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Review

Constrained geometry complexes—Synthesis and applications

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Abstract

Transition metal complexes bearing linked cyclopentadienyl amido ligands, regularly referred to as constrained geometry complexes (CGCs), have found wide interest both in academia and industry since their first description in 1990. Particularly, Group 4 CGCs were applied as catalyst precursors for the polymerisation of α-olefins, often yielding polymers with unique microstructure and material properties. Moreover, the potential of CGCs to mediate transformations other than polymerisation reactions is increasingly acknowledged. The present review aims to give a comprehensive survey about the chemistry of CGCs and covers reports in the open literature between 1990 and spring 2005.

Keywords: Constrained geometry complexes; Cyclopentadienyl amido ligands; α-Olefins

1. Introduction

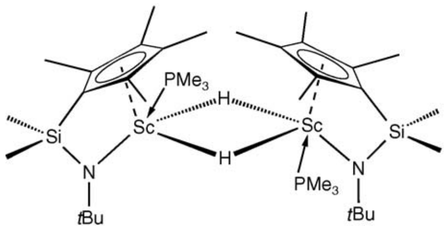
The amount of the classic polyolefins (polyethylene, PE, polypropylene, PP, and polystyrene, PS) currently produced world-wide is well above 130 × 10^6 tonnes per year, thus making up some 60% of the entire production of plastics [1]. Polyolefins (besides low-density polyethylene from the ICI high pressure radical process) are afforded by transition metal catalysts originating from the discovery of Ziegler [2,3] and Natta [4–6] that ethylene and propylene polymerise in the presence of $TiCl_4$ and Et_2AlCl even at low pressure or the discovery of the catalytic activity for olefin polymerisation of chromium oxides (Phillips-type catalysts) by Hogan and Banks [7,8]. A major shortcoming of these early systems was the heterogeneous nature of the catalysts, which prevented a thorough characterisation of the active sites and left many questions concerning the mechanisms involved in polymer growth [9,10].

Stimulated by related developments in other fields of catalysis, homogeneous organometallic compounds were introduced as suitable model systems for a deeper investigation of the polymerisation process at transition metal centres. Metallocenes were particularly attractive for mechanistic studies of Ziegler–Natta type systems, since they exhibit simple coordination geometries, only one type of active site and easily polymerise ethylene when activated by alkylaluminiums [9,11–15]. With the discovery by Kaminsky and co-workers of methylaluminoxane (MAO) as a highly effective activator [16,17], polymerisation rates and yields have been increased to an industrially useful level. These developments combined with the attractive product properties, e.g. well defined structure, little branching and very narrow molar mass distribution, initiated extensive efforts in industry and academia to expand further the capabilities of the system. Besides attempts to alter polymerisation characteristics and product properties by simple variation of the substituents on the cyclopentadienyl ring, more sophisticated alterations were introduced [18]. Since the 1980s, work by Ewen, Brintzinger et al. in particular showed how the controlled, stereoselective polymerisation of propylene and other α-olefins may be achieved by employing catalysts of suitable symmetry and geometry [9,19–23].

More recently, a new family of active polymerisation catalysts was developed by formally exchanging one cyclopentadienyl ring by an amido moiety; these are often referred to as constrained geometry complexes (CGCs), given the chelate bite angle imposed by the cyclopentadienyl and amido donors. Dianionic, bifunctional chelating ligands of this type have been first employed by Bercaw and co-workers for the preparation of Sc(III) complexes, such as **1** (Fig. 1) [24,25]. Only a short time later, reports appeared on the preparation of related Group 4 complexes, such as **2** (Fig. 1) [26] and their exceptional characteristics in ethylene polymerisation and copolymerisation of ethylene and higher α-olefins [27,28].

The superiority of the CGCs for copolymerisation of ethylene and α-olefins when compared to metallocenes and metallocenophanes is generally ascribed to (i) a less crowded coordination sphere, (ii) a smaller $Cp_{centroid}$–M–N bite angle (by 25–30° compared to $\angle Cp_{centroid}$–M–$Cp_{centroid}$ in metallocenes and metallocenophanes) and (iii) a decreased tendency of the bulk polymer chain to undergo chain transfer reactions. The latter, as well as the high activity of such CGCs, most probably result from a more Lewis-acidic transition metal centre (according to the "neutral ligand formalism", an amido moiety can donate, at most, three electrons to the transition metal and thereby two electrons less than a cyclopentadienyl group) [24,25,29]. Another advantage is the higher thermal stability of alkyl and dialkyl CGCs when compared to related metallocenes [30,31] that allows higher polymerisation temperatures.

Since the early 1990s, the chemistry of CGCs experienced a rapid advancement, particularly because catalytic systems based on such compounds gave access to a wide array of polymers with



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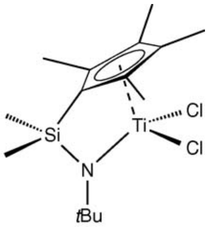

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Fig. 1. First reported scandium and titanium CGCs.

unique material properties and considerable commercial value [32]. Certain aspects of this development were covered by several reviews, however, the most general surveys are dating back to the late 1990s [33–40]. Consequently, the present review aims to give a comprehensive review of the chemistry of CGCs covering the open literature from the early beginnings until at least spring 2005. Synthetic methods for the preparation of CGCs as well as the numerous alterations of the ligand framework will be summarised. Characteristics of CGC catalysed polymerisation reactions will be thoroughly discussed, since they provide a good insight into the versatility and special qualities of this class of compounds that make it so unique. Furthermore, the application of CGCs in the catalysis of transformations other than polymerisations will be examined. The discussion of the catalytic potential of CGCs will highlight the sensitivity of the system to changes in the ligand framework; alterations in the ligand framework also mandate changes in the transition metal or co-catalyst. In addition, various other aspects of the chemistry, such as their immobilisation on heterogeneous supports, their application in concurrent tandem catalysis and C–H activation involving CGCs will be addressed.

2. Definition of constrained geometry complex

The term constrained geometry complex was originally coined by Stevens et al. for complexes in which a π-bonded moiety (e.g. cyclopentadienyl or a derivative) is linked to one of the other ligands on the same metal centre in such a way that the angle at this metal between the centroid of the π-system and the additional ligand is smaller than in comparable unbridged complexes. Stevens et al. claimed in their patent, that such a strain inducing link would improve catalyst performance. Their thesis was supported by a comparison of the polymerisation performance of a series of silanediyl and disilanediyl bridged cyclopentadienyl amido complexes [27].

Obviously, the scope of the definition by Stevens et al. goes far beyond *ansa*-bridged cyclopentadienyl amido complexes and was accordingly used in connection with other more or less related ligand systems, including (i) other *ansa*-complexes with η^5:η^1 coordination, where at least one of the coordinating fragments of bridged cyclopentadienyl-amido complexes is replaced by an isolobal fragment, (ii) other *ansa*-complexes with η^5:η^1 coordination, where at least one of the coordinating fragments is not isolobal to the formally replaced fragments of bridged cyclopentadienyl-amido complexes and (iii) other *ansa*-complexes with a coordination mode different from η^5:η^1 coordination.

Furthermore, the term is frequently used in connection with cyclopentadienyl amido complexes with long *ansa*-bridges, such as –$(CH_2)_n$– ($n > 2$). However, due to the length and flexibility of the bridge in such compounds there is virtually no strain induced [41].

The review presented here spotlights bridged cyclopentadienyl amido complexes and we will refer to such compounds generally as CGCs A few very closely related ligand systems (very similar coordination modes and charge distributions) will be briefly mentioned, but chemically less related systems, e.g. bridged cyclopentadienyl amino ligands will not be considered.

3. Synthesis of CGCs

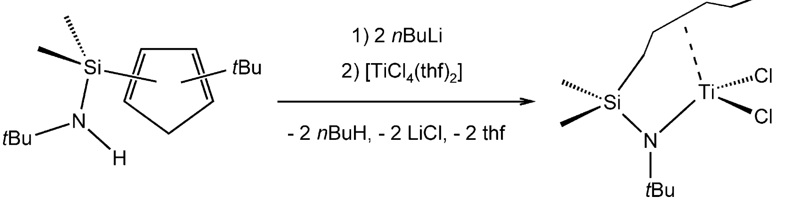
Over the years, various routes for the synthesis of CGCs have been developed. In the following paragraphs, synthetic methods that were reported in the literature for the synthesis of Group 4 CGCs will be described. However, many of these methods can be extended to the synthesis of CGCs of other transition metals as is widely documented in the literature. Two general approaches can be distinguished: (i) the synthesis of the *ansa*-ligand precursor and subsequent complexation to a transition metal and (ii) the introduction of the *ansa*-bridge by reaction in the ligand sphere of a transition metal complex.

3.1. Synthesis of CGCs by complexation of the pre-assembled ansa-ligand precursor

The former approach is by far more extensively studied and a number of variants have been developed. The most successful routes comprise the dimetalation of the ligand precursor (ligand precursor will usually refer to the protonated, neutral species throughout the text) followed by a salt elimination reaction and the direct reaction of the ligand precursor with transition metal amides under amine elimination, respectively. In addition, there are several other routes including toluene elimination, amine assisted HCl elimination and trimethylsilylchloride elimination.

3.1.1. Dimetalation/salt elimination sequence

Dimetalation of the ligand precursor can be usually achieved using two equivalents of alkyl lithium reagents, such as *n*BuLi, *t*BuLi and MeLi. Other lithium reagents, e.g. $LiNR_2$ (R = *i*Pr, $SiMe_3$) and Grignard reagents, e.g. *i*PrMgCl [42], have also been successfully applied for the deprotonation of the ligand precursors. The dimetalated species can then be reacted with suitable Group 4 metal chlorides, e.g. $[TiCl_4(thf)_2]$ [26], $ZrCl_4$ [43], $[ZrCl_4(thf)_2]$ [44], $[ZrCl_2(NEt_2)_2(thf)_2]$ [45] or $HfCl_4$ [43], via salt elimination to give the corresponding CGCs (Eqs. (1)–(3)).



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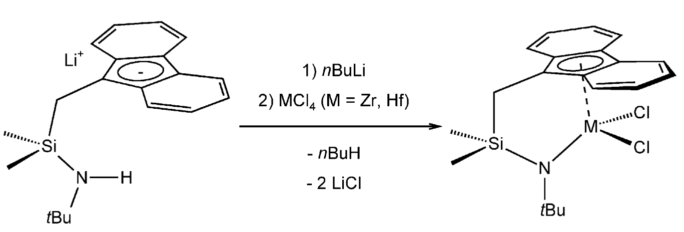

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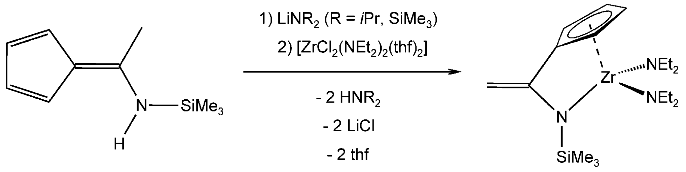
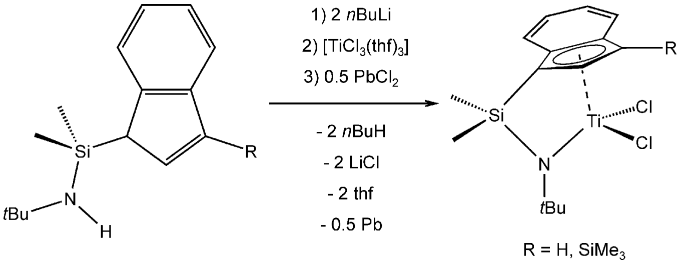


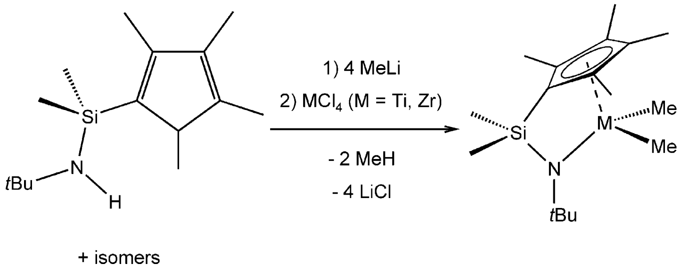
(3)

While this route is quite effective for synthesis of the zirconium and hafnium species, the synthesis of the titanium congeners is often hampered by reduction of the titanium(IV) precursor in the course of the reaction. This obstacle can often be overcome by using $[TiCl_3(thf)_3]$ as the metal source and subsequent oxidation of the resultant titanium(III) complexes with $PbCl_2$ (Eq. (4)) [46].



(4)

More recently, it was also reported that reaction of the dilithiated ligand precursor with MCl_4 (M = Ti, Zr) in the presence of two equivalents of MeLi leads to the corresponding dimethylated CGCs in high yields, i.e. without competitive reduction reactions (Eq. (5)) [47].



(5)

In a variation of the reaction sequence, the dilithiated ligand precursor $[Li_2\{(C_5H_4)(CH_2)_3NMe\}]$ reacts with $[Cp_2ZrCl_2]$ under elimination of one equivalent of both lithium chloride and lithium cyclopentadienide to give $[\{\eta^5:\eta^1-(C_5H_4)(CH_2)_3NMe\}Zr(Cl)Cp]$ [48].

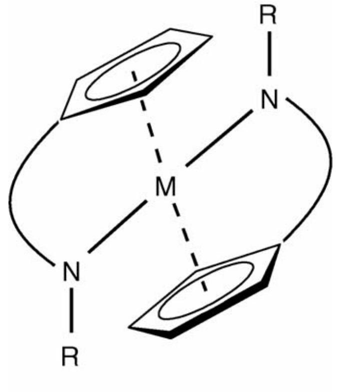


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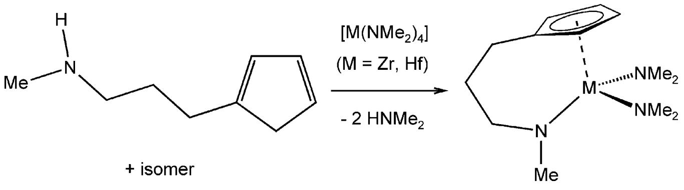
Fig. 2. Metallocene complex with two CGC ligands.

The reaction sequence of dimetalation and salt elimination is widely applicable to a range of differently substituted ligand precursors and different lengths of the *ansa*-bridge. However, substitution of all four chlorides on the metal precursor to give the bis-ligand metallocene (**3**) is frequently observed (Fig. 2).

Examples have been described for $[TiCl_4(thf)_2]$ [45], $ZrCl_4$ [49], $[ZrCl_4(thf)_2]$ [45,50–53] and $[HfCl_4(thf)_2]$ [52] as Group 4 metal precursors. In most of these cases, the metallocene complexes are formed independent of the molar ratio of the starting materials. There is some evidence that the nature of the amido moiety as well as the solvent have some influence on the preference for CGC versus metallocene formation [52].

3.1.2. Amine elimination

Reaction of CGC ligand precursors with Group 4 metal amides $[M(NR_2)_4]$ (M = Ti, Zr, Hf; R = Me, Et) under amine elimination developed into another versatile route to Group 4 CGCs. The first examples were reported for cyclopentadienyl ligands with long C_3H_6 *ansa*-bridges (Eq. (6)) [41] and shortly thereafter for cyclopentadienyl and indenyl ligands with short $SiMe_2$ *ansa*-bridges (Eq. (7)) [54].



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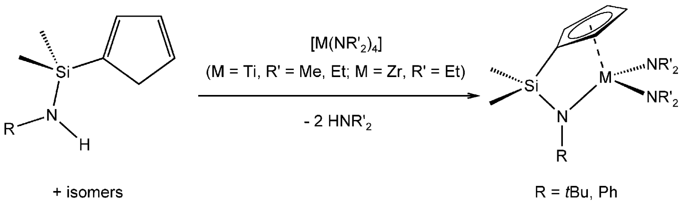
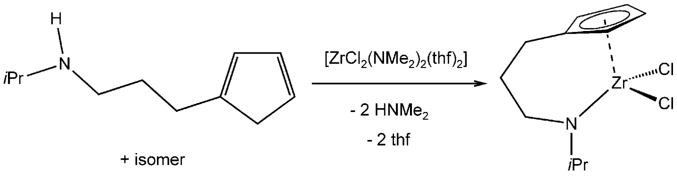


(7)

Examples for substituted tetramethylcyclopentadienyl ligands appeared a few years later [29], while examples for substituted fluorenyl ligands seem to be still absent from the literature. In this context, Alt et al. reported the reaction of ligand precursor $(C_{13}H_9)(SiMe_2)N(H)t$Bu with $[Zr(NEt_2)_4]$ to give the unbridged complex $[(C_{13}H_9)(SiMe_2)N(t\text{Bu})Zr(NEt_2)_3]$. This observation was attributed to the comparably low acidity of the proton on the fluorenyl five-membered ring and the steric demand of the fluorenyl moiety [49]. $[ZrCl_2(NMe_2)_2(thf)_2]$ may as well serve as a suitable precursor for such amine elimination reactions as was demonstrated for a few CGC ligand precursors (Eq. (8)) [55].

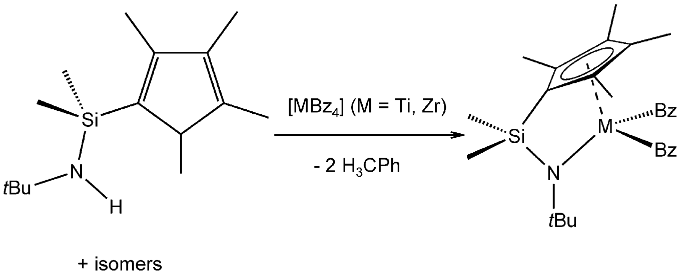


(8)

The amine elimination route usually proceeds very cleanly and gives the desired products in high yields. In contrast to the dimetalation/salt elimination sequence, formation of metallocene type complexes (**3**) is not observed as a side reaction if the starting materials are applied in an equimolar ratio. However, such metallocenes may be obtained if the ligand precursors and the Group 4 metal *per*-amides are combined in a 2:1 molar ratio [56].

3.1.3. Toluene elimination

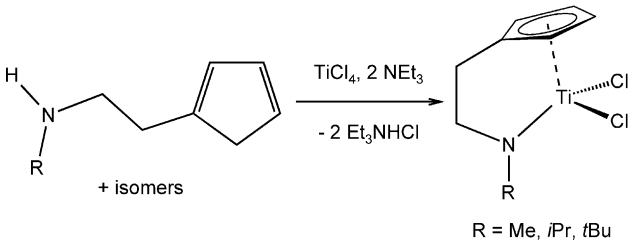
Similar to the amine elimination route, Group 4 tetrabenzyl compounds may be used as precursors for the synthesis of CGCs. This has the added advantage that the pK_a of toluene is much higher than that of any amine and therefore the elimination reaction should be thermodynamically more favoured. While the reaction of $(C_5Me_4H)(SiMe_2)N(H)t$Bu with $TiBz_4$ was reported to give the desired CGC in high yields, the reaction with the zirconium analogue resulted in low conversions and significant amounts of side products (Eq. (9)) [57].



(9)

3.1.4. Amine assisted HCl elimination

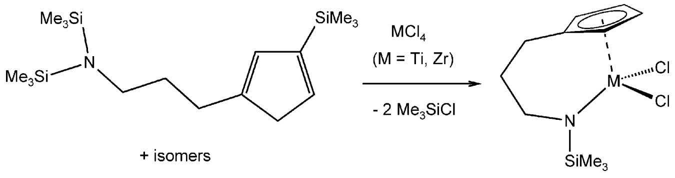
Direct reaction of the neutral ligand precursors with $TiCl_4$ in the presence of triethylamine gave the corresponding dichloro CGCs in moderate yields (Eq. (10)). However, published examples for this HCl elimination reaction include only ligand systems with relatively long C_2H_4 and C_3H_6 *ansa*-bridges and consequently little strain in the *ansa*-ligand [30].



(10)

3.1.5. Me_3SiCl elimination

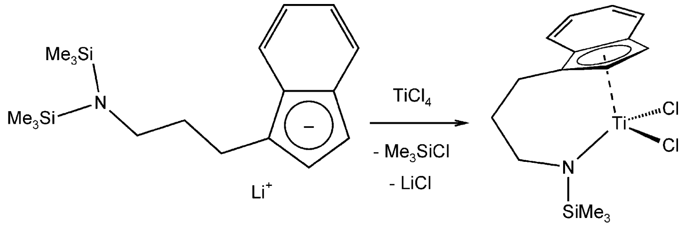
Alternatively, ligand precursors may be utilised where the acidic protons are replaced by trimethylsilyl moieties. Such ligand precursors may react with suitable Group 4 metal halides under Me_3SiCl elimination conditions to give the corresponding CGCs (Eq. (11)). Reported examples are limited to the reaction of $(C_5H_4SiMe_3)(CH_2)_3N(SiMe_3)_2$ with $TiCl_4$, $ZrCl_4$ and $[ZrCl_4(SMe_2)_2]$, i.e. unstrained systems [58,59].



(11)

3.1.6. Combined LiCl and Me_3SiCl elimination

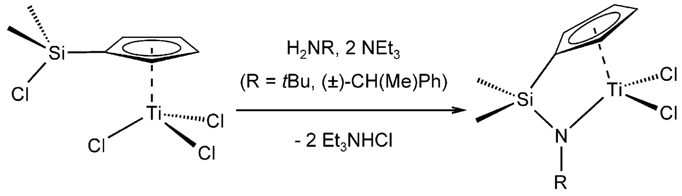
One example has been described that combines the previously described approaches of salt elimination and Me_3SiCl elimination (Eq. (12)). The yield of this synthesis, however, is relatively low. It gives rise to a relatively long C_3H_6 *ansa*-bridge, i.e. a ligand system without strain [60].



(12)

3.2. Synthesis of CGCs by reaction in the ligand sphere of a transition metal

The approach of introducing an *ansa*-bridge by a reaction in the ligand sphere of a suitable half-sandwich complex to create CGCs is much less developed and gives access only to limited variety in terms of ligand design. When $[\{(\eta^5\text{-}C_5H_4)(SiMe_2Cl)\}TiCl_3]$ is treated with either NH_2R and NEt_3 in a 1:1:2 ratio [61], with one equivalent of Li[NHR] in the presence of one equivalent of NEt_3 (Eq. (13)) [61–63], with excess Li[NHR] [64] or even with stoichiometric amounts of Li[NHR] [65] the corresponding CGCs $[\{\eta^5{:}\eta^1\text{-}(C_5H_4)(SiMe_2)NR\}TiCl_2]$ (R = alkyl) are isolated. Similarly, reaction of $[\{(\eta^5\text{-}C_5H_4)(SiMe_2Cl)\}M(\eta^5\text{-}1,3\text{-}t\text{BuC}_5H_3)Cl_2]$ (M = Ti, Zr, Hf) with two equivalents of Li[NH*t*Bu] yields the corresponding CGCs $[\{\eta^5{:}\eta^1\text{-}(C_5H_4)(SiMe_2)\text{N}t\text{Bu}\}M(\eta^5\text{-}1,3\text{-}t\text{BuC}_5H_3)Cl]$ [66]. Surprisingly, the reaction of $[\{(\eta^5\text{-}C_5H_4)(SiMe_2H)\}ZrCl_3]$ with Li[NH*t*Bu] yielded as well the corresponding CGC $[\{\eta^5{:}\eta^1\text{-}(C_5H_4)(SiMe_2)\text{N}t\text{Bu}\}ZrCl_2]$, although this reaction apparently requires the evolution of dihydrogen [67,68].



(13)

Neither the synthesis of indenyl nor fluorenyl analogues has been reported using this route, probably due to difficulties in the preparation of suitable precursors [46].

Only recently, the synthesis of tetramethylcyclopentadienyl analogues by reaction of $[\{(\eta^5\text{-}C_5Me_4)(SiMeClX)\}TiCl_3]$ (X = H, Cl) with two equivalents of LiNH*t*Bu has appeared. It was demonstrated that this reaction proceeds via intermediate formation of $[\{(\eta^5\text{-}C_5Me_4)(SiMeX)N(H)t\text{Bu}\}Ti(Cl)_2N(H)t\text{Bu}]$ and subsequent ring closure under amine elimination [69]. While this route is of interest for facile variation of the amido fragment in silicon bridged CGCs, expansion of this approach to CGCs with other *ansa*-bridges is restricted by the availability of suitable precursors.

Another very specific route is the reaction of fulvene complexes, such as $[\{(C_5H_4){=}C(H)t\text{Bu}\}Ti(Cp^*)Cl]$ with nitriles or *iso*-nitriles. However, these reactions give only access to certain C_2 bridged CGCs and are therefore of limited practical value [70].

3.3. Derivatisation of Group 4 CGCs

Most of the previously described synthetic routes yield the desired CGCs as the dichloro or diamido derivatives. Both may be activated by methylaluminoxane to polymerise olefins. However, further derivatisation of these complexes is often required to obtain CGCs with a certain chemical reactivity, e.g. the dialkyl derivatives that may be activated by $B(C_6F_5)_3$ or $[Ph_3C^+][B(C_6F_5)_4{}^-]$ to give olefin polymerisation catalysts (*vide infra*). Most of these derivatisation reactions seem to be of quite general applicability. The dichloro derivatives can be easily converted to the corresponding diamido derivatives by reaction with two equivalents of $LiNMe_2$ [71]. On the other hand, the diamido derivatives can be converted to the corresponding dichloro complexes using Me_3SiCl [29,72], PCl_5 [29], HCl [29] or $Me_2NH{\cdot}HCl$ [29,41]. In some cases, the dichloro complexes are obtained in the form of their Me_2NH adducts [29,41].

The dichloro complexes and their Me_2NH adducts can be easily converted to the corresponding dialkyl complexes by reaction with two equivalents of lithium alkyls [41,73], potassium alkyls [73] or Grignard reagents [41,46,74]. Selective monoalkylation of the dichloro complexes could as well be achieved by means of one equivalent of $n\text{Bu}_2\text{Mg}$ [31] or $AlMe_3$ [71]. Similarly, reaction of the dichloro complexes with one equivalent of NaCp [75] or lithium aryls [74,76] resulted in selective substitution of one chloride per metal centre. It is noteworthy that CGCs with such substitution patterns are chiral at the metal centre, although resolution of any such system has yet to be accomplished.

The dichloro derivatives can be converted to the corresponding butadiene complexes by reaction with two equivalents of *n*BuLi in the presence of butadienes [77], with magnesium butadiene $[Mg(C_4H_6)]_n$ [78] or with 1,4-diphenylbutadiene magnesium $[Mg(C_4H_4Ph_2)(thf)_3]_n$ [79]. Structural and spectroscopic studies of the resultant complexes revealed that the bonding mode of the butadiene ligand in CGCs is sensitive to the ligand framework and the nature of the transition metal. While the zirconium compounds displayed exclusively a metallacyclic σ^2, π coordination of the butadiene ligand (corresponding to zirconium in the oxidation state +IV) [78,79], the titanium analogues showed both metallacyclic σ^2, π (oxidation state +IV) and conventional π^2 (oxidation state +II) coordination modes dependent on the specific nature of the co-ligands [77,78]. In a similar reaction, $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)\text{N}t\text{Bu}\}TiCl_2]$ was found to undergo reaction with disubstituted 1,3-butadiynes in the presence of magnesium to give the corresponding five-membered titanacyclocumulenes [80].

4. Modification of the ligand system with constrained geometry

To date, a multitude of Group 4 CGCs and closely related compounds have been prepared by the synthetic methods described above. Obviously, the nature of the ligand system may be adjusted either by variation of the cyclopentadienyl moiety, the amido group, the *ansa*-bridge or a combination thereof (Fig. 3).

The following sections aim to give a broad overview of the variations as they are found in the open literature, giving representative examples for each category. Influences of the structure of the CGCs on their polymerisation characteristics will be discussed in an individual section together with other aspects of CGC catalysed polymerisation reactions.

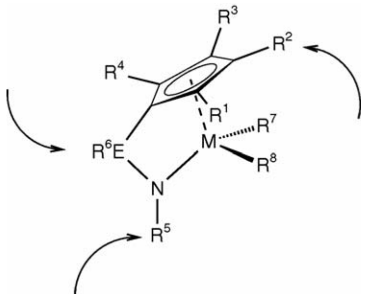


Fig. 3. Sites of modification in ligands with constrained geometry.

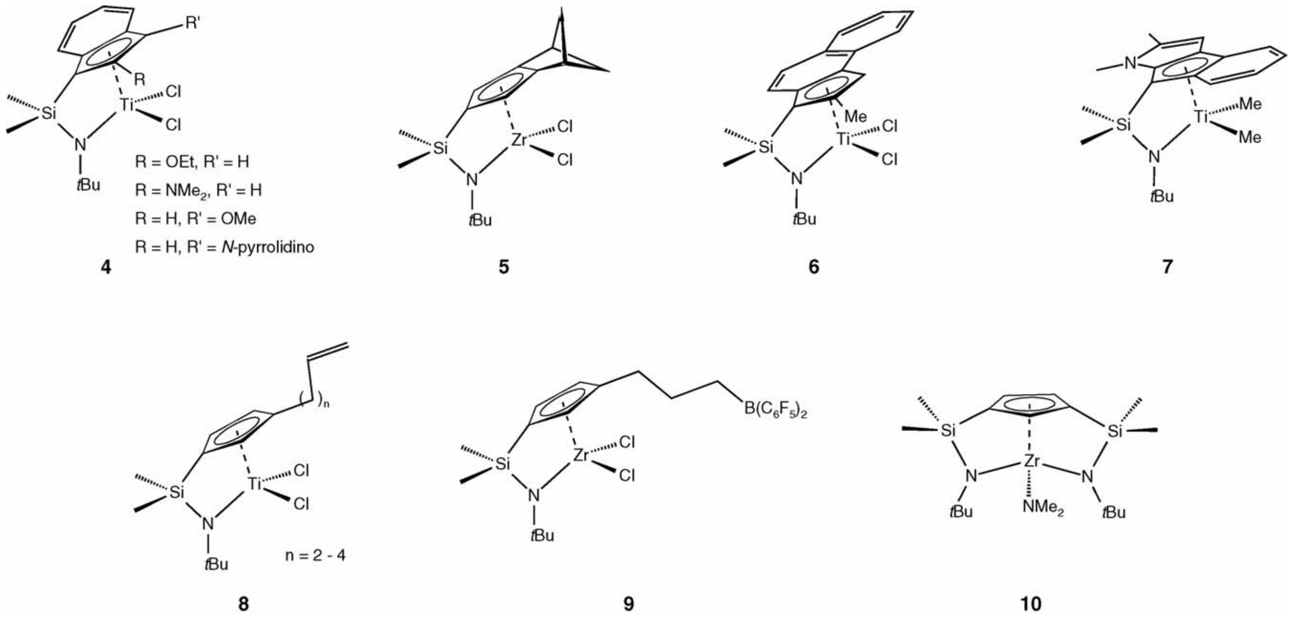


Fig. 4. Variation of the cyclopentadienyl moiety of the CGC ligand.

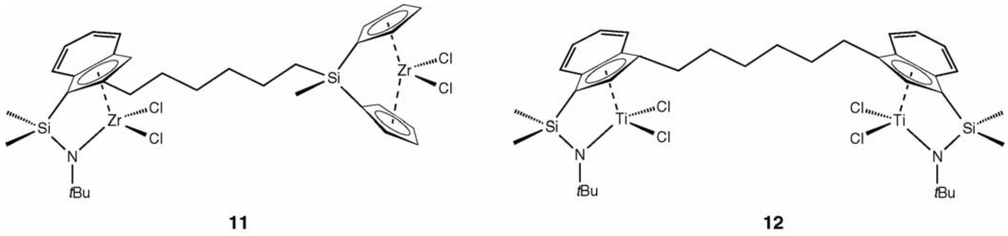


Fig. 5. Bimetallic CGCs with a carbon linker attached to the indenyl moiety.

4.1. Variation of the cyclopentadienyl fragment

Modification of the η^5-coordinated cyclopentadienyl moiety may have significant impact on the chemistry of CGCs through steric and electronic effects. Besides the ubiquitous C_5H_4 (cyclopentadienyl), C_5Me_4 (tetramethylcyclopentadienyl), C_9H_6 (indenyl) and $C_{13}H_8$ (fluorenyl) fragments, a variety of other moieties have been studied (Fig. 4). It should be noted that non-symmetric substitution patterns of the cyclopentadienyl system result in chiral CGCs. Recently, complexes bearing a sterically expanded *ansa*-cyclopentadienyl amido ligand based on a substituted octamethyloctahydrodibenzofluorene were reported. Depending on the ancillary ligands in the complexes, this ligand binds either in a η^5:η^1- or a η^1:η^1-fashion to the transition metal centre [81,82].

Several studies were investigating alkyl and aryl substituted cyclopentadienyl moieties, such as C_5H_3R (R = H, Me, *t*Bu, Bz) [83], C_5H_2(2-Me)(4-Ph) [84] and $CpMe_3R$ (R = H, Me, *n*Bu, 1-methylallyl, 1-methylprop-1-en-1-yl, Ph, 4-fluorophenyl, CMe_2Ph) [85–87]. Similarly, alkyl, aryl (R = Me, *t*Bu, Ph or a combination thereof, in various positions of the ring system) [47] and heteroatom (3-OMe, 2-OEt, 2-NMe_2, 3-*N*-pyrrolidino) [88] substituted indenyl derivatives (**4**) and alkyl substituted fluorenyl (3,6-di-*t*Bu-fluorenyl) [89]

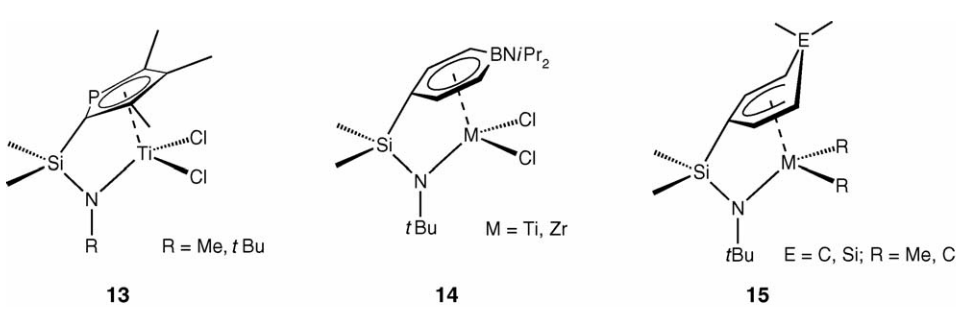


Fig. 6. CGCs containing six-electron donor fragments other than cyclopentadienyl derivatives.

derivatives were studied. Isodicyclopentadienyl based CGCs (**5**) were as well reported [90]. Beside indenyl and fluorenyl, other fused ring systems have been incorporated as the η^5-coordinated moiety in CGCs, such as benz[*e*]indenyl (**6**) [47,91–93] and heterocycle fused indenyl derivatives (**7**) [94].

Furthermore, a series of CGCs with ω-alkenyl substituted cyclopentadienyl and indenyl moieties (**8**) have been prepared and their self-immobilisation during polymerisation by incorporation of the pendant olefinic group into the polymer chain has been explored [95,96]. Specifically, an allyl substituted cyclopentadienyl moiety was further modified by hydroboration to give a derivative with a pendant $B(C_6F_5)_2$ moiety (**9**) [73].

The η^5-coordinated moiety has also been substituted with additional $(SiMe_2)$N*t*Bu amido functionalities (**10**), resulting in a tridentate ligand and consequently a substantial change of the coordination characteristics [97–100].

Bimetallic systems are more than just a curiosity. Here, the CGC fragment is connected via a carbon linker that is attached at its η^5-coordinated moiety to an *ansa*-metallocene [101] (**11**) or a second CGC [102–105] moiety (**12**) (Fig. 5).

Besides cyclopentadienyl derivatives of all sorts, a few examples of CGCs incorporating other monoanionic six-electron donor fragments have appeared in the literature (Fig. 6). These examples include phospholyl (**13**) [106], boratabenzene (**14**) [107] and cyclohexadienyl (**15**) [108] analogues of *ansa*-cyclopentadienyl amido complexes.

4.2. Variation of the amido fragment

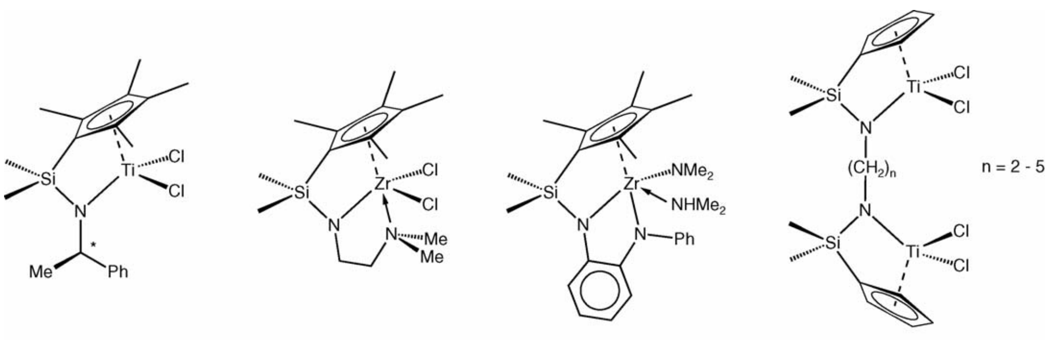
Variation of the amido fragment in CGC ligands may have a marked effect on both the steric and particularly the electronic environment of the ligated transition metal. Simple alkyl and aryl amido fragments in the CGC ligand framework are omnipresent in the literature. Chiral varieties (**16**) of these have been introduced early on, particularly as they allow facile preparation of enantiomerically pure CGCs if suitable enantiomerically pure amines are used in the preparation (Fig. 7) [42,61,62,72,109].

CGCs containing potentially tridentate ligands with additional neutral (**17**) or anionic (**18**) [110] donor sites attached to the amido moiety NR have been reported as well (Fig. 7). Substituents with relatively hard neutral donors (R = CH_2OMe, CH_2NMe_2, CH_2CH_2NHMe, $CH_2CH_2NMe_2$, CH_2CH_2OMe) [51,64,74,76,111–115] as well as softer neutral donor groups (R = *o*-$PhPPh_2$, CH_2CH_2SMe) [116] have been described. Chiral versions of such tridentate CGC ligands have also been published [117]. Furthermore, bimetallic CGCs with carbon spacers between the amido groups of the two CGC moieties (**19**) have been reported (Fig. 7) [114]. A number of CGCs have been reported in the literature, in which the alkyl or aryl amido fragment of *ansa*-cyclopentadienyl amido complexes was formally replaced by a different monoanionic η^1-coordinating moiety.

Besides alkyl and aryl amido moieties, four other nitrogen based groups, i.e. sulfonamido, pyrrolyl, hydrazido and imino groups, have been introduced in such compounds (Fig. 8). Due to the electron-withdrawing characteristics of the sulfonamido moiety, CGCs incorporating this group (**20**) display a significantly elongated Ti–N bond distance when compared to their alkyl or aryl amido counterparts. Similarly, the $Ti–N_{pyrrolyl}$ bond in the linked cyclopentadienyl pyrrolyl complex (**21**) is longer than in related *ansa*-cyclopentadienyl amido complexes, indicating that the pyrrolyl nitrogen is acting only as a one electron donor [118]. The monoanionic hydrazido moiety may adopt a η^1 (**22**) or η^2 (**23**) coordination mode, depending on the co-ligands at the metal centre [119,120]. Bridged cyclopentadienyl imino complex **24** resembles to some extent the bridged cyclopentadienyl amido complexes. However, the electronic situation in the former is quite different, as the formally sp^2-hybridised nitrogen atom acts as a pure σ-donor to the metal since the remaining p-orbital on nitrogen participates in the double bond to the adjacent carbon atom [70].

Examples of complexes in which the amido moiety is replaced by a carbanionic fragment appear in **25** [121], **26** [122] and **27** [123] (Fig. 9) amongst others [124–132]. While the carbanion equivalent is formally isoelectronic to the amido moiety, the former is a pure σ-donor as no suitable lone pair for π-donation to the metal centre is available.

By formal substitution of the nitrogen atom in *ansa*-cyclopentadienyl amido ligands with its higher homologue phosphorus, linked cyclopentadienyl phosphido complexes, such as **28** [133,134], **29** [135] and **30** [136] have been synthesised (Fig. 10) [137–140]. Despite some synthetic difficulties [135], this group of CGCs was studied intensively and a close resemblance to their amido analogues could be demonstrated, e.g. in their (co)polymerisation characteristics.



16 **17** **18** **19**

Fig. 7. Variation of the amido moiety of the CGC ligand.

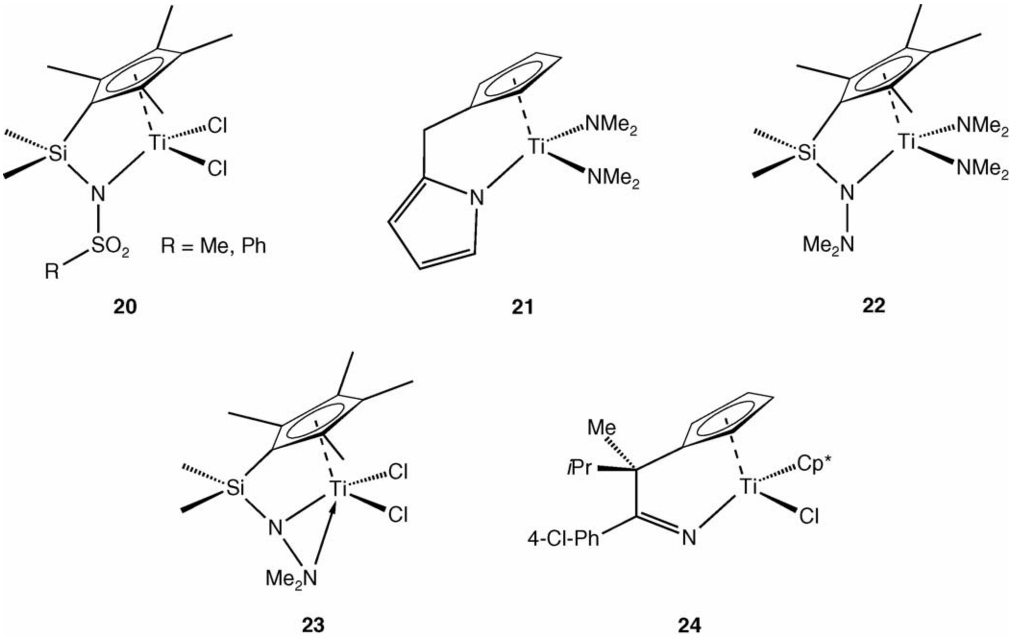


Fig. 8. CGCs containing nitrogen based anionic fragments other than alkyl or aryl amido moieties.

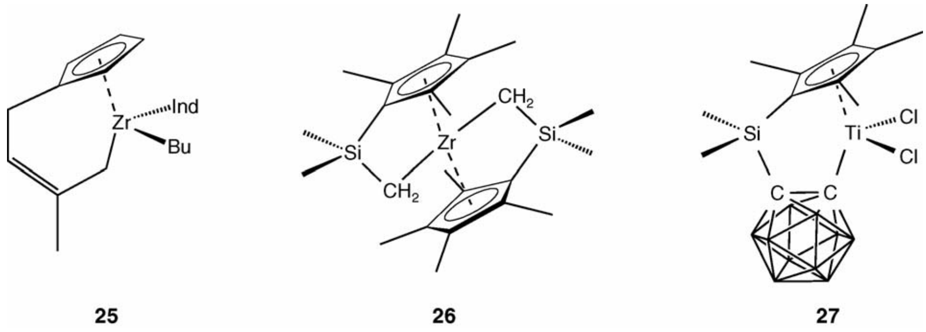


Fig. 9. CGCs in which the amido moiety is formally replaced by carbon based anionic fragments.

Formal replacement of the R_2N^- fragment by isoelectronic RO^- or RS^- fragments is of course also conceivable. Indeed a number of such *ansa*-cyclopentadienyl oxy-complexes, e.g. **31** [141], **32** [45] and **33** [142] have been reported (Fig. 11). Of this class of compounds [143], particularly bridged cyclopentadienyl phenoxy complexes [142,144–149] amongst others [56,150–156] have received a considerable amount of attention due to their structural features that are very similar to their amido counterparts and reasonable catalytic performance. To date, there has been only one report on related sulfur based *ansa*-complexes **34** (Fig. 11) [157].

4.3. Variation of the ansa-bridge

In the original patent by Dow Chemical Co. describing the use of Group 4 CGCs in the polymerisation of olefins, their

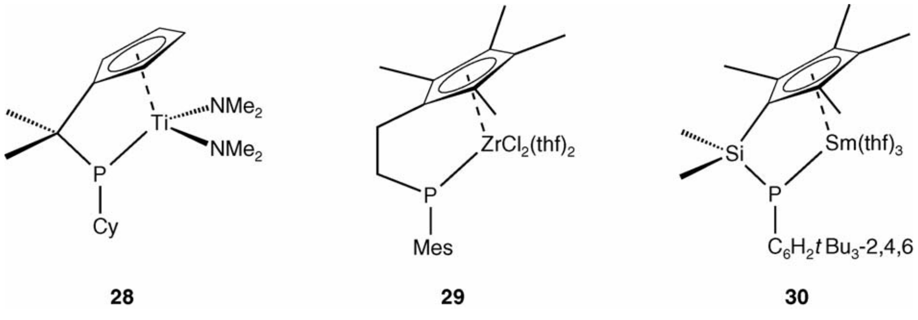


Fig. 10. CGCs in which the amido moiety is formally replaced by phosphido fragments.

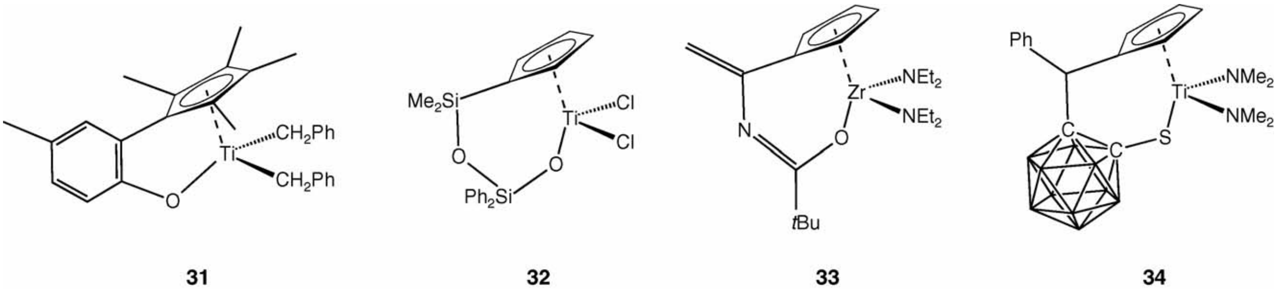


Fig. 11. CGCs in which the amido moiety is formally replaced by Group 16 based anionic fragments.

exceptional characteristics in this reaction was attributed to the strain induced by an *ansa*-bridge between a π-bonded moiety and a second ligand of the same transition metal centre [27]. In the closely related field of metallocene chemistry, the marked effect of an *ansa*-bridge between two cyclopentadienyl moieties on stability and reactivity of these complexes is well documented [158,159]. Owing to the similarity between *ansa*-metallocenes and CGCs, reasonable effort was undertaken to tune the latter by modification of the *ansa*-bridge. However, it should be noted that a recent report critically discussed whether the *ansa*-bridge in CGCs is a true prerequisite for their unique polymerisation characteristics [160]. Notwithstanding the former consideration, the modifications in the *ansa*-bridge as they are found in the literature will be summarised.

The first CGC (**1**) introduced by Bercaw et al. contained a ligand with a $SiMe_2$ moiety between a C_5Me_4 and an amido fragment (Fig. 1). This bridging moiety was previously successfully applied in *ansa*-metallocene chemistry, particularly for Group 4 metallocenes. To date, it is still the most commonly applied bridging moiety in CGC chemistry, probably due to the facile synthetic accessibility and high thermal and chemical stability.

The commonly used $SiMe_2$ *ansa*-bridge has been further modified by replacement of one of the methyl substituents, resulting in a chiral silicon atom (Fig. 12). Replacement by alkyl, alkenyl or phenyl substituents combined with asymmetrically substituted cyclopentadienyl derivatives gives rise to diastereomeric complexes (**35**) [96]. Substitution of one methyl group for hydrogen (**36**) or chlorine (**37**) introduced a reactive site in the *ansa*-bridge that may be used for linking the CGCs to heterogeneous supports [69,161]. In addition, suitable linkers attached to a mono-silicon bridge have been used to connect CGC fragments to *ansa*-metallocene fragments in bimetallic complexes (**38**) [101].

Besides silicon, only a few other elements have been reportedly used to connect the respective ligand fragments in *ansa*-cyclopentadienyl amido complexes by a short, single atom bridge (Fig. 13). These include boron (R_2NB) (**39**) [162–165], carbon in both the sp^2 ($H_2C{=}C$) (**40**) [45,166] or sp^3 (RHC,

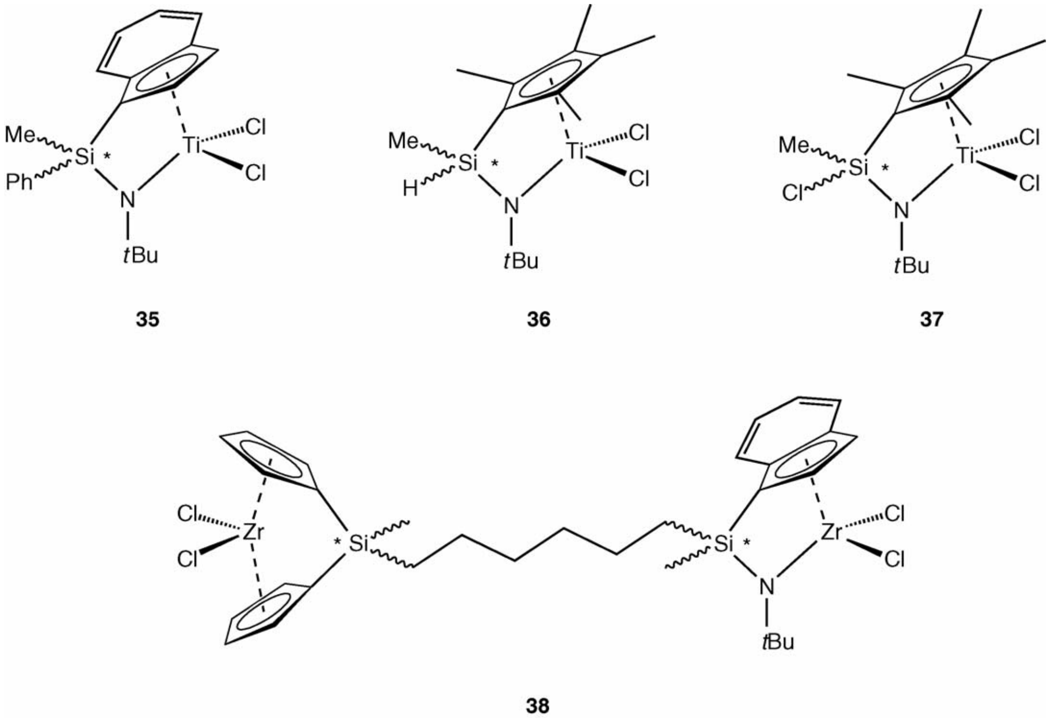


Fig. 12. CGCs with mono-silicon bridges other than $SiMe_2$.

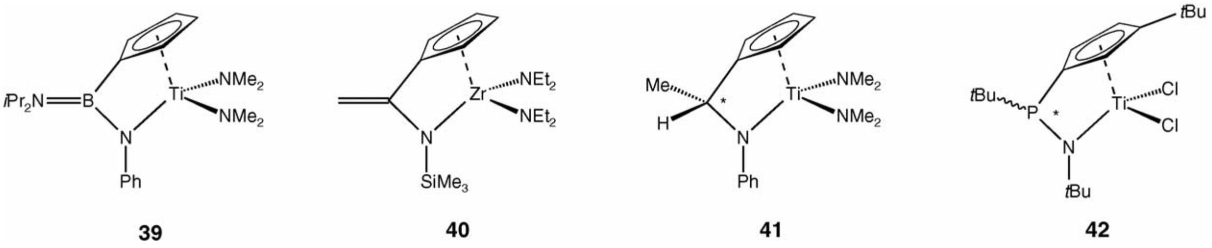


Fig. 13. CGCs with mono-element bridges other than silicon based.

R = alkyl, aryl) (**41**) [133,167] hybridised forms and phosphorous (tBuP) (**42**) [168].

Longer bridges containing two or three atoms in the backbone were also described (Fig. 14). Thus, (SiMe$_2$)$_2$ bridged CGCs (**43**) were used in the patent by Dow Chemical Co. as examples for *ansa*-bridged cyclopentadienyl amido complexes without substantial strain in the ligand framework and subsequently lower polymerisation activity. On the other hand, the CH$_2$SiMe$_2$ bridging moiety, first devised by Dias et al. (**44**) [43], was found to be superior over the short SiMe$_2$ bridge in Group 3 CGC catalysed hydrosilylation (*vide infra*) [169]. Furthermore, numerous CGCs bearing (CH$_2$)$_n$ (n = 2 [30,170–172], 3 [30,173]) bridges (**45**–**47**) have been reported.

4.4. Variation of the metal centre

Linked cyclopentadienyl amido ligands have first been utilised by Bercaw et al. for the synthesis of Sc(III) complexes. Shortly thereafter, Okuda reported the first titanium compounds with such ligands and Dow Chemical Co. and Exxon Chemical Co. issued fundamental patents that claimed unique polymerisation characteristics of the Group 4 congeners. Since then, the vast majority of the open literature focused on the tuning and understanding of properties of Group 4 CGCs. However, linked cyclopentadienyl amido ligands have been extensively applied to Group 3 transition metals and also to the lanthanides and actinides. Furthermore, the same ligand design has been successfully used in the coordination chemistry of other transition metals and even main group elements. The following sections intend to demonstrate the versatility of linked cyclopentadienyl amido ligands for the synthesis of CGCs of transition metals other than Group 4 metals (complexes incorporating CGC type ligands with additional pendant donor functionalities or bearing two CGC type ligands will not be considered here).

Besides the first Group 3 CGCs published by Bercaw and co-workers [24,25,174], various monomeric amido CGCs of Y(III) (**48**) [175], as well as monomeric alkyl [115,176–179] and dimeric hydrido [176–178] CGCs of Y(III), Lu(III), Yb(III), Er(III) and Tb(III) have been reported. Also described are a number of Y(III), La(III) and Nd(III) complexes that bear one or two

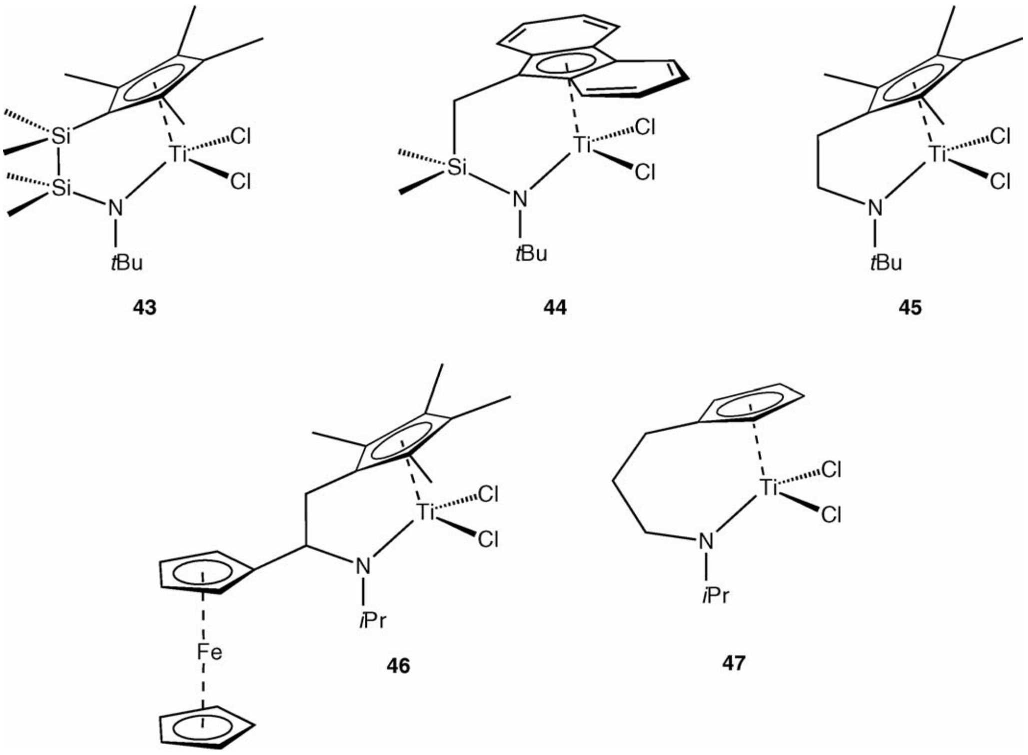
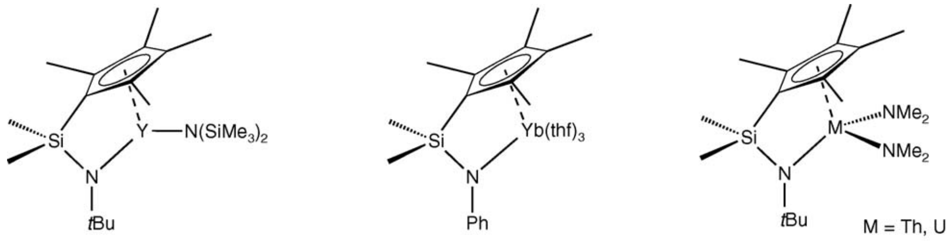
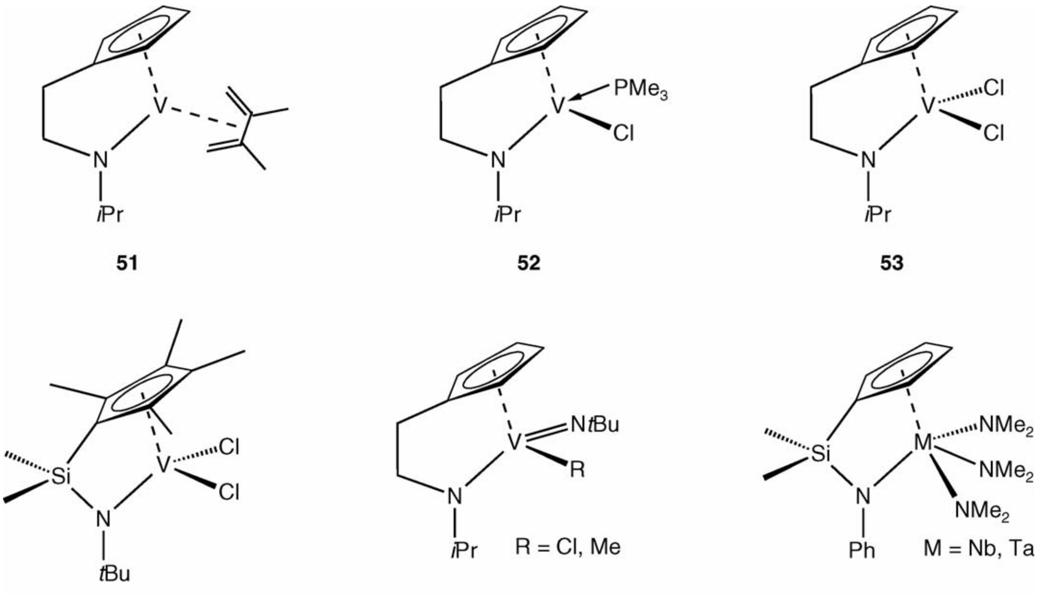


Fig. 14. CGCs with bridges longer than one atom.



48 **49** **50**

Fig. 15. Group 3 CGCs.



51 **52** **53**

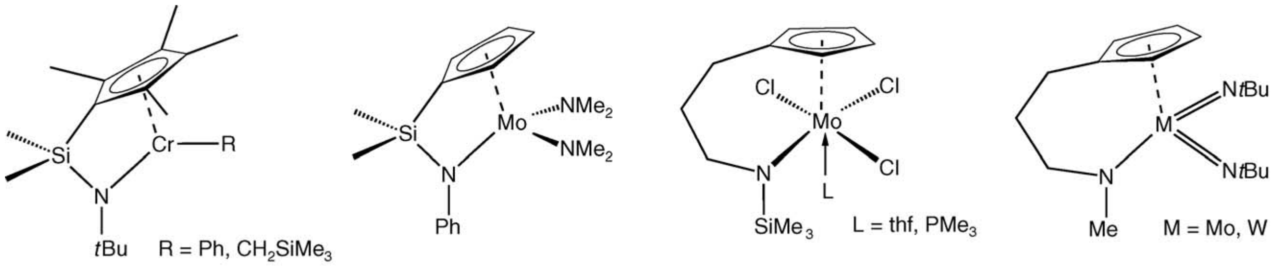
54 **55** **56**

Fig. 16. Group 5 CGCs.

[(3,6-tBu$_2$C$_{13}$H$_6$)(SiMe$_2$)NtBu]$^{2-}$ ligands and which display interesting bonding modes (η^5-, symmetric or non-symmetric η^3-coordination of the substituted fluorenyl moiety depending on the nature of the metal and the co-ligands) [180]. Moreover, monomeric and dimeric CGCs of Yb(II) (**49**) and Sm(II) [181] as well as monomeric, dimeric and tetrameric CGCs of thorium Th(IV) [182,183] and U(IV) [183], such as **50** have been reported (Fig. 15).

Beyond Groups 3 and 4 of the periodic table, numerous examples have been reported for CGCs of other elements, particularly of the earlier groups. For example, vanadium complexes bearing bridged cyclopentadienyl amido ligands were synthesised incorporating vanadium in the oxidation states +II (**51**) [184], +III (**52**) [184], +IV (**53**, **54**) [184,185], +V (**55**) [186]. For the higher Group 5 homologues niobium and tantalum CGCs are only known for the oxidation state +V (**56**) (Fig. 16) [187–190].

CGCs are also known for all the Group 6 metals containing chromium(III) (**57**) [191], molybdenum(IV) (**58**) [192], molybdenum(V) (**59**) [58,59], molybdenum(VI) [48] and tungsten(VI) (**60**) [48], respectively, reflecting the preferred oxidation states for the elements in this group (Fig. 17).



57 **58** **59** **60**

Fig. 17. Group 6 CGCs.

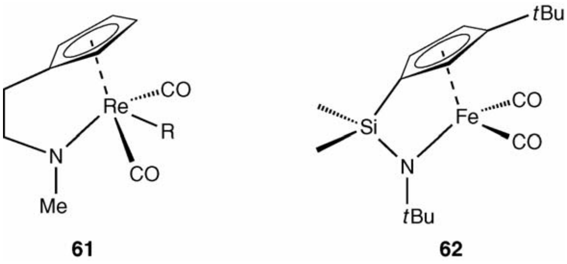


Fig. 18. Groups 7 and 8 CGCs.

The only reported Group 7 complexes bearing a linked cyclopentadienyl amido ligand contain rhenium in the oxidation state +III (**61**) [193,194]. For Group 8, only the Fe(II) complex **62**, albeit only with rudimentary spectroscopic characterisation, has been described (Fig. 18) [26].

Cowley and co-workers reported a number of Group 13 (Al, Ga, In) [195,196] and Group 15 (P, As, Sb) [197] complexes utilising CGC ligands. However, the coordination modes in these compounds are completely different from those found in the previously discussed transition metal complexes, as the main group elements lack suitable orbitals for η^5-coordination of the cyclopentadienyl fragment.

5. Polymerisation with constrained geometry complexes

The first claims of exceptional catalytic activity of Group 4 CGCs for ethylene homopolymerisation, copolymerisation of ethylene with α-olefins, such as 4-methyl-1-pentene, 1-hexene, 1-octene and 4-vinylcyclohexene (as an example of a hindered vinylic monomer) and copolymerisation of ethylene and styrene can be found in the patent literature [27,28]. Such performance triggered intensive research activity to (i) understand, (ii) further improve and (iii) exploit the full catalytic potential of these compounds. Since then, ongoing industrial research into the field is documented in numerous patents [198]. However, the following summary focuses on aspects of CGC catalysed polymerisations as they appear in the open literature.

5.1. Mechanism of the polymerisation reaction

It is generally agreed that the CGC catalysed polymerisation of α-olefins proceeds according to the Cossee–Arlman mechanism [199,200]. This mechanism (Scheme 1) assumes that the catalytically active centre incorporates both an alkyl group and a vacant coordination site that allows π-coordination of the incoming monomer. In a concerted rearrangement via a four-centred transition state, a new bond between the alkyl group and the α-olefinic carbon atom is established, while at the same time a new bond between the β-olefinic carbon atom and the transition metal centre is formed. In this way, both a new alkyl group and a vacant site are generated, providing the conditions for the next propagation step.

Various computational studies specifically on CGC catalysed olefin polymerisation support these assumptions [201–210]. Experimental studies showed a strong influence of the solvent on polymerisation rate [211]. Related computational studies rationalised this observation by demonstrating competition of the counter-ion, monomer and solvent molecules for the vacant coordination sites at the cationic active centre [205,206] and the influence of the solvent on ion-pair separation [205,208–210]. Besides the characteristics of the solvent, the steric demand and ability of the ancillary ligands to stabilise the positive charge on the active centre were found to affect the equilibrium between the contact-ion pair and the solvated, fully separated ion-pair [212].

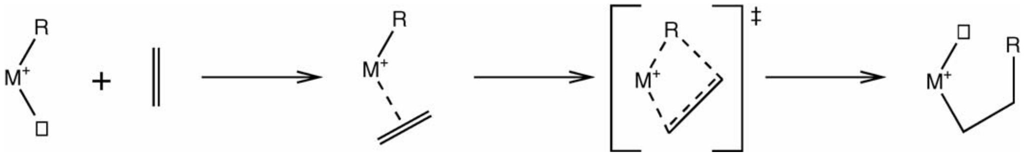
Early in the development of CGCs, the occurrence of long-chain branches in CGC derived polyolefins was observed. It was reasoned that these long-chain branches may stem from incorporation of vinyl-terminated macromonomers formed in the course of the reaction [213]. Indeed, exclusively vinyl terminated polyethylene was obtained with $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO systems [214]. An alternative long-chain branching mechanism via σ-bond metathesis involving transfer of a proton in the growing polymer chain to the α-carbon of the transition metal alkyl cation was excluded based on results from computations [215].

Computational and experimental studies on the potential mechanisms for generation of vinyl terminated macromonomers established that β-hydrogen transfer to the monomer was the energetically most favourable (Scheme 2). Other conceivable mechanisms, such as β-hydride elimination (β-hydrogen transfer to the metal) and σ-bond metathesis involving one equivalent of monomer were found to be energetically highly disfavoured [202,215,216]. Experimental data also suggest that the probability of incorporation of the vinyl terminated macromonomers is enhanced by a low diffusion rate, probably due to entanglement effects [217]. A mathematical model to describe the influence of long-chain branching on the chain length distribution in polyolefins derived from CGCs was also reported [218].

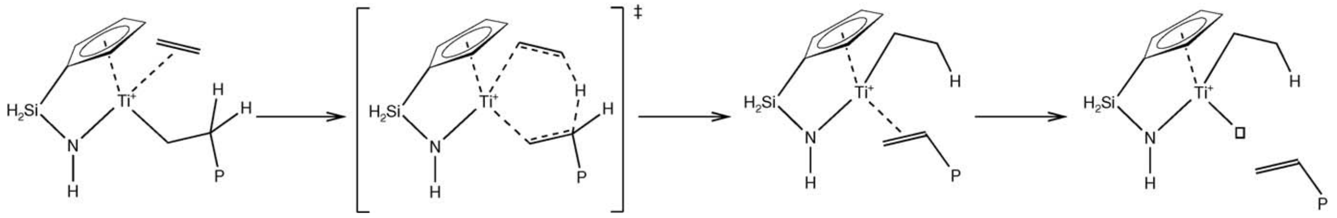
It may be noted that vinyl chloride was utilised in the CGC catalysed polymerisation of ethylene as a chain transfer reagent, producing vinyl terminated macromonomers that are re-incorporated in the growing polymer chain [219].

5.2. Activation of CGC for the polymerisation of α-olefins

Common, neutral Group 4 CGCs have to be converted to the cationic species that are active olefin polymerisation catalysts by



Scheme 1. Cossee–Arlman mechanism for olefin polymerisation on transition metal centres; ancillary ligands and counter-ion omitted for clarity.



Scheme 2. Chain termination with generation of vinyl terminated macromonomer by β-hydrogen transfer to the monomer.

reaction with suitable co-catalysts. The formation of these active species usually involves abstraction of a hydrocarbyl group (e.g. methyl or benzyl) from the metal centre. A suitable co-catalyst should combine both advantageous features in the activation process itself (abstraction) and in the coordination characteristics of the generated anion, which acts as a counter-ion to the cationic active centre. A vast number of different co-catalysts have been reported in the literature [220].

Methylaluminoxane, which can be prepared by controlled hydrolysis of $AlMe_3$ [22], and related activators are currently the commercially most successful co-catalysts, though they exhibit some quite disadvantageous features. Firstly, to obtain optimal polymerisation activities and an acceptable kinetic stability of the polymerisation reactions, high MAO:catalyst precursor ratios of about 10^2–10^4:1 are necessary, making MAO a major cost factor in the process [221]. Secondly, despite prolonged and extensive research in the area, the exact composition and structure of MAO remains unclear [222–224], mainly due to multiple equilibria between different MAO oligomers and residual trimethylaluminium. Both the use of MAO in superstoichiometric quantities and its structural fluxionality and instability prevent a full characterisation of the active species in the polymerisation reaction [225], and consequently make further improvement of the process highly dependent of empirical studies. It should be noted that MAO facilitates the use of dichloro or diamido CGCs as catalyst precursors since MAO (or the $AlMe_3$ residue therein) is a strong methylating agent capable of converting these species to their dimethyl derivatives that are in turn activated by methyl abstraction [226].

Another class of compounds that was successfully applied as co-catalysts in the CGC catalysed olefin polymerisation are highly Lewis-acidic perfluoroarylboranes, particularly $B(C_6F_5)_3$ and a number of other perfluoroarylboranes [227]. Despite lower polymerisation activities of the resulting catalyst systems, they have the great advantage of allowing isolation and thorough characterisation of the ion pairs comprising the catalytically active cationic complexes and their respective counter anions [228,229]. A major drawback of the perfluoroarylboranes in their application as co-catalysts is the considerable interaction of the abstracted methyl group (that is incorporated in the generated $MeBR_3^-$ counter-ion) with the cationic centre. A way to circumvent this problem is the use of the triphenylcarbenium (trityl) salts of the corresponding perfluorotetraarylborates, e.g. $[Ph_3C^+][B(C_6F_5)_4^-]$, as co-catalysts. In these systems, the trityl cation reacts as a strong methyl abstractor generating a neutral hydrocarbon, while the perfluorotetraarylborate moiety acts as a largely non-coordinating anion [227,230]. Other related co-catalysts reportedly utilised in the CGC mediated polymerisation of olefins include $[Ph_3C^+][CN\{B(C_6F_5)_3\}_2^-]$ [231], $[Ph_3C(NC_5H_5)^+][B(C_6F_5)_4^-]$ (NC_5H_5 = pyridine) [232] and $[Ph_3C^+][B(C_6F_4SiR_3)_4^-]$ ($SiR_3 = SiMe_2t$Bu, SiiPr$_3$) [233]. Surprisingly, a beneficial effect of superstoichiometric amounts of $[Ph_3C^+][B(C_6F_5)_4^-]$ was observed in CGC catalysed olefin polymerisation. For example, the $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N t\text{Bu}\}TiCl_2]/Al i\text{Bu}_3/[Ph_3C^+][B(C_6F_5)_4^-]$ system showed a 10-fold increased productivity in propylene polymerisation when pre-catalyst/alkylating agent/co-catalyst were employed in a 1:10:10 ratio compared to a 1:10:1 ratio [234].

Naturally, every co-catalyst displays its specific characteristics in hydrocarbyl abstraction reactivity and interaction of the resulting ion pairs [235]. Therefore, it is not surprising that a strong effect of the combination of catalyst precursor and co-catalyst on polymerisation characteristics is observed. The following sections give an overview about reports that specifically address such dependencies.

The influence of the chosen co-catalyst with respect to the tacticity of the obtained polymer was observed in the polymerisation of propylene with $[\{\eta^5:\eta^1\text{-}(C_{13}H_8)(SiMe_2)N t\text{Bu}\}ZrCl_2]$. The MAO activated system resulted in mainly syndiotactic polymer, whereas the $[Ph_3C^+][B(C_6F_5)^-]/Al i\text{Bu}_3$ activated system yielded mainly isotactic polymer. A change from solvent-separated ion pair in the former to contact ion pair in the latter was suggested as a plausible explanation for this observation [236]. In a consecutive study, $[\{\eta^5:\eta^1\text{-}(C_{13}H_8)(SiMe_2)N t\text{Bu}\}ZrX_2]$ (X = Cl, NMe_2) was demonstrated to act as single site catalyst when activated with MAO, while generating a number of catalytically active species in the presence of $[Ph_3C^+][B(C_6F_5)_4^-]/AlR_3$. At the same time, it was shown that the catalytic performance of such systems is independent of the substituent X; X = Cl or NMe_2 gave identical results [226]. In addition, use of the dimethylated derivative $[\{\eta^5:\eta^1\text{-}(C_{13}H_8)(SiMe_2)N t\text{Bu}\}TiMe_2]$ had a tremendous effect on the observed polymerisation characteristics when the co-catalyst was varied. Systems involving $B(C_6F_5)_3$ as a co-catalyst were capable of polymerising propylene and 1-hexene, respectively, at low temperatures (−50 °C) in a living manner to give syndiotactic-rich homopolymer, but were quickly deactivated at 0 °C [237]. MAO activated systems, in which the added MAO had been freed of all traces of $AlMe_3$, formed polypropylene with high activities and displayed all the characteristics of a living polymerisation system even at 0 °C [238]. Similar catalytic behaviour was reported for related pre-catalysts, albeit producing atactic

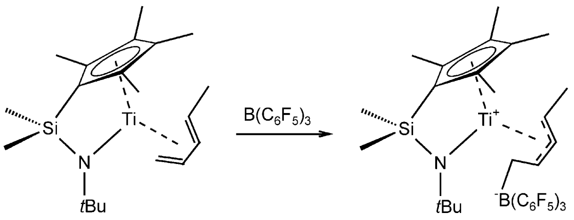
($[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiMe_2]$) [239,240] or isotactically enriched ($[\{\eta^5:\eta^1\text{-}(C_9H_6)(SiMe_2)N\textit{t}Bu\}TiMe_2]$) [241] polypropylenes. Living copolymerisation of ethylene and norbornene was also reported for CGCs activated with dried MAO [242].

Excess $Al(C_6F_5)_3$, in contrast to its boron analogue $B(C_6F_5)_3$, was found to facilitate abstraction of both titanium-bonded methyl groups from $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}\text{-}TiMe_2]$ under formation of the corresponding dicationic complex. This complex produced a copolymer from ethylene and 1-octene with higher efficiency and higher molecular weight than the corresponding cationic catalyst [243].

A marked temperature dependency was observed for the catalyst system $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}ZrMe_2]/[Ph_3C^+][(C_{12}F_9)_3AlF^-]$ ($C_{12}F_9$ = 2-nonafluorobiphenyl). This system was found to be inactive towards the polymerisation of ethylene at 25 °C, but at higher temperatures (60 and 110 °C) a significant polymerisation activity was observed. This change in reactivity may be ascribed to an alteration of the nature of the ion pairing at different temperatures [244].

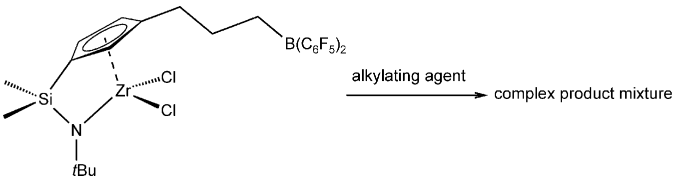
5.3. Zwitterionic CGCs as single component olefin polymerisation catalysts

Devore et al. reported the activation of titanium(II) CGC diene complexes with common activators, such as MAO and $B(C_6F_5)_3$ for the copolymerisation of ethylene and 1-octene [77]. Later, the products of the 1:1 reaction of related diene complexes with $B(C_6F_5)_3$ were found to be well defined, zwitterionic complexes (Eq. (14)). In these complexes, the charge of the cationic transition metal centre is matched by the anionic borate moiety on the original diene ligand [245–247]. Since the zwitterionic complexes contain a cationic transition metal centre with only weak stabilisation by the counter-ion, they can act as single component olefin polymerisation catalysts and no additional co-catalyst is required [248].



(14)

Spence and Piers attempted the incorporation of the co-catalyst into the ligand framework of CGCs by hydroboration of a pendant allyl group on the cyclopentadienyl ring with $[HB(C_6F_5)_2]_n$. The resulting pendant borane moiety was conceived to be sufficiently Lewis acidic to yield a zwitterionic single component catalyst. However, synthetic difficulties prevented a successful realisation of this idea. On one hand, the dichloro derivative with a pendant $B(C_6F_5)_2$ group could be easily prepared, but alkylation failed under various conditions (Eq. (15)). On the other hand, starting from the dimethyl, dibenzyl or bis(trimethylsilylmethyl) derivatives with a pendant allyl group, reaction with the hydroboration reagent was usually not selective and always resulted in undesired products (Eq. (16)) [73].



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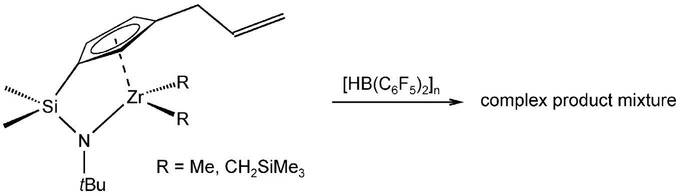


(16)

5.4. Structure–activity relationship for constrained geometry complexes

Since the first publication of CGCs, a wide range of modified and related compounds has been published. Nonetheless, one of the most systematic investigations into the CGC structure–activity relationship for olefin polymerisation is Stevens' report dating back to 1991 [249] that essentially summed up the claims in the initial patent of Dow Chemical Co. [27]. Stevens demonstrated that high catalyst efficiencies and comonomer incorporation are correlated with increased electron density at the metal centre for a series of catalyst precursors. An electron increase at the metal centre can be both induced by variation of the substituted cyclopentadienyl moiety (indenyl < C_5H_4 < C_5Me_4) or the substituent on the nitrogen of the chelating ligand (4-F-C_6H_4 < C_6H_5 < *t*Bu) [250]. Furthermore, it was shown that the nature of the bridge has a strong effect on both catalyst efficiency and comonomer incorporation, with more acute $Cp_{centroid}$–M–N angles giving the better results [251]. Comparison of $SiMe_2$ and $(CH_2)_2$ bridged complexes, which both exhibit $Cp_{centroid}$–M–N angles of about 108°, revealed some electronic influence of the bridge on the polymerisation results: for the dimethyl silyl bridge, comonomer intake is lower, but catalyst activity is higher. A strong influence of the Group 4 metal was also demonstrated, with titanium compounds being generally more efficient and giving polymers with distinctly higher comonomer incorporation than their zirconium analogues. This is in stark contrast to related bis(cyclopentadienyl) Group 4 complexes, were the zirconium derivatives are usually far more active than their titanium counterparts [252].

Compared to metallocenes and *ansa*-metallocenes, CGCs incorporate longer α-olefins to a much higher extent in copolymerisation experiments and without sacrifice of the high molecular mass of the produced polymer [253]. The mechanical properties of such long-chain branched polyolefins resemble in some instances those of cross-linked polymers [254]. A further improvement of comonomer incorporation for a variety of α-olefins was observed for catalyst systems derived from complexes in that two CGC type moieties are connected via a short linker [102,255].

Improved catalyst performance in terms of higher activity, stability, 1-octene incorporation and polymer molecular weight was obtained by replacing the commonly applied C_5Me_4 fragment by either a particular benzannelated cyclopentadienyl derivative, namely a 2-methylbenz[*e*]indenyl moiety [91], or a specific amino functionalised indenyl derivative, namely the 3-pyrrolidino-indenyl group [88]. Copolymerisation of ethylene and 1-octene resulted in poly[ethylene-*co*-(1-octene)] with a high content of 1-octene and oligoethylene side-chains [214]. Virtually ideal copolymerisation of ethylene and propylene was observed with $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$/MAO as a catalyst, a characteristic that could not yet be achieved with any metallocene system [256].

Homopolymerisation of propylene with CGC based systems usually results in atactic products [42,47,257]. However, introduction of suitable amido moieties into the *ansa*-$SiMe_2$-bridged ligand, such as $^{-}N(CHRR')$ (R = alkyl, R′ = aryl), resulted in formation of isotactically enriched polypropylene [211]. Furthermore, it was shown that fluorenyl based CGCs can produce polypropylenes with a high content of syndiotactic or isotactic sequences, depending on the utilised co-catalysts [236,238] and solvents [258,259]. If titanium complexes incorporating heterocycle-fused indenyl [94,260] or 3,6-di-*tert*-butyl fluorenyl [261] based CGC ligands are employed as pre-catalysts, predominantly syndiotactic polypropylene is accessible. Due to its semicrystalline nature, this new type of polypropylene showed unique mechanical properties combining some characteristics of both crystalline syndiotactic polypropylene and amorphous atactic polypropylene, making it an interesting thermoplastic elastomeric material [262].

A strong influence of the nature of the amido group on the molecular weight of obtained polypropylene was reported. While for $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)NR\}TiCl_2]$/MAO, polymer molecular weights increased with increasing bulk of the substituent R, a reversed tendency was observed for $[\{\eta^5:\eta^1\text{-}(C_5H_4)(CH_2)_2NR\}TiCl_2]$/MAO and $[\{\eta^5:\eta^1\text{-}(C_5H_4)\text{-}(CH_2)_2NR\}TiBz_2]/B(C_6F_5)_3$. Differences in cation–anion interactions in the respective catalyst systems were suggested to be a probable explanation for these trends [263].

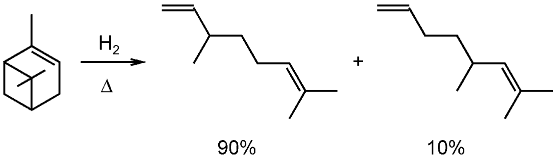
For ethylene bridged ligand systems, a pronounced effect of the nature of the amido moiety (NR) on the activity towards propylene polymerisation was reported. Only for R = Me was the catalytic formation of polypropylene observed, while for R = *i*Pr and *t*Bu the systems were rendered inactive for the polymerisation of propylene. These observations are rather surprising considering that the $(CH_2)_2$ bridged system showed higher activities for the polymerisation of ethylene than the analogous $SiMe_2$ bridged systems, while the latter readily polymerises propylene even for R = *t*Bu [171].

A number of CGCs have also been tested as catalysts for the homopolymerisation of 4-methyl-1-pentene and copolymerisation of this monomer with ethylene. A certain degree of isotacticity (up to 39%) and some irregularities derived from 2,1-insertion were observed in the homopolymerisation experiments, both parameters being distinctly sensitive to variations in the ligand framework. The trends observed in the copolymerisation of 4-methyl-1-pentene with ethylene were similar to those observed in comparable copolymerisation experiments of ethylene with other α-olefins [264].

CGCs with electron-withdrawing groups on the *ansa*-bridged amido moiety (**19**) were studied as catalysts in the homopolymerisation of propylene and styrene and the copolymerisation of ethylene and styrene. Activity for homopolymerisation of propylene and ethylene/styrene copolymerisation was diminished by the electron-withdrawing groups compared to the previously described alkyl amido substituted catalysts. On the other hand, productivity in styrene homopolymerisation was increased, resulting in mainly syndiotactic polystyrene. Overall, the CGCs carrying electron-withdrawing groups on the amido moiety showed a behaviour more similar to non-bridged complexes, such as Cp^*TiCl_3 than to alkyl amido substituted CGCs. This observation was attributed to a cleavage of the titanium amido linkage under polymerisation conditions in the former systems. Hence, it was concluded, that high ethylene polymerisation activity of most CGCs is not solely a result of the constraints induced by a short bridge, but as well a consequence of the donor characteristics of alkyl amido ligands [265].

5.5. Further aspects of (co)polymerisation of ethylene and α-olefins

5,7-Dimethylocta-1,6-diene and 3,7-dimethylocta-1,6-diene, readily available non-conjugated linear dienes from terpene feedstocks (Eq. (17)), are incorporated exclusively via their less hindered double bond into polyethylene copolymers using the $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$/MAO system [266,267]. However, catalyst systems based on $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N(C_{12}H_{23}\}TiCl_2]$ ($C_{12}H_{23}$ = cyclododecyl) were found to facilitate copolymerisation of ethylene with 1,1-disubstituted olefins, e.g. ethylene/isobutylene and ethylene/2-methyl-1-pentene copolymerisation as well as ethylene/propylene/isobutylene terpolymerisation. The obtained ethylene/isobutylene copolymer is substantially alternating, corresponding to a high incorporation of the 1,1-disubstituted olefin that is unique under coordination polymerisation conditions [268]. Formation of poly(ethylene-*co*-isobutylene) with moderate isobutylene incorporation was as well reported utilising mono- or binuclear CGCs in combination with mono- or bifunctional borane co-catalysts [255].



(17)

The capability of CGC based systems to incorporate long-chain vinylic monomers has been utilised in the copolymerisation of ethylene and a decenyl-functionalised silsesquioxane **63** (Fig. 19).

The incorporation of silicon–oxygen cages into the polymer resulted in improved thermal stability of the material and may

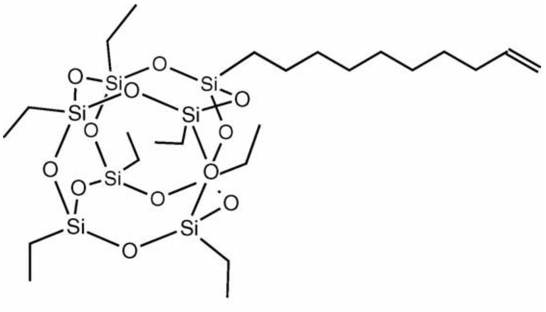


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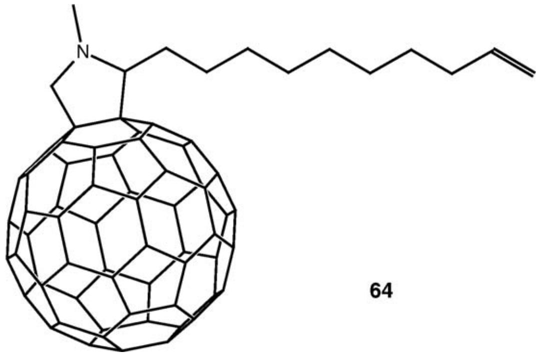
Fig. 19. Decenyl-functionalised silsesquioxane.



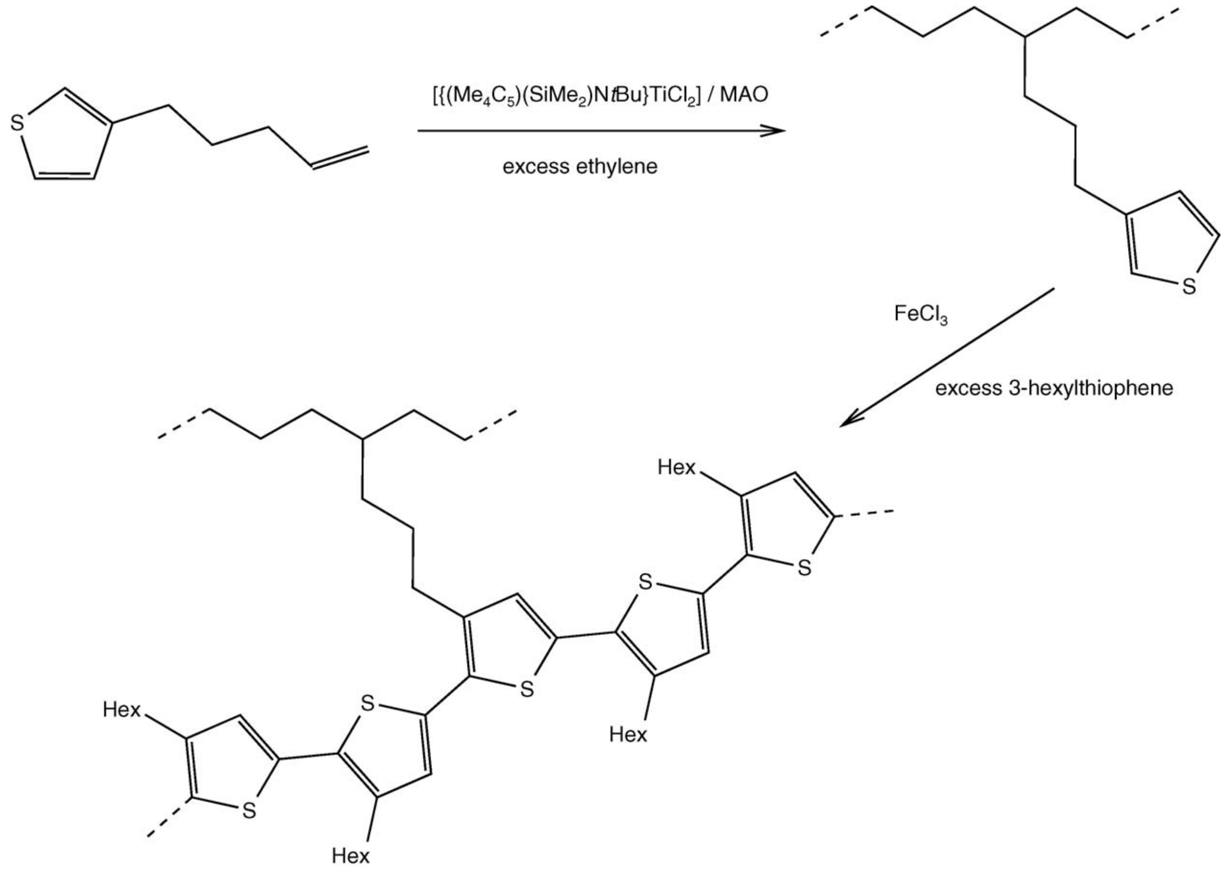
64

Fig. 20. Fullerene-containing 1-alkene monomer.

have further influence on the material properties [269]. The capability to incorporate long-chain vinylic monomers was further established by the copolymerisation of ethylene and vinyl terminated oligoethylene to give long-chain branched polyethylene [214] and the homopolymerisation of ω-undecenyl polystyrene macromonomers, giving access to unique polyethylene-*graft*-(nonyl-*block*-polystyrene) [270].

[{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}$TiCl_2$]/MAO has also been used for the copolymerisation of ethylene and 3-(penten-1-yl)thiophene. The presence of the soft Lewis-base had no detrimental effect on the copolymerisation performance. Subsequent grafting with conjugated poly(3-hexylthiophene) by $FeCl_3$-mediated copolymerisation of the copolymer with 3-hexylthiophene yielded a new material with interesting physical properties, e.g. fluorescence (Scheme 3) [271].

Furthermore, [{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}$TiCl_2$]/MAO has been utilised for the copolymerisation of ethylene and the fullerene containing 1-alkene comonomer **64** (Fig. 20) producing the first fullerene-containing polyolefins. The obtained materials showed a comonomer incorporation of up to 1.5 mol%, corresponding to a content of 25 wt% of C_{60}. The new materials are expected to exhibit interesting electro-optical properties [272].



Scheme 3. Synthesis of a novel ethylene-thiophene copolymer involving CGC catalysis.

5.6. Polymerisation of monomers other than α-olefins

5.6.1. Styrene and derivatives

CGCs were found to be superior catalysts for the production of ethylene/styrene copolymers. On the one hand, commonly used catalysts for the homopolymerisation of styrene, such as $CpTiCl_3$ and related half-sandwich complexes produce predominantly syndiotactic polystyrene in styrene/ethylene mixtures besides traces of copolymer [273]. On the other hand, highly active catalyst systems for the homopolymerisation of ethylene, such as *ansa*-zirconocene dichlorides and related compounds fail to incorporate larger quantities of styrene comonomer due to their crowded coordination sphere [274]. CGCs are bridging this gap by allowing high styrene content in the copolymer, high activity and virtually no contamination by polystyrene [273]. Ethylene and styrene were copolymerised in the presence of $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO. A linear relationship between concentration and styrene incorporation was found only for low styrene concentrations [275].

Mülhaupt and co-workers demonstrated that CGC derived systems incorporate styrene units in the copolymer either in an isolated fashion or with tail-to-tail coupling (Fig. 21). The strict absence of head-to-tail coupling in the polymerisation process limits the maximum number of neighbouring styrene units to two and results in a *pseudo*-random poly(ethylene-*co*-styrene) [276].

Comparison of poly-(ethylene-*co*-styrene) derived from $[(Me_2Si)(C_5Me_4)(NR)TiCl_2]$/MAO (R = *t*Bu, Cy) provided evidence for a significant influence of the amido ligand. While the *t*Bu substituted system displayed some tail-to-tail coupling, the products of the Cy substituted system showed only isolated styrene units despite a higher styrene incorporation [277]. Selectivity of styrene incorporation is as well highly sensitive to variations in the cyclopentadienyl derivative, as was demonstrated by a comparative study on $[\{\eta^5:\eta^1\text{-}(C_5Me_3R)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO (R = H, Me, Bu, Ph, 4-F-Ph, but-2-en-2-yl) [278]. Xu applied a tailored catalyst system, $[\{\eta^5:\eta^1\text{-}(C_{13}H_8)(SiMe_2)N\textit{t}Bu\}TiMe^+][B(C_6F_5)_4{}^-]$ to obtain perfectly alternating poly(ethylene-*co*-styrene) with isotactic arrangement of the styrene units [279].

The preference for isolated incorporation of styrene units in the polymer chain usually limits the styrene content to 50 mol%. However, Marks and co-workers could obtain up to 92 mol% styrene incorporation utilising a bimetallic CGC $[\{\eta^5:\eta^1\text{-}(C_9H_5)(SiMe_2)N\textit{t}Bu\}TiCl_2\}_2(\mu\text{-}C_2H_4)]$, with close proximity of the two active sites. This system apparently facilitates to some extent head-to-tail coupling and tail-to-tail-coupling of styrene units [280]. If the linker between the two CGC units is elongated (6, 9 or 12 carbon atoms), the bimetallic systems behave rather like singular CGCs and styrene incorporation into the copolymer is below 50 mol% [281,282].

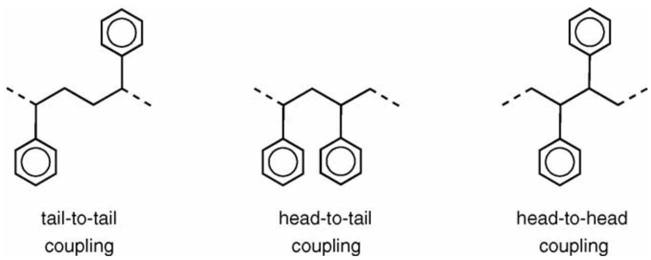


Fig. 21. Possible coupling modes of neighbouring styrene units in styrene polymers.

A study on ethylene/(methyl)styrene copolymerisation using the $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO catalytic system showed an increase in comonomer intake in the order *m*-methylstyrene < *o*-styrene < styrene < *p*-styrene that was attributed both to steric and electronic effects. The good copolymerisation characteristic of *p*-methylstyrene was particularly promising, as the reactivity of the benzylic protons of the methylstyrene moieties allow further functionalisation of the obtained polymers [283]. Contrary to the occurrence of tail-to-tail coupling in ethylene/styrene copolymers derived from CGC catalysis, only isolated *p*-methylstyrene units were observed in the obtained poly(ethylene-*co*-*p*-methylstyrene) [284].

$[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO was also found to facilitate the terpolymerisation of ethylene and styrene or *p*-methylstyrene, respectively, with a variety of termonomers, such as propylene, 1-octene, norbornene and 1,5-hexadiene with high efficiency [285,286]. 1,5-Hexadiene cyclopolymerised under the applied conditions resulting in terpolymers incorporating randomly distributed 1,3-*cis*- and 1,3-*trans*-cyclopentane rings (Fig. 22) [285,287].

Waymouth and co-workers found that CGCs bearing electron-withdrawing amido functions behaved in a distinctively different manner compared to that of the previously described systems and closely resembled the characteristics of non-bridged systems, such as Cp^*TiCl_3, producing predominantly syndiotactic styrene homopolymer even in the presence of ethylene (vide supra) [265].

5.6.2. Cyclic monomers

Ethylene–norbornene copolymers are thermoplastic materials with interesting properties, e.g. they are amorphous, highly transparent and chemically resistant [288]. Ethylene–norbornene copolymerisation using metallocenes and CGCs has been extensively studied by Ruchatz and Fink [289–292]. In most aspects, CGCs were found to behave similarly to the *ansa*-metallocenes investigated in the same studies. All catalytic systems under investigation incorporated norbornene solely in *cis*-2,3-*exo* fashion (Fig. 23) and titanium CGCs were found to incorporate virtually exclusively isolated norbornene units [290,293,294].

On the other hand, the investigated zirconium CGC allowed even homopolymerisation of norbornene [290]. In the case of a bulky amido moiety in the *ansa*-bridged ligand, homopolymerisation can be suppressed and almost perfectly alternating

Fig. 22. Possible microstructures of 1,3-cyclopentane units.

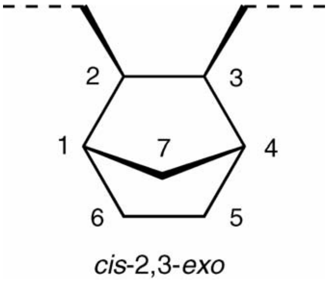


Fig. 23. Preferred microstructure of norbornene units in CGC derived norbornene polymers.

ethylene–norbornene copolymers can be obtained [295]. In these alternating copolymers, subsequent norbornene units arrange largely in an atactic fashion [296]. Copolymerisation activities of CGC based systems were moderate, but frequently lower than those of *ansa*-metallocenes [290]. While *ansa*-metallocenes yielded increased polymer molecular weights with increasing norbornene concentration $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$, gave lower polymer molecular weights with increasing comonomer concentration [292]. At the same time, higher comonomer concentrations correlated with lower numbers of long-chain branches along the polymer chain [297]. These experimental results could be largely rationalised through computational studies [298].

In terpolymerisation experiments, ethylene and norbornene were terpolymerised with 5-vinyl-2-norbornene, demonstrating the exclusive incorporation of 5-vinyl-2-norbornene by reaction of its cyclic double bond. The presence of 5-vinyl-2-norbornene increased the polymer molecular mass of the produced polymers for CGC catalysts, whereas the opposite effect was observed for *ansa*-metallocenes [299].

Sundararajan and co-workers claimed that $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$/MAO can be converted by reaction with phenylacetylene to give a catalytic system that facilitates ring-opening metathesis polymerisation (ROMP) of cyclic olefins, such as norbornene [300,301].

In the copolymerisation of ethylene and cyclopentene, alternating copolymers with 1,2-enchainment of the resulting cyclopentane units were obtained. While catalyst systems based on achiral CGCs $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiR_2]$ (R = Cl, Me) produced highly alternating atactic poly-(ethylene-*co*-cyclopentene), chiral versions of the pre-catalyst incorporating substituted indenyl-moieties produced highly alternating isotactic copolymer (Fig. 24) [93,302]. Analogous observations were reported for copolymerisation of ethylene with cycloheptene and cyclooctene, respectively [93]. Furthermore, catalytic systems based on $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$ were found to facilitate the copolymerisation of ethylene and various cyclic dienes, e.g. cyclopentadiene, 1,3-cyclohexadiene, 1,5-cyclooctadiene, 2,5-norbornadiene and dicyclopentadiene. For the non-conjugated ring systems, exclusive 1,2-enchainment was observed. In those ring systems, where the two olefinic double bonds were separated by three single bonds and therefore sufficiently remote, partial cross-linking through reaction of both double bonds occured [303]. In the case of the conjugated diene cylcopentadiene, both 1,2- and 1,4-insertion modes were detected [303], while 1,3-cyclohexadiene resulted exclusively in the formation of 1,4-cyclohexene units [304].

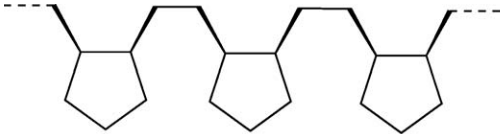


Fig. 24. Section of isotactic poly(*cis*-1,2-cyclopentene-*alt*-ethylene).

In the copolymerisation of ethylene with 7-methylene-bicyclo[4.1.0]heptane $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}MMe^+]$-$[B(C_6F_5)_4{}^-]$ (M = Ti, Zr), catalysed the incorporation of the cyclic monomer via a ring-opening Ziegler polymerisation (ROZP) mechanism (Eq. (18)), involving sequential double-bond insertion and β-alkyl shift ring-opening. The copolymers obtained are of particular interest as they carry *exo*-methylene functionalities that facilitate further derivatisation [305].

(18)

5.6.3. Conjugated dienes

It was demonstrated that CGCs, such as $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}TiCl_2]$, activated with MAO catalyse polymerisation of 1,3-butadiene [306,307] and 1,3-pentadiene [185] with similar activity and produce polymers with comparable microstructure as it is observed for non-bridged systems, i.e. Cp^*TiX_3/MAO. Poly-(ethylene-*co*-1,3-butadiene) could be as well produced with these systems [308]. While activities of Group 4 CGC catalysts were found to be rather poor for the polymerisation of 1,3-pentadiene due to the steric hindrance imposed by the methyl group, the vanadium CGC based system $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\mathit{t}Bu\}VCl_2]$/MAO showed four times higher productivity than its Group 4 analogues under standardised conditions [185]. Characteristics of the copolymerisation of ethylene with cyclopentadiene and 1,3-cyclohexadiene, respectively, mediated by CGCs was already discussed in conjunction with cyclic monomers (vide supra).

5.6.4. Polar monomers

The copolymerisation of polar monomers with olefins using transition-metal complexes is still a great challenge. Correspondingly functionalised copolymers are expected to exhibit desirable material properties of potentially great commercial value [309]. CGCs provided some advancement in this field.

$[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$ was found to facilitate copolymerisation of ethylene and $AlMe_3$ protected polar vinyl comonomers, e.g. $AlMe_3$ protected 5-hexen-1-ol and 10-undecen-1-ol, albeit with low activity. Attempts to incorporate $AlMe_3$ protected vinylic carboxy comonomers, e.g. 10-undecen-1-oic acid, failed [310].

The cationic zirconium enolate complex $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Zr\{OC(OR){=}CMe_2\}(L)]^+$ is capable of producing highly isotactic poly(methyl methacrylate) (PMMA) (Eq. (19)) [311], while its titanium analogue was reported to produce predominantly syndiotactic PMMA [312]. Isoelectronic $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Y(thf)(\mu\text{-}H)]_2$ and $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Y(CH_2SiMe_3)(thf)]$ were shown to catalyse the polymerisation of *tert*-butyl acrylate in a predominantly atactic fashion without addition of a co-catalyst. $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Y(thf)(\mu\text{-}H)]_2$ also showed activity towards polymerisation of acrylonitrile [176]. A group-transfer mechanism was suggested for these reactions [115].

$[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiMe_2]$ was found to be active for methyl methacrylate and *n*-butyl methacrylate homo- and copolymerisation when activated by $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ [75,312].

$Al(C_6F_5)_3$ activated $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Ti(Cp)Me]$ was demonstrated to be an efficient catalyst for the production of PMMA. The lack of a similar reactivity in the analogous borane activated system gave rise to the assumption that the reaction involves enolaluminates as key-intermediates [75].

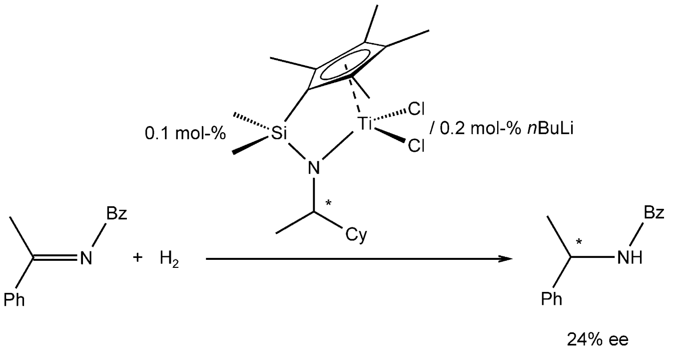
Stepwise copolymerisation of propylene and methyl methacrylate with $B(C_6F_5)_3$ activated $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiMe_2]$ afforded unique *block*-(atactic-polypropylene)-*block*-(syndiotactic-PMMA) beside some homopolymeric material. The diblock structure of the obtained polymers indicates the capability of the catalytic system for mechanism-crossover, specifically the transition from a coordination insertion type polymerisation of propylene to group-transfer type polymerisation of methyl methacrylate [313].

6. Other transformations catalysed by CGCs

Beyond their application in polymerisation reactions, CGCs experience increasing relevance in the catalysis of various other transformations. This section gives an overview about this development.

In a comparative study, Teuben and co-workers demonstrated the catalytic activity of some Group 4 CGCs, namely $[\{\eta^5{:}\eta^1\text{-}(C_5H_4)(CH_2)_3NMe\}MR_2]$ ($MR_2 = TiMe_2$, $Zr(BH_4)_2$, $ZrBz_2$), for the hydroboration of 1-hexene with catecholborane (Eq. (20)). These CGCs showed a much lower catalytic activity than the benchmark catalyst $[Cp^*_2LaCH(SiMe_3)_2]$, but a better stability under the reaction conditions applied [314].

Okuda et al. showed that $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)NR^*\}TiCl_2]$ (R^* = optically pure chiral alkyl group) can efficiently catalyse the hydrogenation of imines, e.g. acetophenone *N*-benzylimine, upon activation with two equivalents of *n*BuLi (Eq. (21)). While conversions were generally high, enantioselectivity was low with a maximum of 24% enantiomeric excess observed in the hydrogenation product [62,109]. Related complexes bearing an additional donor site in the amido moiety (R = –Cy(OCH$_2$Ph)–2) were also tested under the same conditions, but activities were lower while enantioselectivity was not improved [117].



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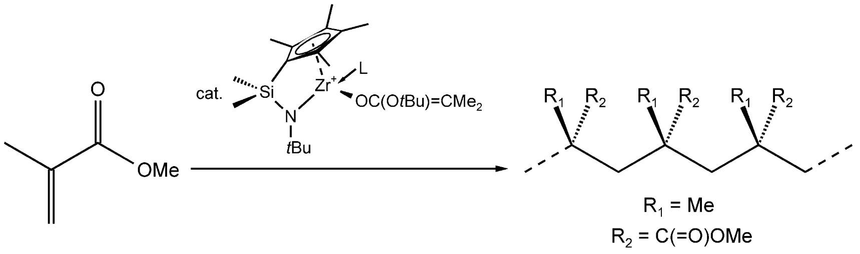

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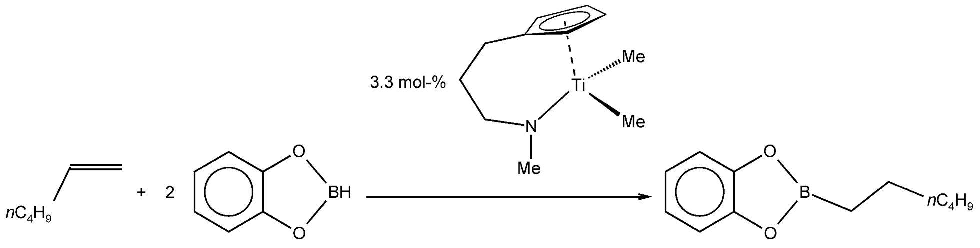

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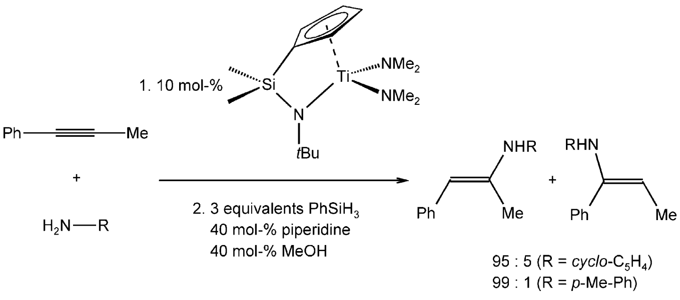
Doye and co-workers employed catalytic amounts of $[\{\eta^5:\eta^1\text{-}(C_5H_4)(SiMe_2)N\textit{t}Bu\}Ti(NMe_2)_2]$ in a sequential hydroamination and hydrosilylation protocol to convert alkynes and primary amines into secondary amines. Activity and regioselectivity of the catalyst system based on the titanium CGC were found to be comparable to the characteristics of $[Cp_2TiMe_2]$ (Eq. (22)) [315].



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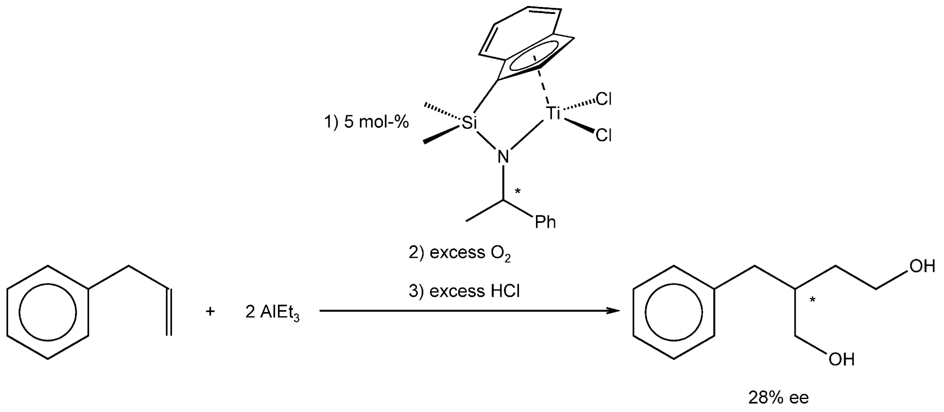
Waymouth and co-workers applied catalytic amounts of titanium CGC $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiMe_2]/[Ph_3C^+][B(C_6F_5)_4{}^-]$ in the presence of $AlMe_3$ and $AlEt_3$, respectively, for the carboalumination of a variety of α-olefins. Strong evidence that supports a mechanism involving olefin insertion into a Ti–C bond followed by transmetalation was given in the report. Catalytic amounts of titanium CGCs $[\{\eta^5:\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$ and $[\{\eta^5:\eta^1\text{-}(C_9H_6)(SiMe_2)N(CH\{Me\}Ph)\}TiCl_2]$ were also reacted with α-olefins in the presence of $AlEt_3$. Analysis of the carboalumination products after work-up strongly suggested a mechanism via a metallacyclic intermediate for this combination of catalyst and alkyl reagent. Enantioselectivity of the chiral catalyst $[\{\eta^5:\eta^1\text{-}(C_9H_6)(SiMe_2)N(CH\{Me\}Ph)\}TiCl_2]$ was moderate with a maximum 28% enantiomeric excess for a specific substrate (allylbenzene) (Eq. (23)) [31].

The same titanium dichloride CGCs were also utilised in ring-opening reactions of 4,5-bis(methoxymethyl)-7-oxabicyclo-2-heptene in the presence of $AlEt_3$. This type of ring-opening of oxabicyclic alkene compounds is of great interest in synthetic organic chemistry. Depending on the amount of $AlEt_3$, either ethyl (two equivalents of $AlEt_3$) or hydride (five equivalents of $AlEt_3$) were transferred to the cyclic substrate upon ring opening. The chiral CGC $[\{\eta^5:\eta^1\text{-}(C_9H_6)(SiMe_2)N(CH\{Me\}Ph)\}TiCl_2]$ catalysed the reaction with up to 34% (ethyl transfer) (Eq. (24)) and 17% (hydride transfer) enantiomeric excess, respectively [316].

Polymerisation of the abundant polar monomer vinyl chloride with activated CGCs has not yet been achieved. Instead, only 1.0 equivalent of vinyl chloride undergoes insertion into the $M\text{–}Me^+$ bond of the catalyst, followed by rapid β-chloride elimination [219,317]. Marks and co-workers reported a detailed study on the reaction of α-chloronorbornene, a vinyl chloride analogue that is conformationally locked and prevents rapid β-chloride elimination, with $M\text{–}Me^+$ in aromatic solvents (Eq. (25)). Rather surprisingly, it was found that $M\text{–}Me^+$ (e.g. activated CGCs) catalyse formation of *exo*-1-chloro-2-arylnorbornanes. The catalytic reaction proceeds via a sequence of olefin addition to the cationic metal moiety, skeletal rearrangement of the bicyclic norbornene system and subsequent electrophilic attack on an aromatic solvent molecule [318].

CGCs of the Group 3 transition metals have also been successfully applied to a number of catalytic organic transformations.



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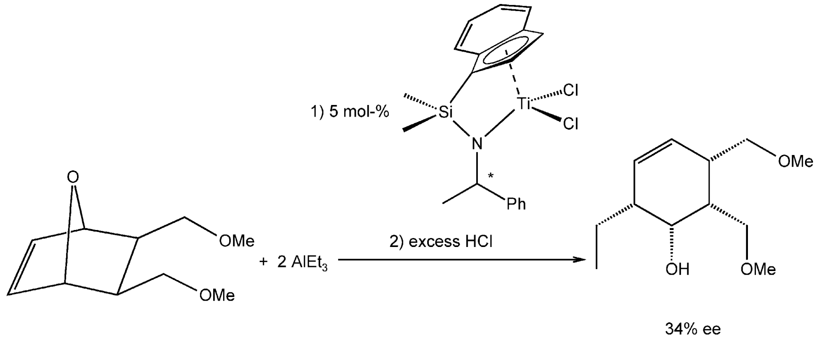

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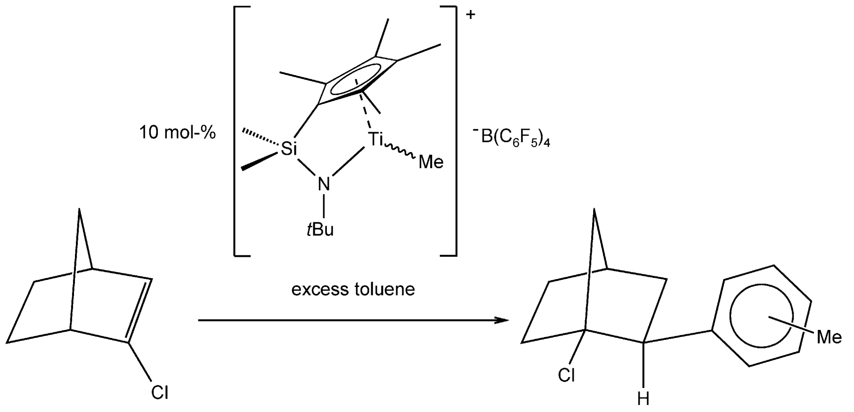
Okuda and co-workers applied [{η^5:η^1-(C_5Me_4)(CH_2SiMe_2)N*t*Bu}Y(thf)(μ-H)]$_2$ and [{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}Y(thf)(μ-H)]$_2$ in the hydrosilylation of olefins with good results. Thus, the former catalyst quantitatively converted 1-decene in the presence of $PhSiH_3$ to the *anti*-Markovnikov product *n*-$C_{10}H_{21}SiH_2Ph$ (Eq. (26)) [169]. Hydrosilylation of acyclic dienes (1,5-hexadiene, 1,7-octadiene) with one equivalent of $PhSiH_3$ in the presence of catalytic amounts of [{η^5:η^1-(C_5Me_4)(CH_2SiMe_2)N*t*Bu}Y(thf)(μ-H)]$_2$ proceeded only with low chemoselectivity, but reaction of 4-vinyl-1-cyclohexene under identical conditions resulted exclusively in the *anti*-Markovnikov hydrosilylation of the *exo*-cyclic double bond [319]. Related dimeric CGCs bearing linked cyclopentadienyl phosphido ligands were also found to be highly active and selective catalysts for the hydrosilylation of a range of substrates [139].

Marks and co-workers reported the high efficiency of lanthanide and actinide CGCs [183,320–322] for the intramolecular hydroamination/cyclisation reaction of various substrates (Eq. (27)). Turnover frequencies were similar or exceeded those of related lanthanocene systems. This reactivity was as well exploited in a key step of the natural product synthesis of (+)-xenovenine, i.e. a catalytic stereoselective tandem bicyclisa-



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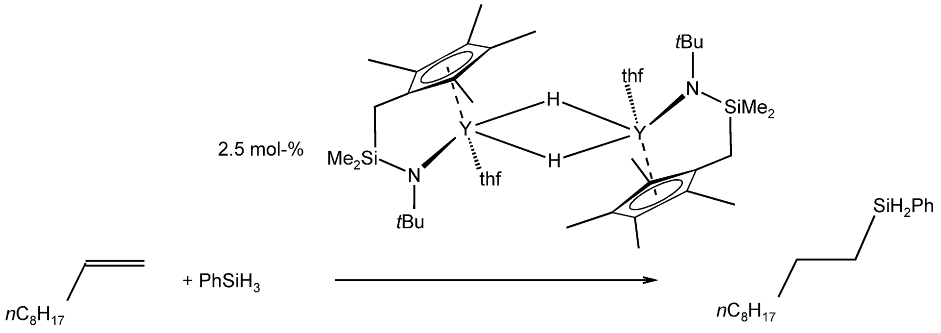

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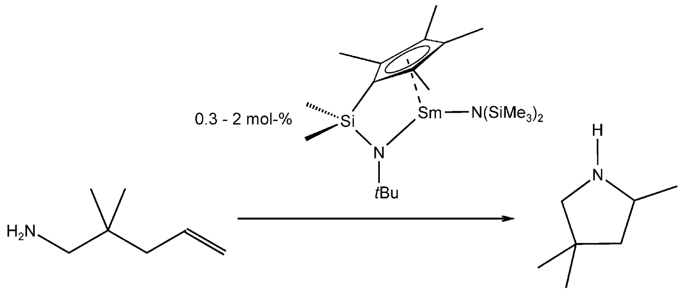

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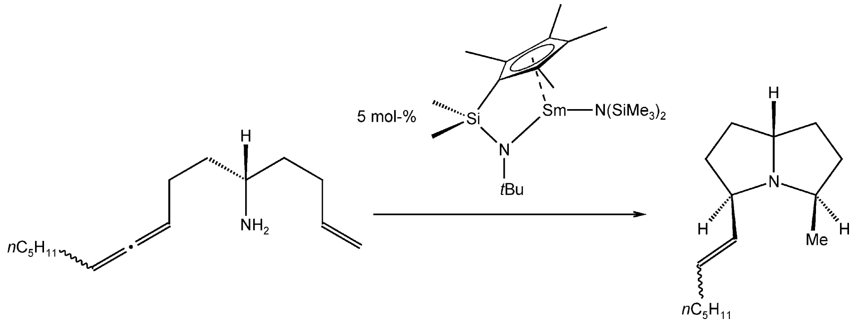
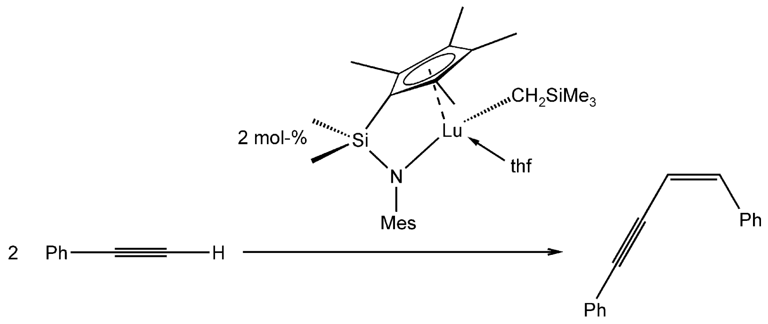


(28)

tion of an intermediate (Eq. (28)). In comparison, conventional hydroamination/cyclisation catalysts yield only a monocyclic product for this substrate [320,321].

Furthermore, $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)NR\}M(CH_2SiMe_3)(thf)_n]$ (M = Y, Yb, Lu; R = *t*Bu, Ph, $C_6H_2Me_3$-2,4,6; $n = 1$, 2) were found to catalyse dimerisation of various terminal alkynes with high activity; almost exclusively head-to-head-(Z)-dimerisation products were formed, exhibiting a high degree of regio- and stereoselectivity (Eq. (29)) [179]. In fact, this reaction presents the first example of such selectivity for aromatic alkynes [323]. The reaction proceeds cleanly even in the presence of carbon-halide bonds that are known to be highly susceptible to reductive cleavage by transition metals [179].



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7. Further aspects

7.1. Supported CGCs

Transition metal complexes, such as CGCs may be immobilised by attachment to organic or inorganic supports either by adsorption, coordination or covalent bonding. Thus, obtained heterogeneous systems are expected to exhibit advantageous catalytic features when compared to corresponding homogenous systems, such as production of polymers with higher molecular masses and melting points. Furthermore, immobilised complexes, unlike their soluble congeners, may be applied in gas-phase and slurry polymerisation processes and prevent the occurrence of reactor fouling [324]. Supported CGCs will be covered in this review by little more than a mere enumeration; the reader may refer to the given references for further details on the complex issues involved in the immobilisation of CGCs.

A first claim of having supported a titanium CGC on dehydroxylated silica can be found in the patent literature. However, no analytical details on the interaction of the CGC with the silica surface and on the characteristics of the obtained polyethylene were provided [27]. Several reports on the immobilisation of CGCs by mixing with silica [101] or MAO supported on silica [325–327] can be found in the open literature. Similarly, a support derived from $MgCl_2$, ethanol and $AlEt_3$ has been used to immobilise and activate $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$ for the polymerisation of ethylene [328].

Several examples of covalent bonding of CGCs via their amido moiety to modified silica [329–336] and cross-linked polystyrene [337] surfaces were also reported. Furthermore, pyridylethylsilane modified silica has been utilised to immobilise CGCs via coordinative interaction [232,338] and the derived systems have been successfully applied in tandem catalysis polymerisation [339]. Self-immobilisation of CGCs with pendant ω-alkenyl moieties through incorporation in the growing polymer chain has also been reported, however, only limited analytical data for this process was provided [95]. In addition, borate modified silica supports have been applied as co-activators in conjunction with trialkylaluminium reagents for the ethylene polymerisation with CGCs [340].

7.2. CGCs in concurrent tandem catalysis polymerisation

In concurrent tandem catalysis, the target product is produced through simultaneous and cooperative action of two or more catalysts in a single reactor [341]. In situ formation of α-olefins from ethylene mediated by one catalyst and simultaneous copolymerisation of this α-olefins with ethylene by a suitable CGC to produce branched polyethylene appears to be an attractive objective. Advantages of this approach include the need for only one monomer feed and the potential control of the number and lengths of the branches by the relative ratio of oligomerisation and polymerisation catalysts. The main challenge of this method is to find suitable sets of catalysts that exhibit the desired reactivity ratio under common reaction conditions [342,343].

The concept of concurrent tandem catalysis involving CGCs to produce branched polyolefins has been realised in a variety of ways utilising (i) a mixture of two mononuclear catalysts and standard co-catalysts, e.g. MAO, MMAO and $B(C_6F_5)_3$, (ii) a mixture of two mononuclear catalysts and a bifunctional co-catalyst and (iii) a bimetallic catalyst combined with a standard co-catalyst ($[Ph_3C^+][B(C_6F_5)_4{}^-]$) (Fig. 25).

Thus, **65** [344,345], **66** [346] and **67** [339], respectively, were applied in the presence of $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiR_2]$ (R = Cl, Me) and MAO or MMAO to yield polyethylene with long-chain branches. The catalytic system **68**/$[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MMAO yielded selectively poly(ethylene-*co*-1-hexene) [347]. The system **69**/$[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}TiCl_2]$/MAO resulted in polyethylene with a distribution of short and long branches [348]. Surprisingly, the catalyst combination **67**/$[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)NMe\}TiCl_2]$/MMAO produced polyethylene exclusively with methyl branches [339]. Co-catalysts, such as MAO that are applied in superstoichiometric amounts naturally affect both the activity and characteristics of the oligomerisation and polymerisation catalysts in the mixture. Improved control over the concurrent catalytic activity could

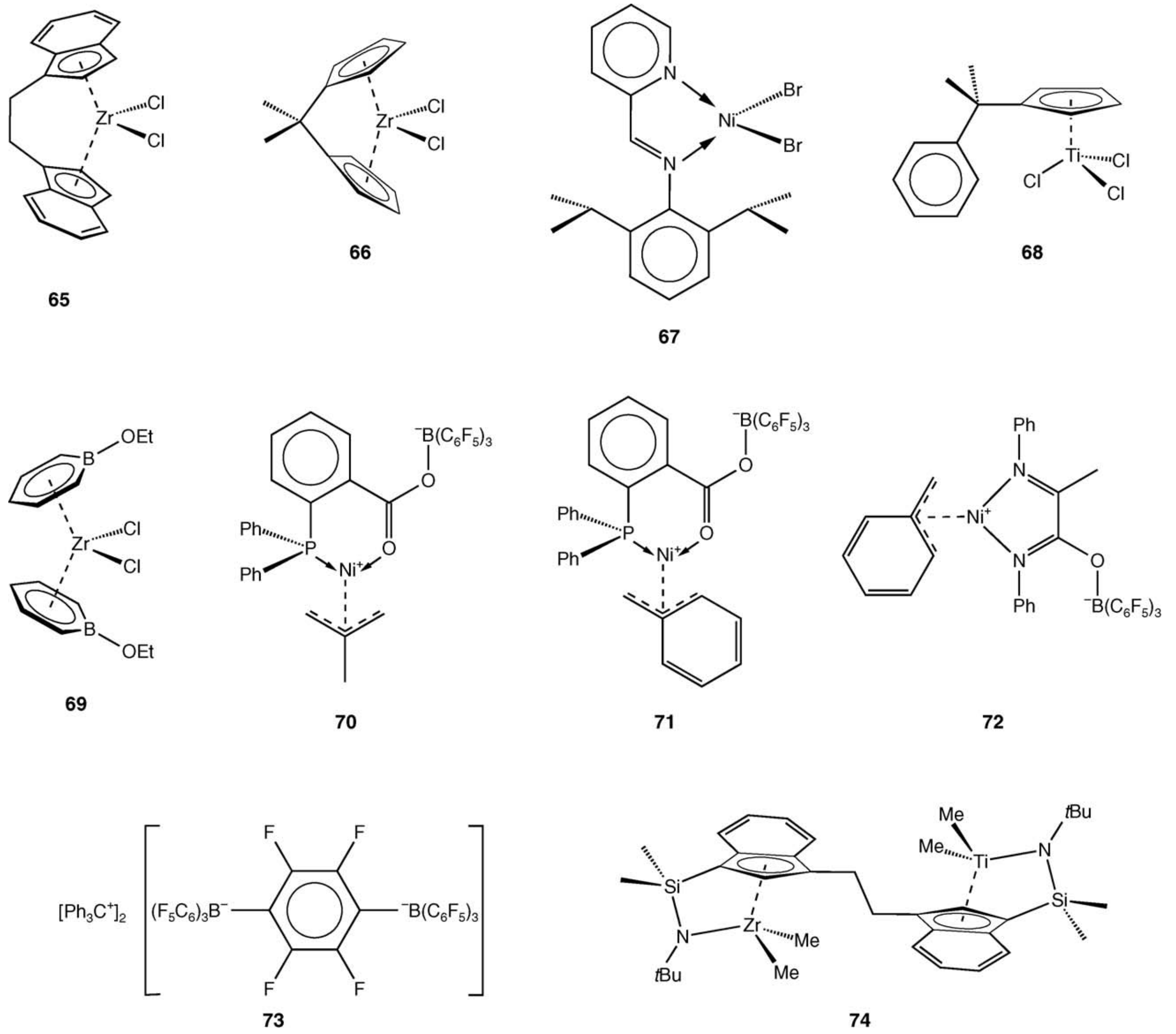


Fig. 25. Oligomerisation catalyst precursors (**65**–**69**), oligomerisation catalysts (**70**–**72**), a bifunctional co-catalyst (**73**) and a bimetallic catalyst precursor (**74**) that have been applied in concurrent tandem polymerisation reactions involving CGCs.

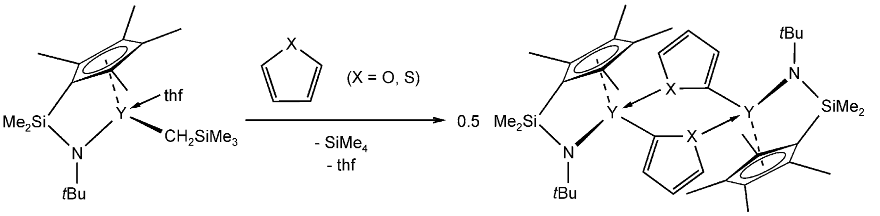
be achieved utilising stoichiometric amounts of $B(C_6F_5)_3$ as a co-catalyst. Examples include the production of poly(ethylene-*co*-1-butene) and polyethylene with a combination of ethyl and butyl branches by the catalyst systems **70** or **71**/[{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}$TiMe_2$]/$B(C_6F_5)_3$ [349,350]. The concurrent tandem reaction of three catalysts **71**/**72**/[{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}$TiMe_2$]/$B(C_6F_5)_3$ to give a polymer containing both ethyl and long-chain branches was also described [351].

A catalytic system involving the bifunctional co-catalyst **73**, the oligomerisation catalyst [{η^5:η^1-($C_{11}H_{10}$)-($SiMe_2$)N*t*Bu}$ZrMe_2$] ($C_{11}H_{10}$ = 3-ethylindenyl) and the polymerisation catalyst [{η^5:η^1-(C_5Me_4)($SiMe_2$)N*t*Bu}$TiMe_2$] yielded as well polyethylene with long-chain branches. The spatial constraint of the catalytic centres that is induced by the bifunctional activator was found to be highly beneficial for the enchainment of produced comonomer when compared to control experiments utilising the monofunctional co-catalyst $[Ph_3C^+][B(C_6F_5)_4{}^-]$ [352].

The concept of spatially constraining the catalytic centres in the tandem catalysis process was further developed with the synthesis of the bimetallic catalyst precursor **74** that allows oligomerisation and polymerisation at two different reactive sites within the same molecule. Indeed, this catalyst precursor in combination with $[Ph_3C^+][B(C_6F_5)_4{}^-]$ facilitates the production of long-chain branched polyethylene from ethylene [104].

7.3. CGCs and CH activation

The mediation of C–H bond activation in both saturated and unsaturated organic substrates by decamethyl lanthanocenes [Ln(η^5-C_5Me_5)$_2$R] (R = H, alkyl) is well documented in the literature [353]. Okuda and co-workers described related C–H activation processes involving the stoichiometric reaction of the CGCs $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(SiMe_2)N\textit{t}Bu\}Y(thf)(CH_2SiMe_3)]$ and $[\{\eta^5{:}\eta^1\text{-}(C_5Me_4)(CH_2SiMe_2)N\textit{t}Bu\}Y(thf)(CH_2SiMe_3)]$, respectively, with a range of aromatic substrates. Both CGCs were found to react with furan and thiophene through activation of an α-methine moiety (Eq. (30)) [354,355]. The latter was also reacted with anisol, phenetole, 3- and 4-methylanisole to yield selectively the *ortho*-metalation products (Eq. (31)), while reaction with 2-methylanisol resulted in activation of the ring methyl group (Eq. (32)) [356].



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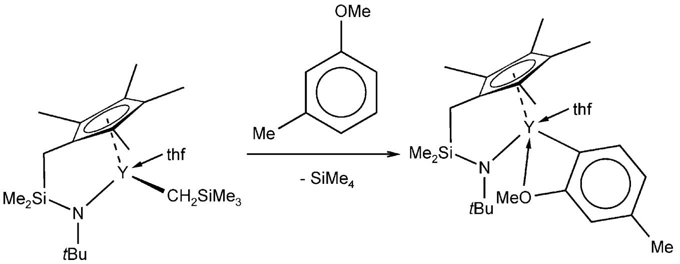

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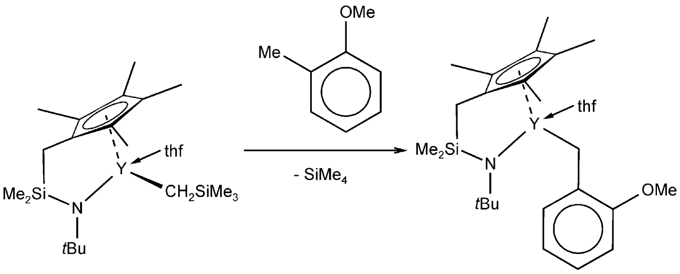

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8. Conclusions

Complexes bearing linked cyclopentadienyl amido ligands, first described in the early 1990s, give access to a wide variety of polyolefins with interesting properties that are often inaccessible with other catalyst systems. While the knowledge about the polymerisation chemistry of CGCs may be regarded as having reached a stage of maturity, reports on other aspects of the chemistry of CGCs, such as their use in the catalysis of organic transformations and tandem catalysis reveal a further potential of these compounds that awaits to be exploited.

Acknowledgements

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