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TUTORIAL REVIEW

Tridentate ligands and beyond in group IV metal α -olefin homo-/co-polymerization catalysisCarl Redshaw^{*ab} and Yong Tang^{*a}

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The opening up of new markets, particularly in the Far East, is expected to increase the industrial demand for more (and new) plastic materials. In turn, this will drive the need for further catalyst development, with increased efficiency and with the capacity to easily control the resulting polymer properties being high on the agenda. With this in mind, tailoring the pre-catalyst structure has proved to be a very successful strategy, and has allowed for the elucidation of a number of structure–activity trends. A particularly fruitful synthetic avenue has been the deployment of multi-dentate ancillary ligands bearing one or more substituents containing additional functionality, capable of weakly binding to the metal. Such a method is versatile and allows for the incorporation of a wide range of functionality. Furthermore, benefits of such an approach include the ability to control the % incorporation of co-monomers, *in situ* screening, low co-catalyst loadings (*versus* activity enhancement) as well as control over the resultant polymer structure. This review underlines the efforts made in the last few years with regard to the use of tridentate ligands and beyond in the field of α -olefin polymerization using catalytic systems based on group IV metals.

1. Introduction

Polymer production is still mostly dominated by the poly(olefin) industry, with polyethylene and polypropylene catering for almost half of Western Europe's annual plastic consumption.¹ The new markets that are opening up in the Far East are expected to follow a similar trend, and so the

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need for new catalysts, which can perform better and which allow for more control, is at a premium.² This is particularly the case in countries such as China, where the need for new IP/technology is also a huge driving force.

With this in mind, single-site, non-metallocene catalysts remain attractive for a number of reasons, such as ease of preparation, high catalytic activity, thermal stability, low co-catalyst loading requirements as well as their ability to perform effectively in a variety of co-polymerizations. It has become clear through much of the recent research efforts that both the electronic and steric effects of the ancillary ligands in the pre-catalyst structure can play a significant role in tuning the properties of the resulting active species. In certain systems, *vide infra*, the choice of activator is also crucial.

Use of multi-dentate ligands which incorporate a functionality capable of weakly binding to a metal and thereby altering either the electronics, steric or both, is proving to be a fruitful avenue for controlling the properties of complexes, both in polymerization catalysis and elsewhere. Of the ligand types studied to-date, impressive results have been achieved by employing either a bis(phenolate)-derived ligand set or a phenoxyimine derivative in titanium-based systems.³ For zirconium, even peripheral changes (involving an extra donor arm) to the pre-catalyst structure have been shown to have a pronounced effect upon catalytic performance, and systems have been shown to be capable of block co-polymerizations. In the case of hafnium, systems were identified which were capable of producing high molecular weight co-polymers at high temperatures (> 100 °C), whilst for propylene polymerization, the use of high through-put synthesis led to rapid commercialization. With the majority of these ligands sets, the introduction of a donor atom has proved to be facile, and the use of donors such as N, O, P or S has met with much success. In ligand sets such as the aminebis(phenol)s, the central donor atom can play a pivotal role in the catalysis, and indeed such a strategy has led to a number of new and versatile catalytic systems. In this review, we will discuss the use of the aforementioned ligand types in α -olefin oligo-/polymerization (and co-polymerization) catalysis, using systems based on the metals of group IV. Comprehensive reviews that cover different aspects of imine-based olefin polymerization catalysis have recently appeared.^{3–6} This review is organized such that for each metal, catalytic systems are discussed in terms of ligand classification. After initially introducing half-metallocene systems for background purposes, post metallocene complexes bearing tridentate chelate ligands are discussed, followed by ligands which incorporate one donor atom in the bridge, and then those utilising two bridging donors (sulfur-bridged systems are not included as they have recently been reviewed elsewhere).^{7,8} Finally, ligands not covered by previous sections are discussed. The referenced works in this review report catalytic activities using a variety of units. Herein, we use where possible only g mmol^{–1} h for consistency, however, it should be noted that polymerization conditions vary from laboratory to laboratory, and so whilst general analogies are possible, more in-depth comparisons are often fruitless.

2. Titanium complexes

2.1 Half-titanocene complexes

The origins of the ‘donor’ approach date back some 20 years, where the focus was to exploit the ability of a pendant donor arm to stabilize a Lewis acidic metal centre, or to enhance other properties, such as solubility.⁹

The first example of a titanium half-sandwich complex, in which the Cp ligand was chelating (see **1**, Fig. 1) was reported here at the SIOC by Qian *et al.*¹⁰ Subsequent work by Flores, Chien and Rausch utilized the related dimethylaminoethyl derivative **2**, and showed that such a complex, in the presence of MAO (Al/Ti = 4000), was about 100 times more active for ethylene polymerization than was [CpTiCl₃].¹¹ Furthermore, both **2** and the permethylated derivative **3** were capable of the efficient polymerization of propylene, affording high molecular weight atactic polymer. Results though for the polymerization of styrene were somewhat less impressive. Subsequent studies from the same laboratory showed that such systems were capable of ethylene/propylene co-polymerizations, as well as ter-polymerizations with either ethylidene norbornene, vinylcyclohexene or 1,4-hexadiene as the third monomer.¹²

Groups such as picolyl, diisopropylaminoethyl and dimethylaminoethyl were appended to both cyclopentadienyl and indenyl groups of titanium triisopropoxide complexes of the type **4** and **5** (Fig. 2).¹³ The indenyl complexes bearing pendant NMe₂ groups proved to be highly active for ethylene polymerization when activated with MAO, but were far less impressive for propylene or styrene polymerization. The indenyl complexes of type **6** bearing NⁱPr₂ or 2-py groups were an order of magnitude less active than **2**, and were inactive towards propylene. In the case of the Cp-containing complexes, those bearing an NⁱPr₂ function also performed poorly towards ethylene, whereas the NMe₂ and picolyl-containing systems, upon activation with MAO (Al/Ti = 2000), were similar in activity to **2**. It was concluded that the NⁱPr₂ moiety in such systems possessed unfavourable sterics, leading to both low activities and low molecular weights.

The number of carbon atoms linking the pyridine ring to the Cp group also seemed to impact dramatically on the observed activity. When three carbons were employed, the activity was

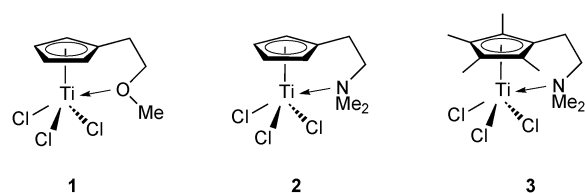


Fig. 1 Early examples of half-sandwich titanocene with donor arms.

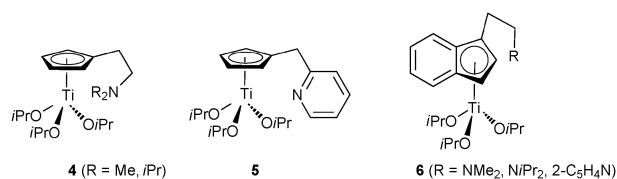


Fig. 2 Titanium isopropoxides with donor arms.

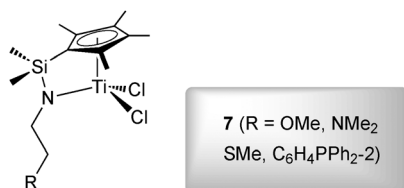


Fig. 3 'Tridentate' amido Cp titanium complexes.

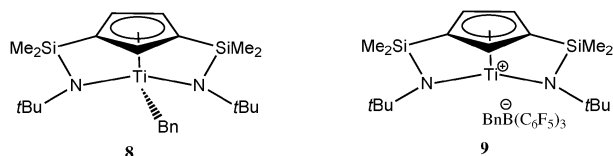


Fig. 4 Doubly silylamido bridged Cp complexes.

far inferior, and this was thought to be due in-part to the extra torsional energy in such a bridge.

Okuda *et al.* examined similar systems, but which incorporated a tridentate linked amido ligand (see **7**, Fig. 3). In such systems, NMR data suggested that the donor was not coordinated to the titanium centre; NOESY spectra indicated this was also the case in resultant dialkyl complexes.¹⁴ However, the presence of these side chains proved to be detrimental in terms of polymerization activity. For example, in the presence of MAO (Al/Ti = 500), **7** (OMe) polymerized ethylene with an activity of 12 g mmol⁻¹ h *cf.* 950 g mmol⁻¹ h for [Ti(η⁵:η¹-C₅Me₄SiMe₂NtBu)Cl₂] under the same conditions.

Okuda *et al.* extended their work to include thioether and phosphino functionalized complexes.¹⁵ Ethylene polymerization screening using the thioether derivative, indicated that in terms of activity, an SMe group was more beneficial than either OMe or NMe₂. This was thought to be due to the softer nature of the SMe group, and so the reduced nucleophilicity allowed for lower stability of the resultant olefin π-complex, and a lower barrier for insertion of ethylene into the growing polymer chain.

Royo *et al.* have prepared the dark red doubly silylamido bridged Cp complex **8** (Fig. 4, left) in quantitative yield *via* the reaction of di(amidosilyl)cyclopentadiene C₅H₄[SiMe₂(NHtBu)]₂ with TiBn₄ in refluxing toluene. Complex **8** was further reacted with B(C₆F₅)₃ at ambient temperature to afford orange **9** (Fig. 4, right) in 60% yield. The molecular structure of **9** was determined and revealed that the Cp centroid, the two amido nitrogen atoms and a *meta* C–H bond (or a *meta* carbon atom) of the phenyl ring of the anion together form a pseudo tetrahedral environment at the cationic titanium centre. The zirconium analogues have been screened to evaluate their potential as ethylene polymerization (and co-polymerization) catalysts (see section 3.1).¹⁶

2.2 Cp containing Schiff-base complexes

A number of mono-Cp containing complexes, which also incorporate tridentate phenoxyimines, have been reported. Qian *et al.* utilized a methoxy containing phenoxyimine, which was reacted in toluene (80 °C, 12 h) with [CpTiCl₃] to afford **10** (Fig. 5, left).¹⁷ Disappointingly, when screened for ethylene

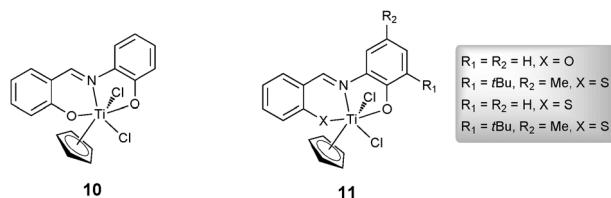


Fig. 5 Cp Titanium complexes bearing tridentate phenoxyimines with O or S donors.

polymerization at 50 °C, in the presence of MAO (Al/Ti = 1000), the observed activity (15.6 g mmol⁻¹ h) was somewhat lower than that observed for the bis(chelate) complex [CpTiCl(PhN=CHC₆H₄O-2)] (18.8 g mmol⁻¹ h). Furthermore, the molecular weight distribution for **10** (4.77) was the highest observed for all the mono-Cp containing complexes screened (2.55–3.2). Complex **10** also performed relatively poorly for the co-polymerization of ethylene with 1-hexene (activity = 0.22 × 10² g mmol⁻¹ h; *M_w/M_n* = 4.9).

More recently, Jin *et al.* reported similar mono-Cp phenoxyimine complexes, and also extended the family to include those bearing an S donor.¹⁸ As mentioned previously, such ligands could be reacted with [CpTiCl₃] *via* their alkali-metal salts. In this way, complexes **11** (Fig. 5, right) were prepared in yields of ≥ 61%. Representative molecular structures were determined by X-ray crystallography, and revealed similar distorted square-pyramidal geometries at titanium, for which the Cp ligand was apical.

These complexes showed only moderate activities (7–77 g mmol⁻¹ h) when screened for ethylene polymerization using MAO as co-catalyst (Al/Ti = 1500). The activities observed for the arylsulfide complexes were higher than for their aryloxy counterparts. The presence of the *ortho tert*-butyl substituent on the non-donor aryloxy ring also appeared to favour high activity. In these polymerization runs, the active species appeared to be quite stable, with ethylene consumption being maintained throughout the procedure (1 h).

Reaction of [Cp'TiCl₃] (Cp' = Cp or Cp*) with the potassium salts 2-(2,6-R¹-4-R²-phenylimino)ethylquinolin-8-olates afforded the pseudo octahedral titanium complexes **12** (R = Me; Fig. 6).¹⁹ Such complexes were found to be highly active for ethylene polymerization, with the Cp* derivatives displaying higher activities (6.52–12.9 × 10² g mmol⁻¹ h) than their Cp counterparts (4.21–8.89 × 10² g mmol⁻¹ h). The activity could be further controlled by variation of the *ortho* substituents about the N-bound aryl group. Co-polymerization of ethylene with 1-hexene, 1-octene or norbornene was also demonstrated, and appreciable co-monomer incorporation

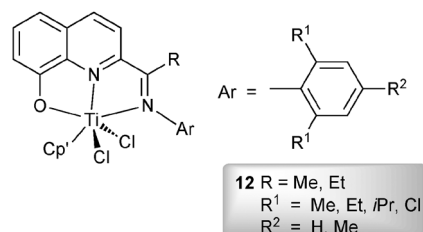


Fig. 6 Iminoquinolinolate Cp titanium complexes.

(10.1 mol%, 1-hexene; 4.22 mol%, 1-octene; 5.87 mol%, norbornene) was achieved.

The related 2-(1-(arylimino)propyl)quinol-8-olates **12** ($R = \text{Et}$, Fig. 6) were also found to possess high activity (up to $6.44 \times 10^3 \text{ g mmol}^{-1} \text{ h}$) for ethylene polymerization. Such complexes also performed well in ethylene co-polymerizations with 1-hexene (up to $5.22 \times 10^2 \text{ g mmol}^{-1} \text{ h}$) or 1-octene (up to $5.04 \times 10^3 \text{ g mmol}^{-1} \text{ h}$); co-monomer incorporations were 11.6 and 6.53 mol%, respectively.²⁰ The 2-(1-(arylimino)-ethyl)quinol-8-olate series, however, exhibited enhanced thermostability during catalysis.

2.3 Complexes based on O,N,P imine ligands

A phenoxyimine ligand bearing a bulky diphenylphosphorus group can be deprotonated by NaH (THF, -78°C) and treated with $[\text{TiCl}_4]$ to afford the trichloride **13** (Fig. 7, top left) in good yield (ca. 80%).²¹ Use of 0.5 equiv. of $[\text{TiCl}_4]$ led to a bis(chelate) complex **14** (Fig. 7, right) in 34% yield. The parent ligand can be reduced with LiAlH_4 (0°C), and then reacted with $[\text{TiCl}_4]$ to afford the imine-amine complex **15** (Fig. 7, bottom left). The molecular structure of **15** was confirmed by X-ray diffraction, and revealed the expected distorted octahedral geometry at titanium. The Ti–P bond length of 2.6484(19) Å was suggestive of only a weak interaction. The open coordination of such complexes was expected to be beneficial for co-polymerization.

In the presence of MMAO, the bis(chelate) **14** afforded only trace polymer, whereas the mono-chelates **13** and **15** were both highly active, even at low co-catalyst loadings ($\text{Ti}/\text{Al} = 50:1$, activity = $5 \times 10^2 \text{ g mmol}^{-1} \text{ h bar}$). Such catalyst systems also proved to be thermally stable, with optimum activities achieved at 50°C . Interestingly, the activities at low temperatures (-30°C) were comparable with those at 100°C , illustrating the ability of this ligand set to stabilize the active species over a wide temperature range. $^1\text{H}/^{13}\text{C}$ NMR spectroscopic analysis of the polyethylene product formed indicated that there were no branches detectable, which was also consistent with the recorded melting points (by DSC = $131\text{--}141^\circ\text{C}$); the molecular weight distribution was 1.54–3.33. Polymer molecular weights were found to be pressure dependent, with higher pressures favouring higher molecular weights, e.g., for **13** at 1 bar $M_w = 22 \times 10^4$ cf. 170×10^4 at 7 bar. Both **13** and **15** were also shown to be capable of the co-polymerization of ethylene with either 1-hexene or norbornene. In each case, it proved possible to control the

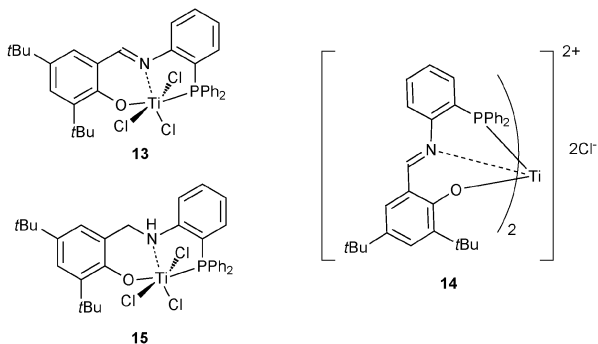


Fig. 7 O,N,P tridentate Schiff bases complexes.

molar% of co-monomer incorporation by variation of the initial co-monomer concentration.

2.4 Complexes based on O,N,S imine ligands

Ligands of the type **1H** (Fig. 8, top) were readily accessible in good yields *via* standard condensation procedures involving 3,5-di-*tert*-butylsalicylaldehyde and the respective 2-phenyl-sulfanylaniline.²² Subsequent treatment with KH in THF at low temperature (-78°C), followed, after work-up, by the addition (in toluene) of $[\text{TiCl}_4]$ afforded complexes of type **16** in good to excellent yields as red crystalline solids.

The crystal structure of **16** ($R^1/R^2/R^3 = \text{H}$) was representative of this class of complex and revealed an octahedral geometry at titanium, which possessed *mer* disposed chloride ligands. The Ti–S bond distance of 2.5908 Å is somewhat larger than the sum of the covalent radii. In the presence of MMAO, such complexes are highly active (typically $2 \times 10^3 \text{ g mmol}^{-1} \text{ h}$) for ethylene polymerization. Whilst there was little variation in activity upon changing the R^2 or R^3 substituents, it was found that the use of either electron donating or electron withdrawing groups promoted high activity (Chart 1).

Furthermore, the use of substituents such as Cl or CF_3 favoured high molecular weight polyethylene products. In the case of the *ortho* substituent R^1 , increasing steric bulk led to decreased catalytic activity (reduction in the rate of chain transfer), but an increase in the polymer molecular weight. A benefit of this catalyst system, like that using **13** and **15**, was that high activities, of the order of $1.88 \times 10^3 \text{ g mmol}^{-1} \text{ h bar}$, were achievable even in the presence of very low (and hence cheaper) co-catalyst loadings ($\text{Al}/\text{Ti} = 100:1$). However, it should be noted that the higher the co-catalyst loading, the lower the resulting polymer molecular weight. Polymer molecular weight was also dramatically effected (chain transfer reactions) by temperature, for example using **16** ($R^1/R^2/R^3 = \text{H}$), at 30°C $M_w = 4.28 \times 10^4$ cf. 1.37×10^4 at 80°C . Good activities were also achievable for the co-polymerization of ethylene with either 1-hexene or norbornene. High incorporation of 1-hexene was possible, for example 30% using **16** ($R^1/R^2/R^3 = \text{H}$).

Extension of this ligand set to side-arms bearing either O- or Se-donor atoms proved facile.²³ In the case of O, a crystal structure determination revealed that the donor O atom was

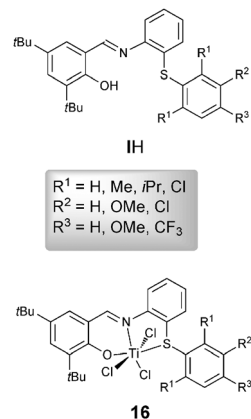
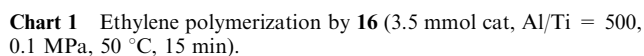
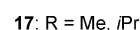


Fig. 8 Type **1H** phenoxyimine ligands and complexes of type **16**.



For the co-polymerization of ethylene with 1-hexene, both sets of complexes bearing either the S- or Se-donor ligand set were highly active, whilst the O-donor containing species gave only low activity. The molecular weight of the co-polymer

The series was further extended to include $R = nPr$, tBu , *noctyl* and *noctadecyl*, all of which were available in yields $\geq 61\%$. Good activities were exhibited (except for the tBu derivative) for a number of co-polymerizations involving ethylene with cyclic olefins, namely norbornene ($1.32\text{--}2.03 \times 10^3 \text{ g mmol}^{-1} \text{ h bar}$), cyclopentene ($1.60\text{--}2.32 \times 10^2 \text{ g mmol}^{-1} \text{ h bar}$) and dicyclopentadiene ($0.99\text{--}8.19 \times 10^2 \text{ g mmol}^{-1} \text{ h bar}$). Systems bearing a linear alkyl group at S showed similar activities, which appeared to be almost independent of the chain length. However, longer chains at S did lead to enhanced thermal stability.²⁶



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These systems (except the *t*Bu derivative) also displayed high activities for ethylene homo-polymerization as well as for the co-polymerization of ethylene with 1-hexene, 1-octene, 1-decene, 1-dodecene and 1-octadecene. As was observed for the cyclic olefin co-polymerizations, the activities were virtually independent of the chain length for the linear alkyls. The degree of incorporation was influenced far greater by the molar ratio of the monomers.²⁷

Co-polymerization of ethylene with 9-decen-1-ol also proved possible using systems of the type **17**. The SME derivative possessed slightly higher activity than did the SPh derivative, with activities of the order of 0.6×10^3 g mmol⁻¹ h bar achievable, and with 3.5 mol% alcohol incorporation.

2.5 β -Carbonylenamine ligands

Our lab (SIOC) has developed a simple one-pot screening method for the evaluation of titanium catalysts for polymerizations/co-polymerizations, in which [TiCl₄(THF)₂] was mixed *in situ* with enamine ligands of the type **II**, and then added to MMAO.²⁸ The optimum ratio of Al/Ti was found to be 1000:1, with highest activities observed at 30 °C. The polyethylene produced contained no branching (by ¹³C NMR spectroscopy), and the molecular weight distribution was 1.33 to 2.70. The molecular weights (*M_w*) were found to be both temperature and co-catalyst concentration dependent.

This one-pot method proved to be quite versatile and allowed for variation of the aniline deployed in the enamine preparation. As shown in Chart 2, it was found that an increase in the steric bulk of the *ortho* substituents led to a large decrease in observed activity, whilst at the same time, increasing the polymer molecular weight.

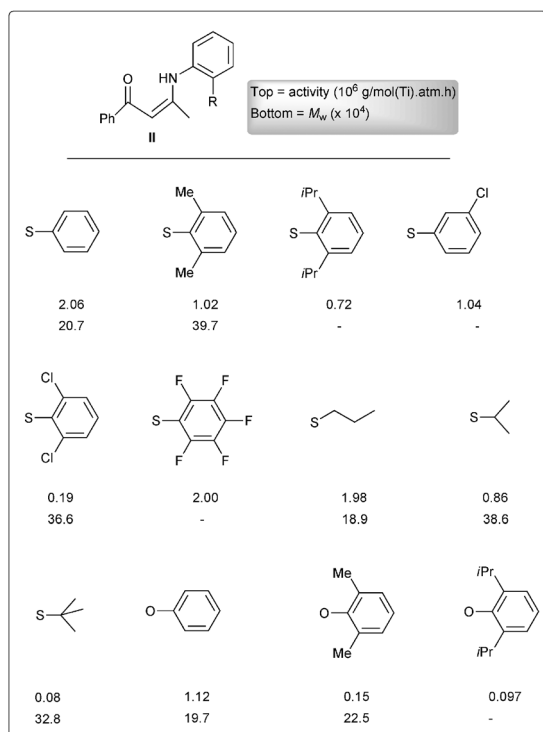


Chart 2 β -Carbonylenamine ligands screened for ethylene polymerization: MMAO (Al/Ti $\approx$ 630), 30 °C, 10 min.

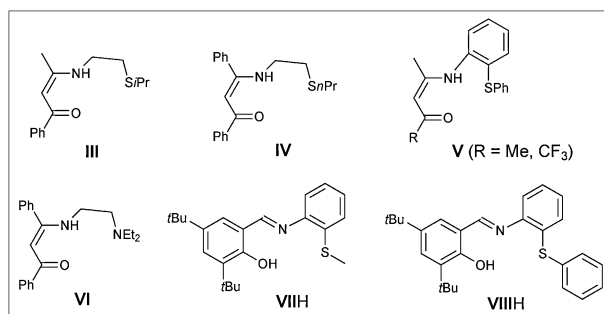


Chart 3 β -Carbonylenamine ligands screened for ethylene polymerization.

The method was further extended to include the ligands **III–VI** (Chart 3). Use of the 2-(isopropylthio)ethanimine-derived ligand led to a slight reduction in activity *cf.* with the *n*-propyl derivative. However, larger reductions in the activity were observed when the ligand contained an S-bound *tert*-butyl group. The diamine derived enamine **VI** led to only poor activity. Other ligands such as **VIIH** and **VIIIH** were also amenable to this one-pot strategy.

In an attempt to elucidate the mechanism of formation of the products formed during this one-pot procedure, the reaction of ligand **IV** with [TiCl₄(THF)₂] was monitored by ¹H NMR spectroscopy. After one hour, a new compound had formed in 61% yield. The reaction was then repeated on a preparative scale, affording a product with an identical ¹H NMR spectrum to that observed *via* the *in situ* route. This product was then recrystallized and subjected to a single crystal X-ray diffraction study. The structure was confirmed to be the complex **18**, for which the chlorines adopted a *mer* configuration about a distorted octahedral titanium centre (Fig. 10). In **18**, the enamine ligand had been converted to the imine form. Use of **18** as a pre-catalyst with MMAO afforded high activity, which was similar, as was the polymer molecular weight and distribution thereof, to that observed by the same ligand and [TiCl₄(THF)₂] when used in the one-pot procedure.

This one-pot method was equally applicable to co-polymerizations, typically of ethylene with other α -olefins. For example, with ethylene/1-hexene, higher activities were readily attainable than when using ethylene alone, whilst increasing the concentration of 1-hexene resulted in both increased polymer molecular weights and enhanced co-monomer content. Cycloalkenes such as cyclopentene and norbornene could also be co-polymerized with ethylene with activities as high as 5.12×10^3 g mmol⁻¹ h bar, and with co-monomer incorporation of 29.7 and 45.6 mol%, respectively.²⁹

By using ligands of the type **IV**, but bearing a methyl group at S, it proved possible to co-polymerize ethylene with

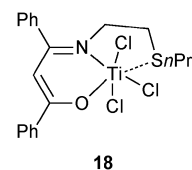


Fig. 10 Complex **18**.

9-decen-1-ol with high co-monomer incorporation (11.2 mol%). Very high activities (1.0×10^4 g mmol⁻¹ h bar) were possible, which were about 16 times higher than those displayed by type **17** (Ar = Ph) complexes. Furthermore, it proved possible to co-polymerize ethylene with 10-undecenoic acid with high activity (1.1×10^4 g mmol⁻¹ h bar) and with 1.6 mol% co-monomer incorporation. Other monomers which could be employed included 4-penten-1-ol and *tert*-butyl(dec-9-enyloxy)dimethylsilane.²⁷

2.6 Complexes based on O,N,N-imine ligands

Using 8-aminoquinoline as the aniline source allowed access to the ligand (*E*)-2-*tert*-butyl-6-[(quinoline-8-ylimino)methyl]-phenol. Conversion to the thallium salt and subsequent treatment with [TiCl₄] afforded the red complex **19** (Fig. 11). The molecular structure was confirmed as distorted octahedral, with *mer* chlorines and a tridentate ligand binding *via* the phenolate oxygen and the imine and quinoline nitrogen atoms.³⁰

Using MAO (Ti/Al = 100) as co-catalyst and an ethylene pressure of 6 bar, yielded 1.2 g polyethylene over 1 h (for [Ti] = 30 μmol), though with a molecular weight distribution of 24, this was not considered single site catalysis. The rather broad distribution was attributed to the presence of the imine bond, which is known to be susceptible to either reduction or alkyl migration *via* the co-catalyst.

In the case of propylene polymerization, the use of MAO as co-catalyst at 50 °C afforded stereoregular and regioregular polypropylene ([*mm*] = 40%, [*mr*] = 34%, [*rr*] = 26%). At 25 °C, 50% of isotactic triads ([*mm*] ~ 50%) were obtained. Extraction of the crude polymer into hexane produced an insoluble isotactic component (80%), together with some insoluble stereoirregular material (20%). Analysis (¹³C NMR spectroscopy) of the soluble fraction revealed mostly blocks of *m* diads bridged by *rr* triads. Less intense resonances were also present, which could be attributed to a regioirregular structure, with a *threo* arrangement of adjacent methyls. Much weaker (*ca.* 10% *cf. threo*) signals due to *erythro* adjacent methyls were also evident. These results were consistent with primary (1,2) and secondary (2,1) insertions operating with the same enantioface selectivity.

At -20 °C, a more homogeneous product was obtained, and indeed all the crude polymer was insoluble in hexane. The ¹³C NMR spectrum revealed a microstructure similar to that observed for the hexane insoluble component at 25 °C with regio-inversions of 5%.

¹H NMR spectroscopic experiments between **19** and dried MAO (Al/Ti = 50) showed resonances attributable to both [LTi(CH₃)₃] and [LTi(CH₃)₃]⁺ in a ratio of 10:1 at 5 min.

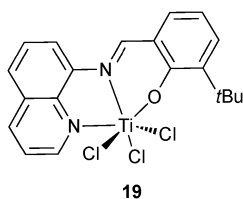


Fig. 11 Complex **19**.

After 10 min, only the cationic species was observed. Similar experiments using Me₃Al (Al/Ti = 50), initially (5 min) revealed only the cationic species, but after 30 min, a second species had appeared with very similar resonances, which was dominant after 1 h. These results, combined with the unusual microstructure found for the polypropylene, suggested that the active species formed were not simple, and that the ligand set was not completely dissociated from the metal.

Aryliminoquinolin-8-olate complexes bearing an ethyl group in the backbone have also been prepared, which on reaction with [TiCl₄(THF)₂], afforded *mer*-complexes **20**, see Fig. 12. Such complexes were shown to be active for ethylene homo-polymerization, as well as co-polymerizations involving ethylene with 1-hexene or 1-octene. The catalytic activity could be enhanced by employing bulky, electron donating alkyl substituents on the N-bound aryl ring.³¹

The series of trichlorotitanium (2-pyridin-2-yliminomethyl)-phenolates **21** (Fig. 13) has been prepared in moderate to good yields (49–86%) *via* the reaction of [TiCl₄(THF)₂] and the potassium salts of the parent ligands.³² Representative molecular structures were determined and confirmed the expected pseudo octahedral geometry at titanium. Good activities (≤ 531 g mmol⁻¹ h) were achievable for ethylene polymerization using MAO as co-catalyst (Al/Ti 5000) at 10 bar ethylene. Such systems exhibited thermal stability with optimum observed activities achieved at 50 °C. Activities for ethylene/1-hexene co-polymerizations were much lower (58–287 g mmol⁻¹ h), but the polymers formed were of high molecular weight (*M_w*–225 000–538 000. Molecular weight distributions (*M_w*/*M_n*) were broad (6.4–10.8), which was thought to be associated with the configurational instability of the pyridyl-containing titanium metallocycle. A 3.28 mol% incorporation of 1-hexene was achieved when using 1.0 mol L⁻¹ 1-hexene. Observed activities for ethylene/1-octene co-polymerizations were higher (233–712 g mmol⁻¹ h), but with lower molecular weight (168 000–285 000) polymers formed. Molecular weight distributions and the degree of co-monomer incorporation was similar to that observed with 1-hexene.

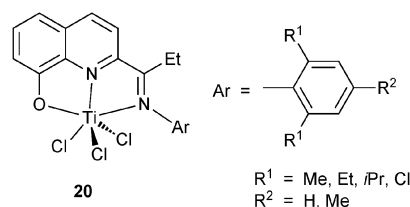


Fig. 12 Aryliminoquinolin-8-olate complex **20**.

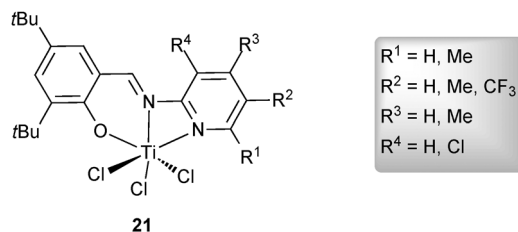


Fig. 13 (2-pyridin-2-yliminomethyl)phenolates of titanium.

2.7 Complexes based on O,O,N-imine ligands

Fujita *et al.* have recently extended their family of FI catalysts to include the use of tridentate phenoximine ligands, which bear either an additional *ortho* alkoxide or aryloxy donor group.³³ Treatment of such ligands with [TiCl₄] afforded the respective trichloride complexes **22** (Fig. 14) in varying yields, *viz* OPh, R = cumyl (27%); OMe, R = cumyl (59%); OMe, R = adamantyl (82%). A crystal structure of the Z = OMe, R = adamantyl derivative confirmed the distorted octahedral geometry at titanium with *fac* tridentate ligation.

Catalytic screening of **22** (Z = OPh, R = cumyl) using MAO as co-catalyst (Al/Ti = 10 000) under 8 bar ethylene afforded 1-hexene and polyethylene in 76.6:23.4 wt%, with an activity of 2.4×10^2 g mmol⁻¹ h. Under the same screening conditions, the use of **22** (R = cumyl), containing a donor OMe group, led to higher selectivity for 1-hexene (86.2 wt%), and with a much increased activity (6.6×10^3 g mmol⁻¹ h). This behaviour quite nicely illustrated how simple variation of the donor group can drastically effect the catalytic performance – in this case producing a highly active and selective trimerization catalyst. It was thought that the donor OMe group played a vital role in stabilizing the proposed Ti(II) intermediates; DFT calculations indicated a shorter Ti–OMe distance (2.31 Å *vs.* 2.43 Å for Ti–OPh).

We note that Ladipo *et al.* had earlier used tridentate phenoxyimines, incorporating a 2-C₆H₄O moiety (as in **10**), which on treatment with varying amounts of [TiCl₄] or [TiCl₄(THF)₂] led to the either mono- or bis(chelate) complexes. However, no polymerization data were presented for these particular complexes.³⁴

A benzimidazolyl group can also be appended to a phenoxyimine-type framework, such as in the ligand **IXH** (Fig. 15). Treatment with NaH, followed by [TiCl₄(THF)₂], yielded the expected trichloride complex **23** (Fig. 15, bottom left). Ligand **IXH** could also be reduced to the secondary amine **XH** (Fig. 15, top right) by reaction with *tert*-butyllithium, followed by aqueous work-up.³⁵

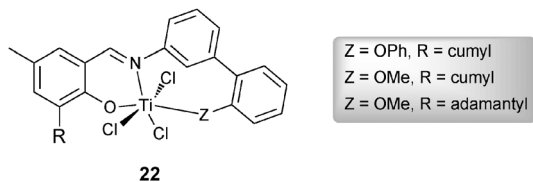


Fig. 14 Tridentate FI pre-catalysts.

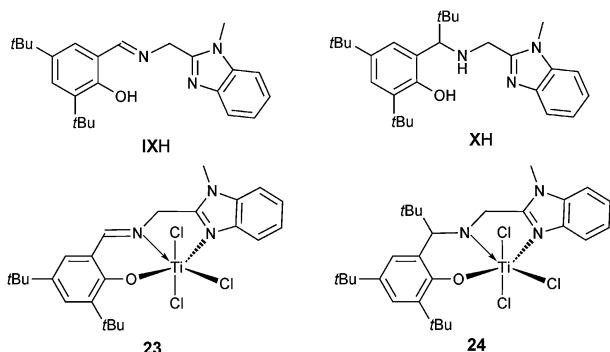


Fig. 15 Benzimidazolyl-containing phenoxyimines of titanium.

Treatment of **XH** with [TiCl₄(THF)₂] led to the trichloride **24** (Fig. 15, bottom right). The change of the hybridization of the nitrogen in the ligand backbone [sp³ in **24** *cf.* sp² in **23**] led to a marked conformational change in the *mer* bound tridentate ligands. Neither complex though produced any polymer (at 25 °C) when MAO (Al/Ti 500) was employed as co-catalyst. Complex **24**, however, did afford an activity of 150 g mmol⁻¹ h bar when Al(*i*Bu)₃/dry MAO was used as co-catalyst at 25 °C; the activity fell to 133 g mmol⁻¹ h bar at 50 °C. In each case, the polymer product produced had *M*_w ~ 500 000 g mol⁻¹, but with very broad molecular weight distribution (47.9 at 25 °C and 23.2 at 50 °C).

2.8 Complexes based on N,N,S ligands

The four or five-coordinate complexes **25** and **26** (Fig. 16), reported by Jin *et al.*, were available in high yield (≥ 78%) by reaction of the parent aniline arylamide arylsulfide ligands with TiCl₄. The formation of type **25** or **26** complexes was dependant on the bulk of the aniline group employed.

In the presence of MAO (Al/Ti = 1000) at 20 °C, the activity was found to be in the order 2,6-*i*Pr₂C₆H₃ (1250 g mmol⁻¹ h) > 2,4,6-Me₃C₆H₂ (600 g mmol⁻¹ h) > C₆H₅ (250 g mmol⁻¹ h). The optimized activity (1500 g mmol⁻¹ h) for the 2,6-*i*Pr₂C₆H₃ derivative **26** was achieved at 40 °C using 1000 equiv. MAO.³⁶

2.9 Complexes based on N,C,N ligands

The bimetallic *i*PrPheBox (2,6-bis(4'-isopropyl-2'-oxazolinyl)-phenyl) gold complex **27** (Fig. 17, left) readily undergoes transmetallation reactions. In the case of titanium, reaction with two equiv. of [TiCl₃(O*i*Pr)] in THF, the complex **28** (Fig. 17, right) was isolated in 73% yield. The distorted octahedral geometry at titanium was confirmed by X-ray diffraction.

Although this complex proved to be inactive as a homogeneous catalyst, when immobilized on an MgCl₂ support, in the presence of either *i*Bu₃Al or Et₃Al, high activity (*e.g.*, 4600 g mmol⁻¹ h bar at 50 °C) was observed. The polyethylene

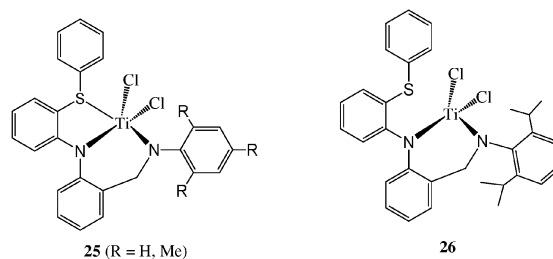


Fig. 16 Complexes **25** and **26**.

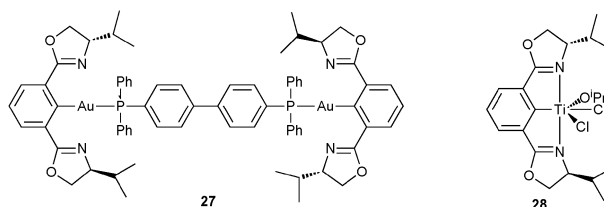


Fig. 17 N,C,N pincer complexes of gold and titanium.

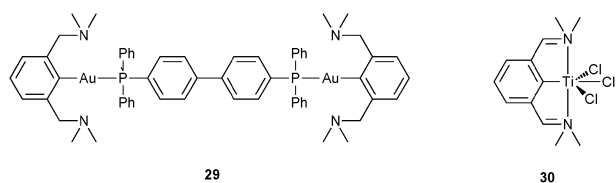


Fig. 18 Dimethylamino N,C,N pincer complexes of gold and titanium.

polymer formed had a molecular weight (M_w) of 1 400 000. Co-polymerization with 1-hexene led to a decrease in activity (down to 3900 g mmol⁻¹ h bar at 50 °C), as well as a decrease in polymer molecular weight (M_w = 870 000). Polydispersities were somewhat narrower for the co-polymerization runs, for example 2.3 *versus* 3.1 at 50 °C. However, the incorporation of the co-monomer was poor, with data suggesting only 0.1 and 0.2 mol% incorporation at 50 and 70 °C, respectively.³⁷

Similar use of the related gold complex **29** (Fig. 18, left) with TiCl₄ led to the isolation of the titanium trichloride complex **30** (Fig. 18, right) in 83% isolated yield. Under 10 bar ethylene pressure at 50 °C, in the presence of MAO, an activity of 110 g mmol⁻¹ h bar was achieved. As in the case of **26**, immobilization on an MgCl₂-based support, in the presence of *i*Bu₃Al, led to increased (by two orders of magnitude) activity. Activities as high as 35 400 g mmol⁻¹ h bar were achievable at 70 °C, though broad M_w/M_n values suggested it was not single site catalysis. High activities ($\leq 23\,200$ g mmol⁻¹ h bar) were also possible for ethylene/1-hexene co-polymerizations, but again M_w/M_n values were broad (≤ 7.1).³⁸

2.10 Bis(aryloxide)s with one additional donor

The pyridine bis(phenolate) ligand set **XIH₂** (Fig. 19, top), employed by Chan *et al.*, can be viewed as a pyridylphenolate bearing an additional phenoxide arm.³⁹ Treatment of **XIH₂** with [TiCl₄(THF)₂] afforded the dark-red, highly crystalline complex [Ti(**XI**)Cl₂(THF)] (**31**, Fig. 19, left). X-ray crystallography confirmed the molecular structure as pseudo octahedral at the metal with *mer* tridentate ligation.

Use of a related unsymmetrical naphthyl ligand set afforded the complex **32** (Fig. 19, right). In the presence of MAO, at 1 °C, both complexes were active (4.4×10^3 and 1.8×10^3 g mol⁻¹ h bar, respectively) for ethylene polymerization. Given that no polymerization took place when THF was

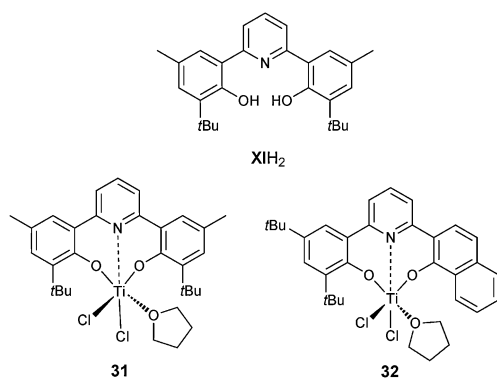


Fig. 19 Ligand **XIH₂** and complexes **31** and **32** reported by Chan *et al.*³⁹

employed as solvent, the presence of the bound THF in **31** and **32** may well be detrimental to the catalysis.

Non-symmetrical fluorine functionalized 2-(2'-hydroxyphenyl)-6-arylpyridine ligands of the type **XIIH** (Fig. 20, top) were accessible *via* the sequential coupling of two substituted acetophenones. Treatment at 25 °C with [Ti(Bn)₄] afforded the red cyclometalated complexes [Ti(**XII**)Bn₂] (**33**, Fig. 20, bottom), *via* a highly regioselective process. Molecular structures of **33** ($R^1 = R^2 = CF_3$, $R^3 = H$; $R^1 = CF_3$, $R^2 = H$, $R^3 = F$; $R^1 = F$, $R^2 = CF_3$, $R^3 = H$) revealed a trigonal bipyramidal geometry at titanium, and η^2 -benzyl ligands that pointed outwards in an unusual *anti*, *anti* configuration. Given the long Ti–F separations (>3.15 Å), the C–H...F–C coupling observed by NMR spectroscopy was not due to M–F coordination. Neutron diffraction studies shed further light on such C–H...F–C interactions (see zirconium section).

In terms of polymerization catalysis, type **33** complexes were found to be highly active (≤ 4460 g mmol⁻¹ h) for ethylene polymerization in the presence of low co-catalyst (MAO) loadings (Al/Ti = 250). The polyethylene product was of high molecular weight ($M_w > 3\,000\,000$). For ethylene/propylene co-polymerizations, the system **33** ($R^1 = F$, $R^2 = CF_3$, $R^3 = H$)/MAO exhibited higher activity than did **33** ($R^1 = R^2 = CF_3$, $R^3 = H$)/MAO, with higher co-monomer incorporation, 40 mol% *cf.* 17 mol%, respectively. Such behaviour was thought to be due to the increased space available at the metal centre when in close proximity to F *vs.* CF₃. Use of *i*Bu₃Al/Ph₃CB(C₆F₅)₄ as co-catalyst led in general to lower activities as well as lower co-monomer incorporation. In ethylene/norbornene co-polymerizations, similar activity trends for type **33** pro-catalysts were noted, with high molecular weights being obtained in all cases. The complex **33** ($R^1 = F$, $R^2 = CF_3$, $R^3 = H$) with either co-catalyst, afforded elastomers with high norbornene incorporations of 19.4 and 20.0 mol%, respectively.⁴⁰

The cyclometallated methodology was extended to the non-fluorinated ligand sets **XIIH** (Fig. 21). When R^1 was either Cl or Br, favourable electronics (electron withdrawing) and sterics led to high activities (*versus* R^1 = methyl). However, activities for ethylene polymerization were slightly lower than those previously observed for the fluorinated systems.⁴¹

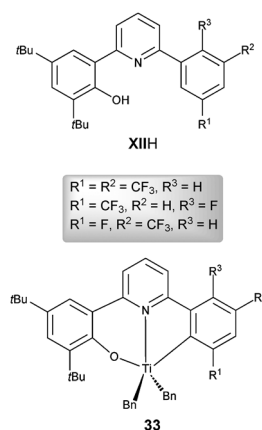


Fig. 20 Fluorinated 2-(2'-hydroxyphenyl)-6-arylpyridine ligands **XIIH** and titanium complexes **33**.

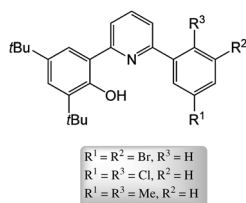


Fig. 21 Non-fluorinated ligand sets XIIIH.

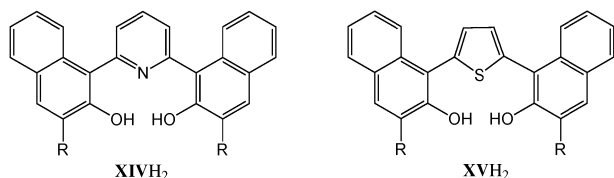


Fig. 22 Bis(naphthoxy)pyridine and bis(naphthoxy)thiophene ligands XIVH₂ and XVH₂.

Bis(naphthoxy)pyridine and bis(naphthoxy)thiophene ligands of the type XIVH₂ and XVH₂ (Fig. 22) were reacted with either [Ti(Bn)₄] or [Ti(O*i*Pr)₄] to afford complexes of the form [Ti(XIV/XV)(X)₂] (for XIV: R = SiPh₃, X = Bn (**34**); R = SiPh₃, O*i*Pr (**35**); R = SiMe₂*i*Bu, X = Bn (**36**); for XV: R = SiPh₃, X = Bn (**37**)) in good to excellent yields (65–95%). Both **34** and **36**, in the solid-state, were found to incorporate *rac*-like binding of the ligand set, whereas in solution, variable temperature ¹H NMR studies revealed both *rac* and *meso* stereoisomers. For **34**, catalytic screening using MAO (1000 equiv.) as co-catalyst led to an observed activity of *ca.* 240 g mmol^{−1} h bar for polyethylene production, and the polymer produced had a bimodal distribution. Activities about an order of magnitude greater were achievable using [Ph₃C](B(C₆F₅)₄)/Al(*i*Bu)₃ (3:200), and the product formed has a monomodal distribution and a melting point in the range 134–140 °C; in the case of propylene (at 50 °C), the system was inactive. For **36**, similar use of [Ph₃C](B(C₆F₅)₄)/Al(*i*Bu)₃ led to a slightly higher activity (2360 g mmol^{−1} h bar). Again, this system was inactive when deployed in propylene polymerization; use of dried MAO also led to inactivity. The thiophene-based complexes were inactive for both ethylene and propylene using either MAO or [Ph₃C](B(C₆F₅)₄)/Al(*i*Bu)₃ as co-catalyst, highlighting the important influence played by the bridging heteroatom.⁴²

Another pyridine bis(alkoxide) was earlier reported by Mach and Eisen. Complex **38** (Fig. 23) was shown, in the presence of MAO (Al/Ti = 4,700, 20 °C, 1 bar), to be effective for the polymerization of either ethylene or propylene, albeit with low activity. In the case of the poly(propylene), ¹³C NMR spectroscopic data was consistent with chain termination by β-hydrogen elimination.⁴³

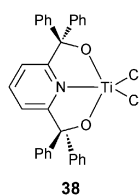


Fig. 23 Pyridine bis(alkoxide) complex **38**.

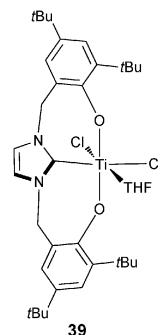


Fig. 24 Bis(aryloxy) carbene complex **39**.

Kawaguchi *et al.* have incorporated a carbene between two aryloxy moieties, and the resulting ligand on further treatment with [TiCl₄(THF)₂] (at −78 °C) afforded the dichloride complex **39** (Fig. 24).⁴⁴ In **39**, the tridentate ligand binds in *meridional* fashion, as confirmed by X-ray crystallography. In the presence of MMAO (Al/Ti = 1000), an activity of 290 g mmol^{−1} h bar was achieved for ethylene polymerization at 30 °C and 9 bar. Polymer characteristics were reported as *M*_n = 3.98 × 10⁴, *M*_w/*M*_n = 4.5 and *T*_m = 135 °C.

Phosphorus-bridged ligands have also been utilized as ancillary ligands in titanium-based ethylene polymerization. For example, the ligand set XVIIH₂ (Fig. 25, top left), on treatment with excess of *n*BuLi followed by [TiCl₄(THF)₂], afforded the complex **40** (Fig. 25, top right) in 45% yield. Use of the precursor to XVIIH₂, namely XVII (Fig. 25, bottom left), and subsequent reaction with [TiCl₄], afforded the THF-free complex **41** (Fig. 25, bottom right) in 60% yield. Similarly, the incorporation of other phosphorus bound substituents allowed for access to the THF-free complexes of type **41** (R = *i*Bu, C₆H₄-2-CH₂NMe₂, C₆F₅). Such complexes were screened for their ability to polymerize ethylene in the presence of either MMAO or TIBA as co-catalyst. Activities were high, with the pre-catalysts bearing the fluorophenyl and dimethylaminobenzyl substituents performing the best with activities of 36.2 and 59.9 × 10³ g mmol^{−1} h, respectively with MMAO and 8.8 and 49.0 × 10³ g mmol^{−1} h, respectively with TIBA. In the case of TIBA, polymers with narrow molecular weight distributions were formed (*M*_w/*M*_n = 2.0 and 2.7, respectively).

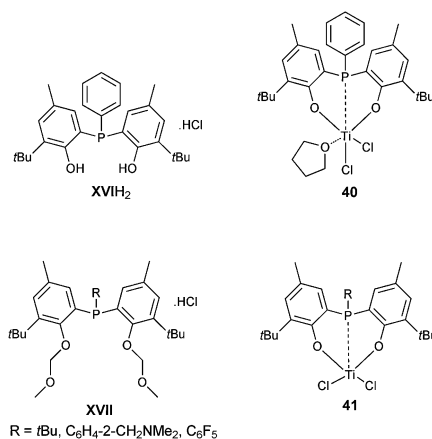


Fig. 25 Phosphorus bridged aryloxy ligands and complexes.

The polymer molecular weight generated by **41** ($R = C_6H_4-2-CH_2NMe_2$) was in excess of 1 000 000, suggesting that the side-arm possessing the nitrogen donor played a role in inhibiting β -elimination. Scaling up the polymerization by using a 300 ml autoclave gave similar impressive activities.⁴⁵

2.11 Bis(aryloxide)s with two additional donors

Work by Kol *et al.* has shown that the presence of an extra amine donor in the side-arm in ligands of the type **XVIIIH₂** (Fig. 26, left) can dictate the nature of the particular complex formed.⁴⁶ In this particular case, the ligand on reaction with $[Ti(OiPr)_4]$ can form either a homoleptic $[L_2Ti]$ complex or an $[L_2Ti(OiPr)_2]$ type complex **42** (Fig. 26, right), depending on which side-arm is built into **XVIIIH₂**.

The pseudo octahedral geometry at titanium was confirmed by X-ray crystallography, and revealed that the isopropoxides were predisposed (*cis*) for α -olefin polymerization catalysis.

Such complexes could readily be converted to dibenzyl complexes such as **43** (Fig. 27, top left) in excellent yields (90%) *via* reaction with Me_3SiCl and then benzyl Grignard.⁴⁷

Alternatively, such complexes could be made in 'one-pot' starting with the parent ligand. The molecular structure of **43** possessed *cis* benzyl groups with a C–Ti–C angle *ca.* 89°. Complex **43** was screened for its ability to polymerize 1-hexene in the presence of $B(C_6F_5)_3$ at ambient temperature. An activity of 30 g mmol^{−1} h was observed, and the polymer isolated had a molecular weight (M_w) of 14 000. Both the narrow PDI recorded (1.18) and the linear time dependence of M_n were suggestive of a living system. By contrast, use of the system containing the non-coordinating alkyl arm, afforded a system with higher activity (56 g mmol^{−1} h), but which yielded a 'polymer' of low molecular weight (M_w 1500). Furthermore, the associated characteristics of this catalysis were not consistent with a living system.

If a methoxy arm is deployed, as in the complex **44** (Fig. 28, top right), then exceptionally high molecular weight poly(1-hexene) was attainable upon activation with $B(C_6F_5)_3$.⁴⁸

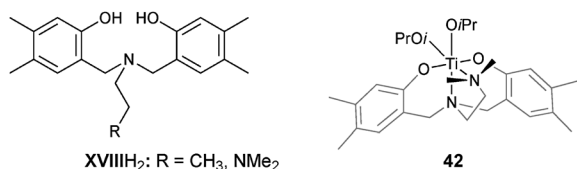


Fig. 26 Ligand **XVIIIH₂** and titanium complex **42**.

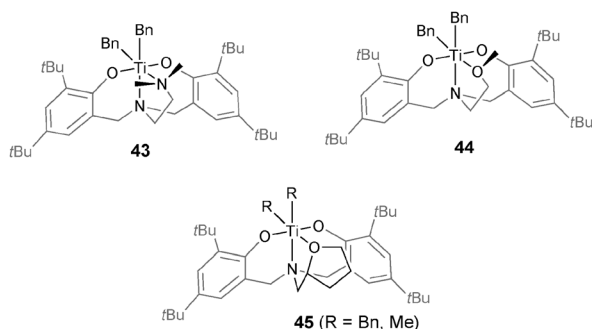


Fig. 27 Dialkyl 'Kol' type complexes.

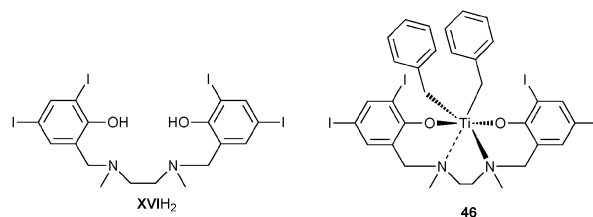


Fig. 28 Diiodosalan ligand **XIXH₂** and complex **46**.

Using neat 1-hexene at ambient temperature, typical activities were observed in the region of 20–35 g mmol^{−1} h, and as a consequence of the long polymerization time (31 h) for which the system exhibited living behaviour, the system was described as being 'immortal'. Such living/immortal behaviour was maintained at 40 °C (in chlorobenzene), but at temperatures above 55 °C, the PDIs began to broaden. The system was also capable of the block co-polymerization of α -olefins at ambient temperature. The system which was reported involved the co-polymerization of 1-hexene with 1-octene, which under the conditions employed, led to an atactic polymer having M_n 11 000 and M_w/M_n 1.2.

It also proved facile to introduce a side-arm containing a THF moiety.⁴⁹ The titanium complex **45** (Bn) was available *via* reaction of the parent ligand with $[TiBn_4]$ in good yield (75%). In the molecular structure, the Ti–O bond length of 2.26 Å was shorter than anticipated for a methoxyalkyl donor. The analogous dimethyl titanium complex **45** (Me) was available in 50% yield *via* reaction of the parent ligand with $[TiCl_4(THF)_2]$ in the presence of Et_3N , followed by subsequent treatment with two equiv. of $MeMgBr$. For 1-hexene polymerization, the dibenzyl complex **45** (Bn) was moderately active (12 g mmol^{−1} h) upon activation with $B(C_6F_5)_3$ in neat 1-hexene. The polymerization was living, and after 48 h, a polymer with a molecular weight (M_w) of 316 000 and M_w/M_n 1.05 could be isolated. The dimethyl complex **45** (Me) exhibited rapid activation, but without the PDI broadening which was exhibited for the dibenzyl system. Under high dilution conditions, the system was living for six days (*i.e.*, immortal), and the polymer isolated had molecular weight (M_w) 816 000 and M_w/M_n 1.09. The dibenzyl system was also capable of the block co-polymerization of 1-hexene with 1-octene.

Use of electron withdrawing chloro groups on the aryl rings, rather than alkyl groups, led to enhanced activity (> 1000 g mmol^{−1} h) for the NMe_2 -containing dibenzyl systems, but not for those bearing the OMe side-arm. The polyethylene obtained using such a chlorinated ligand set was atactic and of ultra-high molecular weight ($M_w > 4 000 000$). Oscillatory rheometry and stress relaxation experiments indicated that the polymer exhibited elasticity at ambient temperature.⁵⁰

Kol *et al.* had previously shown that the use of diaminebis(phenol) ligands bearing alkyl substituents, in combination with zirconium (see section 3), led to low activity catalysts for 1-hexene polymerization. On extending such studies to titanium, the alkyl substituents were replaced with electron withdrawing chloro substituents (at the 3,5-positions). Activation of the dibenzyl complex, formed on treatment of the parent ligand with $[Ti(Bn)_4]$, with 1.2 equivs. of $B(C_6F_5)_3$, afforded a highly active system. Typically, in neat 1-hexene at

ambient temperature, activities were of the order of $200 \text{ g mmol}^{-1} \text{ h}$, affording ultra-high molecular weight (M_w 1 900 000 after 19 h) polymer, which was isotactically enriched [$mm \sim 60\%$]. This and further evidence from ^{13}C NMR spectroscopy, which suggested that the symmetry of the complex (*fac, fac*-isomer identified by ^1H NMR spectroscopy; 'wrapping' mode of the ligand confirmed by X-ray crystallography for dipropoxy analogue) was responsible for the polymer microstructure, rather than the last inserted monomeric unit. Reducing the temperature to 0°C , did not affect the isotacticity.

Use of the bulkier 3,5-dibromo ligand set was also explored, and it was found that this too yielded a highly active system. In fact, activities were somewhat higher, typically $400 \text{ g mmol}^{-1} \text{ h}$ at ambient temperature. Furthermore, polymer molecular weights had increased, for example $M_w \sim 4\,000\,000$ at 19 h, and with increased stereochemical control [$mm \sim 80\%$]. The origin of the high activity in such systems was mostly due to their electron deficiency; related complexes bearing only methyl groups at the 3,5-positions possessed low activity, but with high isospecificity [$mm \sim 90\%$].⁵¹

Diiodosalan-type ligands (see **XIXH₂**, Fig. 28, left) were also synthesized, the dibenzyl complexes prepared (*via* $[\text{Ti}(\text{Bn})_4]$), and polymerization of both propylene and 1-hexene was explored. Upon activation with $\text{B}(\text{C}_6\text{F}_5)_3$, the complex $[\text{Ti}(\text{XIX})(\text{Bn})_2]$ (**46**, Fig. 28, right), which was fairly unstable in solution, exhibited an activity of $1500 \text{ g mmol}^{-1} \text{ h}$, affording a polymer with molecular weight 410 000 and with M_w/M_n 1.4. ^{13}C NMR spectroscopic analysis suggested that an enantiomorphic site control mechanism was in operation. This postulation was based on the isolation of a polymer with high isotacticity, [$mmmm$] 87%, and with only an *mrrm* pentad as well as *mmmr*/*mmrr* overlap with *mmmm* as the only impurities.⁵²

Polymerization of propylene using MAO as co-catalyst $[\text{Al}/\text{Ti} = 500]$ was initially conducted *via* cryogenic condensation of propylene into the reactor vessel. Whilst the use of this technique did not allow for activity calculations, it was found that the resulting polymer was of high isotacticity with [$mmmm$] at 80%. Data was again suggestive of an enantiomorphic site control mechanism operating, whilst the white crystalline polymer isolated was of ultra-high molecular weight ($M_w > 1\,000\,000$).

Using a more conventional approach, *i.e.*, passing propylene through a toluene solution of **40** (generated *in situ*) and MAO ($\text{Al}/\text{Ti} = 500$) at ambient temperature (27°C) and 1 bar, an activity of $390 \text{ g mmol}^{-1} \text{ h}$ was achieved with M_n 157 000 and M_w/M_n 1.12. At 50 min, M_n was 240 000 with only a slight broadening of the polydispersity values, which indicated good control. The isoselectivity of the polymers under these conditions reached [$mmmm$] 82%, with melting transitions in the range $120.9\text{--}123.8^\circ\text{C}$. X-Ray powder diffraction of the polymer indicated the presence of only the α -form of the isotactic PP.⁵²

Salalen-type ligands, which can be viewed as hybrids comprising half-salan/half-salen, preferentially adopt *fac-mer* binding at the metal. With this in mind, the family of salalen ligands **XXH₂** (Fig. 29, left) bearing alkyl substituents (R^1, R^2) on the phenolate ring nearest the imine-bond, and halides (R^3) on the phenolate ring nearest the amine, was prepared. Further reaction with either $[\text{Ti}(\text{Bn})_4]$ or $[\text{Ti}(\text{O}i\text{Pr})_4]$ gave the

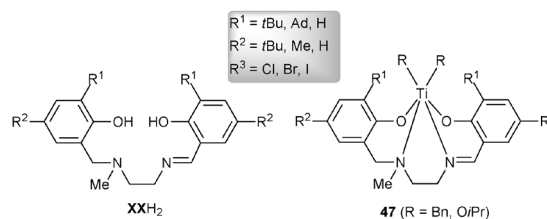


Fig. 29 Salalen ligands and zirconium complexes.

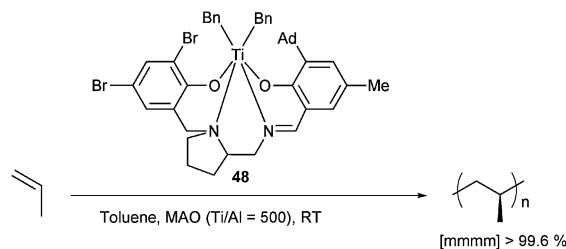
C_1 symmetric complexes $[\text{Ti}(\text{XX})(\text{R})_2]$ (**47**: $\text{R} = \text{Bn}, \text{O}i\text{Pr}$ —Fig. 29, right), respectively. The structure of the isopropoxide derivative was determined by X-ray crystallography, and confirmed the *fac-mer* binding mode for the Salalen ligand set.⁵³

1-Hexene polymerization using the complexes (activated with $\text{B}(\text{C}_6\text{F}_5)_3$ for which $\text{R}^1 = \text{R}^2 = t\text{Bu}$, occurred with only moderate activities ($4.5\text{--}18 \text{ g mmol}^{-1} \text{ h}$), but with narrow molecular weight distributions ($M_w/M_n \sim 1.04$), *i.e.*, a living process. However, it appeared that the pre-catalyst had only undergone partial activation, as the high molecular weights obtained ($M_w = 360\,000\text{--}390\,000$) were far in excess of the calculated values ($M_{\text{calc}} = 9300\text{--}48\,000$). The size of the halide (R^3) present played a crucial role in determining the isotacticity. ^{13}C NMR spectroscopic experiments revealed [$mmmm$] = 63% for Cl, 79% for Br and 94% for I. Interestingly, variation of the size of the substituents in the other phenolate ring (*tBu* *versus* adamantyl or H) had little effect on the isotacticity, and so, under the conditions employed, were not important stereo-directors.

It also proved possible to utilize the dibenzyl systems (**47**) for propylene polymerization, using MAO ($\text{Ti}/\text{Al} = 500$) as co-catalyst. The *tBu*-bearing ligand set afforded crystalline, highly isotactic polypropylene with [$mmmm$] in the range 90–96% (by ^{13}C NMR spectroscopy). Use of $\text{R}^1 = \text{adamantyl}$ gave [$mmmm$] $\geq 99\%$, whereas for $\text{R}^1 = \text{R}^2 = \text{H}$, stereoirregular polypropylene was mostly formed.

The high isotacticities noted for the propylene runs *versus* 1-hexene, particularly in the case of the adamantyl system, were unexpected, and so with this in mind, polymerization of 1-hexene was also conducted using MAO ($\text{Ti}/\text{Al} = 500$) as co-catalyst. In this case, activities were high ($\leq 11\,700 \text{ g mmol}^{-1} \text{ h}$), and except for the $\text{R}^1 = \text{R}^2 = \text{H}$ system, in all cases higher [*cf.* $\text{B}(\text{C}_6\text{F}_5)_3$] isotacticities were achieved ([$mmmm$] 76–96%). Impressively, 50 equiv. of MAO was enough to generate a highly active ($600 \text{ g mmol}^{-1} \text{ h}$) system using the adamantyl ligand set.

In the case of propylene, even higher isotacticities proved possible using the complex **48**, which possessed a backbone comprised of an aminomethylpyrrolidine (see Scheme 2).⁵³



Scheme 2 Highly isotactic polypropylene *via* the aminomethylpyrrolidine-based system **48**.

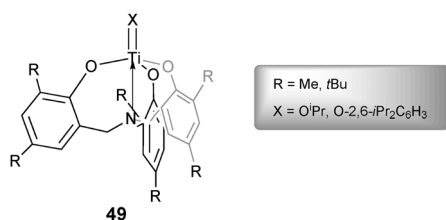


Fig. 30 Triaryloxoamine titanium complex **49**.

2.12 Other ligand sets

Nomura *et al.* have employed complexes of the type **49** (Fig. 30), containing a triaryloxoamine ligand, to polymerize ethylene. The co-catalyst used was dried MAO, from which residual Me_3Al had been removed. High activity was observed at high temperature, for example $241 \text{ g mmol}^{-1} \text{ h}$ at 100°C in toluene, when using $\text{R} = \text{Me}$, $\text{X} = \text{OiPr}$ and $\text{Al/Ti} = 500$. The activity could be further increased by increasing the amount of co-catalyst used ($\leq 40\,000$ equiv.). At lower temperatures ($\leq 80^\circ\text{C}$), activities were low ($< 62 \text{ g mmol}^{-1} \text{ h}$). The system $\text{R} = \text{tBu}$, $\text{X} = \text{OiPr}$ displayed the highest activity at 100°C ($1850 \text{ g mmol}^{-1} \text{ h}$). Use of octane rather than toluene as solvent allowed for increased activity at 120°C ($2290 \text{ g mmol}^{-1} \text{ h}$). The addition of small amounts (10 equiv.) of Me_3Al led to increased activity, for example $4740 \text{ g mmol}^{-1} \text{ h}$ at 120°C in octane. However, increased amounts (100 equiv.) of Me_3Al , led to a reduction in activity. Use of other co-catalysts such as Me_3Al ($\text{Al/Ti} = 100$), Et_2AlCl ($\text{Al/Ti} = 100$) or $\text{Et}_2\text{AlCl/Me}_3\text{Al}$ ($\text{Al/Ti} = 100:10:1$) led to only poor activities ($< 3 \text{ g mmol}^{-1} \text{ h}$). Similarly, the use of $\text{Al}(\text{iBu})_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_3$ ($\text{Al/B:Ti} = 250:1.5:1$) gave poor results ($< 50 \text{ g mmol}^{-1} \text{ h}$). Attempts to polymerize styrene yielded only negligible amounts of atactic polystyrene.⁵⁴

3. Zirconium complexes

3.1 Cp-containing systems

In the mid-1990s, Jutzi and Kleimeier prepared a number of group IV species bearing 'pendant' aminoalkylcyclopentadienyl ligand set. Amongst the complexes prepared was the zirconium complex **50** (Fig. 31), which was shown to possess a bound dimethylamino function.⁵⁵

In terms of catalysis, a number of Cp-bearing zirconium systems have shown promise, including as outline below (section 3.2), species bearing an additional tridentate ligand set. However, one other system also worthy of note was based on the tropidinyl ligand set **XXI** (Fig. 32, left).⁵⁶ Ligand **XXI** is isoelectronic with the Cp ligand, but with a split 4π (the allyl)

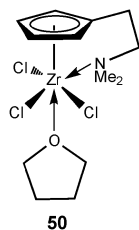


Fig. 31 DimethylaminoethylCp complex **50**.

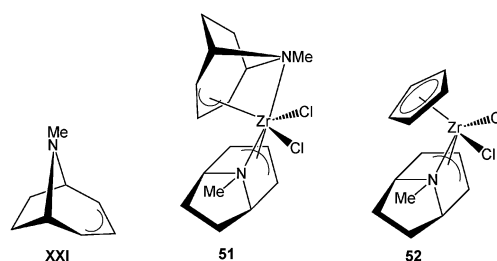


Fig. 32 Tropidinyl ligand **XXI** and complexes **51** and **52**.

and 2π (the amine) electron donor set. Zirconium complexes bearing either one or two such tropidinyl ligands, namely **51** (Fig. 32, middle) and **52** (Fig. 32, right), have been prepared. Each synthesis involved transmetallation of a stannylated allyl functionality with a zirconium halide, namely $[\text{ZrCl}_4]$ or $[\text{CpZrCl}_3]$.

Both **51** and **52**, in the presence of MMAO ($\text{Zr/Al} = 1000$), were active for ethylene polymerization, albeit with very different activities of 8 and $9860 \text{ g mmol}^{-1} \text{ h bar}$, respectively. Use of $\text{B}(\text{C}_6\text{F}_5)_3$, in combination with the dimethyl derivative of **52**, afforded an activity of $3750 \text{ g mmol}^{-1} \text{ h bar}$. Complex **52/MMAO** was also shown to oligomerize ($\text{C}_{12}\text{--C}_{27}$) propylene at 0°C .

Okuda *et al.* prepared and structurally characterized a family of zirconium complexes **53** bearing tridentate Cp-amido ligands (Fig. 33). The donor group can be OMe, NMe_2 or SMe, and in contrast to the related titanium complexes (see 7, Fig. 3), this donor group binds to the metal (axial position) to afford a trigonal bipyramidal geometry at zirconium.¹⁴

In the case of the OMe containing complexes, further treatment with either methylmagnesium chloride or *n*-butyllithium allowed for the isolation of the respective dialkyl complexes **53** ($\text{X} = \text{Me}$) and **53** ($\text{X} = n\text{-butyl}$) in good yields ($\geq 61\%$). NOE experiments revealed that there was intramolecular coordination of the side-arm. Such complexes were active for ethylene polymerization in the presence of MAO ($\text{Al/Zr} = 500$), generating high molecular weight polymer, for example $M_w = 970\,000$ for the *n*-butyl derivative.

The SMe containing complex **53** ($\text{D} = \text{SMe}$, $\text{X} = \text{Cl}$), when screened for ethylene polymerization, was found to be an order of magnitude less active than its titanium counterpart 7.

Doubly silylamido bridged Cp complexes **54** and **55** (Fig. 34) (analogues of 8 and 9, Fig. 4) have been screened for ethylene polymerization. For **54**, using MAO as co-catalyst and hexane as solvent, an activity of $7.4 \times 10^2 \text{ g mmol}^{-1} \text{ h bar}$ was achieved at 70°C and 4 bar ethylene, affording high molecular weight ($M_w = 5.4 \times 10^5$; $M_w/M_n = 1.9$) polymer. Co-polymerization of ethylene with 1-hexene proved possible (activity = $3.5 \times 10^2 \text{ g mmol}^{-1} \text{ h bar}$) using **54**, affording a

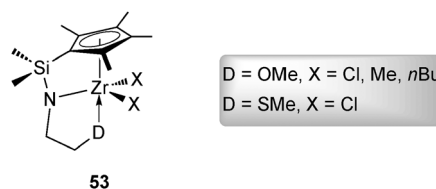


Fig. 33 Complexes of the type **53**.

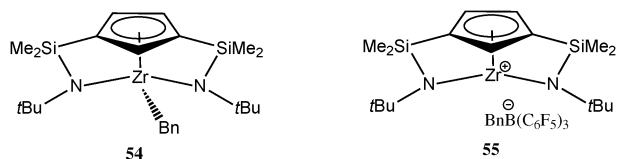


Fig. 34 Doubly silylamido bridged Cp complexes **54** and **55**.

polymer with $M_w = 4.1 \times 10^5$ with 0.7 mol% incorporation of 1-hexene. The alkyl-free complex **55** was also found to be capable of ethylene polymerization at ambient temperature and pressure.¹⁶

3.2 Cp containing Schiff base complexes

Huang *et al.* reported mono-Cp containing Schiff base complexes of the type $[\text{CpZrCl}(\text{THF})(2\text{-OMeC}_6\text{H}_4\text{N}=\text{CH})\text{C}_6\text{H}_4\text{O}]$ (**56**, Fig. 35, left). These yellow complexes were available, following work-up, in high yields ($\geq 67\%$) *via* treatment of the parent ligand with *n*BuLi in THF (-78°C), followed by the addition of $[\text{CpZrCl}_3(\text{DME})]$. The distorted octahedral molecular structure of **56** ($\text{R}^1 = \text{R}^2 = \text{H}$) was confirmed by X-ray diffraction, and a wide Cl–Zr–Cl angle of $151.71(3)^\circ$ was observed. As for titanium, prolonged heating of these systems (THF, 4h) led to loss of the methoxy group (as CH_3Cl) and formation of the zirconoxacycle $[\text{CpZrCl}(\text{THF})(2\text{-OC}_6\text{H}_4\text{N}=\text{CH})\text{C}_6\text{H}_4\text{O}]$ **57** (Fig. 35, right). Alternatively, **57** could be prepared from $[\text{CpZrCl}_3(\text{DME})]$ and the dilithium salt of the parent ligand; a THF ligand was retained in the product using either method.⁵⁷

In the presence of MAO ($\text{Zr}/\text{Al} = 2000$), systems **56** and **57** were active and thermally stable for ethylene polymerization. The wide Cl–Zr–Cl angle mentioned above was thought to be responsible for the lower activities compared to the system $[\text{Cp}_2\text{ZrCl}_2]/\text{MAO}$. Both the Cp and the Schiff base substituents were capable of influencing the activity of the system. For example, at 80°C , the system **56** ($\text{R}^1 = \text{R}^2 = \text{H}$) exhibited an activity two to three times higher than that observed for the other systems screened. Increasing the size of either R^1 or R^2 decreased the observed activity, though this had little effect on polymer weight. The lower activity of the zirconoxacycle **57** was attributed to the lack of chloride ligands (one *versus* two for the other complexes). Over the temperature range 30 to 80°C , lower temperatures afforded decreased activities, whereas the molecular weights (M_w) increased. ^{13}C NMR spectroscopic analysis of the polymer obtained at 70°C by **56** ($\text{R}^1 = \text{R}^2 = \text{H}$)/MAO showed it to be linear, whilst polymer formation occurred with unimodal molecular weight distribution. The system **56** ($\text{R}^1 = \text{R}^2 = \text{H}$)/MAO did not co-polymerize ethylene with 1-hexene, whereas the zirconoxacycle **57** exhibited high activity, albeit with low 1-hexene

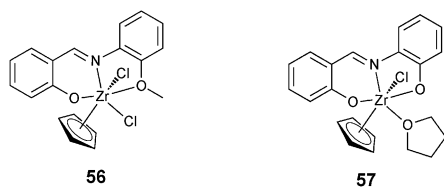


Fig. 35 Complexes **56** and **57**.

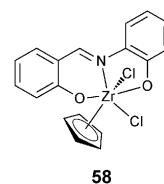


Fig. 36 Complex **58**.

incorporation (1.1%). These poor co-polymerization results reflected the less open environment around the zirconium centre.

Jin *et al.* also reported a zirconium complex $[\text{CpZrCl}\{(2\text{-OC}_6\text{H}_4\text{N}=\text{CH})\text{C}_6\text{H}_4\text{O}\}]$ (**58**, Fig. 36) analogous to the titanium complexes of the type **11**. The molecular structure was shown to be distorted octahedral, due to the presence of an additional THF donor (not present in the titanium complexes). In the presence of MAO ($\text{Al}/\text{Zr} = 1500$), the observed activity for **58** ($150\text{ g mmol}^{-1}\text{ h}$) was about twice that observed for the best of the titanium analogues.¹⁸

3.3 Complexes based on O,N,N-imine ligands

The quinoline-containing phenolate complex **59** (Fig. 37) can be prepared in the same way as the titanium complex **19** (Fig. 11), with which it is isostructural. At 25°C and 1 bar ethylene, combining **59** with a variety of co-catalysts afforded only poor activity. Under more robust conditions (50°C , 6 bar), the yield of polymer (linear by ^{13}C NMR spectroscopy) increased more than 10-fold. Hydrolysis of the catalytic system **59**/MAO afforded a mixture of ligands, including a reduced by-product containing an amine donor.

In propylene polymerization, the product obtained at 50°C (upon activation with MAO), possessed a stereoirregular [*mm*] 34%, [*mr*] 39%, [*rr*] 27% microstructure. At 25°C , the system was virtually inactive.³⁰

High throughput screening methodology of an ' 8×3 ' ligand library was used to identify which ligand sets might be capable of forming highly active 1-octene polymerization

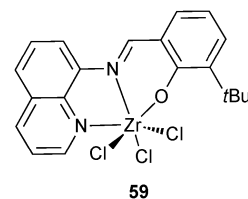


Fig. 37 Complex **59**.

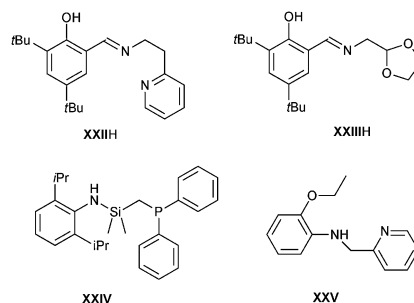


Fig. 38 Selected ligands employed in the ' 8×3 ' high throughput screening.

catalysts on combination with $[\text{Zr}(\text{Bn})_4]$, in the presence of a variety of co-catalysts including $[\text{Me}_2\text{PhNH}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{B}(\text{C}_6\text{F}_5)_3]$ in combination with either Et_3Al or $i\text{Bu}_3\text{Al}$. The library contained the ligand sets **XXIII**–**XXV** (Fig. 38), however, none of these, under the conditions employed, were identified as good catalysts candidates.⁵⁸

3.4 Other N,N,O ligands

(Quinolin-8-ylamino)phenolate and (quinolin-8-ylamido)-phenolate complexes of type **60** and **61** (Fig. 39) have been reported.⁵⁹ Complex **60** exhibited a distorted octahedral geometry, whilst **61** adopted a distorted trigonal bipyramidal geometry, as determined by DFT calculations. Polymerization screening using MAO as co-catalyst revealed only low activities ($<10 \text{ g mmol}^{-1} \text{ hr bar}$) for both **60** and **61**; the products were high molecular weight ($M_n = 328\,000$ – $627\,000$), linear ($T_m = 133.0$ – 142.6°C) polyethylenes. Complex **60** was also screened for propylene polymerization, in the presence of MAO, under 6 bar propylene. The product was mostly isotactic ($[\text{mm}]:[\text{mr}]:[\text{rr}] = 59:26:15$). Similar runs using higher olefins, namely 1-butene, 1-pentene or 1-hexene also resulted in mostly atactic polymer. The trend of increased amount of isotactic pentads with increasing size of monomer was noted, for example 50% for polypropylene *cf.* 98% for poly(1-hexene).

NMR experiments on **60** suggested that MAO deprotonated the monoanionic ligand set, thereby resulting in the formation of a common active species for both **60** and **61**.

3.5 Complexes based on N,O,N ligands

Tridentate diamido complexes have been reported by Schrock *et al.* Early work focussed on the $\text{R} = i\text{Bu}_{\text{d6}}$ ligand set, which when reacted sequentially with $[\text{Zr}(\text{NMe}_2)_4]$, MeI and MeMgI afforded the complex $[(\text{RNONR})\text{ZrMe}_2]$ (**62**, Fig. 40, left). On further treatment with $\text{B}(\text{C}_6\text{F}_5)_3$, it proved possible to isolate and crystallize the yellow complex $[(\text{RNONR})\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**63**, Fig. 40, middle). A molecular structure determination revealed that the borane had partially abstracted the apical methyl group $[\text{Zr}-\text{C} = 2.487(12) \text{ \AA}]$. Given that the $\text{Zr}-\text{O}$

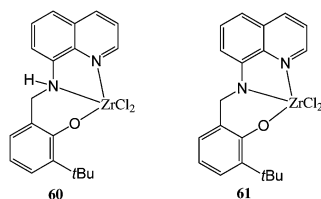


Fig. 39 (Quinolin-8-ylimino)phenolate and (quinolin-8-ylamido)phenolate complexes.

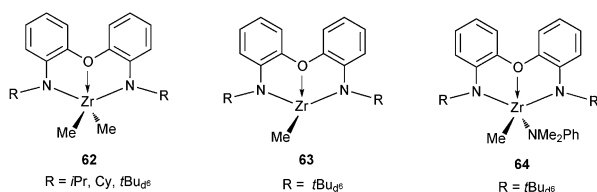


Fig. 40 Zirconium diamido complexes of the type **62**–**64**.

donor bond distance was $2.256(8) \text{ \AA}$, there was clearly a role here in terms of stabilizing the cationic metal centre.

^1H NMR spectroscopic data observed on treatment of **62** ($\text{R} = i\text{Bu}_{\text{d6}}$) with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ was consistent with dimethylaniline coordination at the metal, *i.e.*, $[(\text{RNONR})\text{ZrMe}(\text{PhNMe}_2)][\text{B}(\text{C}_6\text{F}_5)_4]$ (**64**, Fig. 40, right). Both **63** and **64** were shown to be capable of ethylene polymerization with activities of $\sim 10^2 \text{ g mmol}^{-1} \text{ h}$ and $8 \times 10^2 \text{ g mmol}^{-1} \text{ h}$, respectively. Complex **64** was also shown to be capable of 1-hexene polymerization, with an activity of $2 \times 10^2 \text{ g mmol}^{-1} \text{ h}$ ($M_n = 45\,000$), in near neat 1-hexene. Use of chlorobenzene as solvent at 0°C , led to increased polymer molecular weight, and the behaviour of the system was living for up to 1000 equiv. of 1-hexene. The poly(1-hexene) was atactic (by ^{13}C NMR spectroscopy).⁶⁰

^{13}C NMR spectroscopic experiments using a ^{13}C labelled methyl group at zirconium, carried out in bromobenzene- d_5 , were consistent with insertion of 1-hexene into the $\text{Zr}-\text{Me}$ bond in a 1,2 manner. Similar results were observed for 1-nonene.⁶¹

These five-coordinate dimethyl complexes and the borane activated species thereof, were able to adopt 'twisted'-type trigonal bipyramidal *fac* structures, in which the amido nitrogens were in equatorial positions, *i.e.*, inequivalent alkyl groups. Indeed, molecular structures ($\text{R} = i\text{Pr}$) confirmed the *mer* coordination of the NON ligand set, with the donor oxygen planar. The two R^1 groups were observed to equilibrate rapidly on the NMR timescale, even at low temperature (-80°C), and so it was proposed that the *fac* structure was in equilibrium with a *mer* structure (Fig. 41). Such a *mer* structure was thought to be of high energy for the $\text{R} = i\text{Bu}$, due to steric crowding (R vs. R^1). It was therefore proposed that living polymerization will occur if the 'twisted' *fac* structure was of lower energy. In the case of $\text{R} = i\text{Pr}$, Cy systems (cationic complexes which were only stable below 10°C), only slow oligomerization was observed ($\text{R} = \text{Me}$, 0°C , 50 equiv. 1-hexene, $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$), which was thought to be due to more facile β -elimination and the ability to 2,1 insert; the resultant less reactive insertion product being less stable toward β -elimination. By contrast, the more crowded $\text{R} = i\text{Bu}$ system was proposed to encourage 1,2-insertion, thereby slowing down β -hydride elimination.⁶²

Subsequent studies revealed that $\text{R} = i\text{Bu}$ was a prerequisite for the living polymerization of 1-hexene using such systems; $\text{R} = \text{mesityl}$ behaved in a similar fashion to $\text{R} = i\text{Pr}$ and Cy.⁶³ Investigation of the kinetics revealed that at 0°C , the polymerization of 1-hexene, in the presence of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, was first order for both the 1-hexene and for the metal ($k_p = 9.9 \pm 0.7 \text{ M}^{-1}\text{min}^{-1}$).⁶⁴

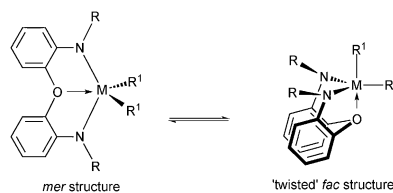


Fig. 41 *mer* and 'twisted' *fac* configurations for trigonal bipyramidal NON complexes **62** ($\text{R} = i\text{Pr}$, Cy, $i\text{Bu}$; $\text{R}^1 = \text{Me}$, Et, $i\text{Bu}$, CH_2CH_3 , allyl).

Replacement of the O-donor by S proved facile, however cationic complexes generated from $[(\text{RNSNR})\text{ZrMe}_2]$ (**65**) ($\text{R} = t\text{Bu}, i\text{Pr}$; Fig. 42) were unstable at ambient temperature, and were inactive for the controlled polymerization of 1-hexene.⁶⁵

In parallel studies, Schrock *et al.* also investigated the potential of complexes bearing tridentate diamido ligands of the form $[(\text{ArNCH}_2\text{CH}_2)_2\text{O}]^{2-}$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2-2,6$ or $\text{C}_6\text{H}_3i\text{Pr}_2-2,6$). Zirconium dialkyl complexes **66** (Fig. 43, left) were readily prepared by treatment of the parent ligands with $[\text{Zr}(\text{NMe}_2)_4]$, and subsequent reaction with Me_3SiCl (generating the dichloride) and then Grignard reagent. The molecular structure of the dimethyl complex with $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2-2,6$ was determined, which revealed that the Zr-N bonds were axial. The $\text{R} = \text{Me}, \text{CH}_2\text{CHMe}_2$ complexes were activated with either $[(\text{Ph}_3\text{C})[\text{B}(\text{C}_6\text{F}_5)_4]]$ or $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, and were then screened for 1-hexene polymerization at 0°C in chlorobenzene. Activities were high, but molecular weights were much lower than the calculated values, suggesting that chain termination was competing with propagation, with the catalyst remaining active and initiating the polymerization of a new chain. Interestingly, the analogous titanium complexes were poor, with only 75% consumption of 25 equiv. of 1-hexene. Systems of this type were poisoned by the addition of 2,4-dimethylaniline.⁶⁶

The series of ligands was extended to include $\text{Ar} = \text{C}_6\text{H}_3\text{Et}_2-2,6$ and $\text{C}_6\text{H}_3i\text{Pr}_2-2,6$, whilst the related S-donor ligands $[(\text{ArNCH}_2\text{CH}_2)_2\text{S}]^{2-}$ with $\text{Ar} = \text{C}_6\text{H}_3\text{Me}_2-2,6$ or $\text{C}_6\text{H}_3\text{Et}_2-2,6$ were also prepared. Generated (*via* protonation or oxidation cleavage of the alkyl) cationic alkyl intermediates proved to be quite stable, despite an apparent low electron count, particularly when formed in the presence of an oxygen donor such as diethylether. The S-donor systems were not as stable though as their O-donor counterparts. Both families of complexes were capable, upon activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, of efficiently polymerizing 1-hexene, albeit affording poly-(1-hexene) of limited molecular weight ($\sim 20\,000$ – $25\,000$). The complex $[(\text{ArNONAr})\text{ZrMe}(\text{Et}_2\text{O})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**67**, Fig. 42, right) was found to be incapable of the polymerization of either

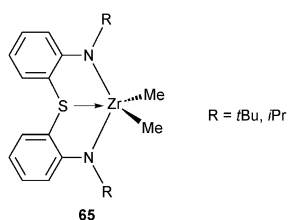


Fig. 42 Complex **65**.

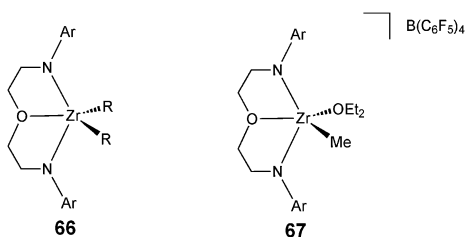


Fig. 43 NON complexes of the type **66** ($\text{R} = \text{C}_6\text{H}_3\text{Me}_2-2,6$, $\text{C}_6\text{H}_3\text{Et}_2-2,6$, $\text{C}_6\text{H}_3i\text{Pr}_2-2,6$ and **67** ($\text{R} = \text{C}_6\text{H}_3i\text{Pr}_2-2,6$).

ethylene or 1-hexene at ambient temperature. It was postulated that the solvated 5-coordinate cation was required to lose solvent, so that reaction with the α -olefin could take place; the chain length was limited by β -hydride elimination in the four-coordinate cation.⁶⁷

Ligands akin to those in complex **66**, but incorporating a phosphorus donor, namely $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_2\text{PPh}]^{2-}$ and $[(\text{RNSiMe}_2\text{CH}_2)_2\text{PPh}]^{2-}$ ($\text{R} = t\text{Bu}, 2,6\text{-Me}_2\text{C}_6\text{H}_3$), were readily available, and complexes of the type **68** (Fig. 44, left) were readily prepared from $\text{Zr}(\text{NMe}_2)_4$. However, the resulting alkyl cations were unstable, and this was thought to be associated with the presence of the trimethylsilyl substituents (possibly involved in unwanted CH activation or Si–N bond cleavage). In an attempt to overcome such instability, a dimethylsilyl group was placed in the backbone of the ligand, whilst $t\text{Bu}$ or $2,6\text{-Me}_2\text{C}_6\text{H}_3$ groups were employed at the amido nitrogen atoms. However, resulting cationic species generated from the dimethyl complex **69** ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$; Fig. 44, right) were not stable (-35 to -25°C in bromobenzene- d_5) and were incapable of the polymerization of 1-hexene (0°C over 30 min.).⁶⁸

The symmetrical (**XXVI**) and unsymmetrical (**XXVII**) diamido O-donor ligands (see Fig. 45, top) readily reacted with $[\text{Zr}(\text{NMe}_2)_4]$, and subsequently Me_3SiCl and MeMgBr to afford the respective dimethyl complexes $[(\text{XXVI}/\text{XXVII})\text{ZrMe}_2]$ (**70**, Fig. 45, bottom). Activation of **70** with $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ gave observable cations, which were stable (for hours at ambient temperature) to exchange with dimethylaniline. By contrast, use of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ as activator led to less stable, unobservable (no well-defined methyl resonances) species. However, this ill-defined system was found to be capable of 1-hexene polymerization at 0°C in chlorobenzene, affording polymers with molecular weights $\leq 45\,000$. Use of the system generated *via* $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ was only partly active (or $K_p \gg K_i$), which was probably due to problems associated with dissociation of the base. This same system also proved capable of the polymerization of propylene at 0°C , affording atactic (by ^{13}C NMR spectroscopy) polymer.⁶⁹

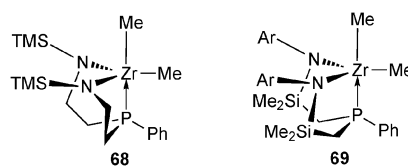


Fig. 44 Complexes **68** and **69**.

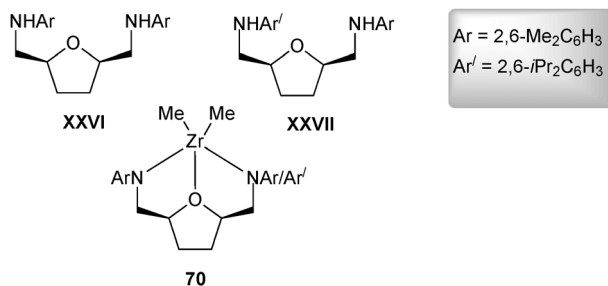


Fig. 45 N,O,N ligands **XXVI** and **XXVII**, and complex **70**.

3.6 Complexes based on N,N,N ligands

Arylated diamido pyridine ligands have proved to be successful for 1-hexene polymerization catalysis. The mesityl substituted version of the ligand set was initially studied, and the dimethyl and diisobutyl complexes (see **71**, Fig. 46, top) thereof were prepared. Using $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ as activator led to quite different polymerization behaviour. The resulting cationic isobutyl complex was shown to polymerize 1-hexene (100 equiv.) in a well-behaved manner up to temperatures of 10 °C, although the light sensitivity associated with the diisobutyl precursor proved problematic. In the case of the methyl system, activation of the dimethyl complex resulted predominantly in the inactive complex $[(\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{Zr}_2\text{-Me}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**72**, Fig. 46, bottom), but also a small amount (*ca.* 10%) of the desired cationic alkyl. Results from scaled-up polymerizations of 1-hexene using the methyl systems were consistent with only 10% of the metal centers being active.^{70,71}

Versions of these ligands containing electron withdrawing fluoro and chloro 2,6-substituents on the aryl group have also been utilized for 1-hexene polymerization – see Hafnium (section 4).

Using the same type of strategy, Schrock *et al.* utilized diamidoamine ligands, whereby the O- or S-donor in type **56** complexes was replaced by the NR moiety ($\text{R} = \text{H}, \text{Me}$). Such complexes were found to adopt *mer* structures in the solid-state, due to the flexibility inherent in the two arms connecting the amide/amine nitrogens. Minimal steric interactions precluded the need for a 'twisted' *fac* structure. The cationic alkyl $\{[(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**73**) was found to polymerize 1-hexene, but not in a living manner. Decomposition of this salt in bromobenzene occurred *via* C–H activation of an *ortho* methyl group in the mesityl substituent, liberating methane (Fig. 47). Investigations showed that the intermediates in the polymerization process also decomposed by this route. It proved possible to eliminate this decomposition pathway, whilst at the same time not altering the sterics of the system too much by using a 2,6- $\text{Cl}_2\text{C}_6\text{H}_3$ group. Indeed, cationic complexes containing the ligand set $(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}^{2-}$ were found to be fairly

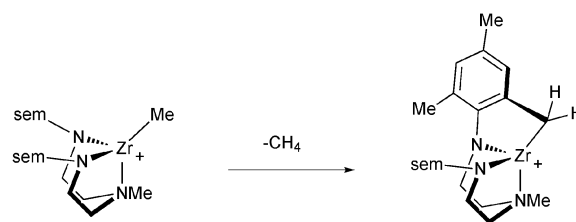


Fig. 47 CH activation in complexes of the type **73**.

stable (*e.g.*, hours at 0 °C), and polymerized 1-hexene in a living manner (0 °C, chlorobenzene).^{72–74}

Asymmetric variations of this type of diamide N-donor ligand set have been synthesized (see **XXVIII**, Fig. 48, left), which contained ethylene/*o*-phenylene arms. As before, treatment of the bis(dimethylamido) complexes, prepared *via* $[\text{Zr}(\text{NMe}_2)_4]$, with two equiv. of trimethylsilylchloride and then methyl magnesium bromide, led to dimethyl complexes of the type **74** (Fig. 48, right). In the case of $\text{R} = \text{mesityl}$, the cation generated using $[(\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ was an effective polymerization catalyst; at 0 °C, 100 equiv. 1-hexene was polymerized in <5 min. The polymer produced was atactic (by ^{13}C NMR spectroscopy), with $M_w/M_n \leq 2.43$. Similar use of $\text{R} = \textit{t}\text{Bu-d}_6$ afforded a dimeric monocation of the type $[(\text{XXVIII})_2\text{Zr}_2\text{Me}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, which was long-lived when using 0.5 equiv. of activator. This dimeric cation slowly reacted with the activator to afford a monomeric cation $[(\text{XXVIII})\text{ZrMe}]^+$. Polymerization of 1-hexene with this monomeric cation was much slower (6 h), and polymer M_n values much lower, than observed in the mesityl case. ^1H NMR spectroscopic studies suggested that the active catalyst was decomposing, thought to be *via* β -hydride elimination, during the polymerization. Lowering the temperature to –25 °C, seemed to impede the decomposition process somewhat, and higher M_n values were obtained.⁷⁵

Use of N,N,N-diamido/donor ligands bearing electron withdrawing substituents allowed access to complexes of the form **75** (Fig. 49). Generation of cations with a variety of activators produced systems that were active for the living

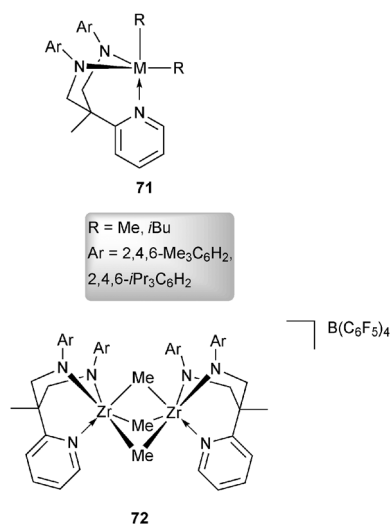


Fig. 46 Diamidopyridyl complexes of the type **71** and **72**.

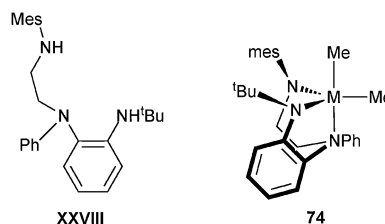


Fig. 48 Asymmetric ligand **XXVIII** and complexes of the type **74**.

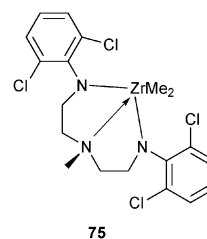


Fig. 49 Complexes of the type **75**.

polymerization of 1-hexene (first order in 1-hexene). The activity was higher than that observed for complexes of the type $[(\text{ArNCH}_2)_2\text{C}(\text{Me})(2\text{-C}_5\text{H}_4\text{N})\text{HfR}][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{R} = \text{Me}$, $i\text{Bu}$; $\text{Ar} = \text{mesityl}$ or $2,6\text{-Cl}_2\text{C}_6\text{H}_3$), see hafnium (section 4).⁷⁶

3.7 Complexes based on O,N,O ligands

The pyridinebis(menthol) ligand **XXIXH**₂ (Fig. 50, top left) on reaction with $[\text{Zn}(\text{Bn})_4]$ afforded the yellow complex **76** (Fig. 50, top right) in good yield (75%). The molecular structure of **76** revealed a distorted trigonal bipyramidal geometry at the metal with a *mer* bound tridentate ligand set. One of the benzyl groups bound in η^2 -fashion, with the complex overall possessing approximate C_2 symmetry. The zwitterionic adduct **77** (Fig. 50, bottom left) was formed in quantitative yield (by NMR spectroscopy) by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to **76**. Further treatment of **77** with one equivalent of diethylether was found to release the anion $[\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]^-$, thereby forming the salt **78** (Fig. 50, bottom right).

By contrast, use of the activator $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ did not lead to a clean NMR spectrum, though addition of diethylether afforded the cation seen in **78**, namely $[\text{Zr}(\text{XXIX})-(\eta^2\text{-CH}_2\text{Ph})(\text{OEt}_2)]$. Both **76** and **77** were shown to be inactive for ethylene polymerization using MAO as co-catalyst when conducted at ambient temperature and 1–6 bar. When solutions of **78** and the ‘NMR mix’ were exposed to ethylene, despite the decoloration, there was no apparent formation of polyethylene. Indeed, *in situ* NMR studies of **77** indicated complete conversion to the zwitterionic complex $[\text{Zr}(\text{XXIX})(\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph})][(\eta^6\text{-PhCH}_2)\text{B}(\text{C}_6\text{F}_5)_3]$ (**79**–Fig. 51, top left), whereas the ‘NMR mix’ led to the salt $[\text{Zr}(\text{XXIX})(\eta^1:\eta^6\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ (**80**, Fig. 51, top right). Both **79** and **80** were the result of stoichiometric ethylene insertion into a Zr–C bond. In **79**, a phenyl group of the γ -substituted *n*-propyl ligand was believed to stabilize the cationic centre *via* π -bonding. This chelation, involving the *n*-propyl/phenyl, prevented further ethylene coordination,

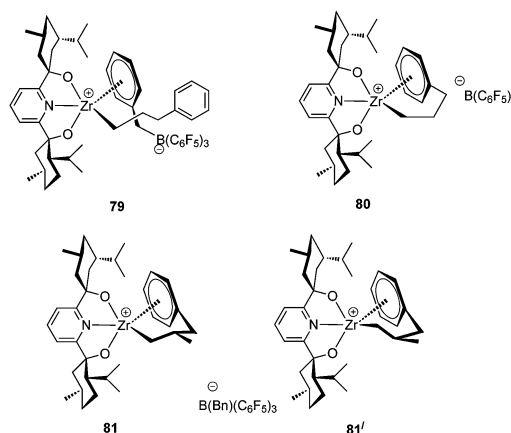


Fig. 51 2,6-Bis(menthoxy)pyridine complexes with chelating alkyl ligands.

whilst in **80**, it was the strength of the anion binding that was thought to be responsible for the inactivity.⁷⁷

In the case of exposure of **77** to propylene, regiospecific 1,2-insertion resulted in the complex $[\text{Zr}(\text{XXIX})(\eta^1:\eta^6\text{-CH}_2\text{CHMeCH}_2\text{Ph})][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$, which was found to exist (by NMR spectroscopy) as two diastereoisomers **81** and **81'** (45 : 55) – Fig. 51 (bottom). Exposure of **77** to 1-hexene led to a mixture of diastereoisomers (50 : 50) of formula $[\text{Zr}(\text{XXIX})(\eta^1:\eta^6\text{-CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph})][\text{B}(\text{CH}_2\text{Ph})(\text{C}_6\text{F}_5)_3]$ (**82/82'**, Fig. 52), *i.e.*, low diastereoselectivity was observed. In the case of exposure to 4,4'-dimethyl-1-pentene, the opposite diastereoselectivity to propylene was observed, and it was postulated that a second directing effect was in operation as well that produced by the chiral ligand **XXIX**. This was thought to probably involve the non-symmetric orientation of the benzyl group in an intermediate. Styrene was also observed to 1,2-insert into the Zr–C bond of **77**, whilst reaction with 1,5-cyclooctadiene proved much slower, and afforded only a single observable isomer.

Zirconium complexes of the ligand **XIH**₂ (Fig. 19) have been synthesized and screened for ethylene polymerization in the presence of MAO. In particular, the zirconium analogue of **30**, namely $[\text{Zr}(\text{XI})\text{Cl}_2(\text{THF})]$ (**83**, Fig. 53, left), was found to be notably active at 20 °C (7.03×10^3 g mmol^{−1} h bar). Use of diethylether as solvent led to the related complex $[\text{Zr}(\text{XI})\text{Cl}_2(\text{Et}_2\text{O})]$ (**84**, Fig. 53, right), which similarly exhibited high activity when activated with MAO. The high activities observed here are consistent with the presumed strong binding of the pyridine at zirconium.³⁹

Reaction of the ligand set **XIII** (Fig. 20) with either $[\text{Zr}(\text{Bn})_4]$ or $[\text{Zr}(\text{Bn})_2\text{Cl}_2(\text{OEt}_2)_2]$ afforded yellow/orange solids of the form $[\text{Zr}(\text{XII})(\text{Bn})_2]$ (**85**, Fig. 54). In the case of $\text{R}^1 = \text{F}$,

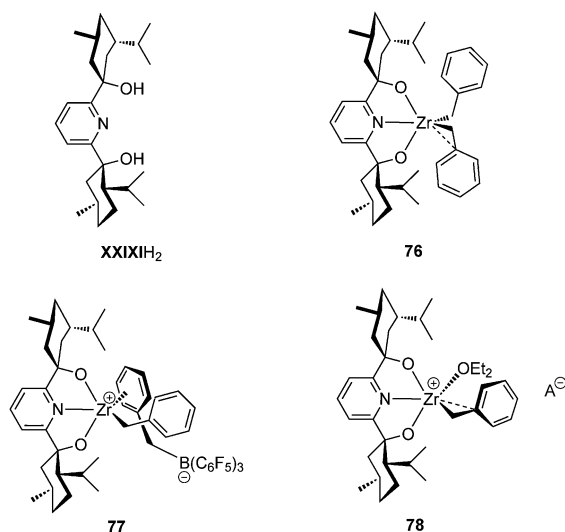


Fig. 50 2,6-Bis(menthoxy)pyridine ligand **XXIXH**₂ and zirconium benzyl derivatives (A = anion).

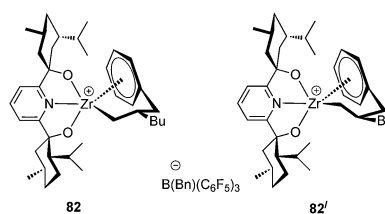


Fig. 52 Diastereoisomers **82**.

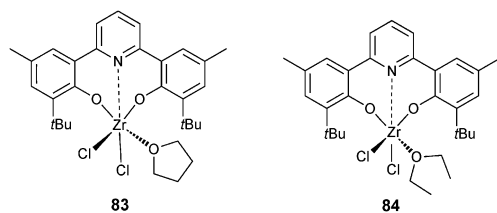


Fig. 53 Complexes 83 and 84.

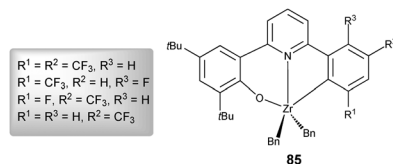


Fig. 54 Fluorinated 2-(2'-hydroxyphenyl)-6-arylpyridine complexes 85.

$R^2 = CF_3$, $R^3 = H$, the presence of a donor THF was beneficial for complex isolation.

As well the derivatives that were prepared for titanium, the zirconium family was extended to include the $R^1 = R^3 = H$, $R^2 = CF_3$ derivative. For the $R^1 = R^2 = CF_3$, $R^3 = H$ derivative, neutron diffraction studies, conducted at 20 K, enabled the C–H...F–C interaction to be characterized. Given that this technique can accurately determine the position of the hydrogen, it was found that the H–F distances and C–H...F angles were appropriate for C–H...F–C interactions. The neutron experiment also suggested that the orientation of the benzyl group towards the CF_3 group might be better described as orientated away from the *tert*-butyl groups, due to the proximity of the latter to the benzyl methylene protons.

Interestingly, complex 84 displayed the opposite co-catalyst trends for the co-polymerization of ethylene with propylene to those observed for titanium, *i.e.*, higher activities and co-monomer incorporation was observed with $iBu_3Al/Ph_3CB(C_6F_5)_4$ as co-catalyst. Such systems also exhibited poor incorporation of norbornene.⁴⁰

Use of the non-fluorinated ligand sets **XIIIIH** (Fig. 21) led to systems for which the effect of R^1 variation was less pronounced on catalytic activities than observed for the titanium case. This was thought to be due to the increased size of the central metal.⁴¹

Dibenzyl complexes incorporating bis(naphthoxy)pyridine ligands (see **XIVH₂**, Fig. 22) have been prepared in good ($R = SiMe_2tBu$, 60%) to excellent ($R = SiPh_3$, 90%) yield. In the solid-state, the structure of the $R = SiMe_2tBu$ derivative was found to possess a ligand with *meso*-like coordination (*cf.* *rac*-like for titanium, complex 36), whilst in solution *rac* and *meso* stereoisomers were observed (as for titanium). For ethylene polymerization, complex 86 (Fig. 55, left) performed well in the presence of $[Ph_3C][B(C_6F_5)_4]/Al(iBu)_3$ achieving an activity of 3010 g mmol^{−1} h bar at 60 °C. This system though was inactive for propylene polymerization when using either dried MAO or $[Ph_3C][B(C_6F_5)_4]/Al(iBu)_3$ as co-catalyst. By contrast, the derivative 87 bearing $R = SiMe_2tBu$ (Fig. 55, right) was active for propylene polymerization in the presence of MAO, both at 25 (490 g mmol h bar) and 50 °C

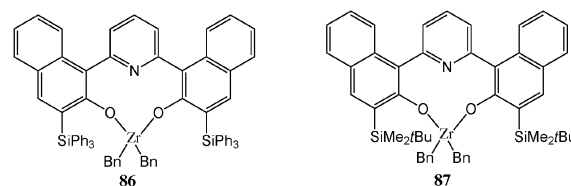


Fig. 55 Complexes 86 and 87.

(320 g mmol^{−1} h bar). The use of dried MAO led to a similar activity (413 g mmol h bar), whereas with $[Ph_3C][B(C_6F_5)_4]/Al(iBu)_3$ as co-catalyst, the system was inactive.⁴²

3.8 Complexes based on N,N,C ligands

Building on earlier work, much of which appeared in the patent literature,⁷⁸ pyridylamido complexes of the type **88** (Fig. 56) were prepared *via* lithiation of the parent ligand, followed by addition of $[ZrCl_4]$ (110 °C, 1h) and then excess (3 equiv.) methylmagnesium bromide (~10 °C). Rotation about the 2-*i*Pr phenyl group attached to the chiral centre led to the formation of two isomers (ratio 93 : 7).

In the presence of MMAO, the activator $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$ and **75** (ratio 10 : 1.2 : 1) and hydrogen, at 120 °C and 400 psi ethylene/250 g 1-octene, ethylene/1-octene were co-polymerized with an activity of 8400 g mmol^{−1} over 15 min. The activity dropped to 3800 g mmol^{−1} at 150 °C. The molecular weight (M_w) of the polymer was 870 000 (at 120 °C) and 301 000 (at 150 °C), with mol% 1-octene incorporation of 8.5 and 8.4, respectively.

For propylene polymerization, using the same combination of activator mix, **88** afforded isotactic polypropylene with an activity of 1 400 g mmol^{−1} (120 °C) or 7 200 g mmol^{−1} (60 °C). Molecular weights were 67 400 (120 °C) and 168 000 (60 °C), with melting points suggesting lower tacticities than for the polymer obtained with the corresponding hafnium-based system (see section 4).⁷⁹

3.9 Complexes based on C,N,C ligands

The lithiated bis(σ-aryl)amine ligand **XXXLi₂** (Fig. 57, top left) was reacted with $[Zr(Bn)_2Cl_2(Et_2O)]$ to afford the crystalline complex **89** (Fig. 57, top right) in 30% yield. The molecular structure was determined and revealed a distorted trigonal bipyramidal geometry at zirconium. The two σ-bond carbons are positioned axially, whilst one of the benzyl groups has η²-character $[Zr-C-C = 97.7^\circ]$. Treatment of **89** with $[Ph_3C][B(C_6F_5)_4]$ led to the formation of the salt **90** (Fig. 57, bottom), possessing an η²-benzyl group. NMR tube experiments revealed that **90** would polymerize both ethylene or propylene. In autoclave runs (4 bar, 25 °C, bromobenzene, 30 min), **90** afforded atactic poly(propylene), with a catalytic

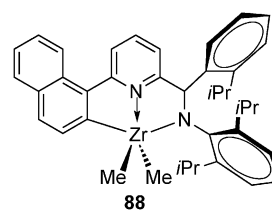


Fig. 56 Pyridylamido zirconium complex 88.

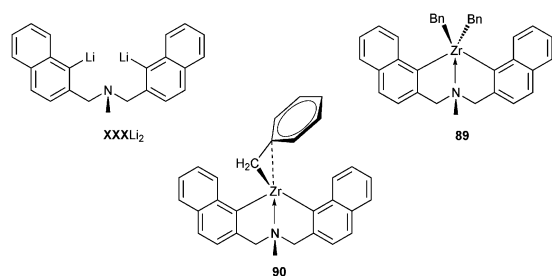
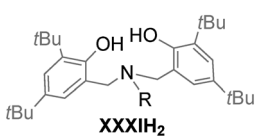


Fig. 57 Bis(s-aryl)amine ligand XXXLi_2 and complexes $\mathbf{89}$ and $\mathbf{90}$.

activity of $26 \text{ g mmol}^{-1} \text{ h}$. GPC analysis revealed a main peak at 21 000, which possessed a shoulder to higher molecular weights.⁸⁰

3.10 Bis(phenolate) ligands with one additional donor

Minor changes to the peripheral framework in ligands of the type XXXIH_2 (Chart 4) were shown to play a major role in the catalytic behaviour of their resultant zirconium-based systems. ^1H NMR spectroscopy indicated rigid ligand binding at the metal, whilst solid-state structures possessed similar (as identified by X-ray crystallography) cores. As a consequence, differing behaviour was determined to be the result of the donor side arm. Indeed, the lack of such an arm afforded a system which rapidly deactivated and afforded only trace oligomers. By contrast, a strong donor arm, capable of forming a 5-membered ring at zirconium, can lead to extremely high polymerization activity. The ligands screened included those shown in Chart 4, and results revealed that either changes to the nitrogen hybridization or to the aryl substituents had little effect. However, an increase in the size of the zirconacycle (formed by the donor arm) afforded either negligible activity (when no binding) or moderate activity (strong binding). The steric bulk of the donor group was also found to weaken the $\text{Zr-N}(\text{donor})$ bond, and resulted in a moderate oligomerization catalyst. Chart 4 also highlights

 XXXIH_2			
R	Activity	M_w	M_w/M_n
$\text{CH}_2\text{CH}_2\text{NMe}_2$	21,000	35,000	3.5
Pr	trace	oligomers	
$\text{CH}_2\text{CH}_2\text{CH}_2\text{NMe}_2$	trace	oligomers	
$\text{CH}_2\text{py-2}$	5,700	15,000	4.5
$\text{CH}_2\text{CH}_2\text{py-2}$	65	102,000	1.7
$\text{CH}_2\text{CH}_2\text{NEt}_2$	60	1,100	1.6

Performed in neat 1-hexene using 13 mmol pre-cat. and 1 equiv. of $\text{B}(\text{C}_6\text{F}_5)_3$; activities in g/mmole.h

Chart 4 Variation of the donor arm R in amine bis(phenolate) zirconium complexes.

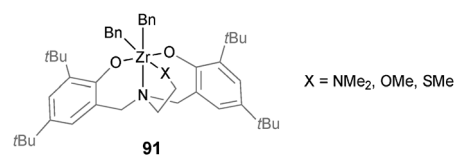


Fig. 58 Dibenzyll 'Kol' type complexes $\mathbf{91}$.

the wide range of polymerization behaviour that can be found for such systems.⁸¹

The family of ligands XXXIH_2 was expanded by Kol *et al.* to include those bearing OMe and SMe donor groups. Such ligands, as well as those bearing an NMe₂ donor group, were reacted with $[\text{Zr}(\text{Bn})_4]$ to afford the zirconium complexes $[\text{Zr}(\text{Bn})_2(\text{XXXI})]$ ($\mathbf{91}$, Fig. 58) in quantitative yields. Screening for 1-hexene polymerization revealed the activity ratio $\text{OMe (5)} > \text{NMe}_2 \text{ (2)} > \text{SMe (1)}$. The highest activity was $50\,000 \text{ g mmol}^{-1} \text{ h bar}$, affording a polymer with molecular weight 80 000. Analysis of the three molecular structures revealed very similar geometrical parameters, except in the case of the OMe derivative, where partial η^2 -binding was evident for the 'axial' benzyl group. This partial η^2 -binding resulted in a widening of the angle between the two benzyl ligands [$\text{C-Zr-C} = 106^\circ$]. The zirconium-donor atom bond distances [$\text{Zr-O } 2.24$, $\text{Zr-N } 2.59$, $\text{Zr-S } 2.86 \text{ \AA}$] were longer than those observed in related systems. NMR (NOESY) spectroscopic studies on both the complexes and the active species thereof, generated upon the addition of $\text{B}(\text{C}_6\text{F}_5)_3$, suggested that the side-arm remained bound to the metal. Furthermore, $^1\text{H}/^{19}\text{F}$ /NOESY NMR spectroscopic studies supported the formation of a relatively stable (hours at room temp, days at -30°C), well separated ion-pair, in which the abstracted benzyl group was not coordinated to the metal (the remaining benzyl group occupied an axial position). The higher activity of the OMe derivative *versus* the NMe₂ derivative was postulated to be due to steric effects.⁸²

3.11 Bis(phenolate) ligands bearing two additional donors

Kol *et al.* extended their zirconium work to include the diamine bis(phenol) ligand set XXXIIH_2 (Fig. 59; $\text{R} = \text{Me}$, $\text{R}^1 = t\text{Bu}$, $\text{X} = \text{CH}_2\text{CH}_2$), which were readily available as colourless solids *via* a one-pot Mannich condensation. Reaction with $[\text{Zr}(\text{Bn})_4]$ at 65°C afforded a C_2 -symmetric complex $[\text{Zr}(\text{Bn})_2(\text{XXXII})]$ ($\mathbf{92}$), possessing *cis*-benzyl groups [$\text{C-Zr-C } 110.5^\circ$], see Fig. 60. Activation with $\text{B}(\text{C}_6\text{F}_5)_3$ in neat 1-hexene afforded poly(1-hexene) with an activity of $18 \text{ g mmol}^{-1} \text{ h}$ and with $M_w = 12\,000$. Data was consistent with a living, isospecific 1-hexene polymerization ($>95\%$ isotactic). Similar use of the ligand XXXIIH_2 ($\text{R} = \text{R}^1 = \text{Me}$, $\text{X} = \text{CH}_2\text{CH}_2$) led to higher activity ($35 \text{ g mmol}^{-1} \text{ h}$) affording atactic polymer with M_w 23 000.⁸³

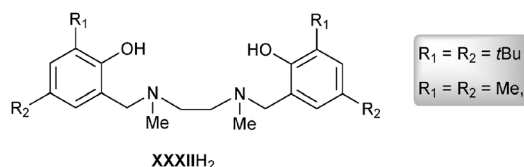


Fig. 59 Ligand XXXIIH_2 .

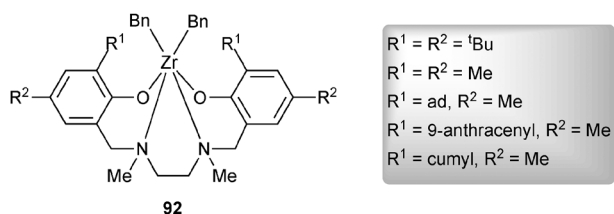


Fig. 60 C_2 -symmetric zirconium complexes employed by Kol, Busico *et al.*

Incorporation of $R^1 = \text{Cl}$ in such systems proved to be highly beneficial in terms of catalytic activity ($\leq 5400 \text{ g mmol}^{-1} \text{ h}$), but unlike their titanium counterparts, led to the isolation of low molecular weight ($M_w = 9100$), atactic polymer.⁵⁰

Busico *et al.* have also utilized such complexes to polymerize propylene, in the presence of either MAO or $i\text{Bu}_3\text{Al}/[\text{HMe}_2\text{N}(\text{C}_6\text{H}_5)][\text{B}(\text{C}_6\text{F}_5)_4]$. Fast chain transfer to aluminium was observed, with loss of living character (*cf.* Kol systems), and formation of isotactic polypropylene with $[mmmm] = 0.8$, $[mrrm] = 0.037$. Subsequent studies utilized $[\text{HMe}_2\text{N}(\text{C}_6\text{H}_5)]-[\text{B}(\text{C}_6\text{F}_5)_4]$ and a pre-formed alkylaluminium aryloxide, the later being generated from equimolar amounts of $i\text{Bu}_3\text{Al}$ and 2,6-di-*tert*-butylphenol. Homo-polymerizations of either ethylene or propylene with such a co-catalyst mixture (and **92**; $R^1 = R^2 = t\text{Bu}$), were found to be ‘quasi-living’, that is there was only slow chain transfer over the timescale of the experiment. Indeed, data indicated that on average it took 6 and 30 min for chain growth of polyethylene or polypropylene, respectively. With this in mind, it proved possible to form a block co-polymer, comprising only of a diblock of PE and of PP; there was no evidence for the formation of the respective homo-polymers. ^{13}C NMR spectroscopic data estimated the average block lengths of polyethylene (PE) at 130 ± 30 and polypropylene (PP) at 120 ± 30 monomeric units. The block co-polymer was insoluble in refluxing hexane, and possessed a melting peak of 120°C (by DSC) for the PE block, which blended in with a broader peak for the PP. On cooling, separate crystallization isotherms were recorded.⁸⁴

Quantum/molecular mechanics calculations indicated that the R^1 group was crucial to both the enantioselectivity and to the ease of monomer-induced chain transfer. Systems bearing the R^1 groups shown in Fig. 60 were prepared and their behaviour in propylene polymerization was compared against that predicted by the calculations. The complex bearing $R^1 = \text{adamantyl}$ afforded isotactic polypropylene with very low *rr* stereo-defects (0.3 mol%), with a melting point of 151°C . The enantioselectivity however had increased to 99.7% (*cf.* 96% for $R^1 = R^2 = t\text{Bu}$), with average growth time from less than 30 mins to around 9 h. Such a system was thus capable of the block co-polymerization of ethylene with propylene, affording a block co-polymer for which there were two distinct melting peaks (by DSC) at 126°C (PE block) and 152°C (PP block). Use of $R^1 = 9\text{-anthracenyl}$, led to only oligomeric, oily polypropylene, which was consistent with the predicted behaviour. Use of $R^1 = \text{cumyl}$, afforded higher than expected molecular weights, the discrepancy (*cf.* predicted results) was thought to be due to the conformational flexibility of the cumyl substituent.⁸⁵

Other NMR spectroscopic experiments and DFT calculations suggested that the bis(phenoxamine) complex **92** ($R^1 = \text{cumyl}$, $R^2 = \text{Me}$), upon activation with $\text{B}(\text{C}_6\text{F}_5)_3$, underwent a change in the ligand binding from *cis*-(*N,N*)-*trans*-(*O,O*) to *cis*-(*N,N*)-*cis*-(*O,O*) upon ion-pair formation.⁸⁶

Calculations and experiments have also been performed on the closely related complex, but with $R^1 = R^2 = \text{cumyl}$, which revealed that when combined with MAO, entropy loss due to monomer capture was one of the key factors responsible for the low chain propagation rates occurring within this system.⁸⁷

The influence of a variety of co-catalysts/activators on the ion-pair structure and the catalytic performance was investigated, both for dibenzyl and for dimethyl complexes. In particular, the ion-pairs, where $R^1 = t\text{Bu}$, $R^2 = \text{OMe}$, were synthesized for both the dibenzyl and dimethyl complexes and screened for their ability to polymerize propylene, in the presence of the anions $\text{MeB}(\text{C}_6\text{F}_5)_3$ (dimethyl complex only), $\text{BnB}(\text{C}_6\text{F}_5)_3$ (dibenzyl complex only) and $\text{B}(\text{C}_6\text{F}_5)_4$ (both complexes). Interestingly, the various co-catalysts/activators has little influence on the observed catalytic activity. In each of the cases shown, using NMR/DFT experiments, three isomers were observed, *viz mer-mer* (most stable), *fac-mer* and *fac-fac* (least stable). The anion occupied a position in the second coordination sphere. The energy of the *fac-fac* isomer was found to be influenced much more by the R group which, given that the active centre was proposed to be of the *fac-fac* form, was consistent with the lack of fluctuation of activity on changing the co-catalyst/activator.⁸⁸

Salophan ligands bearing secondary N-methyl groups (see **XXXIIIH₂**, Fig. 61, top) were prepared *via* nucleophilic substitution of bromomethylated phenols with the N,N'-methylated diaminobenzene (prepared *in situ*). Salophan ligands were also prepared, in good yields, for which R or $R' = \text{Cl}$ or $t\text{Bu}$. Reaction of **XXXIIIH₂** ($R = \text{H}$, $R^1 = t\text{Bu}$) with $[\text{Zr}(\text{OtBu})_4]$ afforded $[\text{Zr}(\text{XXXIII})(\text{OtBu})_2]$ (**93**, Fig. 61, bottom) as an isomeric (kinetic/thermodynamic) 1 : 1 mixture. Use of the other ligand sets afforded just the one isomer. All were of C_2 -symmetry, and the molecular structure, confirmed by X-ray crystallography, for the $R^1 = t\text{Bu}$ derivative revealed the *fac-fac* binding mode of the ligand. Similarly, use of

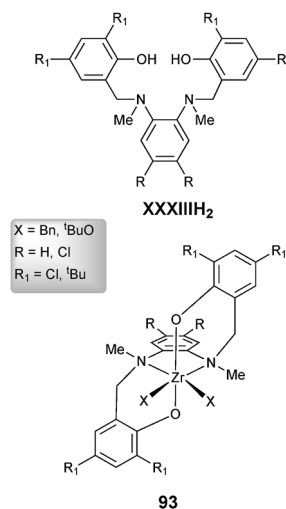


Fig. 61 Salophan ligands and zirconium complexes.

$[\text{Zr}(\text{Bn})_4]$ led to C_2 -symmetric complexes, though it was found necessary to heat the systems to 75 °C for complete conversion.

Upon screening for 1-hexene polymerization, using $\text{B}(\text{C}_6\text{F}_5)_3$ as activator, it was found that the dibenzyl complexes bearing ligands with chloro substituents on the phenolate rings afforded extremely high activities, of the order of 20 000 g mmol⁻¹ h bar (higher than those observed for the salan complexes **92** (Fig. 60), when such ligands also possessed chloro substituents). Furthermore, only poor activity (≤ 5.6 g mmol⁻¹ h) was observed for those ligand sets bearing *tert*-butyl substituents. By contrast, the presence of chloro substituents in the bridge (*i.e.*, $\text{R} = \text{Cl}$) had little impact on the observed activity. ¹³C NMR spectroscopic experiments indicated that these systems bearing salophan ligands possessed lower stereochemical control *versus* related salan complexes.⁸⁹

On reaction with $[\text{Ti}(\text{O}i\text{Pr})_4]$, such ligands also formed C_2 -symmetric complexes of the type $[\text{Ti}(\text{XXXIII})(\text{O}i\text{Pr})_2]$, but such titanium complexes were not screened for polymerization catalysis.

Related chiral N-Me substituted salan ligands can be wrapped around zirconium. Use of $[\text{Zr}(\text{Bn})_4]$ afforded access to the respective dibenzyl complexes in excellent yields (90%), as single diastereoisomers (*cf.* mixtures for titanium). NMR spectroscopic evidence was indicative of a C_2 -symmetric structure, whilst an X-ray structure determination revealed an *R,R*-salan ligand and Δ binding. For 1-hexene polymerization (25 °C), those systems possessing non-bulky substituents ($\text{R}^1/\text{R}^2 = \text{Cl}, \text{Br}$; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$) afforded atactic polymers, whereas for $\text{R}^1/\text{R}^2 = t\text{Bu}$; $\text{R}^1 = \text{adamantyl}, \text{R}^2 = \text{Me}$, highly isotactic poly(1-hexene) was formed. The $\text{R}^1 = \text{adamantyl}, \text{R}^2 = \text{Me}$ system proved to be more active than $\text{R}^1/\text{R}^2 = t\text{Bu}$, with a very high degree of isotacticity (no *mmmr* errors *etc.*). For $\text{R}^1/\text{R}^2 = \text{Cl}$ or Br , very high activity was observed, affording high molecular weight polymers. Both 4-methyl-1-pentene and 1,5-hexadiene could also be polymerized, with the systems bearing $\text{R}^1/\text{R}^2 = \text{Cl}$ or Br affording high activity, and in the case of 4-methyl-1-pentene, a high molecular weight stereoirregular polymer.⁹⁰

In the case of 1,5-hexadiene polymerization conducted at about 55 °C, the $\text{R}^1/\text{R}^2 = t\text{Bu}$ system yielded only trace polymer. This contrasted with the behaviour of the $\text{R}^1 = \text{adamantyl}, \text{R}^2 = \text{Me}$ system, the single diastereoisomeric *R,R* form ($[\alpha]_D = +265$) of which was shown by X-ray crystallography to possess adamantyl groups which were orientated in such a way that they blocked specific regions of potential olefin coordination and growth (see Fig. 62).⁹¹ As a consequence, polymerization of 1-hexene using this diastereoisomer resulted in highly isospecific induction and formation of a soluble polymer ($[\alpha]_D -24$), a situation that was reminiscent of the directing ability observed for $[(\text{EBTHI})\text{Zr}(\text{BINOL})]$ (EBTHI = ethylenebis(tetrahydro-1-indenyl); BINOL = 1,1'-bi-2-naphthalate) by Waymouth and Coates.⁹²

For vinylcyclohexane polymerization, salan catalysts bearing electron withdrawing substituents exhibited very high activities, specifically 1800 g mmol⁻¹ h ($\text{R}^1 = \text{R}^2 = \text{Cl}$) and 3600 g mmol⁻¹ h ($\text{R}^1 = \text{R}^2 = \text{Br}$). Such high activities indicated that the performance of this class of catalyst was not hampered by the bulk of the monomer. The polymer products were shown to be highly isotactic, irrespective of

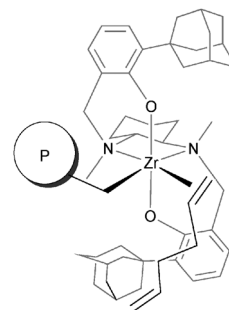


Fig. 62 Sterics associated with olefin growth for $\text{R}^1 = \text{adamantyl}, \text{R}^2 = \text{methyl}$ system.

the size of the phenolate group (*i.e.*, for all variations of R^1/R^2), with high melting points (*ca.* 360 °C). Such high melting points prompted an investigation into the ability of such polymers to act as nucleating agents for polypropylene crystallization. DSC measurements were encouraging and indicated efficient nucleating ability.⁹³

If differently substituted phenol arms are deployed, as in XXXIVH₂ and XXXVH₂ (Fig. 63), then C_1 symmetric single *fac-fac* isomers are obtained from the precursor $[\text{Zr}(\text{Bn})_4]$. Upon activation with $\text{B}(\text{C}_6\text{F}_5)_3$, such systems polymerized 1-hexene, and activities indicated that the electron withdrawing influences of the substituents were the dominant effect. For example, in the case of dichlorophenolate/di-*tert*-butylphenolate arms, the activity was 1300 g mmol⁻¹ h, whereas replacing the former with a diiodophenolate arm led to a dramatic reduction in activity (180 g mmol⁻¹ h). However, the bulk of the substituents played a dominant role in determining the degree of isotacticity of the polymer. The more rigid diaminocyclohexane derived systems were the less active family of catalysts.⁹⁴

Zirconium analogues of the benzimidazolyl bearing titanium complexes **23** and **24** (Fig. 15) were found to be inactive for ethylene polymerization, either in the presence of MAO or $\text{Al}(i\text{Bu})_3/[\text{Ph}_3\text{C}]/[\text{B}(\text{C}_6\text{F}_5)_4]$.³⁵

Diphosphanyl-biphenoxide O,P,P,O ligands have been synthesized, following work-up ($\text{AcOH}/\text{H}_2\text{O}/\text{NH}_3$), from $\text{Ph}(\text{Cl})\text{PC}_2\text{H}_4\text{P}(\text{Cl})\text{Ph}$ and *ortho*-lithiated MOM-protected 2-*tert*-butylphenol. *rac*- and *meso*-diastereoisomers were formed (1:1), which could be separated using methanol. Treatment of each diastereoisomer with $[\text{Zr}(\text{Bn})_4]$ afforded *cis-α* and fluxional *cis-β* structures **94** (Fig. 64), respectively.

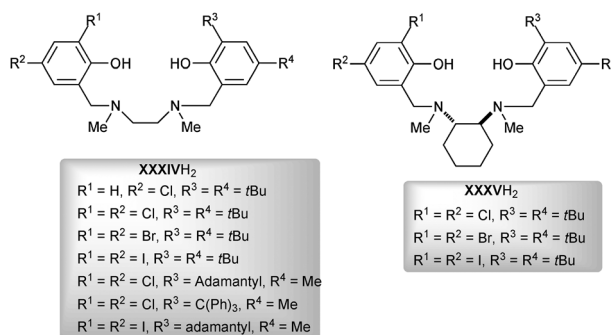


Fig. 63 Non-symmetric salan ligands used in zirconium-based 1-hexene polymerization.

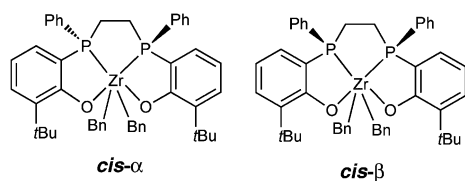


Fig. 64 Diastereoisomers **94** bearing O,P,P,O ligands.

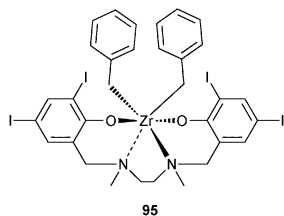


Fig. 65 Complex **95**.

Cationic alkyl species were generated with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, which in the presence of $i\text{Bu}_3\text{Al}$, were found to polymerize ethylene with an activity of ≤ 5450 (*cis*- α) and 116 (*cis*- β) $\text{g mmol}^{-1} \text{ h bar}$. Such systems were also capable of propylene polymerization, affording oligomeric products with an activity of about 210 $\text{g mmol}^{-1} \text{ h bar}$ (*cis*- α), and 43 $\text{g mmol}^{-1} \text{ h bar}$ (*cis*- β). Mostly 1-hexene (84 wt%) was formed in the *cis*- α system, whilst for the *cis*- β system, higher oligomers were identified (up to C_{30}).⁹⁵

The zirconium dibenzyl complex of the ligand **XVII**₂ (Fig. 28), namely $[\text{Zr}(\text{XVI})(\text{Bn})_2]$ (**95**, Fig. 65), was somewhat more stable than its titanium counterpart. The structure adopted was the same C_2 -symmetric geometry with *fac*-*fac* wrapping of the ligand and *cis*-benzyl groups. The zirconium-based system was more active (3800 $\text{g mmol}^{-1} \text{ h}$) than either the titanium or hafnium-based systems, for 1-hexene polymerization (neat 1-hexene, ambient temperature). The polymerization however was not living ($M_w/M_n = 2.0$), and the polymer obtained was of low molecular weight ($M_w = 14000$). The polymer was isotactic (by ^{13}C NMR spectroscopy) with $[mmmm] = 33\%$.

Polymerization of propylene was possible using solid MAO as co-catalyst and solid pre-catalyst in neat propylene (ambient temperature, 16 h). The oily polymer product obtained was near atactic ($[mmmm] = 6\%$), with molecular weight 4000. Chain end analysis identified both vinylene and *n*-propyl groups as the major chain ends, implying 1,2-insertion prior to hydride transfer termination.⁵²

3.12 Other ligand systems

The C_2 -symmetric diaminobinaphthylpyridine ligands **XXXVI**, (Fig. 66) prepared *via* reductive amination of *rac*-2,2'-diaminobinaphthalene with 6-methylpyridinecarboxaldehyde, when

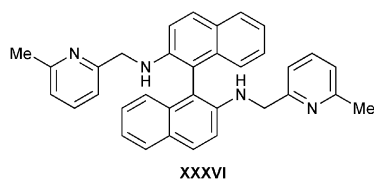


Fig. 66 Ligands of the type **XXXVI**.

utilized to make zirconium (and hafnium) dialkyls, failed, upon activation, to polymerize 1-hexene.⁹⁶

4. Hafnium

4.1 Cp-containing complexes

Although hafnium has received less attention than its lighter congeners, a number of interesting polymerizations systems have been reported.

The methoxy functionalized amido-Cp ligand, utilized in both the titanium **7** (Fig. 3) and zirconium **53** (Fig. 33) systems, was also employed in hafnium chemistry. Activation of the di-*n*-butyl complex **96** (Fig. 67) with MAO ($\text{Al}/\text{Hf} = 500$) at 25 °C and 3 bar ethylene, afforded high molecular weight polymer with a melting point of 130.7 °C. The activity of the system was 32 $\text{g mmol}^{-1} \text{ h bar}$, which decreased to 12 $\text{g mmol}^{-1} \text{ h bar}$ on elevating the temperature to 70 °C.¹⁴

4.2 Complexes based N,N,O-imine ligands

The complex $[(\text{XXXIV})\text{HfCl}_3]$ (**97**, Fig. 68), where **XXXIV** = 2-*tert*-butyl-6-[(quinoline-8-ylimino)methyl]phenolate, was screened for both ethylene and propylene polymerization, in the presence of MAO. At 6 bar ethylene and 50 °C, the observed activity was lower than that seen for either titanium (**19**, Fig. 11) or zirconium (**59**, Fig. 37), as was the polymer molecular weight ($M_w = 274000$). A broad polydispersity index (22) suggested the presence of multiple active species. Complex **97** was virtually inactive for propylene polymerization (25 °C or 50 °C, 3 mmol MAO, 6 bar propylene).³⁰

The hafnium complex **98** (Fig. 69) has been reported, for which NMR data suggested that the tridentate ligand was not as tightly bound as for the analogous zirconium complex. Screening for ethylene polymerization, using MAO as co-catalyst, produced a worse performance than with zirconium (complexes **60** and **61**, Fig. 39).⁵⁹

4.3 Complexes based on N,N,C ligands

Klosin *et al.* at the Dow Chemical Company prepared the hafnium complex $\{[2-(\text{C}_{10}\text{H}_6)_6, 6-(2-\text{iPr}(\text{Ph})\text{NC}_6\text{H}_3(\text{iPr})_2-2,6)-\text{C}_5\text{H}_5\text{N}\}\text{HfMe}_2$ **99** (Fig. 70), which was made by the same method as used for the zirconium analogue **88** (Fig. 56).

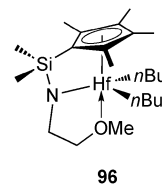


Fig. 67 Hafnium complex **96**.

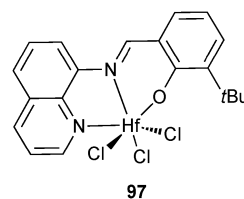


Fig. 68 Complex **97**.

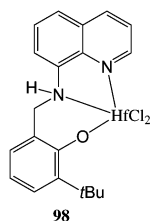


Fig. 69 Complex 98.

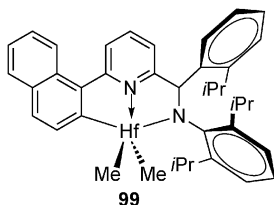


Fig. 70 Pyridylamido zirconium complex 99.

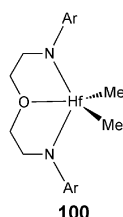
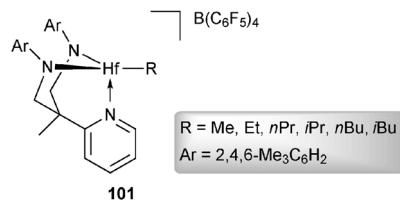
Activities for **99** were far higher than observed for **88**. In the case of ethylene/1-octene co-polymerization, **99** was some 60% more active at elevated temperatures. Also levels of co-monomer incorporation were higher (≤ 12.7 mol%), for which the polymers exhibited very high molecular weights ($M_w = 1\,420\,000$ at 120°C and $565\,000$ at 150°C).

For propylene polymerization, the activity was twice that of the zirconium-based system **88**. At 120°C , the poly(propylene) produced had two distinct 2,1 insertion regioerrors. The minor regioerror was the same as that generated when using metallocene catalysts for poly(propylene) production.⁷⁹

4.4 Complexes based on N,N,N ligands

Schrock *et al.* activated the complex $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{O}]\text{-HfMe}_2$ (**100**, Fig. 71) with either $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, at 0°C in chlorobenzene, and observed 1-hexene polymerization behaviour comparable to the zirconium system (**66**, Fig. 43).⁶⁶ Further studies on this system found that the cationic species were best isolated in the presence of a base, typically diethylether or dimethylaniline. The polymerization results (for both Hf and Zr) were interpreted in terms of ease of loss of the base from the 5-coordinate base adduct. However, the ether adduct $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{HfMe}(\text{ether})][\text{B}(\text{C}_6\text{F}_5)_4]$, at 25°C and 1 bar, was inactive. The hafnium systems at 0°C (in chlorobenzene) were the best behaved in terms of polymer molecular weight *versus* monomer consumed and polydispersity (low).

Extension of this hafnium work to the analogous sulfur donor ligands found, as for zirconium, that such systems were less stable.⁶⁷

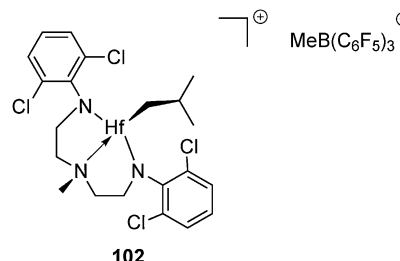
Fig. 71 Complex 100 (Ar = $\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6}$).Fig. 72 Diamidopyridyl complexes of the type **101**.

The same group have also isolated cationic hafnium alkyl complexes of type **101** (Fig. 72), which bear arylated diamidopyridine ligands, as employed in the zirconium system **71** (see Fig. 46). Such complexes were stable below 10°C , and were active for the living polymerization of 1-hexene. The complications that were observed for zirconium upon activation were not seen with hafnium, and it proved possible to isolate and fully characterize the family of alkyl cations $[(\text{mesNpy})\text{HfR}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**101**: R = Et, *n*Bu, *i*Bu, *n*Pr and *i*Pr). Furthermore, such systems operated *via* 1,2-insertions into the Hf–C bond, though the polymerization rate was only half that observed for zirconium.⁹⁷ As an example, polymerization of 1-hexene using $[(\text{mesNpy})\text{Hf}(\text{iBu})][\text{B}(\text{C}_6\text{F}_5)_4]$ at 0°C (in deuterated bromobenzene) followed first order kinetics, and was well-behaved on warming to 10°C . On a preparative scale, 600 equiv. of 1-hexene were polymerized over 40 mins at 0°C , to afford atactic polymer with $M_w/M_n \leq 1.05$. The polymerization could be inhibited by diisopropylether, hexyltrimethylsilylether, triethylamine and tributylamine, in a controlled fashion. Use of either diphenylether or dimethylaniline led to complications of CH activation.

The incorporation of *ortho* chlorides or fluorides on the amido aryl groups, led to a further decrease in the polymerization rate and a preference for β -hydride elimination.⁹⁸

The presence of such electron withdrawing groups in other N,N,N-diamido/donor ligands also proved to be problematic in terms of significant β -hydride elimination (*cf.* zirconium analogues, see Fig. 49), though when using complexes of the type $\{[\text{ArClN}_2\text{NMe}]\text{Hf}(\text{iBu})\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ **102** (Fig. 73), the product, following β -hydride elimination, was capable of re-initiating the 1-hexene polymerization.⁷⁶

Asymmetric diamido ligands **XXVIII** (see Fig. 48) also proved to be useful in hafnium-based 1-hexene polymerization. Abstraction of a methyl group was facile using $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_4)_4]$, and the resulting cations formed atactic poly(1-hexene). In the case of the *t*Bu- d_6 containing ligand set, activation initially afforded a dimeric cation, which ultimately afforded a monocation capable of 1-hexene polymerization.⁷⁵

Fig. 73 Hafnium complex **102**.

The non-fluorinated ligand sets **XIIH** (Fig. 21) produced systems which proved to be inactive in the presence of MAO (500 equiv.) at 25 °C.⁴¹

Dibenzyl and bis(dimethylamine) complexes incorporating the ligand set **XIVH₂** (Fig. 22, R = SiPh₃) have been prepared in excellent yields ($\geq 84\%$). In the solid-state, the dibenzyl complex was found to possess a *fac*-like bound chelating ligand, whereas the diamine complex (characterized as the NHMe₂ adduct) contained *meso*-like ligation. The additional amine can readily be removed under vacuum. The 'amine-free' complex was capable of ethylene polymerization at 50 °C using MAO (1000 equiv.) as co-catalyst, producing an activity of 48 g mmol⁻¹ h bar. When [Ph₃C](B(C₆F₅)₄)/Al(*i*Bu)₃ was used as co-catalyst, the system was inactive.⁴²

4.5 Bis(aryloxide) ligands bearing two additional donors

As for zirconium, hafnium complexes of **XIXH₂** (Fig. 28) were more stable than those of titanium. Activities for 1-hexene polymerization were similar to those of titanium ($\sim 1\,500$ g mmol⁻¹ h). Similarly, higher (*versus* Zr) molecular weight polymer was produced ($M_w = 320\,000$), with $M_w/M_n = 1.7$, which was of higher (*cf.* Zr) isotacticity, $[mmmm] = 50\%$. As for both titanium and zirconium, the solid hafnium pre-catalyst with solid MAO could polymerize propylene. The resultant highly viscous oil had molecular weight 37 000.⁵²

The complex {Hf(Bn)₂[(3,5-*i*Bu₂C₆H₂O-2)CH₂]₂N(2-CH₂-C₄H₇O)} (**103**), bearing a bis(phenolate) ligand containing a donor THF side-arm was shown, upon activation with B(C₆F₅)₃ (1.2 equiv.) in neat 1-hexene, to be highly active for 1-hexene polymerization. The system was slower than that employing zirconium, but more efficient than the titanium system **45** (Fig. 27), and generated, with an activity of 4000 g mmol⁻¹ h, a polymer with molecular weight (M_w) of 59 000. Use of chlorobenzene as solvent, led to lower activity (1000 g mmol⁻¹ h), but similar molecular weight.⁴⁹

Diaminobinaphthyl dipyrindine ligands (see **XXXVI**, Fig. 66), when coordinated to bisneopentyl hafnium, proved to be inactive for 1-hexene polymerization using a variety of activators, this despite the formation of observable cationic alkyls.⁹⁶

5. Conclusions

From the work described herein, it is clear that the use of tridentate chelate ligands bearing additional donor atoms capable of weakly binding to the metal has opened up many new fertile areas in α -olefin polymerization catalysis. Many of the ligand sets described in this review can be prepared simply, often by one-pot procedures in near quantitative yields. The incorporation of an extra donor function can dictate the structure of the metal complex formed, *e.g.* mono- *versus* bis(chelate), and this control can lead to systems with less steric hinderance at the catalytically active site. Indeed, the wide variation of donor groups available allows for the control of both the steric and electronics, and this can have a dramatic effect on the catalytic performance, through stabilization (the donation can impart resistance to reduction) of metal cations. Even when the changes are made at the periphery of the coordination sphere, without change of the basic core, the range of products that can be obtained from the catalytic

procedure can vary from oligomers through to high molecular weight polymers. For example, the presence of donor side arms has been noted to restrict β -elimination in the catalytically active species, thereby allowing for the formation of ultra high ($> 1\,000\,000$) molecular weight polyethylene.

Many of the systems herein exhibit living behaviour or even 'immortal' behaviour, and in certain cases, unstable pre-catalysts can lead to well-behaved systems. The 'quasi-living' nature of some of the systems described herein allows for the construction of block co-polymers, without the concomitant occurrence of homo-polymerization. High molecular weight co-polymers are also accessible at high temperatures (> 100 °C), whilst isotactic induction is also possible in some systems.

Going down the group, the larger size of the metal can lead to different coordination modes for specific ligand types (*e.g.*, *meso* *vs.* *rac* for **XIVH₂**, R = SiMe₃*t*Bu). Observed activities for a particular ligand set can also vary dramatically from metal to metal. In some cases, the titanium derivative can exhibit higher activity (*e.g.*, **7** *vs.* **53**), whereas for others zirconium can easily outperform titanium (*e.g.*, **58** *vs.* **11**). Similarly, hafnium for certain ligands can exhibit the best performance in terms of activity, particularly for co-polymerizations (*e.g.*, **98** *vs.* **88**). Furthermore, the hafnium systems are often better behaved (*e.g.*, **100** *vs.* **66**) than their zirconium counterparts.

Many of the catalyst systems can operate efficiently at very low co-catalysts loadings (*e.g.*, Al:M = 50:1), which is clearly important from a commercial point of view.

The presence of the additional donor atoms can also allow for the observation of hitherto not seen presumed active species.

As for the metallocene-based systems, well-defined structure-activity relationships have been identified. However, there is clear potential for the pre-catalyst systems herein to yield products not available *via* the use of more traditional (*e.g.*, metallocene-based) catalysts. An additionally attractive feature is the ability to zipper catalysts onto PE, which allows for PE to be used as a cheap and recoverable catalyst support.

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