makes the study on these systems difficult. However, the development of alternative methods for the generation of cationic species has led to an extensive research in this field. Here we will describe three of these methods, all of which use neutral metal alkyl complexes (preferably methyl or benzyl species) as catalyst precursor.



Scheme 3

Alkyl abstraction from the di-alkyl complex L_nMR_2 ($R = \text{Me}$ or CH_2Ph) with the Lewis acidic borane compound $B(\text{C}_6\text{F}_5)_3$ generates $[L_nMR][\text{RB}(\text{C}_6\text{F}_5)_3]$ (Scheme 3).²⁰ The $[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ anion can remain coordinated to the cationic metal center (by the methyl²⁰ or phenyl²¹ group), or dissociate, depending on the circumstances (for instance: solvent polarity, steric hinderance of L, ect.).

Alkyl abstraction with the trityl cation of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ generates a cationic complex with a weakly coordinating anion, $[L_nMR][\text{B}(\text{C}_6\text{F}_5)_4]$ and Ph_3CR (Scheme 3).²² Although a weak interaction of the fluorine atoms of the anion with the cationic metal center in $[\text{Cp}^*\text{ThMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ is observed in the solid state,²³ the anion is dissociated in solution.

Protonation of L_nMR_2 with the Brønsted acid $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ generates $[L_nMR][\text{B}(\text{C}_6\text{F}_5)_4]$, RH and PhNMe_2 (Scheme 3).²⁴ This last method generates a cationic metal center with the weakly coordinating $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion, but the PhNMe_2 that is also generated can block the free coordination site on the metal. This can be overcome by using amines with large substituents.²⁵

1.5 Well-defined vanadium catalysts

The studies on ligand systems and cocatalysts described above have almost all been performed on group 4 metal complexes. Only relatively recently have well-defined catalysts based on middle and late transition metals been

described in literature.¹⁸ Despite the increasing number of metals used in olefin polymerization, the number of well-defined vanadium catalysts is very limited.

In analogy to the group 4 single-site catalysts, the vanadocene dichloride Cp_2VCl_2 was investigated as a catalyst precursor. The vanadium complex is activated by aluminum halo alkyls to generate an ethene polymerization catalyst, however, there are indications that the Cp_2V moiety does not remain intact.²⁶ This was further demonstrated by the generation of the cationic species $[\text{Cp}_2\text{VMe}]^+$, which is unreactive towards ethene under a variety of reaction circumstances (various counter anions, solvents, temperatures and ethene pressures).²⁷ Apparently the 14 valence electron species $[\text{Cp}_2\text{TiR}]^+$ is an active catalyst, while the 15 valence electron species $[\text{Cp}_2\text{VR}]^+$ is not. Probably, the extra electron in the vanadium complex occupies the orbital necessary for monomer coordination (Scheme 2). Similar differences are found between the isostructural Cp^*_2ScH and Cp^*_2TiH . While the 14 valence electron scandium species is active in olefin polymerization,²⁸ the 15 valence electron titanium species only reacts by a single ethene insertion.²⁹

The isolobal relationship between the group 4 metallocenes and the group 5 half-sandwich imido complexes (Figure 2A), has led to the investigation of these last species, and their isolobal hydrotris(pyrazolyl)borate (Tp) analogues (Figure 2B), as possible catalyst precursors.³⁰ Both type of complexes are activated by MAO to polymerize ethene, although the exact nature of the active species is unknown.

More recently, new non-Cp vanadium complexes have been investigated as possible catalyst precursors (Figure 2C - F).³¹ Although these complexes are active catalysts when activated by aluminum halo alkyls (complexes C and D) or MAO (complexes E and F), no significant activities were observed after activation of the di-alkyl species of complexes D - F with $\text{B}(\text{C}_6\text{F}_5)_3$.

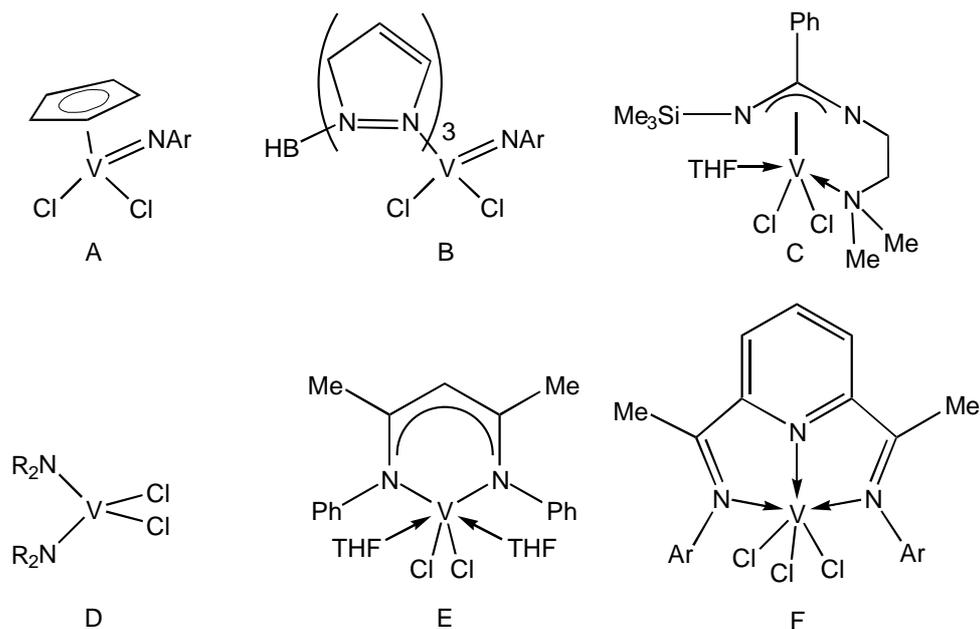


Figure 2: Example of soluble vanadium catalyst precursors.

Theopold *et al.* report that the cationic vanadium(III) alkyl complex $[LVMe(OEt_2)(THF)][B\{3,5-(CF_3)_2-C_6H_3\}_4]$ (L = N,N-diphenyl-2,4-pentadiimine, Figure 3) is an active polymerization catalyst. Unfortunately, characterization of the catalyst and details about the polymerization experiments have not been reported so far.^{31d}

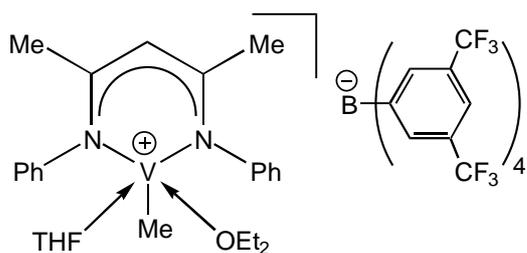


Figure 3: Cationic vanadium(III) alkyl complex.

1.6 Aspects of organo-vanadium chemistry

In general the organometallic chemistry of vanadium complexes is not as well developed as that of its group 4 neighbor, titanium. There are several reasons for this. First of all, vanadium has a more extensive redox chemistry than titanium, and oxidation states in organometallic compounds range from +5 to -1.³² Furthermore, most vanadium complexes are paramagnetic, which makes study by NMR spectroscopy difficult. Even complexes with an even number of d-electrons tend to have multiple unpaired electrons, unless the complexes are 18 valence electron species. Although IR spectroscopy and elemental analysis give valuable information about functional groups and stoichiometry, characterization often has to be based on single crystal X-ray diffraction.

For diamagnetic vanadium complexes (mostly d^0 vanadium(V) compounds), ^{51}V NMR spectroscopy is a much used tool (^{51}V nucleus: Spin number $I = 7/2$, natural abundance $> 99\%$). So far, it has mostly been used to observe trends within series of structurally related complexes,³³ and characterization based only on the chemical shift is not possible. Although ^{51}V NMR resonances are often broad, information about coupling constants (especially $J_{\text{V-N}}$) is reported.³³ The quadrupolar ^{51}V nucleus broadens ^1H , ^{13}C and ^{31}P NMR resonances of groups close to the metal center, which can be used in assigning resonances. However, much information about coupling constants in these spectra is lost, even though lowering the temperature can help to make resonances more narrow.³⁴

A limitation in the organometallic vanadium chemistry is the relatively low stability of vanadium alkyl complexes. Furthermore, vanadium in the +5 and +4 oxidation state is a strong oxidant, and often alkylation leads to reduction of the metal center. These features are especially important for the chemistry of well-defined vanadium catalysts, since this requires the synthesis of vanadium di-alkyl species. So far, only few vanadium di-alkyl species have been reported,³⁵ the most surprising is probably the bis-*n*-butyl complex, $\text{LV}(n\text{-Bu})_2$ ($\text{L} = N,N$ -diphenyl-2,4-pentadiimine), reported by Budzelaar *et al.*^{31c} This complex, which contains four β -hydrogens, can be crystallized from warm hexane (50°C), without significant decomposition.

1.7 Aim of the research

The aim of this research is (1) to develop the chemistry of vanadium complexes containing the amido functionalized cyclopentadienyl (Cp-amido) ligand; (2) to study the nature and reactivity of well-defined cationic vanadium species; (3) to synthesize Cp-amido vanadium complexes that are isostructural to known titanium complexes, and compare their properties in catalytic olefin polymerization.

The Cp-amido ligand $C_5H_4(CH_2)_nNR$ is chosen for this study, since the corresponding titanium complexes are active olefin polymerization catalysts. The 15 valence electron species $[Cp_2VR]^+$ is not active in olefin polymerization, but the cationic $[(Cp\text{-amido})VR]^+$ is a 13 valence electron species and could therefore be an active catalyst. This gives an opportunity to compare isostructural d^0 and d^1 catalyst systems.

1.8 Contents of the thesis

In Chapter 2 the synthesis of Cp-amido vanadium(V) complexes is described. Various ways to introduce the Cp-amido ligand on the metal center have been explored, and the synthesis and stability of a series of Cp-amido vanadium(V) alkyl complexes studied. An additional imido ligand is used to stabilize the high valence vanadium center.

Starting from neutral vanadium(V) methyl complexes, Chapter 3 describes the generation and characterization of well-defined cationic complexes. Although these complexes are not suitable as polymerization catalysts, since they lack a metal alkyl bond for olefin insertion, the study of their reactivity towards C-C unsaturated substrates provided useful information on the reactivity of these species. For instance, although the V-N(imido) bond is inert, the V-N(amido) bond shows the unprecedented insertion of non-activated di-olefins and alkynes.

Simple olefins like ethene and propene coordinate to the cationic vanadium(V) center, which is the first time that adducts of these olefins with d^0 metal centers were characterized. An extensive study of these adducts is found in Chapter 4.

Chapter 5 describes the synthesis of a Cp-amido vanadium(IV) dichloro complex, by a route which also gives entry to vanadium complexes in the oxidation state of +2 and +3. The vanadium(IV) complex is activated by MAO to generate an active catalyst for ethene polymerization, although the activity is lower than that of the isostructural titanium(IV) complex.

Parts of this research have been communicated: Witte, P.T.; Meetsma, A.; Hessen, B.; Budzelaar, P.H.M., *J. Am. Chem. Soc.*, **1997**, *119*, 10561. Witte, P.T.; Meetsma, A.; Hessen, B., *Organometallics*, **1999**, *18*, 2944.

1.9 References

- (1) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H., *Angew. Chem.*, **1955**, *67*, 541.
- (2) Mülhaupt, R., in: Fink, G.; Mülhaupt, R.; Brintzinger, H.H. (Editors), *Ziegler catalysts, recent scientific innovations and technological improvements*, Springer report, Berlin, **1995**.
- (3) (a) Natta, G., *Angew. Chem.*, **1956**, *68*, 393. (b) Natta, G.; Pasquon, I.; Giachetti, E., *Angew. Chem.*, **1957**, *69*, 213.
- (4) Moore, E.P. Jr., *Polypropylene*, in: Salamone, J.C. (Editor), *The polymeric materials encyclopedia* (on CD-ROM), CRC Press, **1996**.
- (5) Parshall, G.W.; Ittel, S.D., *Homogeneous catalysis, the applications and chemistry of catalysis by soluble transition metal complexes*, 2nd Edition, Wiley & Sons inc., New York, **1992**, Chapter 4.
- (6) Polymer 'molecular weight': M_n = number average, M_w = weight average; Polydispersity = M_w/M_n . When the chain growth and termination are of a constant rate and independent of the chain length, $M_w/M_n = 2$. See: Parker, D.B.V., *Polymer chemistry*, Applied Science Publishers, London, **1974**, pp. 134 - 141.
- (7) Lee, D-H., *Olefin polymerization catalysts*, in: Salamone, J.C. (Editor), *The polymeric materials encyclopedia* (on CD-ROM), CRC Press, **1996**.
- (8) Sinn, H.; Kaminsky, W., *Adv. Organomet. Chem.*, **1980**, *18*, 99.

- (9) Davis, S.C.; Von Hellens, W.; Zahalka, H.A.; Richter, K-P., *Ethylene-propylene elastomers*, in: Salamone, J.C. (Editor), *The polymeric materials encyclopedia* (on CD-ROM), CRC Press, **1996**.
- (10) Henrici-Olivé, G.; Olivé, S., *Angew. Chem.*, **1971**, *83*, 782.
- (11) See for instance: Adisson, E.; Deffieux, A.; Fontanille, M.; Bujadoux, K., *J. Pol. Sci. A, Pol. Chem.*, **1994**, *32*, 1033.
- (12) Huang, B.; Tian, H., *Metallocene catalysts*, in: Salamone, J.C. (Editor), *The polymeric materials encyclopedia* (on CD-ROM), CRC Press, **1996**.
- (13) Kaminsky, W.; Bark, A.; Steiger, R., *J. Mol. Catal.*, **1992**, *74*, 109.
- (14) See for instance: Jordan, J.F., *Adv. Organomet. Chem.*, **1991**, *32*, 325.
- (15) (a) Cossee, P., *J. Catal.*, **1964**, *3*, 80. (b) Arlman, E.J.; Cossee, P., *J. Catal.*, **1964**, *3*, 99.
- (16) Ewen, J.A., *J. Am. Chem. Soc.*, **1984**, *106*, 6355. For a recent review see: Brintzinger, H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M., *Angew. Chem. Int. Ed. Eng.*, **1995**, *34*, 1143.
- (17) Shapiro, P.J.; Bunel, E.; Schaefer, W.P.; Bercaw, J.E., *Organometallics*, **1990**, *9*, 867. For a recent review see: McKnight, A.L.; Waymouth, R.M., *Chem. Rev.*, **1998**, *98*, 2587.
- (18) Johnson, L.K.; Killian, C.M.; Brookhart, M., *J. Am. Chem. Soc.*, **1995**, *117*, 6414. For a recent review see: Britovsek, G.J.P.; Gibson, V.C.; Wass, D.F., *Angew. Chem. Int. Ed. Eng.*, **1999**, *38*, 428.
- (19) Sinn, H., *Macromol. Symp.*, **1995**, *97*, 27.
- (20) Yang, X.; Stern, C.L.; Marks, T.J., *J. Am. Chem. Soc.*, **1994**, *116*, 10015.
- (21) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A., *Organometallics*, **1993**, *12*, 4473.
- (22) Chien, J.C.W.; Tsai, W-M.; Rausch, M.D., *J. Am. Chem. Soc.*, **1991**, *113*, 8570.
- (23) Yang, X.; Stern, C.L.; Marks, T.J., *Organometallics*, **1991**, *10*, 840.
- (24) Bochmann, M.; Lancaster, S.J., *J. Organomet. Chem.*, **1992**, *434*, C1.
- (25) Lin, Z.; le Marechal, J-F.; Sabat, M.; Marks, T.J., *J. Am. Chem. Soc.*, **1987**, *109*, 4127.
- (26) Karapinka, G.L.; Carrick, W.L., *J. Pol. Sci.*, **1961**, *55*, 145.
- (27) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P., *Organometallics*, **1995**, *14*, 4471.
- (28) Parkin, G.; Bunel, E.; Burger, B.J.; Trimmer, M.S.; van Asselt, A.; Bercaw, J.E., *J. Mol. Catal.*, **1987**, *41*, 21.
- (29) Luinstra, G.A.; ten Cate, L.C.; Heeres, H.J.; Pattiasina, J.W.; Meetsma, A.; Teuben, J.H., *Organometallics*, **1991**, *10*, 3227.
- (30) (a) Coles, M.P.; Gibson, V.C., *Polym. Bull.*, 1994, *33*, 529. (b) Scheuer, S.; Fischer, J.; Kress, J., *Organometallics*, **1995**, *14*, 2627.
- (31) (a) Brandsma, M.J.R.; Brussee, E.A.C.; Meetsma, A.; Hessen, B.; Teuben, J.H., *Eur. J. Inorg. Chem.*, **1998**, 1867. (b) Desmangles, N.; Gambarotta, S.; Bensimon, C.; Davis,

- S.; Zahalka, H., *J. Organomet. Chem.*, **1998**, 562, 53. (c) Budzelaar, P.H.M.; van Oort, A.B.; Orpen, G.A., *Eur. J. Inorg. Chem.*, **1998**, 1485. (d) Kim, W-K.; Fevola, M.J.; Liable-Sands, L.M.; Rheingold, A.L.; Theopold, K.H., *Organometallics*, **1998**, 17, 4541. (e) Reardon, D.; Conan, F.; Gambarotta, S.; Yap, G.; Wang, Q., *J. Am. Chem. Soc.*, **1999**, 121, 9318.
- (32) Berno, P.; Gambarotta, S.; Richeson, D., *Comp. Organomet. Chem.*, **1995**, 5, 1.
- (33) see for instance: (a) Maatta, E.A., *Inorg. Chem.*, **1984**, 23, 2560. (b) Preuss, F.; Steidel, M.; Vogel, M.; Overhoff, G.; Hornung, G.; Towae, W.; Frank, W.; Reiss, G.; Müller-Becker, S., *Z. Anorg. Allg. Chem.*, **1997**, 623, 1220.
- (34) Mann, B.E.; Taylor, B.F., *¹³C NMR data for organometallic compounds*, Academic Press, London, **1981**, pp 2-5.
- (35) (a) Wills, A.R.; Edwards, P.G., *J. Chem. Soc. Dalton Trans.*, **1989**, 1253. (b) Danopoulos, A.A.; Edwards, P.G., *Polyhedron*, **1989**, 8, 1339. (c) Hessen, B.; Teuben, J.H.; Lemmen, T.H.; Huffman, J.C.; Caulton, K.G., *Organometallics*, **1985**, 4, 946. (d) Hessen, B.; Meetsma, A.; Teuben, J.H., *J. Am. Chem. Soc.*, **1989**, 111, 5977. Vanadium tris-alkyl species have also been reported: (e) Buijink, J-K.F.; Meetsma, A.; Teuben, J.H., *Organometallics*, **1993**, 12, 2004. (f) Murphy, V.J.; Turner, H., *Organometallics*, **1997**, 16, 2495.