DOI: 10.1002/masy.200650405

# Single-Site Organochromium Catalysts: Synthesis, Characterisation by Paramagnetic NMR and Olefin Polymerisation

*Markus Enders*

**Summary:** Chromium(III)-complexes with monoanionic spectator ligands allow the preparation of highly active catalysts for ethylene polymerisation. We summarize the synthesis and NMR-spectroscopic investigations of precatalysts with quinolyl-functionalised Cp-ligands. These complexes have advantageous properties. For spectroscopic investigations the rigidity of the ligand framework helps to identify the species present in solution as fewer conformers are possible. For the application as polymerisation catalysts the high stability of the activated catalyst is important. We obtained meaningful analytical data by paramagnetic NMR, combined with DFT-calculation of the spin-density. These and other investigations lead to the conclusion, that the active species is a cationic chromium(III)alkyl complex. However, at present we have not enough information about the exact structure of this species in the absence of coordinating solvent molecules.

**Keywords:** chromium single-site catalysts; olefin polymerisation; paramagnetic NMR

## Introduction

Chromium based catalysts play a significant role in coordination polymerisation of α-olefins. Heterogeneous silica-supported systems, like the Phillips[1] or Union Carbide[2] catalysts, are among the most important catalysts for the production of polyethylene. The Phillips-catalyst show several important differences compared to Ziegler-Natta-type heterogeneous (e.g. $MgCl_2/TiCl_4/AlR_3$) or many homogenous single-site catalysts (e.g. Zirconocene/MAO). Some characteristics of the Phillips-system are:[3] a) an oxidic support is necessary, b) no co-catalyst is required, as the ethylene itself activates the catalytic centres (induction period), c) the catalyst is able to trimerize the α-olefin, d) hydrogen does not lead to a significant effect on the molecular weight distribution of the polymer, e) the oxidation state of most chromium centres in the active catalyst is +2, f) different catalytically active sites are present (multi-site catalyst).

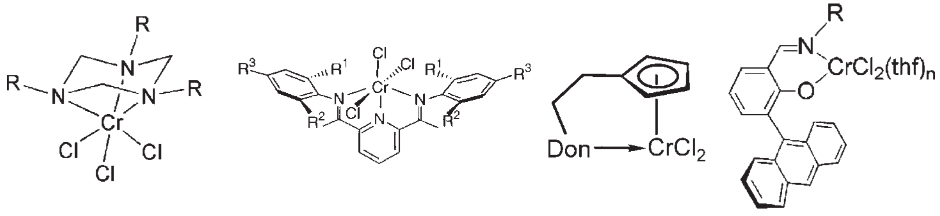
Several molecular, single-site chromium catalysts have been developed, but only a few systems have chromium(II)-centres.[4] In this context it is surprising that nearly all molecular chromium polymerisation catalysts bear the metal in the oxidation state +3. Several ligand types have been used, which can be categorised in the following way:

1. neutral tridentate donor ligands which coordinate a) facially (e.g. **1**[5]); b) meridionally (e.g. **2**[6]); 2. monoanionic chelate ligands which are sufficiently large for the protection of a $CrX_2$-fragment (X = halogen atom) realised as a) donorfunctionlised Cp-ligands (**3**[7]) or as b) bidentade or tridentate ligands with one anionic donor atom like the sterically demanding phenoxy-imine system **4**[8].

Dianionic chelate ligands are less favourable as only one reactive, anionic substituent could remain in neutral chromium(III)-complexes. If the monoaninic spectator ligand is not demanding enough, undesired

---

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany
E-mail: markus.enders@uni-hd.de



**1** **2** **3** **4**

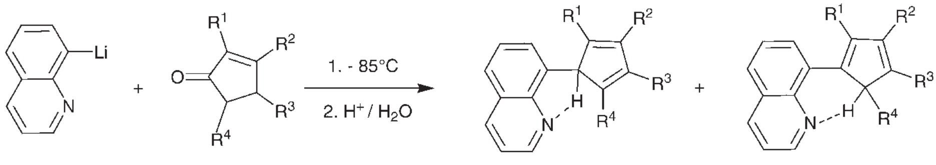
*Figure 1.*
Examples of chromium(III)complexes which lead to highly active ethylene polymerisation catalysts.

complexes with two such ligands may form. Therefore donorfunctionlised Cp-ligands are ideally suited for the development of improved Cr(III)-catalysts. It has been shown before, that half sandwich Cr(III)-compounds which are coordinated by an additional nitrogen donor exhibit high polymerisation activities for ethylene, some of them are also capable of copolymerizing ethylene with higher $\alpha$-olefins.[9] However, many of the systems described, decompose slowly after activation or are unstable during polymerisations at high temperatures (>80 °C), which is important for industrial applications. In order to increase the stability of Cr(III) half sandwich compounds, quinolyl or N,N-dimethylanilinyl functionalised cyclopentadienyl ligands have been introduced by us. These ligands have an ideal, rigid geometry for the formation of half sandwich compounds. Consequently stable chromium(III)complexes have been obtained and used as precatalysts for olefin polymerisation.

## Ligand and Complex Synthesis

We used several standard and newly developed routes for the synthesis of cyclopentadienyl-ligands functionalised with aromatic substituents and a neutral N-donor function.[10] The main synthetic method for quinolylcyclopentadienes (**7**) is the addition of 8-lithioquinoline (**5**) to substituted cyclopentenones or indanones (Figure 2). The reactions are successful when at least the R$^2$-substituent is different from H. In derivative **H7a** a C–H–N-hydrogen bridge is present in solution and in the solid state. For all derivatives studied the isomer **H7b** is the thermodynamic product. Analogous syntheses have been performed for Cp-ligands substituted with o-N,N-dimethylaniline (see complex **16** in Figure 4).

Treatment of **5** with the non-substituted cyclopentenone **6** (R$^1$ – R$^4$ = H) does not lead to satisfactory results as side reactions like deprotonation of **6** and polymerisation of the formed cyclopentadiene dominate. Therefore 8-lithioquinoline (**5**) has been added to cobaltocenium iodide. The cobaltocenium cation $[(\eta^5\text{-}C_5H_5)_2Co)]^+$ can be described as a complex between the unstable $C_5H_5$-cation and a neutral CpCo-fragment. From this description it is obvious, that anionic C-nucleophiles add to the formally positive $C_5H_5$-ring and a neutral $\eta^4$-bound $C_5H_5R$-ligand is formed (Figure 3). The new



**5** **6** **H7a** **H7b**

*Figure 2.*
Synthesis of quinolylcylcopentadienes.

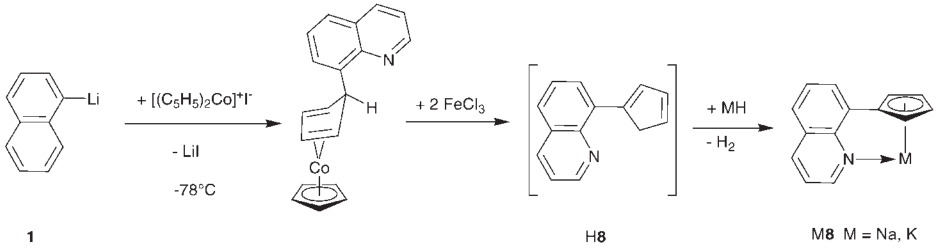


*Figure 3.*
Addition reaction to [Cp2Co]+-salts and liberation of the ligand H**8**.

cyclopentadiene H**8** can then be liberated by oxidation with $FeCl_3$. Without coordination to the cobalt, H**8** is thermally unstable, so it has to be transformed at low temperatures into its stable alkali metal salt M**8** (M = Na or K).

The formation of the desired chromium complexes is straightforward: The respective ligand precursors are deprotonated by lithiumalkyls or favourably by sodium- or potassium hydride. Succeedingly chromiumtrihalide salt is added and under elimination of the alkali halide the complexes form in moderate to good yields. Depending on the solubility of the complex, the separation and purification is easy but sometimes problematic.

For the synthesis of **15** we treated $[CrCl_2Me(THF)_3]$[11] with the potassium salt K**17** and obtained a mixture of the desired compound together with the dichloro-derivate **13**. The product mixture is maintained after crystallisation (proven by a single-crystal X-ray analysis where the $CH_3$-group is statistically replaced by Cl-atoms).

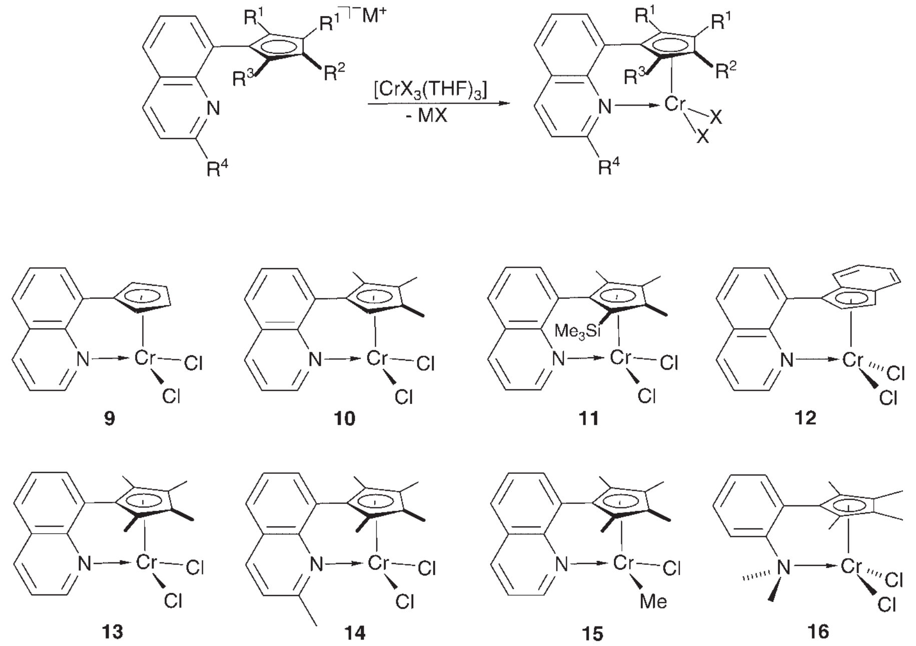


*Figure 4.*
Synthesis of chromium(III)complexes with rigid, N-functionlised Cp-ligands and molecular formulas of the complexes **9–16**.

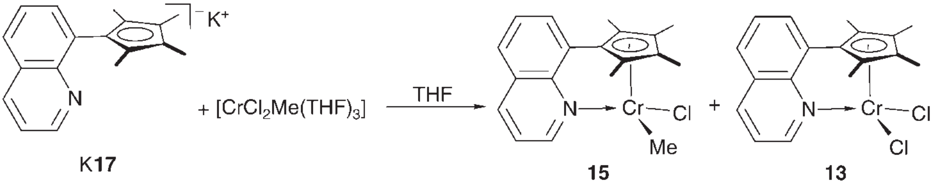


***Figure 5.***
Reaction of K**17** with [$CrCl_2Me(THF)_3$].

## NMR-Studies with Paramagnetic Organochromium Complexes

NMR-spectroscopy is a powerful tool for the investigation of catalyst/cocatalyst combinations in the presence of the reactive substrates. With diamagnetic catalyst/cocatalyst systems, NMR studies have led to a detailed knowledge of initiation, propagation and termination steps of the polymerization process.[12] In the case of chromium(III)-based compounds the paramagnetic character leads to strong shifts and broadening of the NMR signals.[13] In addition, the assignment of the experimental NMR shifts to nuclei of the known compound is not always possible. These NMR-properties have led to the belief that NMR spectroscopy is less useful for the characterization of paramagnetic compounds. Therefore, the literature often do not report NMR shifts of such molecules although it is often quite easy to obtain their $^1$H-NMR spectra.[14]

In many cases, the catalysts have to be activated with a cocatalyst, so that significant overlap of the NMR-signals of the catalyst and the cocatalyst has to be avoided. Therefore these investigations are generally carried out with non standard activating agents and/or isotopically marked systems. If methylaluminoxane (MAO) is used for the activation, at least 50 equivalents of Al per catalyst molecule are necessary. Thus, the normal window for $^1$H-NMR is dominated by the excess of cocatalyst. In these cases, paramagnetic systems are advantageous for NMR studies, as the NMR-signals are dispersed over a larger region and therefore overlap with the signals of diamagnetic species (like for example the co-catalyst) is less important. The unpaired electrons lead to electron spin polarization of the surrounding electrons which themselves shield or deshield the nuclear spins. Consequently the NMR signals of the nuclei are shifted to higher or lower frequencies, depending whether the spin density is positive or negative. This allows the observation of well-resolved signals wide apart from the normal ‘‘diamagnetic region’’. For some paramagnetic chromium complexes, systematic NMR-investigations were carried out, mainly by the group of Köhler. From these studies on mono- and bimetallic complexes, the authors obtained spin density maps of several molecules, assignments and interpretations of $^1$H- and $^{13}$C-NMR data. However, up to now it is difficult and sometimes even impossible to predict paramagnetic shifts of organometallic compounds.

In many cases the Fermi contact interactions dominate the isotropic shifts experienced by NMR active nuclei. Thus, calculations of Fermi contact coupling constants based on ab initio and density functional methods have been reported in order to predict the hyperfine shifts. The theoretical studies have mainly focused on small organic paramagnetic systems,[15] whereas the application to transition metal-based systems have been accomplished only recently by a few groups.[16] Organochromium complexes previously studied by NMR have up to five different $^1$H-NMR signals, complexes **9** and **13** have already eight and **10**–**12** up to eleven $^1$H-NMR signals (Figure 4). However, due to the rigidity of these complexes, static molecular structures obtained by DFT-calculations represent well the species present in solution. This is a big advantage when using the technique described below.

In Figure 6 the $^1$H-NMR of **13** is shown as an example (upper spectrum). Six resonances outside the "diamagnetic region" are observed together with a verybroad and weak signal around $-80$ ppm. The eighth signal of **13** lies in the diamagnetic region and is hidden by residual solvent signals and diamagnetic impurities. Integration allows the assignment of the signals at $+28$ and $-41$ ppm to the methyl groups at the Cp-ring (six H-atoms compared to one H-atom for the other signals). At a first sight, the chemical shifts of the methyl groups with negative and positive signs are not expected, as the number of bonds between the H-atoms and the $Cr^{3+}$-centre are identical and therefore the signs of the spin densities should also be the same. However, a similar behaviour was reported for octamethyldiphosphachromocene, where the phosphorous atoms lead to a lower symmetry.[17] In complex **13**, the coordination of the quinoline moiety to the chromium centre leads to the fixation of the Cp-ring orientation relative to the orbitals of the $CrCl_2$-fragment. This allows for the alternation of spin-density in the $\eta^5$-bonded ring. The signals in the heterocyclic part of the quinoline are at similar positions as reported by Köhler for dichlorocyclopentadienyl-pyridinechromium(III).[14b] The assignments are consistent with the typical feature of the Fermi-contact shift: the sign changes with the number of bonds between the paramagnetic centre and the observed nucleus.[13] For an odd number of bonds, a negative spin density and therefore a negative contact shift is expected, whereas for an even number of bonds the inverse signs should be observed. In our case, the $H^2$-hydrogen atom at the quinoline is close to the metal so that both, dipole-dipole interaction and Fermi-contact shift contribute to the chemical shift and line broadening. The line broadening associated to the dipolar shift is proportional to $r^{-6}$, ($r =$ distance between the paramagnetic centre and the nucleus under study). This fact leads a very broad signal at $-78$ ppm for the hydrogen atom of

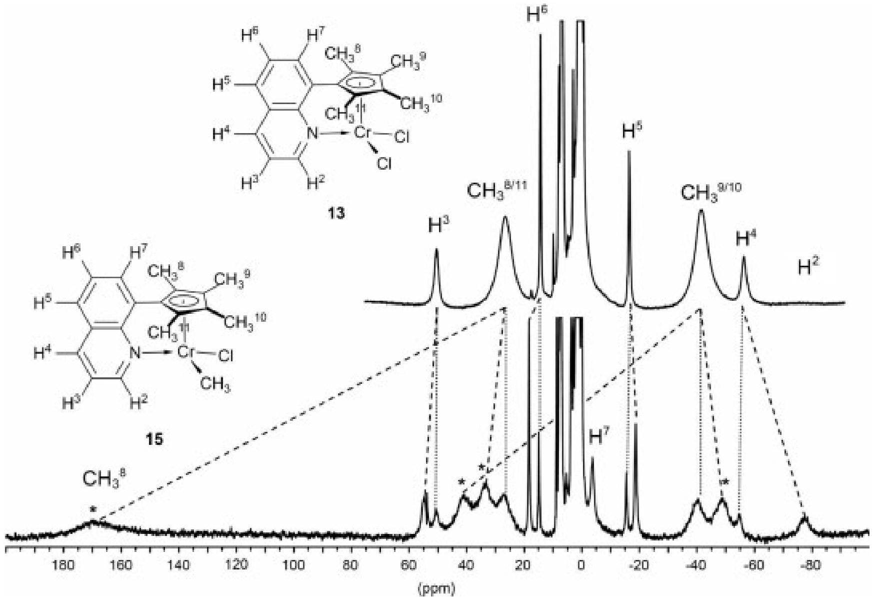


***Figure 6.***
$^1$H-NMR spectra of **13** (top) and a 3:1 mixture of **15** and **13** (bottom). The dotted lines connect signals of **13**, while the dashed lines point to corresponding signals in **15**. Asterisks show the signals of the four inequivalent $CH_3$-groups in **15**.

the quinoline closest to the metal ($H^2$ signal only visible after amplification of the spectrum).

### Theoretical Prediction of Paramagnetic $^1$H-NMR Chemical Shifts

The chemical shift in paramagnetic compounds is a sum of diamagnetic and paramagnetic contributions ($\delta_{obs} = \delta_{dia} + \delta$-$_{dpara}$). The paramagnetic shift, $\delta_{para}$, is the sum of the Fermi-contact and the dipolar contribution ($\delta_{para} = \delta_{con} + \delta_{dip}$). The Fermi-contact shift is directly proportional to the contact spin density, $\rho_{\alpha\beta}$, at each nucleus. For the chromium compounds investigated, $S = 3/2$ so that the relationship between the Fermi-contact shift (in ppm) and the contact spin density (atomic units per ppm) can be expressed as:

$$\delta_{con} = 2.0051 \cdot 10^5\ \rho_{\alpha\beta} \qquad (1)$$

A rough estimation of the dipolar contribution to the chemical shift shows, that only $H^2$ which is sufficiently close to the metal centre could have significant dipolar shifts. Depending on the magnetic axis present in the compounds studied, this contribution lies in the range between $-11.7$ and $+23.4$ ppm and is even for this position much less important than the Fermi-contact contribution ($-85$ ppm for $H^2$). For all other H-atoms the maximum dipolar contribution is calculated in the range from $-3$ to $+6$ ppm.[18]

The determination of the spin-density distribution by quantum-chemical methods allows the calculation of the contact shift ($\delta_{con}$) and hence the interpretation of observed NMR-shifts. After validation of the model by comparing calculated shifts with experimental values, NMR-shifts of new compounds or reaction intermediates can be predicted. As several chromium(III)-complexes with similar, well defined geometries are available, the theoretical model could be well validated. In order to get satisfactory results, it was necessary to calculate the minimum energy structures on a relatively high level of theory (UB3LYP/6-311G(d)). Difficulties arise for the positions where several rotational isomers are present in solution which is true for the $CH_3$-groups. For these groups it is necessary to take the average of corrected, angular dependent spin-densities by using the formula: $\rho_{\alpha\beta} = B\ \cos^2(\varphi)\ \rho_{\alpha\beta(calc)}$. The best results are obtained with a B-value of 1.0. The calculated spin-densities correlate very well when a constant of proportionality between $\rho_{\alpha\beta}$ and $\delta_{obs}$ of $1.8862 \cdot 10^5$ is used (instead of the theoretical value in formula (1), see above). A comparison of the experimental and the calculated values of different quinolyl-Cp-chromium complexes is given in Figure 7. It can be seen, that the values correlate well, and that prediction of chemical shifts is possible. This correlation indicates that the NMR hyperfine shifts are dominated by the Fermi contact shift.

The methodology has led to a complete assignment of the experimental $^1$H-NMR-shifts in the complexes **8**–**16**. Deviations between the calculated NMR-shifts, based on the calculated spin densities and the experimental NMR data could result from dipolar shift contributions. These differences can be used to gauge the contribution of dipolar shift to the overall shift. As shown in Figure 6, the $^1$H-NMR-spectrum of the methyl-chloro complex **15** was compared with the spectrum of the dichloro derivative **13**. The resonances are wider apart from the diamagnetic region than those of **13**. This fact can be explained by the calculated contact spin densities of the geometry-optimised molecule. For all hydrogen atoms, the absolute value of the contact spin density at the nuclei is larger than in **13**. The values are particularly different at the methyl groups. The spin densities at the hydrogens of the $CpCH_3$-groups located at position trans relative to the Cr-$CH_3$-group, is very high so that a strongly shifted NMR resonance should result. Indeed, this is the case for one $CH_3$-group in the $^1$H-NMR of **15** (observed 168 ppm, predicted 146 ppm, see Figure 6).

### Polymerisation Results

The complexes **9**–**14**, **16** and several other derivatives are precursors for highly active

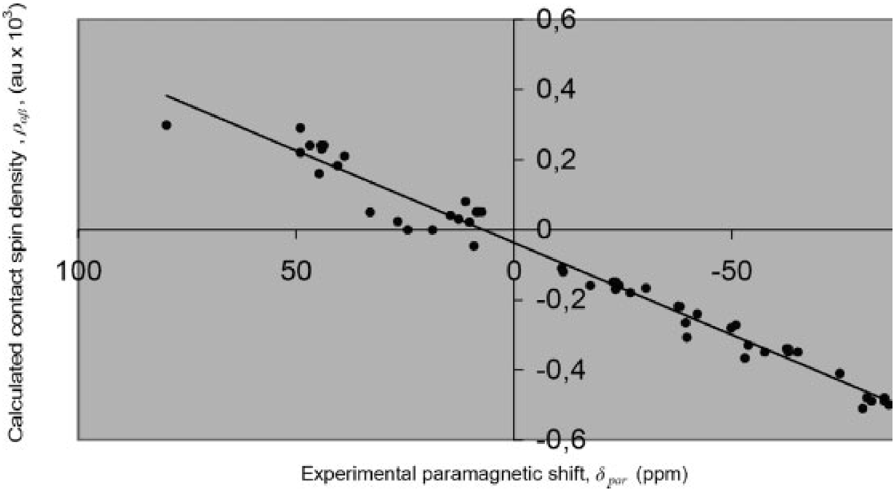


**Figure 7.**
Paramagnetic shift vs. contact spin density at hydrogen atoms in complexes **1** – **8** calculated with UB3LYP/6-311g(d).

polymerisation catalysts for ethylene.[19] Higher α-olefins are polymerised as well but with much lower catalytic activity. All compounds need a co-catalyst, which is able to alkylate the metal as well as to abstract an anionic ligand. For this purpose methylaluminoxanes (MAO) are ideal. We monitored the activation process by paramagnetic NMR-, EPR- and UV-vis-spectroscopy. General observations are:

*Activation of Catalyst*
MAO was used for activation. After addition of 50 equivalents of Al per chromium atom, the activation is complete. We have no evidence from spectroscopy, that more MAO changes the catalytic species. The colour of the solution changes from blue or green (depending on the derivative used) to pink-violet upon addition of the co-catalyst. A combination of alkylating agent and a proton source with a weakly coordinating anion (e.g. $R_2Mg$/N,N-dimethylalinium-BArF) is also a successful co-catalyst.[20]

*Solubility of the Active Catalyst*
The activated catalyst is soluble in toluene to a small extent. The solubility is sufficient for homogeneous catalyst solutions in typical polymerisation experiments (catalyst concentration $< 10^{-5}$ mol/l). Considerably higher concentrations lead to precipitation of the active catalyst as an intensely coloured violet, viscous oil. This oil is well soluble in polar solvents like THF or *o*-diflourobenzene.

*Stability of the Catalyst*
Decomposition of the catalyst into an inactive form is always accompanied by a disappearance of the typical pink colour of the active system. Therefore the stability can be monitored easily by following this colour change but also by EPR-spectroscopy. In addition we have tested the polymerisation activity of systems at high temperatures and after a delay of several days. In the absence of air, humidity or reactive solvents, the active catalysts are stable for at least one week at room temperature or one hour in boiling toluene. Some derivatives can be transformed back to the precatalyst by addition of acidified water and extraction with dichloromethane.

*Structure of the Active Catalyst*
We have determined the magnetic moments in solution and the temperature dependence of the paramagnetic NMR-

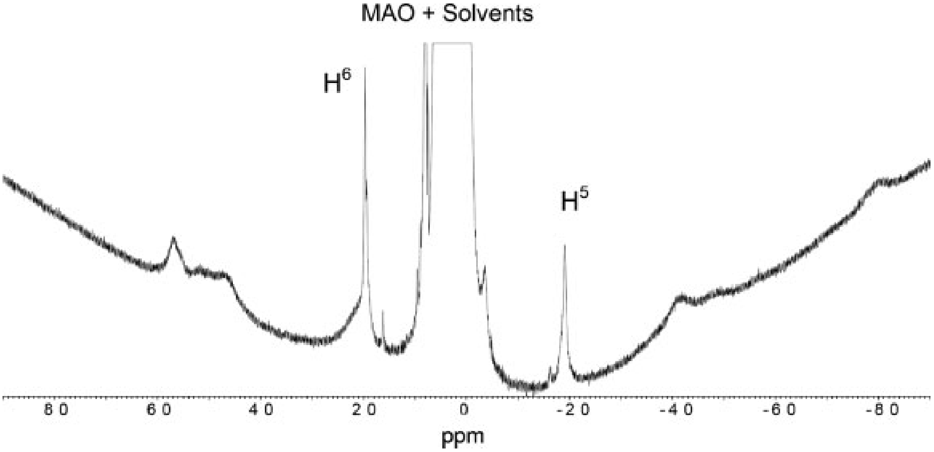


***Figure 8.***
$^1$H-NMR-spectrum of **13** and MAO (50 eq. Al) in d$^8$-THF.

shifts. These measurements give us information about the nuclearity of the molecules in solution, as aggregation should lead to different magnetic suszeptibilities and to deviations from the temperature behaviour described by the Curie-law. As expected, all precatalysts are monomeric in solution. The activated catalyst is also monomer when a donor solvent like THF is present. The question whether the activated complexes aggregate in non-coordinating solvents cannot be answered at this stage. A paramagnetic $^1$H-NMR of a catalyst solution in d$^8$-THF is shown in Figure 8. The observed signals are consistent with a cationic chromium(III)complex and a coordinated THF-molecule. This has been confirmed by calculation of the spin-density distribution for the model compound shown in Figure 9.

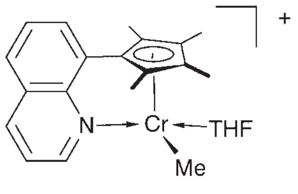


***Figure 9.***
Model for the activated catalyst in the presence of coordinating THF-solvent.

*Catalytic Activity*

The activity in ethylene polymerisation was measured by running polymerisation experiments at temperatures between 25 °C and 100 °C in toluene solution for 30 min and weighing the produced polyethylene. In addition the ethylene gas consumption was monitored with a mass flow meter. The activity decreases only slightly during polymerisation. In a typical run, the gas flow after 30 minutes is about 2/3 of the gas flow in the first 5 minutes (for technical reasons we cannot measure the activity in the first minute of the polymerisation). This behaviour comes from the gradual inclusion of the active centres in the produced polymer and is consistent with the described stability of

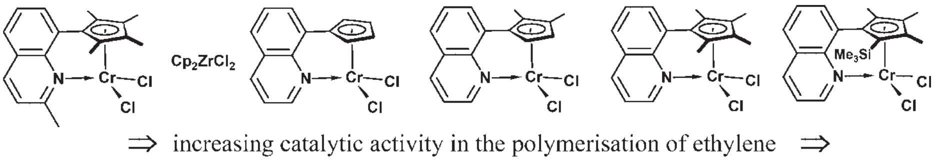


***Figure 10.***
Activity sequence for selected catalyst precursors after activation with MAO.

the active form of the catalyst. At atmospheric pressure and room temperature, catalyst activities lie between 1200 and 2500 Kg product per mol catalyst per hour. At higher pressure much higher activities are observed as the concentration of ethylene in the toluene solvent is much higher and there are fewer limitations due to slow gas diffusion. At 5 bar ethylene pressure for example the pressure normalised activities lie around 5000 kg(PE) $mol^{-1}$(cat) bar $^{-1}$. The substitution pattern of the spectator ligand influences the catalytic activity in the following way: Substituents in the 2-postion of the quinoline lower the activity considerably. Substituents at the Cp-ring increase the activity. For comparison we determined the activity in ethylene polymerisation with the catalyst $C_5H_5ZrCl_2$/MAO. The sequence from lower to higher activities for selected examples is shown in Figure 10.

## Conclusion

Molecular chromium complexes are promising candidates for industrially applicable single-site polymerization catalysts. The systems described in this report profit from high stability and the spectroscopic investigations profit form the rigid and therefore well defined geometries of the compounds. The investigation of catalytically active species by NMR-techniques has to be combined with quantum chemical calculations. This technique leads to a better understanding of homogeneous paramagnetic chromium catalysts. At this stage it is difficult to predict the effects of the ligand framework on the catalyst characteristics and on the properties of polymer produced. Therefore more information about the elemental steps in the olefin formation have to be obtained in future.

[1] (a) J. P. Hogan, R. L. Banks, (Phillips Petroleum Co.) Belg Patent 530,617, **1955**; U.S. Patent 2825,721, **1958**. (b) J. P. Hogan, *J. Polym. Sci. A* **1970**, *8*, 2637.

[2] a) G. L. Karapinka, U.S. Patent 3,709,853, **1973**. (b) F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson, W. L. Garrick, *J. Polym. Sci. A* **1972**, *10*, 2621.

[3] E. Groppo, C. Lamberti, S. Bordiga, G. Spoto, A. Zecchina, *Chem. Rev.* **2005**, *105*, 115.

[4] a) P. Crewdson, S. Gambarotta, M.-C. Djoman, I. Korobkov, R. Duchateau, *Organometallics*; **2005**; *24*, 5214. b); A. Jabri, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, *Organometallics*; **2006**; ASAP Web Release Date: 06-Jan-2006.

[5] R. D. Köhn, M. Haufe, S. Mihan, D. Lilge*Chem. Commun.* **2000**, 1927

[6] M. A. Esteruelas, A. M. López, L. Méndez, M. Oliván, E. Oñate, *Organometallics*, **2003**, *22*, 395–406.

[7] a) A. Döhring, J. Göhre, P. W. Jolly, B. Kryger, J. Rust, and G. P. J. Verhovnik, *Organometallics*, **2000**, *19*, 388. A. Döhring, V. R. Jensen, P. W. Jolly, W. Thiel, J. C. Weber, *Organometallics*, **2001**, *20*, 2234.

[8] a) D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, *Chem. Commun.* **2002**, 1038–1039. b) D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2005**, *127*, 11037.

[9] a) K. H. Theopold, *Eur. J. Inorg. Chem.* **1998**, 15. b) Y. Liang, G. P. Yap, A. L. Rheingold, K. H. Theopold, *Organometallics* **1996**, *15*, 5284. c) R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger, G. P. J. Verhovnik, *Organometallics* **1997**, *16*, 1511. d) P. W. Jolly, K. Jonas, G. P. J. Verhovnik, A. Döhring, J. Göhre, J. C. Weber, WO-98/04570, **1998**. e) A. Döhring, J. Göhre, P. W. Jolly, B. Kryger, J. Rust, G. P. J. Verhovnik, *Organometallics* **2000**, *19*, 388.

[10] For a review on the Synthesis of Cp-ligands with aromatic substituents see: M. Enders, R. W. Baker, *Curr. Org. Chem.* **2006**, *10*, in press.

[11] K. Nishimura, H. Kuribayashi, A. Yamamoto, S. Ikeda, *J. Organomet. Chem.* **1972**, *37*, 499.

[12] a) L. Li, C. L. Stern, T. J. Marks, *Organometallics* **2000**, *19*, 3332; b) K. P. Bryliakov, N. V. Semikolenova, V. A. Zakharov, E. P. Talsi, *J. Organomet. Chem.* **2003**, *683*, 23; c) K. P. Bryliakov, E. P. Talsi, M. Bochmann, *Organometallics* **2004**, *23*, 149; d) P. A. Deck, M. M. Konaté, B. V. Kelly, C. Slebodnick, *Organometallics* **2004**, *23*, 1089; e) P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1994**, *116*, 4623; f) L. H. Shultz, D. J. Tempel, M. Brookhart, *J. Am. Chem. Soc.* **2001**, *124*, 11539.

[13] a) G. N. La Mar, W. Horrocks, Jr., R. H. Holms, Eds., "*NMR of Paramagnetic Molecules: Principles and Applications*" Academic Press, NY, **1973**; b) I. Bertini, C. Luchinat, G. Parigi, "*Solution NMR of Paramagnetic Molecules*", Elsevier2001; c) F. H. Köhler, "*Magnetism: Molecules to Materials*" Wiley-VCH Verlag GmbH, Weinheim, Germany, **2001**, 379.

[14] a) R. A. Heintz, T. G. Neiss, K. H. Theopold, *Angew. Chem.* **1994**, 106, *22*, 2389; b) B. Bräunlein, F. H. Köhler, W. Strauss, H. Zeh, *Z. Naturforsch.* **1995**, *50b*, 1739.

[15] a) V. Barone, C. Adamo, N. Russo, *Chem. Phys. Lett.* **1993**, *212*, 5; b) L. A. Eriksson, O. L. Malkina, V. G. Malkin, D. R. Salahub, *J. Chem. Phys.* **1994**, *100*, 5066; c) M. J. Cohen, D. P. Chong, *Chem. Phys. Lett.* **1995**, *234*, 405; d) C. Adamo, V. Barone, A. Fortunelli, *J. Chem.*

*Phys.* **1995**, *102*, 384; e) P. J. O'Malley, S. J. Collins, *Chem. Phys. Lett.* **1996**, *259*, 296.

[16] a) S. J. Wilkens, B. Xia, F. Weinhold, J. L. Markley, W. M. Westler, *J. Am. Chem. Soc.* **1998**, *120*, 4806; b) J. Mao, Y. Zhang, E. Oldfield, *J. Am. Chem. Soc.* **2002**, *124*, 13911; c) C. Sporer, H. Heise, K. Wurst, D. Ruiz-Molina, H. Kopacka, P. Jaitner, F. H. Köhler, J. J. Novoa, J. Veciana, *Chem. Eur. J.* **2004**, *10*, 1355.

[17] R. Feher, F. H. Köhler, F. Nief, L. Ricard, S. Rossmayer, *Organometallics* **1997**, *16*, 4606.

[18] The estimation was done by applying the formula of Kurland and McGarvey with a simplified model of axial symmetry: R. J. Kurland, B. R. McGarvey, *J. Magn. Reson.* **1970**, *2*, 286.

[19] a) M. Enders, P. Fernández, G. Ludwig, H. Pritzkow, *Organometallics* **2001**, *20*, 5005. b) M. Enders, S. Mihan, D. Lilge, G. Schweier, PCT Int. Appl. **1999**, WO 0112687 A1; c) S. Mihan, D. Lilge, P. De Lange, G. Schweier, M. Schneider, U. Rief, U. Handrich, J. Hack, M. Enders, G. Ludwig, R. Rudolph, U. S. Patent. 6,437,161 B1 **2001**; d) G. Kohl, M. Enders, H. Pritzkow, *Organometallics* **2004**, *23*, 3832.

[20] M. Enders, P. Fernández, S. Mihan, H. Pritzkow, *J. Organomet. Chem.* **2003**, *687*, 125.