Available online at www.sciencedirect.com

ScienceDirect

Journal of Organometallic Chemistry 692 (2007) 4411–4423

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

How to synthesize a constrained geometry catalyst (CGC) – A survey

Jesus Cano [a,*], Klaus Kunz [b]

[a] *Dpto de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain*
[b] *Bayer CropScience AG, Research, 40789 Monheim, Germany*

Received 30 March 2007; received in revised form 8 May 2007; accepted 10 May 2007
Available online 18 May 2007

Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Since the discovery of titanium- and zirconium complexes with linked cyclopentadienyl amido ligands, this new polymerization catalyst class (constrained geometry catalysts "CGCs") has attracted the interest of many research groups in industry and academia. In order to improve or modify the catalytic and polymer properties, numerous changes in the environment of the catalyst have produced a huge family of CGCs. The aim of this contribution is to provide a concise overview on synthetic entries to these structurally highly diverse catalysts – an organometallic guide to CGCs.

Keywords: Constrained geometry catalysts; Cyclopentadienyl amido ligands; Titanium; Zirconium; Polymerization

1. Introduction

Synthetic polymers have made their arrival in almost all parts of our daily life and have become indispensable materials in all kinds of industries. Nearly half of the quantity produced in a year comprises polyolefins such as polyethylene (PE) and polypropylene (PP), which for the most part are manufactured by classical "high-pressure" and "normal-pressure" procedures [1].

The development of well-defined, homogeneous metallocene catalysts (single-site-catalysts, SSC) and suitable cocatalysts such as methylalumoxane (MAO) in the early 1980s raised high expectations for industrial applications of the new, tailor-made polymers [2], but it took another 10 years until the polymer industry pushed the first "SSC-polyolefins" into the market. Nowadays analysts expect growth rates of up to 25% for these materials, while conventional manufactured polyolefins are forecast to disappear [3].

While the first generation of SSCs were dominated by metallocenes (mainly titanocenes and zirconocenes), the researchers' interest in the 1990s was more and more drawn to non-metallocene complexes covering early and late transition metals and culminating in the investigation of highly active Fe and Ni catalysts [4]. However, the starting point for these activities was the exploration of the more "metallocene-like" half-sandwich Cp-amido complexes of groups III and IV metals that were initially investigated by Bercaw and Shapiro (scandium) [5–7] and Okuda (titanium) [8] (Fig. 1).

When compared to metallocenes these catalysts showed improved stabilities towards high temperatures and MAO and remarkably increased incorporation rates of higher olefins in copolymerizations with ethylene. Attracted by these features many research groups in industry and academia focused on the new catalyst class and the economic impact appeared attractive enough to Dow [9] and Exxon [10] to provoke a patent controversy lasting for years. The open nature of the catalysts' active site is forced by the short bridge between the Cp- and amido donor and earned them the name "constrained geometry catalysts"

---

[*] Corresponding author. Tel.: +34 918854584; fax: +34 918854683.
E-mail address: jesus.cano@uah.es (J. Cano).

0022-328X/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2007.05.015

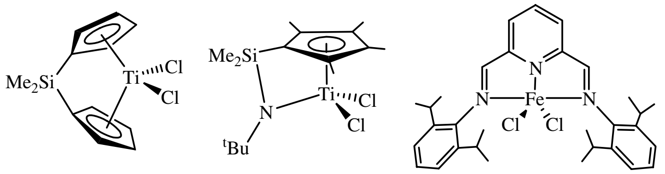


Fig. 1. Metallocenes, CGCs and Fe-catalysts.

(CGCs). A closer look in the academic and the patent literature reveals the massive interest in these compounds (Chart 1).

Since the publication of McKnight's and Waymouth's first review [11], intense progress in synthetic and technical terms was achieved. Only recently Braunschweig gave a very detailed analysis of the class focusing on the structure–activity relationship and catalytic performance [12]. The aim of this contribution is to provide a concise overview on synthetic entries to these structurally highly diverse catalysts – an organometallic guide to CGCs.

Fig. 2 gives an idea of the diversity of constrained geometry catalysts produced up to the end of 2006. As illustrated only group(IV) metals and dianionic CGC ligands are discussed, neutral donor functionalities X such as amino- or alkoxy moieties are not included [13].

In order to "simplify" the following discussions, the authors propose a nomenclature which is based on the chelating ligand (Fig. 2).

2. Synthetic strategies to constrained geometry catalysts

Synthetic pathways to attach functional groups to the cyclopentadienyl moiety in metallocenes or monocylopentadienyl compounds strongly depend on the nature of the metal: while complexes of (d^8–d^{10})-elements are particularly stable and can be transformed by typical methods such as aromatic substitution, metallation or Friedel–Crafts-Acylation, the early transition metals (d^0) allow pre-formation of the functionalized cyclopentadienyl ligand before complexation in most cases (Scheme 1).

Furthermore different stabilities of various ligand types towards oxidation and decomposition determine feasible routes to the catalysts – a careful choice of the metal precursor is essential for a successful transformation. All these restrictions are exemplified in the installation of constrained geometry ligands at group(IV) metals. In the past 15 years, numerous approaches to CGCs have been established which can be classified into three general categories: metathesis, metallation and template approach (see Scheme 2).

Metathesis and metallation go along with typical metallocene formation approaches, while template-based strategies are basically tailor made for the installation of CGC ligands. Representative examples for each method are given below.

2.1. Metathesis

The first group(IV) constrained geometry catalyst was synthesized by Okuda in 1990 via the metathesis route by treating $TiCl_4(THF)_2$ with 1 equiv. of $Li_2\{(C_5H_3\textit{t}Bu)SiMe_2N\textit{t}Bu\}$ [8] (Scheme 3). It may be noted that solvent adducts such as $TiCl_4(THF)_2$, $ZrCl_4(THF)_2$ or $ZrCl_4(Et_2O)_2$ are superior to simple tetrachlorides in terms of handling and solubility and thus in many cases are the precursors of choice.

However, the yield of 35% of this initial experiment led to further optimization. In the course of the next few years several protocols and reagents were developed – each useful for a special type of ligand. The choice of a titanium(III)species – $TiCl_3(THF)_3$ – followed by $PbCl_2$ oxidation gave better results in terms of yield and reproducibility [16] but turned out to be applicable only for substituted Cp ligands [17–19]. The corresponding Cp-permethylated zirconium complex $\{(C_5Me_4)SiMe_2N\textit{t}Bu\}ZrCl_2$ was prepared following the original route by employing $ZrCl_4(THF)_2$ as a precursor, while analogous attempts with $Li_2\{(C_5H_4)SiMe_2N\textit{t}Bu\}$ exclusively gave the spiro-type bis ligated compounds [20]. Obviously increasing the steric demand of the cyclopentadienyl moiety allows the use of simple group(IV)metal chlorides (Scheme 4).

In order to avoid time and yield losses related to the isolation of lithium salts, a convenient one-pot synthesis was reported by Resconi et al. [21] for the synthesis of dimethylmetallocenes by the reaction of cyclopentadiene ligands with a 2-fold excess of MeLi and MCl_4 (M = Ti, Zr, Hf).

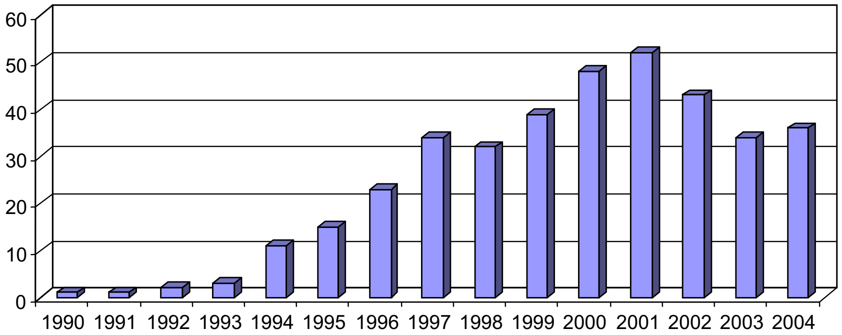


Chart 1. Publications and patents bearing "constrained geometry catalyst" in title or abstract (SciFinder).

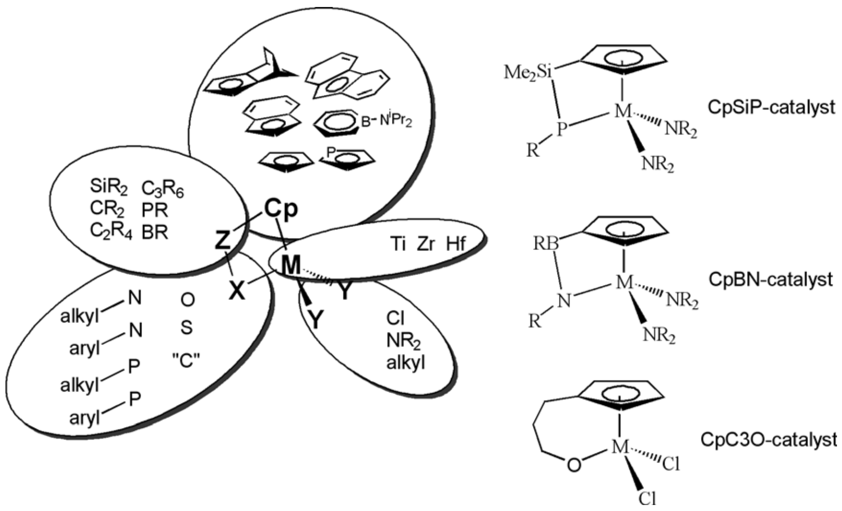
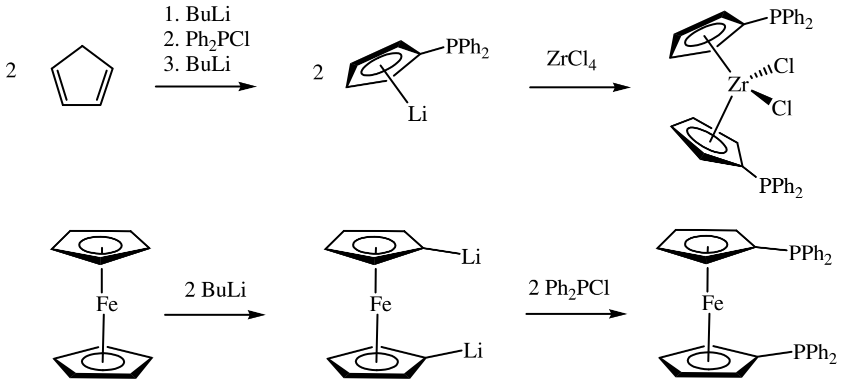
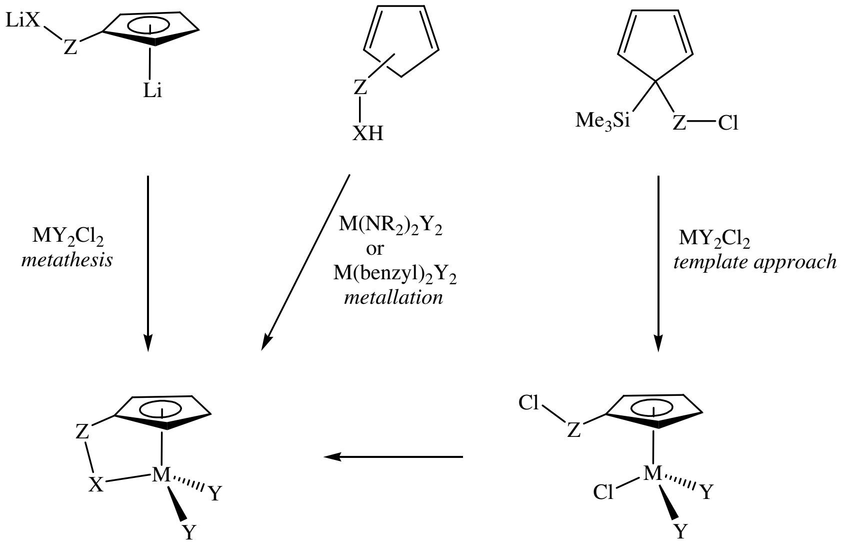


Fig. 2. Structural diversity and classification of constrained-geometry-catalysts.

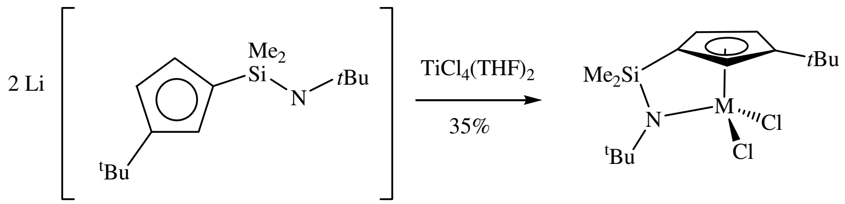


Scheme 1. Synthesis of $(C_5H_4PPh_2)_2ZrCl_2$ [14] and $(C_5H_4PPh_2)_2Fe$ [15].

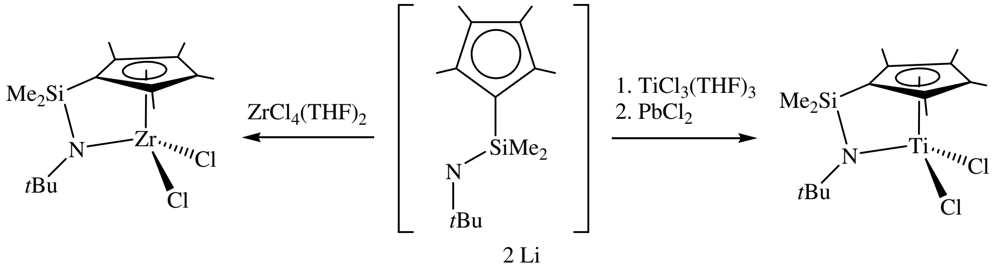


Scheme 2. Metathesis, metallation and template approach.

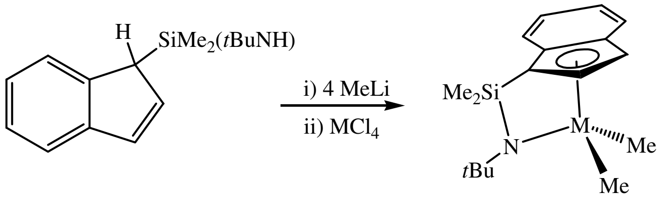
This method simplifies the synthesis of a large number of metal methyl complexes. Subsequently, a series of CG indenyl amido titanium and zirconium dimethyl complexes, by means of the direct synthesis from the ligand, a 2-fold excess of MeLi, and MCl_4 (M = Ti, Zr) were reported [22] (Scheme 5).



Scheme 3. Synthesis of $\{(C_5H_3t\mathrm{Bu})SiMe_2Nt\mathrm{Bu}\}TiCl_2$ [8].



Scheme 4. Synthesis of $\{(C_5Me_4)SiMe_2Nt\mathrm{Bu}\}TiCl_2$ [16] and $\{(C_5Me_4)SiMe_2Nt\mathrm{Bu}\}$ $ZrCl_2$ [20].



Scheme 5. Synthesis of CG indenyl amido titanium and zirconium dimethyl complexes.

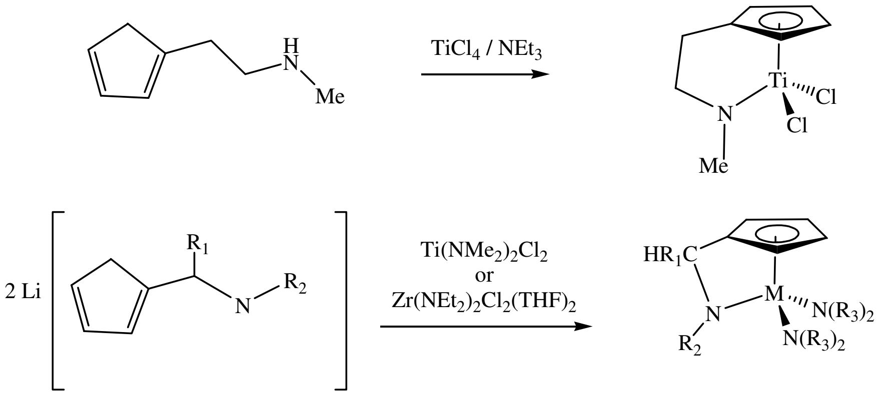
Dianionic ethylene-bridged ligand systems may be formed by milder deprotonation with NEt_3 before subsequent reaction with $TiCl_4$ gives the corresponding complexes in high yields [23] (Scheme 6). In the case of methylene-bridged CGCs, bis(amido)dichlorocomplexes such as $Zr(NEt_2)_2Cl_2(THF)_2$ and $Ti(NMe_2)_2Cl_2$ proved to be successful [24–26].

Silylene- [27] and methylene- [25,28] bridged Cp phosphido ligands were successfully transformed in the same way, while other attempts utilizing metal tetrachlorides or metallation reactions failed. The metathesis method was also applicable for Cp analogues such as the fluorenyl- [29], cyclohexadienyl- [30] and boratabenzene [31] -amido catalysts. A further remarkable example is the challenging 7-step-synthesis of a phospholyl-amido Ti complex: in this rare case the dilithiated ligand was transmetallated to the distannyl before reaction with $TiCl_4$ (Scheme 7) [32].

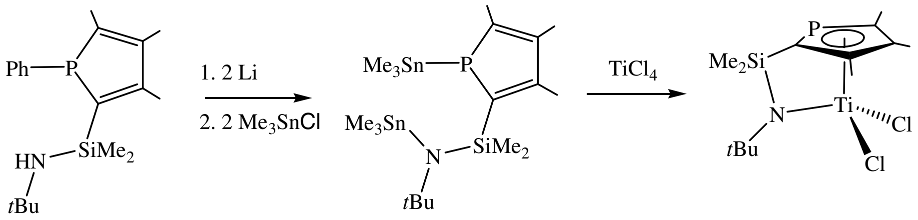
2.2. Metallation (amine and alkane elimination)

Analogous to the carefully investigated and well established metallocene syntheses, neutral CGC ligand precursors may react with homoleptic metal tetraamides (e.g. $Ti(NMe_2)_4$, $Zr(NEt_2)_4$) with the loss of 2 equiv. of dialkylamine to form the desired complexes under moderate reaction conditions. This methodology was first applied by Teuben et al. in the preparation of CGCs with ethylene and propylene-bridged ligands [23,33,34] (Scheme 8).

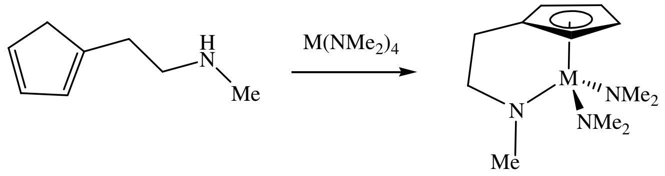
The formation of volatile dialkylamines as the driving force of the reaction offers an easy workup with often



Scheme 6. Synthesis of $\{(C_5H_4)\ (CH_2)_2NR\}TiCl_2$ [23] and synthesis of $\{(C_5H_4)CR_2NR\}M(NR_2)_2$ [25].



Scheme 7. Synthesis of {(C$_4$PMe$_3$)(SiMe$_2$)NR}TiCl$_2$ [32].



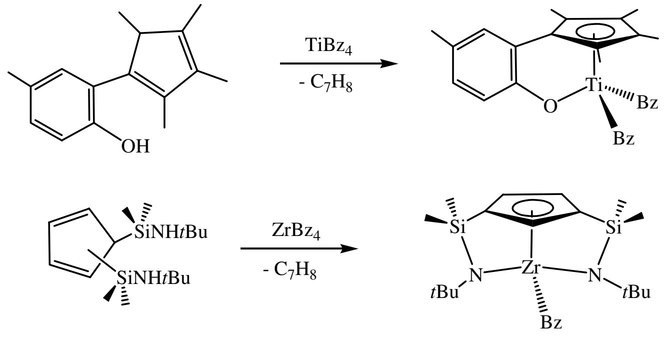
Scheme 8. Amine elimination synthesis using M(NR$_2$)$_4$, M(NR$_2$)$_2$Cl$_2$(THF)$_{0,2}$ [33].

almost quantitative yields. In contrast to the metathesis approach increasing the steric demand of the ligand is unfavorable: while propylene bridged methylamido units may be linked to the metal center, the corresponding tert-butylamido species are not deprotonated. The method has been applied in the syntheses of various types of CGCs including ligand variations such as CpC$_3$S- [35] or CpBN- [36] patterns. A straightforward entry to dichloro CGCs is accessed when bis(amido)dichloro complexes such as Zr(NMe$_2$)$_2$Cl$_2$(THF)$_2$ are employed [37].

Alkane elimination is a related approach which was reported by Piers et al. in 1996 [38] and later described by Marks et al. for the metallation of Cp amido and Cp oxo type ligands [39] (Scheme 9). The method appeared to be limited to Ti complexes until attachment of double silylamido functionalized Cp ligands to Zr was reported only recently [40,41].

2.3. Template synthesis

This approach is characterized by a stepwise attachment of the ligand to the metal center and was first applied by Royo et al. [42,43]. It turned out that further substitution at the Cp moiety as well as employment of Zr precursors affords mixtures of products (Scheme 10).

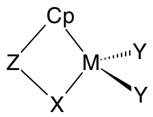


Scheme 9. Alkane elimination reactions [39,40].

The advantage of this method is the late introduction of the amido- (or oxo-) fragment giving way to broad catalyst screenings. An interesting example for an application in organic synthesis was published by Okuda et al. who prepared a small library of chiral CpSiN catalysts for asymmetric imine hydrogenation investigations [44]. First CpPN catalysts [45] and aminosilica-based immobilized CGCs [46] were also prepared by the template approach. The first example precoordinating a neutral ligand species to a metal precursor followed by double deprotonation was reported by Mu et al. for the synthesis of a Cp oxo catalyst system bearing sterically demanding tetramethylcyclopentadienyl fragments [47]. A highly efficient one-step synthetic strategy with HCl elimination [48] was described recently by the direct reaction of TiCl$_4$ with substituted cyclopentadienes without adding any other deprotonating reagent (Scheme 11). Notably, attempts using metathesis and metallation methodology failed completely.

3. Diversity of constrained geometry catalyst systems

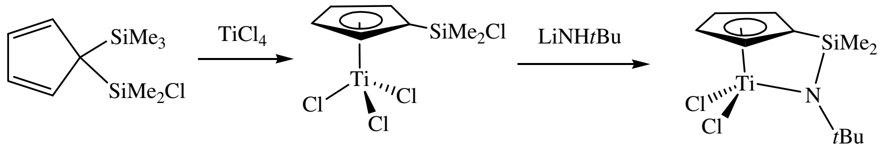
As ligand design allowed the exploration of new catalysts capable of controlling polymerization parameters such as activity, molecular weight, stereoregularity and polydispersity, many efforts have been made to modify the environment of the active metal center. As already elucidated in the introduction, we will classify the catalysts by the different modifications on the metal center environment.



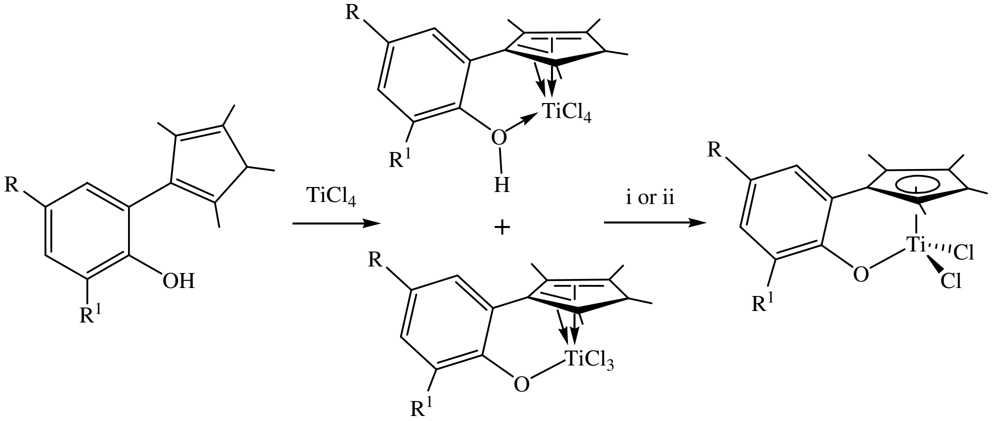
3.1. Variations of donor X (NR, PR, S, O, C)
3.2. Variations of bridge Z (Si, C1-C3, P, B, others)
3.3. Modifications of the Cp-ring.
3.4. Other CGC.

3.1. Changing donor X

The traditional X-motif in CGCs is the alkylamido moiety represented by N-*t*Bu in the first Scandium complex of Shapiro and Bercaw [5–7] and subsequently in Okuda's Titanium catalyst **1** [8]. Later several modifications in the



Scheme 10. First template approach to a CGC by Royo.



Scheme 11. Precoordination of a neutral ligand by Mu et al. (i) 2*n*BuLi, rt. [47]; (ii) 40 °C, 12 h [48].

amido substituent have been made to try to enhance the catalytic activity: more electron-withdrawing aromatic groups such as C_6H_5 [49], smaller and bulkier alkyl groups (cyclododecyl or adamantyl) [50] or chiral substituents [51]. However, despite intense screening activities, no superior substitute for the bulky and synthetically easily accessible *t*Bu has been discovered to date. In a further approach Okuda et al. described ligands containing an additional 2-electron donor function such as –OMe, $–NMe_2$ [18,52,53], –SMe, $–PPh_2$ [54] attached to the amido-nitrogen. While in X-ray crystal structure analyses the coordination of the σ-donor was proven (changing the complex geometry to a trigonal bipyrimidal arrangement), in solution reversible dissociation is observed. These more "metallocene-like" catalysts exhibit low to moderate polymerization activities as also observed for the corresponding hydrazido derivatives of Park et al. [55] (Fig. 3).

While amido-derived CGCs have been widely explored, other ring-closing moieties have been far less investigated. In a first attempt to construct a CpSiO bridge, Royo et al. obtained dimeric complexes [42,43]; in the case of the zirconium system, bridging μ^3-O atoms were found. In careful experimental and theoretical studies, Erker et al. elucidated the same tendency for CpC1O compounds to form dimeric rather than monomeric catalysts which were found for CpC1N complexes [56]. Only in the case of elongated C2- and C3-bridges was it possible to obtain monomeric "CpC_nO" MX_2 complexes [39,57,58].

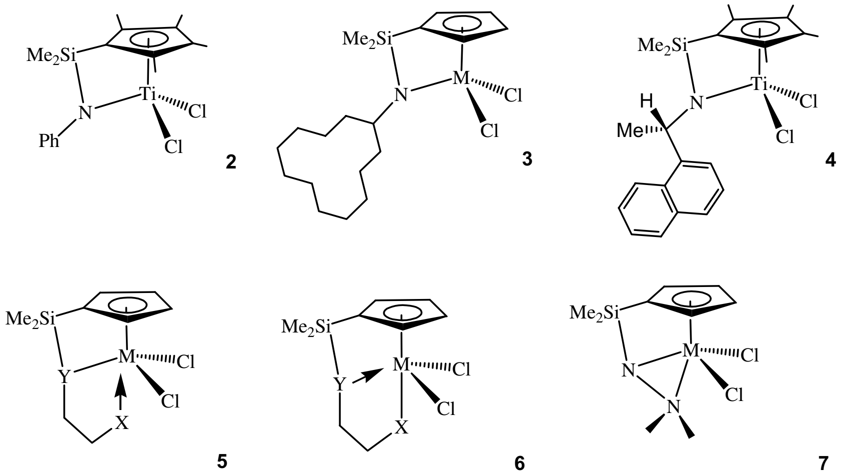


Fig. 3. Amido derived CGSs with different terminal substituents.

CpSiP- and CpCP-catalysts were reported only recently by Erker et al. [25,27,28]. In contrast to CpSiN-complexes the phosphido analogues reveal a distorted geometry, due to the chiral, non-planar coordination mode of the phosphorus atom. Notably, some of the methylene-bridged complexes performed with excellent polymerization activities, superior to the corresponding CpSiN-, CpSiP- and CpCN-catalysts.

Catalysts containing constrained geometry carboranyl ligands have been reviewed only recently by Xie [59]. In this special area the carboranyl moiety may serve as Cp- or as σ-donor formally affording CpAC catalysts. Very high activities in polymerization/copolymerization have been observed, but in contrast to CpSiN- or related systems Zirconium complexes were significantly superior to the corresponding Titanium analogues. The only sulfur-bridged CGC reported to date (CpC3S) also contains a carboranyl linkage [35] (Fig. 4).

3.2. Changing bridge Z

The bridge in ansa-metallocene complexes has an important effect on their structures and reactivity compared with their unbridged counterparts. The degree of distortion from the normal metallocene geometry that is caused by the bridge is reflected in the geometric parameters and the catalytic activity. Whereas a single-atom bridge can cause substantial distortions (by as much as 20°) in these angles in bent metallocene systems, the effect of two-atom-bridges on these angles is insignificant [60] (Fig. 5).

The same effect is observed in CG derivatives. However, the constrained bridge in CGC causes the angle α(Cp(centroid)–M–N) to be around 25–30° lower than the corresponding angle α(Cp(centroid)–M–Cp(centroid)) in ansa-metallocene complexes, forcing the opening of the supplementary angle β and therefore opening the coordination site. This structural feature is commonly considered to be responsible for the branches in PE free from comonomers and their application in the copolymerization of ethylene with long chain olefins [11,12].

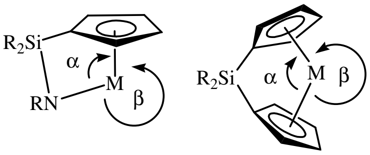


Fig. 5. Effect of the bridge in CGCs and ansa-metallocenes.

As observed in ansa-metallocenes, the geometric parameters in CGC may be modified with the introduction of alternatives to the original silylamido bridge and on the Cp ring.

Employing a methylene instead of a silylene bridge induces a larger opening of the coordination sphere compared to the (CpSiN)MIV analogues (around 10° in the angle Cp(centroid)–M–N) [25,26,61]. The slight relaxation of the bridge on changing from $SiMe_2$ to $(CH_2)_2$- [23,33,62,63] results in a drastic decrease in the activity of polymerization. Notably, CpC2N catalysts bearing bulky substituents at the amido nitrogen were inactive in propene polymerization, while methyl substituted derivatives showed sufficient activities. A phenylene-bridged analogue was published only recently by Lee et al. [64] (Fig. 6).

Other chemical groups have been introduced in place of the dimethylsilyl bridge, such as the phosphanyl-substituted cyclopentadienyl described by Lemenovskii et al. [45] and the bridging boron derivative described by Braunschweig et al. [36,65–67] producing high molecular weight PE (see Table 1).

Chlorine substituted silylene bridges offer the possibility to introduce various functionalities and are useful precursors for supported catalysts [68].

3.3. Modifications of the Cp-ring

In order to induce steric and electronic changes at the metal center, several efforts have been made to modify

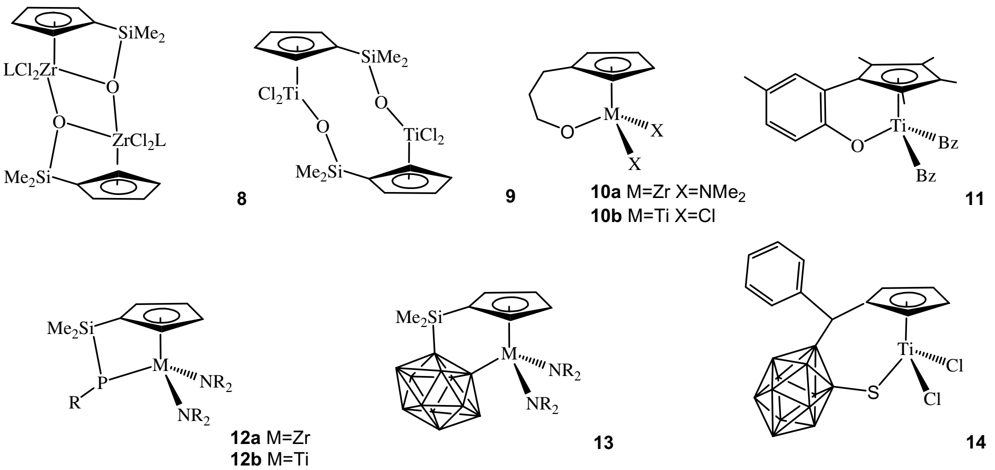


Fig. 4. Oxygen-, phosphorous-, carbon- and sulfiur-derived CGCs.

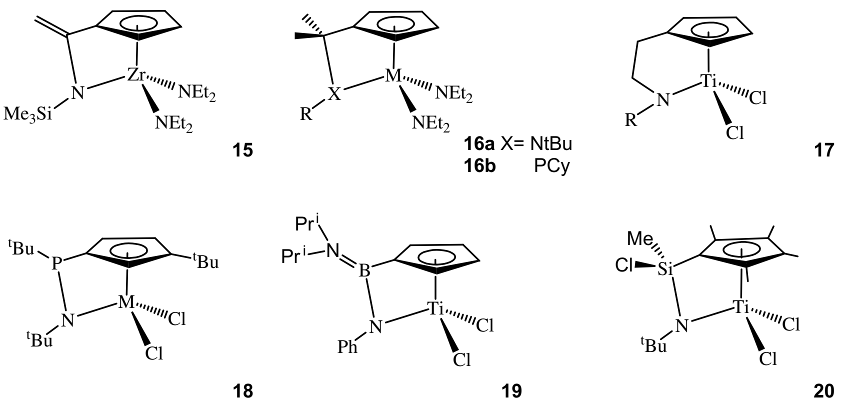


Fig. 6. Shortening and elongating the bridge in CGCs.

Table 1
Effect of bridge variations on the catalyst's constraint

CGC type	Compound	Cp(centroid)–M–N	Lit.
CpSiN	$\{(C_5H_4)SiMe_2N\textit{t}Bu\}TiCl_2$	107.0	[20]
CpC1N	$\{(C_5H_4)(CH\textit{t}Bu)N(4\text{-}MeO\text{–}Ph)\}TiCl_2$	96.1	[61]
CpC2N	$\{(C_5H_4)(CH_2)_2N\textit{i}Pr\}TiCl_2$	104.4	[23]
CpC3N	$\{(C_5H_4)(CH_2)_3N\textit{i}Pr\}TiCl_2$	112.6	[23]
CpBN	$\{(C_5H_4)(BN\textit{i}Pr_2)NPh\}TiCl_2$	99.7	[65]

the Cp ring. First indenyl- (IndSiN) and fluorenyl- (FluSiN) derivatives were prepared by Okuda et al. by the metathesis reaction of the lithium salts of the ligands with the corresponding group 4 tetrachlorides [17,29]. A significant increase in the polymerization activity [69] and the formation of slight stereoregular polypropylene [70] has been reported with these indenyl-CGC derivatives.

The introduction of bulky substituents or alkoxy and amino substituents attached to a second and third indenyl-position surprisingly revealed an enormous substituent effect in the catalytic process [71]. Notably, the permethylated cyclopentadienyl fragment still remains as the most frequently used unit for most catalytic applications. Other fused ring systems such as isocyclopentadienyl-based CGCs [72], heterocycle fused indenyl derivatives [73] or sterically expanded fluorenyl CGC [74] with unprecedented incorporation rates in the copolymerization process have been reported as well.

Heteroaromatic five-membered ring systems bearing phosphorus or boron were reported by the groups of Spence [32] and Ashe [31], respectively. Alt et al. employed alkenyl substituents in view of readily occurring self-immobilization in copolymerization processes [75,76] (Fig. 7).

3.4. Other constrained geometry catalysts

$(CpAX)MCl_2$ CGCs may be transformed in the same way as already described for the corresponding metallocenes: alkylation and cation formation by methyl abstraction [19,33,42,43,61,77,78] or butadiene and betain formation [49,61,79,80] are well established methods to generate highly active catalysts and catalyst precursors, respectively. In the following we want to focus on some more CGC-specific ligand systems.

3.4.1. Binuclear CGCs

Substituents of the Cp ring have also been employed to connect two active metal centers to study the cooperative effects between the two active sites [81–86]. With Marks' bifunctional activators, these tailor-made binuclear systems showed a 11-fold increase in ethyl branching in ethylene homopolymerization studies when compared to the mononuclear analogues [81]. Incorporation rates of higher α-olefins such as 1-hexene or 1-pentene were also significantly higher (Fig. 8).

Alt combined a CGC motif with a metallocene [84] via the cyclopentadienyl fragments, whereas Cuenca et al. [86] anchored the ligands at the bridging silylene and the terminal alkyl, respectively.

3.4.2. Monoalkyl metal-constrained geometry catalysts

A new class of monoalkyl metal-constrained geometry catalysts was reported by Royo et al. using two silylamido bridges providing a double constrained geometry catalyst [40,41,87,88], which was active in the polymerization of ethylene and copolymerization of ethylene/1-hexene. Another example of a monoalkyl complex with a silylamido bridge is the dicyclopentadienyl catalyst system $\{(C_5H_4)SiMe_2N\textit{t}Bu\}\{(C_5H_5)MX$, which was independently reported by Royo [89] and Chen [90] (Fig. 9).

3.4.3. Spiro-metallocene complexes

If two CGC ligands are installed at one metal center, chiral *spiro*-metallocenes with a *C*2-symmetry are obtained (Fig. 10). These compounds were initially observed as byproducts in the syntheses of CGCs and have been described only rarely in the literature [18,26,39,91,92].

While corresponding Yttrium complexes proved to be highly efficient polymerization catalysts for ε-caprolactone [93,94], group(IV) analogues have found no interesting application to date.

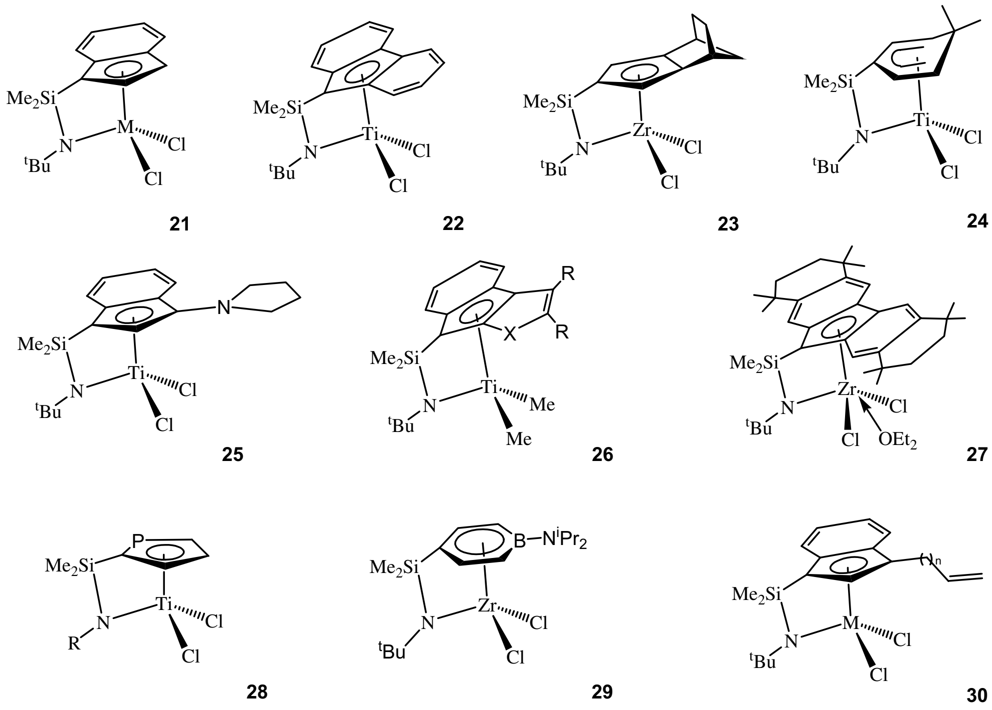


Fig. 7. Modifications of the Cp fragment.

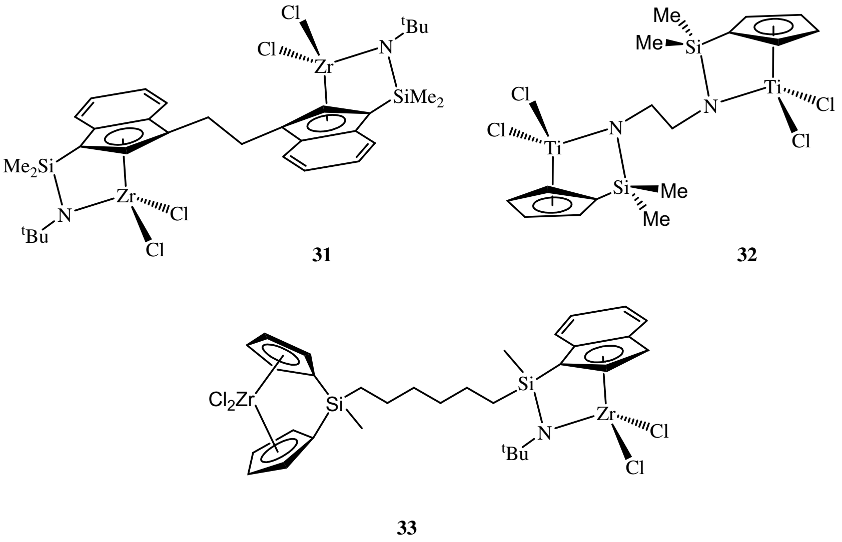


Fig. 8. Binuclear CGCs.

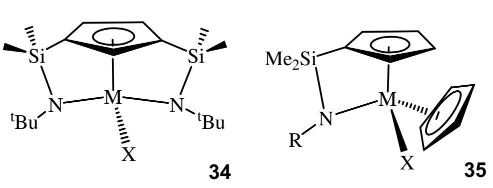
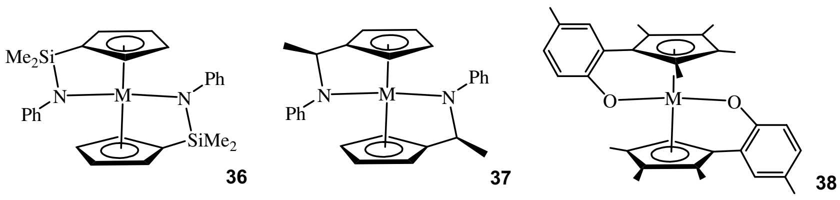


Fig. 9. Double constrained geometry catalysts and a constrained geometry metallocene.

3.4.4. Immobilized CGCs

A few reports on immobilized CGCs have been published. Eisen [95], Pakkanen [96] and Jones [46] anchored the catalysts to a silica surface. Interestingly they used different approaches: While Eisen introduced a reactive center at the terminal alkyl substituent of the CpSiN ligand and connected the preformed Titanium complex to the surface, Pakkanen's CpSiN ligand was prefixed before the metal



36 37 38

Fig. 10. Chiral spiro-metallocenes with two CGC ligands.

centers were introduced by the metallation methodology. As already noted in Section 2.3, Jones made use of the template strategy, connecting the amide function to the metal center and the bridging silylene in one step (Fig. 11).

A well defined (aminomethyl)polystyrene surface was charged with CGCs by Coughlin et al. [97].

3.5. Fine tuning the structure

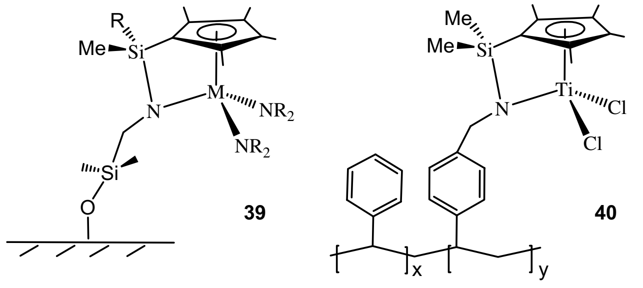
The geometric parameters in CGC maybe modified by a careful choice of the ligand parameters Cp, Z and X. Taking the original ligand system CpSiN as a standard (Fig. 12), the impact of changes on the constraint (measured by the Cp(centroid)–M–N angle) is summarized:

The following modifications result in an opening of the coordination sphere compared to the (CpSiN)MX_2 analogues:

- the introduction of a methylene (C1) bridge (M = Zr, 89.9°) [26] in place of a silylene bridge (around 10° in the angle Cp(centroid)–M–N),
- the substitution of a $B=NR_2$ bridge (M = Ti, 99.2°) [36] in place of the $SiMe_2$ moiety (around 5° in the angle Cp(centroid)–M–N),
- the introduction of X = PR (M = Ti, 103.9°; M = Zr, 98.2°) [27] in place of the original NR (around 2°),
- CG complexes of Zr have a larger coordination sphere than Ti derivatives (around 5°).

On the other side, relaxation of the bridge produces a closing of the coordination site:

- changing from $SiMe_2$ to $(CH_2)_3$–N (M = Ti, 112.5°) [23] results in a closing of the coordination sphere site and in a drastic decrease in the activity [62] of polymerization;



39 40

Fig. 11. Immobilized CGCs.

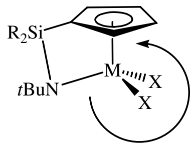


Fig. 12. Effect of the constraint in the Cp(centroid)–M–N angle.

- the same effect is observed on changing from $SiMe_2$ to C3S (M = Ti, 113.5°) [35] or exchanging the NR group for a CC bond part of a closoborane (M = Zr, 108.5°) [98].

A slight closing of the coordination site is also observed when bulkier ligands than Cp, such as indenyl (M = Zr, R = C_9H_5R, 102.8°) [81] or fluorenyl (M = Zr, R = $C_{13}H_8$, 103.4°) [29], are attached to the metal center (around 2°). This effect is even more significant when these ligands are substituted (M = Ti, R = $C_9H_5(OMe)$, 110.1° [71]; R = $C_9H_5(NC_4H_8)$, 111.0°) [71] or (M = Ti, R = 2-methylindenothiophene-$C_{13}H_6$, 110.7°) [73].

Finally, a special effect is observed when the NR bridge is exchanged with O. Only in systems containing ethylene (C2) (M = Ti, 100.8°) [99] or propylene (C3) (M = Ti, 113.8°) bridges are monomolecular complexes formed. The angle in the CpC2O derivative is one of the closest observed in CG complexes with Ti. If the bridge is then shortened to Cp–SiMe2–O- [43] or Cp–C–O- [56], the tension of the molecule is too high and an intermolecular reaction takes place forming a non-constrained dimeric structure (M = Ti, 119°) [43].

4. Overview: synthetic pathways to CGC

Table 2 exemplifies synthetic entries to CGCs, ordered by Cp fragment, bridge Z, donor X and metal center M. Although this list is not exhaustive, it will provide access to the structurally diverse area of CGCs.

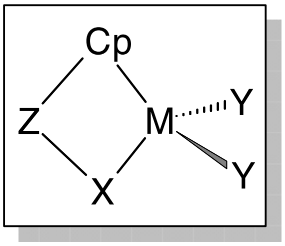


Table 2
Synthetic pathways to structurally diverse CGCs

No.	Cp	Z	X	M	Y	Method	Lit.
1	Cp*	Si	*N*-alkyl	Ti	Cl	A	[16]
2	Cp*	Si	*N*-alkyl	Zr	Cl	A	[20]
3	Cp	Si	*N*-alkyl	Ti,Zr,Hf	NMe_2	B	[20]
4	Cp	Si	*N*-aryl *N*-alkyl	Ti, Zr	Cl	C	[42,43]
5	Cp	Si	*N*-alkyl (chiral)	Ti	Cl	A,C	[51]
6	Ind, Flu	Si	N-*t*Bu	Ti,Zr	Cl	A	[17,29]
7	C_5H_4B	Si	N-*t*Bu	Zr	Cl	A	[31]
8	C_4Me_3P	Si	N-*t*Bu	Ti	Cl	A	[32]
9	Cp	C1	*N*-aryl *N*-alkyl	Ti, Zr	NR_2	A	[25,26]
10	Cp	C1	*N*-aryl *N*-alkyl	Ti, Zr	Cl	A	[61]
11	Cp	C2	*N*-alkyl	Ti	Cl	A	[23]
12	Cp	C2	*N*-alkyl	Ti, Zr	NMe_2	B	[33,34]
13	Cp	C3	*N*-alkyl	Ti,Zr	NMe_2	B	[33,34]
14	Cp	B	*N*-aryl	Ti	NMe_2, Cl	B	[36,65]
15	Cp	B	*N*-aryl	Zr, Hf	NMe_2	B	[66]
16	Cp	B	*N*-alkyl	Ti	NMe_2	B	[67]
17	Cp	P	N-*t*Bu	Ti	Cl	C	[45]
18	Cp	Si	O	Ti, Zr	Cl	C	[43,42]
19	Cp	C1	O	Ti, Zr	NR_2	A	[56]
20	Cp	C2	O	Ti, Zr	Cl	B	[39]
21	Cp*	C2	O	Ti	Cl	C	[47]
22	Cp	C3	O	Ti	Cl	C	[58]
23	Cp*	Si	*P*-alkyl	Ti, Zr	NR_2	A	[27]
24	Cp	C1	*P*-alkyl	Ti,Zr	NR_2	A	[25,28]
25	Cp	C3	S	Ti	NMe_2, Cl	B	[35]

5. Outlook

CGCs are well known for their use in the synthesis of ethylene/α-olefin copolymers with unique material properties. Ligand design has been tailored with respect to particular catalytic activities or polymer properties.

The main advantages of CGCs lie in their high stability towards high temperatures and MAO, permitting the use of these catalysts in industrial scale processes, and their open coordination sites, affording the incorporation of bulky olefins into polyethylene.

These features make these systems appropriate candidates to be used in concurrent tandem catalysis [100,101], a highly topical challenge for chemists in industry and academia [102], where multiple catalysts operating simultaneously avoid the time and yield losses associated with isolation and purification of intermediates. Moreover, CGC properties may be exploited in the so-called "chain-shuttling polymerization" [103], where two different catalysts that produce different polymer structures are used. In recent years, CGCs have been applied in some organic transformations such as hydroamination [104,105] for the synthesis of imines (using enatiomerically pure amines) [106] or pyrroles [107,108], or even in a one-pot hydroamination/hydrosilylation sequence [109].

The synthesis of new families of CGC catalysts will depend on the application of these types of complexes in these chemical processes. Undoubtedly, the future of constrained geometry complexes in catalysis is far from over.

Acknowledgements

J.C. acknowledges the MCyT (project MAT2004-02614 and *programa Juan de la Cierva*) for financial support.

References

[1] PlasticsEurope Deutschland (Eds.), Plastics Business Data and Charts, Frankfurt 2005, http://vke.de.

[2] For an excellent review see: H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. 107 (1995) 1255;
H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143.

[3] A.H. Tullo, Chem. Ing. News 78 (2000) 35.

[4] Review: S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.

[5] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867.

[6] W.E. Piers, P.J. Shapiro, E.E. Bunel, J.E. Bercaw, Synlett (1990) 74.

[7] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 116 (1994) 4623.

[8] J. Okuda, Chem. Ber. 123 (1990) 1649.

[9] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, Eur. Patent. Appl. EP (1991) 416.

[10] J.M. Canich, Eur. Patent. Appl. EP (1991) 420.

[11] (a) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587;
(b) , For other reviews see also:J. Okuda, T. Eberle, in: A. Togni, R.L. Haltermann (Eds.), Metallocenes, vol. 1, Wiley-VCH, Weinheim, 1998, p. 415;
(c) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.

[12] H. Braunschweig, F.M. Breitling, Coord. Chem. Rev. 250 (2006) 2691.

[13] (a) For reviews see: P. Jutzi, T. Redeker, Eur. J. Inorg. Chem. (1998) 663;
(b) U. Siemeling, Chem. Rev. 100 (2000) 1495.
[14] C.P. Casey, R.M. Bullock, W.C. Fultz, A.L. Rheingold, Organometallics 1 (1982) 1591.
[15] J.J. Bishop, A. Davison, M.L. Katcher, D.W. Lichtenburg, R.E. Merrill, J.C. Smart, J. Organomet. Chem. 27 (1971) 241.
[16] G.A. Luinstra, J.H. Teuben, J. Chem. Soc.-Chem. Commun. (1990) 1470.
[17] F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 245.
[18] K.E. Duplooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3129.
[19] J. Okuda, T. Eberle, T.P. Spaniol, Chem. Ber.-Recl. 130 (1997) 209.
[20] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, Organometallics 15 (1996) 1572.
[21] D. Balboni, I. Camurati, G. Prini, L. Resconi, S. Galli, P. Mercandelli, A. Sironi, Inorg. Chem. 40 (2001) 6588.
[22] L. Resconi, I. Camurati, C. Grandini, M. Rinaldi, N. Mascellani, O. Traverso, J. Organomet. Chem. 664 (2002) 5.
[23] P.J. Sinnema, L. vanderVeen, A.L. Spek, N. Veldman, J.H. Teuben, Organometallics 16 (1997) 4245.
[24] L. Duda, G. Erker, R. Frohlich, F. Zippel, Eur. J. Inorg. Chem. (1998) 1153.
[25] K. Kunz, G. Erker, S. Doring, R. Frohlich, G. Kehr, J. Am. Chem. Soc. 123 (2001) 6181.
[26] M. Kunz, G. Erker, S. Doring, S. Bredeau, G. Kehr, R. Frohlich, Organometallics 21 (2002) 1031.
[27] G. Altenhoff, S. Bredeau, G. Erker, G. Kehr, O. Kataeva, R. Frohlich, Organometallics 21 (2002) 4084.
[28] S. Bredeau, G. Altenhoff, K. Kunz, S. Doring, S. Grimme, G. Kehr, G. Erker, Organometallics 23 (2004) 1836.
[29] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1995) 789.
[30] S.G. Feng, J. Klosin, W.J. Kruper, M.H. McAdon, D.R. Neithamer, P.N. Nickias, J.T. Patton, D.R. Wilson, K.A. Abboud, C.L. Stern, Organometallics 18 (1999) 1159.
[31] A.J. Ashe, X.G. Fang, J.W. Kampf, Organometallics 18 (1999) 1363.
[32] S.J. Brown, X.L. Gao, D.G. Harrison, L. Koch, R.E.V. Spence, G.P.A. Yap, Organometallics 17 (1998) 5445.
[33] A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1936.
[34] A.K. Hughes, S.M.B. Marsh, J.A.K. Howard, P.S. Ford, J. Organomet. Chem. 528 (1997) 195.
[35] J.H. Wang, C. Zheng, J.A. Maguire, N.S. Hosmane, Organometallics 22 (2003) 4839.
[36] H. Braunschweig, C. von Koblinski, U. Englert, Chem. Commun. (2000) 1049.
[37] P.J. Sinnema, K. Liekelema, O.K.B. Staal, B. Hessen, J.H. Teuben, J. Mol. Catal. A-Chem. 128 (1998) 143.
[38] Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, V.G. Young, Organometallics 15 (1996) 2720.
[39] Y.X. Chen, P.F. Fu, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 5958.
[40] J. Cano, P. Royo, M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio, Angew. Chem.-Int. Ed. 40 (2001) 2495.
[41] J. Cano, P. Royo, H. Jacobsen, O. Blacque, H. Berke, E. Herdtweck, Eur. J. Inorg. Chem. (2003) 2463.
[42] S. Ciruelos, T. Cuenca, R. Gómez, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 15 (1996) 5577.
[43] S. Ciruelos, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, Organometallics 14 (1995) 177.
[44] J. Okuda, S. Verch, R. Sturmer, T.P. Spaniol, J. Organomet. Chem. 605 (2000) 55.
[45] V.V. Kotov, E.V. Avtomonov, J. Sundermeyer, K. Harms, D.A. Lemenovskii, Eur. J. Inorg. Chem. (2002) 678.
[46] K.Q. Yu, M.W. McKittrick, C.W. Jones, Organometallics 23 (2004) 4089.
[47] Y.T. Zhang, Y. Mu, C.S. Lu, G.H. Li, J.S. Xu, Y.R. Zhang, D.S. Zhu, S.H. Feng, Organometallics 23 (2004) 540.
[48] Y.T. Zhang, Y. Mu, Organometallics 25 (2006) 631.
[49] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, Organometallics 14 (1995) 3132.
[50] J.A.M. Canich, (Exxon). PCT Int. Appl. 1996, WO96/00244.
[51] R. Kleinschmidt, Y. Griebenow, G. Fink, J. Mol. Catal. A-Chem. 157 (2000) 83.
[52] F. Amor, A. Butt, K.E. du Plooy, T.P. Spaniol, J. Okuda, Organometallics 17 (1998) 5836.
[53] F. Amor, K.E. du Plooy, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 558 (1998) 139..
[54] J. Okuda, T. Eberle, T.P. Spaniol, V. Piquet-Faure, J. Organomet. Chem. 591 (1999) 127.
[55] J.T. Park, S.C. Yoon, B.J. Bae, W.S. Seo, I.H. Suh, T.K. Han, J.R. Park, Organometallics 19 (2000) 1269.
[56] K. Kunz, G. Erker, G. Kehr, R. Frohlich, H. Jacobsen, H. Berke, O. Blacque, J. Am. Chem. Soc. 124 (2002) 3316.
[57] W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, Angew. Chem.-Int. Ed. Engl. 33 (1994) 1946.
[58] E. Gielens, J.Y. Tiesnitsch, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 1652.
[59] Z.W. Xie, Coord. Chem. Rev. 250 (2006) 259.
[60] B.Q. Wang, Coord. Chem. Rev. 250 (2006) 242.
[61] C. Wang, G. Erker, G. Kehr, K. Wedeking, R. Frohlich, Organometallics 24 (2005) 4760.
[62] D. van Leusen, D.J. Beetstra, B. Hessen, J.H. Teuben, Organometallics 19 (2000) 4084.
[63] P.T. Gomes, M.L.H. Green, A.M. Martins, J. Organomet. Chem. 551 (1998) 133.
[64] D.J. Cho, C.J. Wu, S. Sujith, W.S. Han, S.O. Kang, B.Y. Lee, Organometallics 25 (2006) 2133.
[65] H. Braunschweig, F.M. Breitling, C. von Koblinski, A.J.P. White, D.J. Williams, Dalton Trans. (2004) 938.
[66] H. Braunschweig, F.M. Breitling, K. Radacki, F. Seeler, J. Organomet. Chem. 690 (2005) 5000.
[67] H. Braunschweig, F.M. Breitling, C. Burschka, F. Seeler, J. Organomet. Chem. 691 (2006) 702.
[68] A.B. Vázquez, P. Royo, E. Herdtweck, J. Organomet. Chem. 683 (2003) 155.
[69] H.G. Alt, K. Fottinger, W. Milius, J. Organomet. Chem. 572 (1999) 21.
[70] A.L. McKnight, M.A. Masood, R.M. Waymouth, D.A. Straus, Organometallics 16 (1997) 2879.
[71] J. Klosin, W.J. Kruper, P.N. Nickias, G.R. Roof, P. De Waele, K.A. Abboud, Organometallics 20 (2001) 2663.
[72] S. Gentil, N. Pirio, P. Meunier, J.C. Gallucci, J.D. Schloss, L.A. Paquette, Organometallics 19 (2000) 4169.
[73] C. Grandini, I. Camurati, S. Guidotti, N. Mascellani, L. Resconi, I.E. Nifant'ev, I.A. Kashulin, P.V. Ivehenko, P. Mercandelli, A. Sironi, Organometallics 23 (2004) 344.
[74] L.J. Irwin, J.H. Reibenspies, S.A. Miller, J. Am. Chem. Soc. 126 (2004) 16716.
[75] H.G. Alt, A. Reb, W. Milius, A. Weis, J. Organomet. Chem. 628 (2001) 169.
[76] H.G. Alt, A. Reb, J. Mol. Catal. A-Chem. 175 (2001) 43.
[77] H.V.R. Dias, Z.Y. Wang, S.G. Bott, J. Organomet. Chem. 508 (1996) 91.
[78] L. Kloppenburg, J.L. Petersen, Organometallics 15 (1996) 7.
[79] A. Spannenberg, W. Baumann, S. Becke, U. Rosenthal, Organometallics 21 (2002) 1512.
[80] G. Erker, Chem. Commun. (2003) 1469.
[81] L.T. Li, M.V. Metz, H.B. Li, M.C. Chen, T.J. Marks, L. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 124 (2002) 12725.
[82] J.X. Wang, H.B. Li, N. Guo, L.T. Li, C.L. Stern, T.J. Marks, Organometallics 23 (2004) 5112.
[83] N. Guo, L.T. Li, T.J. Marks, J. Am. Chem. Soc. 126 (2004) 6542.

[84] H.G. Alt, R. Ernst, I.K. Bohmer, J. Organomet. Chem. 658 (2002) 259.
[85] S.K. Noh, J. Lee, D.H. Lee, J. Organomet. Chem. 667 (2003) 53.
[86] G. Jiménez, P. Royo, T. Cuenca, E. Herdtweck, Organometallics 21 (2002) 2189.
[87] J. Cano, M. Sudupe, P. Royo, M.E.G. Mosquera, Angew. Chem.-Int. Ed. 45 (2006) 7572.
[88] J. Cano, M. Sudupe, P. Royo, M.E.G. Mosquera, Organometallics 24 (2005) 2424.
[89] S. Ciruelos, A. Sebastián, T. Cuenca, P. Gómez-Sal, A. Manzanero, P. Royo, J. Organomet. Chem. 604 (2000) 103.
[90] J.Z. Jin, D.R. Wilson, E.Y.X. Chen, Chem. Commun. (2002) 708.
[91] U. Bohme, K.H. Thiele, J. Organomet. Chem. 472 (1994) 39.
[92] F. Amor, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4765.
[93] K.C. Hultzsch, T.P. Spaniol, J. Okuda, Organometallics 16 (1997) 4845.
[94] K.C. Hultzsch, J. Okuda, Macromol. Rapid Commun. 18 (1997) 809.
[95] M. Galan-Fereres, T. Koch, E. Hey-Hawkins, M.S. Eisen, J. Organomet. Chem. 580 (1999) 145.
[96] H. Juvaste, T.T. Pakkanen, E.I. Iiskola, Organometallics 19 (2000) 1729.
[97] R.M. Kasi, E.B. Coughlin, Organometallics 22 (2003) 1534.
[98] H.P. Wang, Y.R. Wang, H.W. Li, Z.W. Xie, Organometallics 20 (2001) 5110.
[99] G. Trouve, D.A. Laske, A. Meetsma, J.H. Teuben, J. Organomet. Chem. 511 (1996) 255.
[100] Z.J.A. Komon, G.M. Diamond, M.K. Leclerc, V. Murphy, M. Okazaki, G.C. Bazan, J. Am. Chem. Soc. 124 (2002) 15280.
[101] K. Musikabhumma, T.P. Spaniol, J. Okuda, J. Mol. Catal. A-Chem. 192 (2003) 223.
[102] J.C. Wasilke, S.J. Obrey, R.T. Baker, G.C. Bazan, Chem. Rev. 105 (2005) 1001.
[103] D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, Science 312 (2006) 714.
[104] I. Bytschkov, S. Doye, Eur. J. Org. Chem. (2003) 935.
[105] S. Doye, Synlett (2004) 1653.
[106] F. Pohlki, I. Bytschkov, H. Siebeneicher, A. Heutling, W.A. Konig, S. Doye, Eur. J. Org. Chem. (2004) 1967.
[107] B. Ramanathan, A.J. Keith, D. Armstrong, A.L. Odom, Org. Lett. 6 (2004) 2957.
[108] A.L. Odom, Dalton Trans. (2005) 225.
[109] A. Heutling, F. Pohlki, I. Bytschkov, S. Doye, Angew. Chem.-Int. Ed. 44 (2005) 2951.