Transition Metal Imido Compounds as Ziegler–Natta Olefin Polymerisation Catalysts

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Dedicated to Professor Richard R. Schrock on the occasion of his 60th birthday in appreciation of his many contributions to organometallic chemistry.

Abstract: Transition metal imido compounds having the general formula $[(L)_nM(NR)]$ [where $(L)_n$ is a supporting ligand or ligand set, and R typically is alkyl or aryl] have been known for nearly 50 years, and during the last two decades have been the focus of considerable attention. Relatively recently their potential application in the Ziegler–Natta polymerisation of olefins has been realised. In this contribution we review the Ziegler–Natta polymerisation of olefins by transition metal imido compounds. A general introduction to homogeneous Ziegler–Natta olefin polymerisation and key aspects of transition metal imido chemistry is given, followed by a short description of a related imido-based polymerisation process, namely ring-opening olefin metathesis polymerisation catalysed by imido-supported molybdenum and tungsten alkylidenes. A summary of the "design principles" that have been employed in the development of certain imido-based Ziegler–Natta catalysts is presented, followed by a comprehensive survey of the literature in the title area.

Keywords: homogeneous catalysis; imido compounds; olefin polymerisation; transition metals; Ziegler–Natta catalysis

1 Introduction

1.1 Homogeneous Ziegler–Natta Olefin Polymerisation

This short review describes the present state-of-the-art with regard to the Ziegler–Natta polymerisation of olefins by homogenous (or supported molecular) transition metal imido compounds. Imido compounds contain the formally dianionic NR ligand where R is typically a bulky alkyl or *ortho*-substituted phenyl group. Aspects of the reactivity and applications of transition metal imido compounds in general are summarised in Section 1.2 below.

The present intense interest in the homogenous polymerisation of olefins owes much to Ziegler and Natta's well-documented[1–3] discovery some 50 years ago of the heterogeneous polymerisation of olefins by metal halides in the presence of alkylaluminium co-catalysts. Also of vital industrial significance are the chromium-based Phillips catalysts[4,5] which polymerise ethylene to high molecular weight. These compounds require no alkylaluminium or methylaluminoxane (MAO) co-catalyst. Mechanistically they are much less well understood than the Ziegler–Natta systems.

Homogeneous olefin polymerisation is attractive because of the exquisite control of key macromolecular properties such as polymer molecular weight, polydispersity and stereochemistry that can (in principle) be built into the products through ligand design and co-catalyst selection. The importance of the co-catalyst cannot be underestimated as is exemplified by Sinn and Kaminsky's discovery[6] that while $[Cp_2ZrCl_2]$ in the presence of $AlMe_3$ is inactive for olefin polymerisation, this catalyst system becomes highly active upon the addition of

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Philip Mountford gained a D.Phil. degree at the University of Oxford (1986 to 1989) under the supervision of Professor M. L. H. Green. After a further period in Oxford as a Junior Research Fellow and Lecturer at Keble College, he was appointed to a lectureship at the University of Nottingham in 1992. In 1998 he returned to Oxford where he is a Reader in Inorganic Chemistry and a Tutorial Fellow at St Edmund Hall. He is a Fellow of the Royal Society of Chemistry, and a past recipient of the Royal Society of Chemistry's Sir Edward Frankland Fellowship. He has recently been a visiting professor at the Université Louis Pasteur, Strasbourg and the Université Bordeaux I, France, and the University of Heidelberg, Germany. He is interested in the structure, bonding and reactivity of organometallic and coordination compounds of the early transition metals, and is author of over 160 articles and reviews in these areas.

Paul Bolton gained an MChem degree in chemistry from Oxford University and Wadham College in 2002, having carried out his final year masters project with Philip Mountford. He also spent a period of time working on Schrock alkylidenes for Dr Christophe Copéret at LCOMS, ESCPE Lyon, France. He is presently a DPhil student in Philip Mountford's research group working on the stoichiometric and catalytic applications of cationic imido-alkyltitanium compounds.

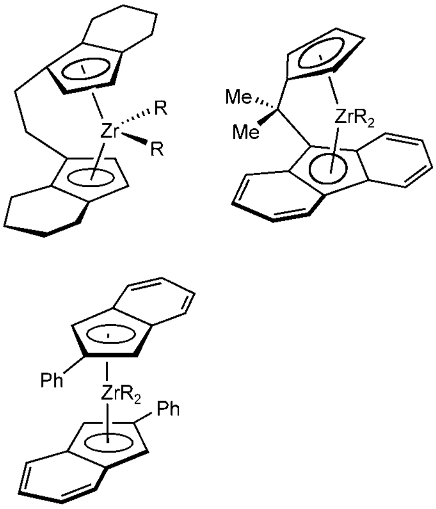
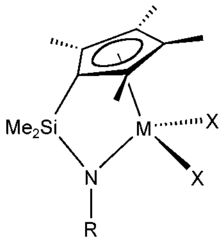


Figure 1. Some of the key ligand architectures in group 4 metallocene Ziegler–Natta polymerisation catalysts.

water. This effect was traced to the conversion of $AlMe_3$ to MAO, the first member of a family of potent aluminium-based co-catalysts extensively used in many transition metal polymerisation systems.[7] A wide range of other activators (co-catalysts), mostly borane- or borate-containing systems, are also now routinely employed.[8,9]

The 1980s and 1990s witnessed many advances in the design and performance of early transition metallocene catalysts, as well as elegant mechanistic studies of the underlying processes. Some of the key ligand architectures are illustrated in Figure 1. This work has been comprehensively reviewed.[10–17] During this period the group 4 "constrained geometry catalyst" (CGC) systems (**1**) were developed based on cyclopentadienyl-amido ligand combinations. Replacing the 5-electron pentahapto-cyclopentadienyl ligand of a metallocene with the 3-electron donor monohapto amide moiety (first developed by Bercaw for organoscandium chemistry) permitted the highly efficient incorporation of higher chain α-olefins.[18]



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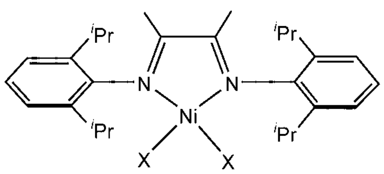
By the early 1990s a huge research effort from academic and industrial laboratories into the development of olefin polymerisation catalysts from across the whole of the transition series was underway. By way of example, some of the key classes of group 4 compound are illustrated in Figure 2.[19–23] Two main consequences of this effort have been (i) the development of a very wide range of what are now termed "post-metallocene" (i.e., non-metallocene) early metal catalysts, and (ii) the discovery of very active and tuneable later transition metals based in particular on diimine complexes of nickel, palladium, cobalt and iron (see, for example, **2** and **3**). Comprehensive reviews charting the development and current state of the art are again available.[17,24,25]



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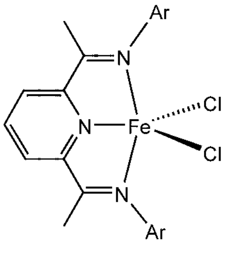

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It was within the context of early to mid-transition metal Ziegler–Natta polymerisation catalysis that a number of research groups identified the potential application of transition metal imido compounds.

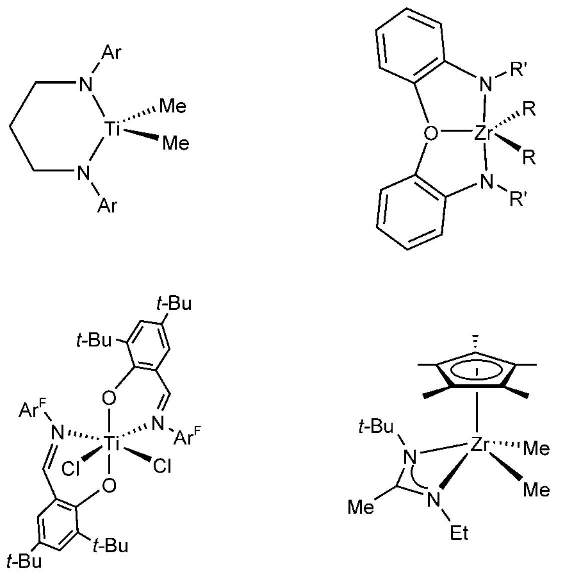


Figure 2. Examples of important milestones in group 4 post-metallocene Ziegler–Natta polymerisation chemistry.

1.2 Aspects of Transition Metal Imido Chemistry

Terminal (i.e., having at least one non-bridging NR group) transition metal imido complexes have been known since the late 1950s,[26,27] but it was only during the last two decades that a particularly intense effort was made in exploring their syntheses, structures and reactivity. Several general reviews[28–30] and a number of more specific ones are now available.[31–42] The bonding in imido compounds is now well understood.[34] When the R–N=M angle is greater than 155–160° the dianionic ligand normally acts as a net six-electron donor to the metal, and the metal-nitrogen bond order is formally three (a $\sigma^2\pi^4$ configuration). As a π-donor ligand, the imido group promotes high oxidation state coordination and organometallic chemistry. Importantly, both the structural and reaction chemistry of metal imido compounds can be profoundly changed by modification of the N-substituent.

Apart from their potential use in materials chemistry as sources of the corresponding metal nitrides (e.g., *via* chemical vapour deposition),[43] the main current interest in imido compounds is with regard to their stoichiometric or catalytic reactions. The reactions can be divided into two types: those where the M=NR bond itself is the reactive site, and those in which the imido ligand acts as a "spectator" or "supporting" ligand. The most reactive metal-imido linkages have been found for group 4 compounds,[31,36,37,40] although many examples of M=NR group reactivity are know for other metals.

It is the second type of reactivity (imido group as a spectator ligand) that is most relevant to the catalytic chemistry described in this review. One of the best examples of this type of reactivity is the ring-opening metathesis polymerisation of olefins by imido-supported group 6 alkylidene catalysts. A short overview of this very relevant topic is given in the next section.

1.3 Ring-Opening Olefin Metathesis Polymerisation with Imido-Supported Molybdenum- and Tungsten-Alkylidene Catalysts

While the main focus of this review is the Ziegler–Natta (insertion) polymerisation of olefins by imido compounds, the living ring-opening metathesis polymerisation (ROMP) of olefins with imido-supported molybdenum- and tungsten-alkylidene catalysts [M(NAr)=(CHR)(OR')$_2$] (Ar typically = 2,6-i-Pr$_2$C$_6$H$_3$) has been known for over 15 years. This followed from original discoveries by Schrock and co-workers.[44,45] Schrock's 1990 review[46] of the early part of this work has nearly 500 literature citations, and one of the first full papers on the molybdenum imido alkylidene metathesis catalysts, also appearing in 1990,[47] has nearly 630 literature citations. Recent comprehensive reviews of this and related organic-focussed metathesis chemistry are available.[48–50] Although the tungsten systems were disclosed first,[44] the molybdenum congeners are superior: the intermediate metallacyclobutanes formed by the [2 + 2] cycloaddition of an olefin and the M=CHR bond more readily undergo ring opening, and the Mo systems are more functional group tolerant. The ROMP of norbornene by a general catalyst [M(NAr)(CHR)(OR')$_2$] is shown in Figure 3. Note that in living ROMP systems such as that illustrated, the polymer is finally cleaved from the propagating species by addition of a capping reagent, typically benzaldehyde.

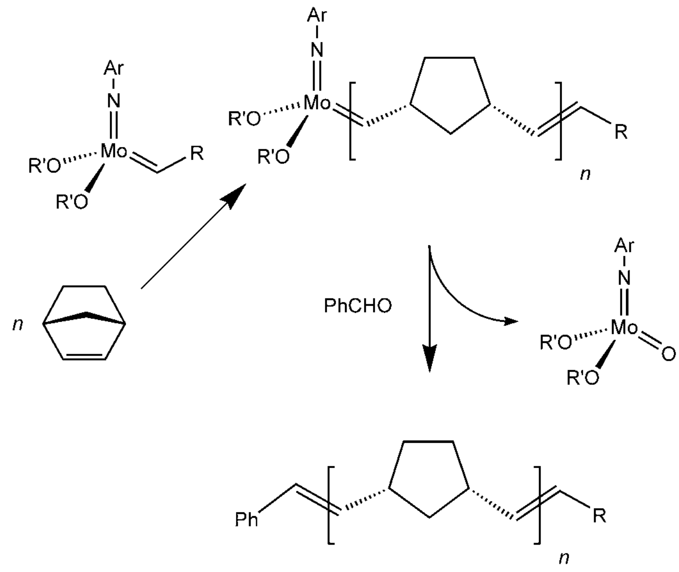


Figure 3. The ROMP of norbornene by a general catalyst [$M(NAr)(CHR)(OR')_2$].

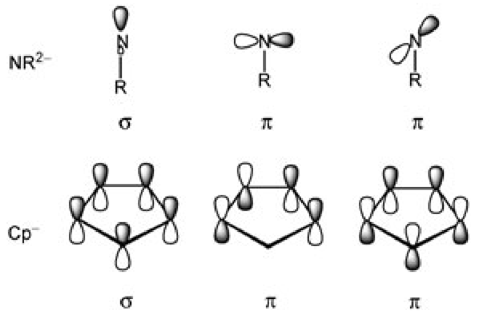


Figure 4. Frontier orbital symmetries of NR^{2-} and Cp^- ligands.

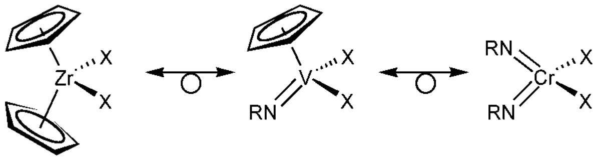
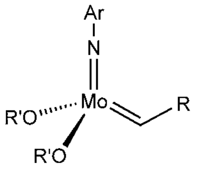


Figure 5. Isolobal relationship between group 4 metallocene and imido complexes of groups 4–6.

The compounds [$M(NAr)(CHR)(OR')_2$] can exist as *syn* (**4**) or *anti* (**5**) isomers. Although the former is usually thermodynamically more favoured, the rate of reaction of the latter can be orders of magnitude higher. Importantly, from a mechanistic point of view, it was found that the origin of the varying degrees of *cis* or *trans* double bond content in the ROMP polymer could be traced to whether the *syn* or *anti* isomer (respectively) was involved in the [2+2] cycloaddition step. The use of electron-withdrawing alkoxide ligands (OR′) produces the most active catalysts and, in general, the rates of reaction depend on the electronic and steric characteristics of the CHR group and the olefin. Use of racemic diolate co-ligands as "$(OR')_2$" can afford excellent enantiomorphic site control of the polymer tacticity.



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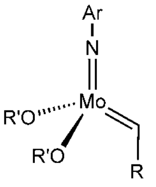

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2 Imido Compounds as Ziegler–Natta Catalysts: Design Principles

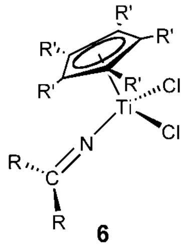
One possible approach to producing new alternative catalysts to the group 4 metallocenes is to make use of the isolobal analogy[51] in order to find suitable ligands to replace cyclopentadienide. By combining different metal ions with ligands possessing similar frontier orbital energies and symmetries to those of cyclopentadienide it should be possible to build up fragments with electronic properties approximately equivalent to [Cp_2M]$^{2+}$ (M = group 4 metal). Clearly then, since cyclopentadienide is a monoanionic ligand, for a group 4 system (where the metal is in the +4 oxidation state) it is necessary to use a combination of either two monoanionic ligands or one dianionic along with one neutral ligand in order to retain the balance of charge. Moving across the transition series the increasing charge required for a d^0 metal centre must be taken into account. Thus for vanadium(V) the overall charge of the two supporting ligands must be −3. A detailed account of this approach has been given by Gibson.[52]

As mentioned, in its most common bonding mode the formally dianionic imido ligand NR^{2-} can be considered to donate six electrons to a metal centre through a combination of one σ and two π bonds. The frontier donor orbital energies and symmetries are somewhat similar to the cyclopentadienide ligand (Figure 4). Taking into account the dianionic nature of the imido ligand, one can envisage an isolobal series across groups 4–6 of the transition series for formally d^0, 16-valence electron metal centres (Figure 5). The potential use of imido ligands in new catalysts provides much scope for tuning both the electronic and steric requirements of the metal centre by virtue of the number of alternative NR substituents that may be incorporated in a family of compounds.

3 Survey of Systems

3.1 Group 4

The possibility of preparing active group 4 imido olefin polymerisation catalysts can be anticipated from two



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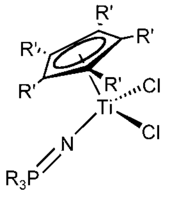

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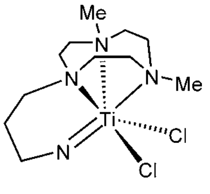

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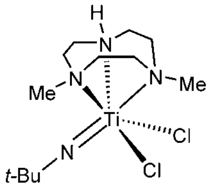

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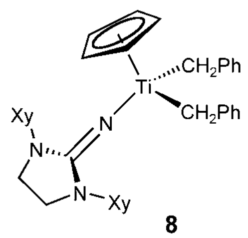

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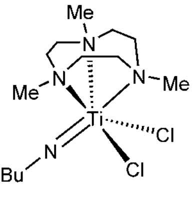

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other highly active families, namely the ketimide system **6**[53] and the phosphinimide system **7**,[54] both supported by cyclopentadienyl ligands. It is believed that in these systems the activity is enhanced by imido-type resonance contributions that increase the π-donor capability of the ligand. Indeed Hessen and co-workers have reported the synthesis of [CpTi{NC(NXyCH$_2$)$_2$}(CH$_2$Ph)$_2$] (Xy = xylyl) (**8**), a close relative of the ketimides.[55]

It is possible in the case of a guanidinate-type anion to draw zwitterionic resonance structures reminiscent of imido anions (Figure 6). The complex **8** was found to display a marked increase in catalytic activity over the otherwise equivalent ketimide [CpTi(NC-*t*-Bu$_2$)(CH$_2$Ph)$_2$] for the polymerisation of ethylene when activated with B(C$_6$F$_5$)$_3$ (1600 kg mol^{-1} h^{-1} bar^{-1} *vs.* 464 kg mol^{-1} h^{-1} bar^{-1}) under the same conditions, probably due to the favourable electronic factors imparted by the guanidinate-type ligand.

The first group 4 terminal imido catalysts were reported by Mountford et al. in 2000.[56] Neutral 1,4,7-triazacyclononane ligands were used in combination with divalent imido ligands to give titanium(IV) complexes isolobal with titanocene dichloride. A series of *ansa*-linked macrocycle-imido complexes (e.g., **9**) along with their non *ansa*-linked analogues (e.g., **10**) were synthesised and tested for their olefin polymerisation activity with MAO (methylaluminoxane) co-catalyst. The observed activities were low (0.7–4.0 kg mol^{-1} h^{-1} bar^{-1}) and showed no enhancement for the *ansa*-linked compounds. The polymer produced had high molecular weight which hampered analysis, and where GPC analysis was possible the polyethylene had very poor polydispersity indices ($M_w/M_n = 50-70$).

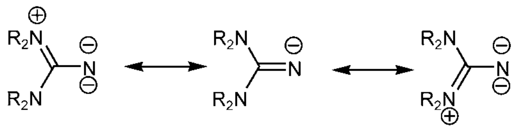
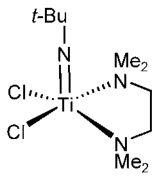


Figure 6. Resonance forms of guanidinate-type ligands.

More recently it has been demonstrated that this class of compound can be highly active.[57] At room temperature the complex [Ti(N-*t*-Bu)(Me$_3$[9]aneN$_3$)Cl$_2$] (**11**) displays a moderate activity of 22 kg mol^{-1} h^{-1} bar^{-1}. However, at 100 °C in pentamethylheptane solvent with MAO co-catalyst the same complex gives an activity in excess of 10^5 kg mol^{-1} h^{-1} bar^{-1}. These compounds were found to be amenable to high-throughput screening strategies resulting in a library of compounds with varying imido substituents. From the library of 47 compounds, 7 were found to have activities in the range 3,400–10,340 kg mol^{-1} h^{-1} bar^{-1}.

Some closely related work was reported by Nielson et al. in which the triazacyclononane ligand is replaced by a TMEDA (tetramethylethylenediamine) ligand.[58] Since the TMEDA ligand only possesses two nitrogen donors the resulting compounds possess 14 valence electrons in contrast to the 16 valence electron complexes discussed above. In addition to the compound with a *tert*-butyl imido group (**12**), two further compounds were synthesised, each having arylimido groups with bulky *ortho* substituents. The compounds were screened for ethylene polymerisation activity with MAO under various conditions and it was found that the arylimido compounds were moderately active ([Ti(N-2-*t*-BuC$_6$H$_4$)Cl$_2$(TMEDA)] (**13**) = 12.8 kg mol^{-1} h^{-1} bar^{-1} and [Ti(N-2-PhC$_6$H$_4$)Cl$_2$(TMEDA)]$_2$ (**14**) = 12.5 kg mol^{-1} h^{-1} bar^{-1}) in contrast to the low activity of the *tert*-butylimido compound **12** (3.2 kg mol^{-1} h^{-1} bar^{-1}). Interestingly the complex with an *ortho*-phenyl group (**14**) was found to be dimeric in the solid state with bridging chloride ligands.

Other dimeric titanium systems have been reported (*vide infra*), although these feature bridging imido ligands. Heterogenisations were also attempted by using



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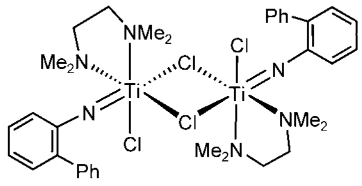

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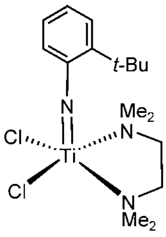

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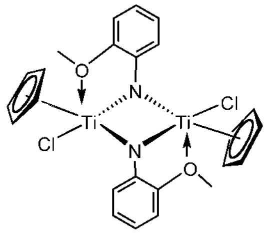
modified polystyrene resins containing TMEDA groups.[58] However, preliminary results showed that these compounds were inactive [in contrast to the situation for the supported vanadium(V) catalysts of Gibson et al. discussed below].



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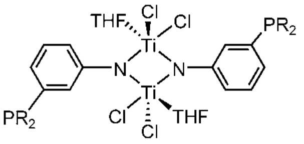

R = 3,5-$(CF_3)_2C_6H_3$

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In 2000 Qian and co-workers reported the synthesis of imido-bridged dimeric half-sandwich compounds of the type $[CpTiCl(\mu\text{-}NR)]_2$ (R = aryl or pyridyl).[59] It was shown that the complex $[CpTiCl(\mu\text{-}N\text{-}2\text{-}(OMe)C_6H_4)]_2$ (**15**) polymerises styrene in the presence of MAO. The same year a patent was taken out by Equistar on structurally similar catalysts $[M(\mu\text{-}NR)XL]_2$ (where M = group 3–10 metal; R = alkyl; X = R, halogen, alkoxy, siloxy; L = general anionic ligand) for the polymerisation of α-olefins.[60] Although metals from groups 3–10 were included, particular emphasis was placed on the group 4 systems.

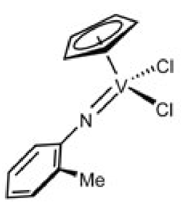
Recently, a reasonably active dimeric titanium μ-imido-bridged catalyst was reported by Bochmann et al.[61] When activated with MAO the species $[TiCl_2(THF)\{\mu\text{-}N\text{-}3\text{-}(PR_2)C_6H_4\}]_2$ [R = 3,5-$(CF_3)_2C_6H_3$] (**16**) displayed activities in the range 440–620 kg mol^{-1} h^{-1} bar^{-1}. Reaction of this complex with $[Ni(cod)_2]$ gave coordination polymers with the phosphine groups bound to nickel. The coordination polymers were also active catalysts with activities of the same order of magnitude (400 kg mol^{-1} h^{-1} bar^{-1}), therefore showing the tolerance of these catalysts to PR_3 functional groups whether complexed or non-complexed. The chloride species could also be alkylated with methyllithium, resulting in an imido bridged alkyl species. This suggested that the Ti_2N_2 framework is unlikely to be affected by MAO during catalysis.

Although beyond the scope of this review, we note that titanium and zirconium imido complexes have been found to be catalysts for the polymerisation of MMA (methyl methacrylate) *via* cycloaddition to M=NR bonds of the precatalyst. In this work Chen and co-workers reported MMA polymerisation by $[Cp_2Zr(NR)(THF)]$ (R = *t*-Bu, 2,6-*i*-$Pr_2C_6H_3$), $[Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^2\text{-}C_9H_6)Ti(N\text{-}t\text{-}Bu)(THF)]$ and $[rac\text{-}Me_2Si(Ind)_2Zr(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)]$.[62]

3.2 Group 5

3.2.1 Cyclopentadienyl and Tris(pyrazolyl)borate Compounds

As previously discussed, in order that M(V) complexes of group 5 metals should be isoelectronic and isolobal with the group 4 metallocenes, a monoanionic supporting ligand is required in addition to a dianionic imido ligand. The first example of a group 5 imido-supported olefin polymerisation catalyst was reported by Gibson et al. in 1994.[63,64] The complex $[CpV(N\text{-}2\text{-}MeC_6H_4)Cl_2]$ (**17**) was tested for ethylene polymerisation with both Et_2AlCl and MAO activators and moderate activities of 15 and 27 kg mol^{-1} h^{-1} bar^{-1}, respectively, were observed at room temperature. These catalysts were only active for the first few minutes of a 60 minute run, and subsequent results have indicated that bimolecular deactivation occurs following alkylation.[65]



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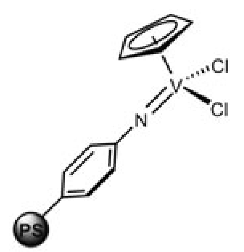

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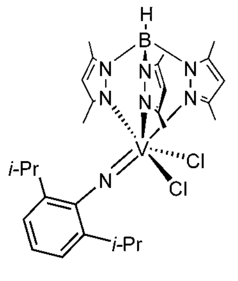
As a means of preventing such deactivation pathways Gibson et al. prepared vanadium(V) imido complexes supported on polystyrene.[66] Attachment of the catalyst through the imido ligand was achieved by an imide-exchange reaction of a *tert*-butylimido compound with an amino-functionalised polystyrene (PS) resin. The supported catalyst $[Cp(PS\text{-}N)VCl_2]$ (**18**) yielded activities of 7.6 kg mol^{-1} h^{-1} bar^{-1} with Et_2AlCl and 8.0 kg mol^{-1} h^{-1} bar^{-1} with MAO. This was a ten-fold increase in activity over that of unsupported [CpV(N-*t*-Bu)Cl$_2$] (0.7 kg mol^{-1} h^{-1} bar^{-1}) although a lower activity than for the corresponding homogeneous 2-methylphenylimido complex **17**. Significantly, however, there was a large improvement in catalyst lifetime for the supported system, with a steady uptake of ethylene over the course of a 60-minute run.

In 1995 Kress and co-workers reported a series of vanadium(V) imido complexes supported by tris(pyrazolyl)borate ligands.[67] Four different complexes were synthesised with either the parent Tp [tris(pyrazolyl)borate] or Tp* (the 3,5-dimethyl ring-substituted analogue) ligand and *tert*-butyl- or 2,6-diisopropyl-substituted imido ligands. When activated with MAO, all four compounds polymerised ethylene as exemplified by an activity value of 14 kg mol^{-1} h^{-1} bar^{-1} for [Tp*V(N-2,6-*i*-Pr$_2$C$_6$H$_3$)Cl$_2$] (**19**).



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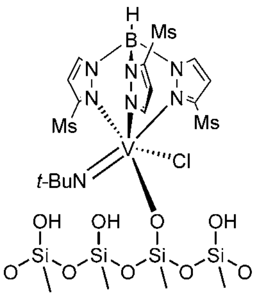

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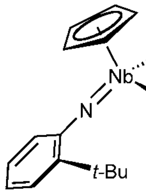
Some closely related work has recently been published by Santos et al. in which tris(pyrazolyl)borate imidovanadium(V) complexes have been immobilized onto various inorganic supports.[68] The compound [Tp$^{\mathrm{Mes}*}$V(N-*t*-Bu)Cl$_2$] was grafted onto SiO$_2$ (**20**), MAO-modified SiO$_2$, SiO$_2$-Al$_2$O$_3$, MCM-41, MgO and MgCl$_2$ [Tp$^{\mathrm{Mes}*}$ = HB(3-N$_2$C$_3$H$_2$Mes)$_2$(5-N$_2$C$_3$H$_2$Mes)]. Activities for the supported systems ranged from 8.1–88.8 kg mol^{-1} h^{-1} bar^{-1}, the highest activity being observed for the silica-supported catalyst **20** activated by a mixture of TiBA (triisobutylaluminium) and MAO. In comparison, the corresponding homogeneous system displayed a high activity of 922 kg mol^{-1} h^{-1} bar^{-1} when activated with MAO.

In order to compare catalysts of first and second row transition metals Gibson et al. tested the niobium complex [CpNb(N-2-*t*-BuC$_6$H$_4$)Cl$_2$] (**21**), reporting an activity of 0.6 kg mol^{-1} h^{-1} bar^{-1} when activated with Et$_2$AlCl, i.e., lower than for the related vanadium catalyst.[64] In the same study, dialkyl complexes of both niobium and tantalum, [Cp*Nb(N-2,6-*i*-Pr$_2$C$_6$H$_3$)Me$_2$] and [Cp*Ta(N-*t*-Bu)(CH$_2$Ph)$_2$] (the bulkier Cp* ligand was necessary to stabilise the dialkyl species), were screened for ethylene polymerisation with the anilinium borate activator [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. Negligible activities were recorded in each case.



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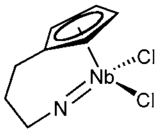

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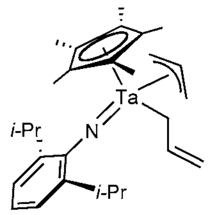
Green and co-workers have reported attempts to synthesise niobium-based olefin polymerisation catalysts. In 1992 these researchers reported the synthesis of the *ansa*-linked compound [Nb{η:σ-C$_5$H$_4$(CH$_2$)$_3$N}Cl$_2$] (**22**).[69] Later attempts were made to alkylate **22**; this resulted in various species all of which were found to be catalytically inactive.[70] The dichloride precursor also displayed no polymerisation activity when activated with MAO. It was postulated that this lack of activity is due to the frontier orbitals of these compounds being too dissimilar to those of bent metallocenes.

In 1997 Stryker et al. reported some work using half-sandwich tantalum imido complexes.[71] Having previously shown that [Cp*$_2$Zr(C$_3$H$_5$)][BPh$_4$] is a single-component ethylene polymerisation catalyst, they targeted cationic allyl complexes of tantalum, in the hope that they would be more stable than the corresponding alkyl compounds. The fluxional bis(allyl) complex [Cp*Ta(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(η^3-C$_3$H$_5$)(η^1-C$_3$H$_5$)] (**23**) was synthesised and tested for catalytic activity towards ethylene with [Ph$_3$C][B(C$_6$F$_5$)$_4$] activator in fluorobenzene solvent. The activity was low (6.9 kg mol^{-1} h^{-1} bar^{-1}) and the polymer produced had a rather high polydispersity index of 17.4, implying that this is not a single-site catalyst. Stryker also noted that the parent dichloride [Cp*Ta(N-2,6-*i*-Pr$_2$C$_6$H$_3$)Cl$_2$] is inactive with MAO co-catalyst. For comparison, the compounds [Cp*Ta(NSi-*t*-Bu$_3$)Cl$_2$] (**24**) and [Cp*Ta(NSi-*t*-Bu$_3$)(η^3-C$_3$H$_5$)(η^1-C$_3$H$_5$)] (**25**) were also prepared. In this case the dichloride **24** gave an activity of 13.6 kg mol^{-1} h^{-1} bar^{-1} when activated with MAO but the bis(allyl) **25** was inactive in the presence of either [Ph$_3$C][B(C$_6$F$_5$)$_4$] or B(C$_6$F$_5$)$_3$. The steric protection provided by the bulky tris(*tert*-butyl)silyl groups, which could help prevent dimerisation and attack of MAO at the imido nitrogen, could explain why this dichloride species displays moderate activity whilst no activity is observed when the diisopropylphenylimido group is used. Why the bis(allyl) species **25** in this case is inactive is unclear.

Another tantalum(V) imido catalyst was recently reported by Chen et al.[72] Methylation of [(η^5-C$_5$Me$_4$H)-Ta(N-*t*-Bu)Cl$_2$] with MeMgBr yielded [(η^5-C$_5$Me$_4$H)-Ta(N-*t*-Bu)Me$_2$] (**26**) which was then tested for ethylene/1-octene co-polymerisation with either PMAO-IP or [HNMe(C$_{18}$H$_{37}$)$_2$][(C$_6$F$_5$)$_3$AlNC$_3$H$_3$NAl(C$_6$F$_5$)$_3$] activators. With PMAO-IP an activity of 88 kg mol^{-1} h^{-1} bar^{-1} was recorded (at 130 °C). However, with the Al-



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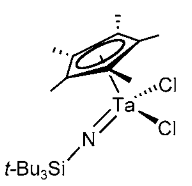

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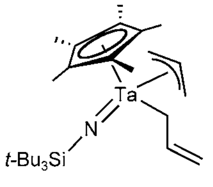

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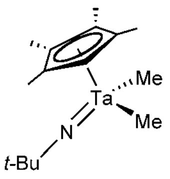

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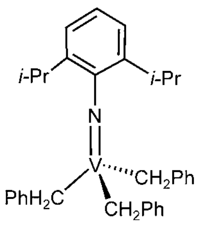
imidazolide activator the activity was as high as 1190 kg mol^{-1} h^{-1} bar^{-1} at 140 °C. The high molecular weight ($M_w = 127{,}000$) of the polymer produced, along with its low density (0.898 g mL^{-1}), are believed to indicate a high incorporation of octene in the copolymer. This system is clearly highly active, although the unusual activators and conditions (including the type of polymerisation) make it difficult to compare with other systems in the literature.

3.2.2 Other Vanadium(V) Compounds

Although both Gibson and co-workers and Teuben and co-workers have found a propensity for reductive dimerisation of vanadium(V) alkyl species,[65,73] in 1997 Murphy and Turner at Exxon reported the synthesis and structural characterisation of [V(N-2,6-*i*-$Pr_2C_6H_3$)-($CH_2Ph)_3$] (**27**).[74] The bulky 2,6-diisopropylphenylimido substituent was used because it was believed that it would afford steric protection around the vanadium(V) centre. It may also be the case that the benzyl groups provide extra stability compared to methyl groups, since reductive dimerisation was in fact observed for the corresponding methyl complexes. Although the reactions of **27** with various reagents to yield dibenzyl-alkoxide, -aryloxide and -amido derivatives were reported, the use of these compounds in olefin polymerisation catalysis has not been disclosed.



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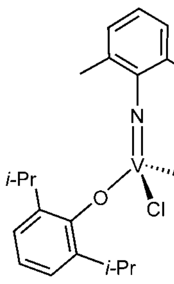

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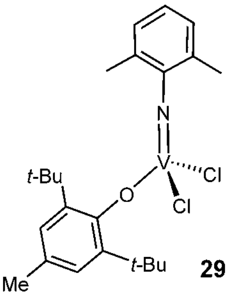

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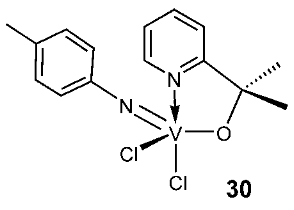
Nomura and co-workers reported two new vanadium(V) imido complexes with aryloxide coligands in 2001.[75] The first of these compounds, [V(N-2,6-$Me_2C_6H_3$)(O-2,6-*i*-$Pr_2C_6H_3$)Cl_2] (**28**), had a high activity of 119 kg mol^{-1} h^{-1} bar^{-1} when activated with d-MAO (solid MAO with $AlMe_3$ and toluene removed) at 25 °C. This activity dropped off at lower temperatures. [V(N-2,6-$Me_2C_6H_3$)(O-2,6-*t*-Bu-4-MeC_6H_2)Cl_2] (**29**) diplayed a moderate activity of 60 kg mol^{-1} h^{-1} bar^{-1} with the same co-catalyst at 60 °C, and even lower activities at 25 °C. The authors suggest that their catalysts are more active than those of Gibson[63,64] and Kress[67] due to the low coordination number around the vanadium centre. The dibenzyl complex [V(N-2,6-$Me_2C_6H_3$)(O-2,6-*i*-$Pr_2C_6H_3$)($CH_2Ph)_2$] was prepared by an analogous procedure to that used by Murphy and Turner,[74] and could be used as a catalyst for ROMP. Subsequent work by Nomura et al. has been directed at gaining an understanding of how substituents on the aryloxide ligand affect the catalytic activity, and also the effect of changing the reaction conditions for catalysis.[76,77] It was found that when activated with Et_2AlCl, under optimised conditions [V(N-2,6-$Me_2C_6H_3$)(O-2,6-*i*-$Pr_2C_6H_3$)Cl_2] (**28**) displayed activities up to 1024 kg mol^{-1} h^{-1} bar^{-1}, an order of magnitude higher than when activated with d-MAO. Lower temperatures were found to give higher activities in this case, the exact opposite trend to that with d-MAO. To investigate the role of substituents on the aryloxide ligand two new compounds in this family were synthesised, having either phenyl or methyl groups in the 2- and 6- positions of the aryloxide ligand. The O-2,6-$Ph_2C_6H_3$-supported compound was found to have the lowest activity, possibly due to the large steric bulk of the phenyl groups. Generally it was found that the optimum conditions for ethylene polymerisation were dependent on the catalyst precursor.

O,N-Chelating ligands have been used along with either oxo or imido ligands in vanadium(V) complexes by van Koten and co-workers.[78] The imido compound {V(N-4-MeC_6H_4)Cl_2[$OCMe_2$(2-C_5H_4N)]} (**30**) gave low activities of 0.8–2.2 kg mol^{-1} h^{-1} bar^{-1} for ethylene polymerisation with Et_2AlCl activator under various conditions, significantly lower than the activities of 57–107 kg mol^{-1} h^{-1} bar^{-1} observed for the corresponding



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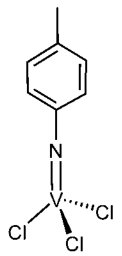

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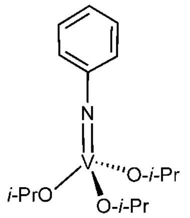

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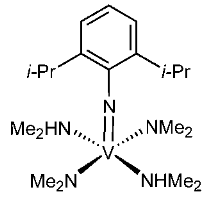
oxo compound [$VOCl_2\{OCMe_2(2\text{-}C_5H_4N)\}$]. Two of the classes of compound used as starting materials in this study were also screened. Of the compounds tested, the most active at 114–215 kg mol^{-1} h^{-1} bar^{-1} was [$V(N\text{-}4\text{-}MeC_6H_4)Cl_3$] (**31**), although this could not be directly compared to the value obtained for [$VOCl_3$] since in this case some precipitate formed during preactivation. [V(NPh)(O-*i*-Pr)$_3$] (**32**) gave activities of 9–53 kg mol^{-1} h^{-1} bar^{-1} compared with 30–135 kg mol^{-1} h^{-1} bar^{-1} for [VO(O-*i*-Pr)$_3$] (note that ranges of activities are quoted here since many different conditions were used by these authors). In all cases very high molecular weight polymer was produced making GPC analysis difficult, and no information on the molecular weight distribution was reported. The authors surmise that the imido compounds are less active due to the inability of the imido nitrogen to form a Lewis adduct with an aluminium species, in contrast to the oxo unit. It was postulated that formation of a Lewis adduct would decrease π-donation to the metal centre making insertion of ethylene into a vanadium-carbon bond more favourable.

A DFT study of olefin polymerisation by some *neutral* vanadium(V) imido catalysts has been carried out by Bühl.[79] The model compounds chosen were of the type [$V(NR)Me_3$] [R = H, *t*-Bu, $C(CF_3)_3$, C_6H_5, 4-$OMeC_6H_4$, 2,4-$(NO_2)_2C_6H_3$ and 2-$(COMe)C_6H_4$]. The barrier for insertion of ethylene into a V–C bond, along with ^{51}V chemical shifts, were calculated for each of these compounds. The calculations predicted that placing a suitable group in the *ortho* position of an arylimido substituent could lead to anchimeric assistance for ethylene insertion. For example, an *ortho* nitro group leads to a stabilisation of the transition state by an intramolecular V···O interaction and also to a large deshielding of the ^{51}V resonance.

3.2.3 *Vanadium(IV) Compounds*

In 2000 Choukroun et al. reported two new d^1 vanadium(IV) imido-based polymerisation catalysts, [V(N-2,6-*i*-$Pr_2C_6H_3$)$(NMe_2)_2(NHMe_2)_2$] (**33**) and [V(N-2,6-*i*-$Pr_2C_6H_3$)$Cl_2(NHMe_2)_2$] (**34**).[80] Preliminary ethylene polymerisation results showed that the dichloride **34** is moderately active with MAO co-catalyst (activity 59 kg mol^{-1} h^{-1} bar^{-1}), and displays a higher activity of 120 kg mol^{-1} h^{-1} bar^{-1} when activated with $EtAlCl_2$. The bis(amido) compound **33** was tested with $EtAlCl_2$ co-catalyst and this gave an activity of 22 kg mol^{-1} h^{-1} bar^{-1}. The polymer produced from the $EtAlCl_2$-activated catalyst system had a high molecular weight, and in all cases reasonable polydispersity indices of approximately 3.0 were recorded.



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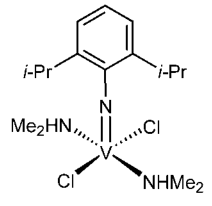

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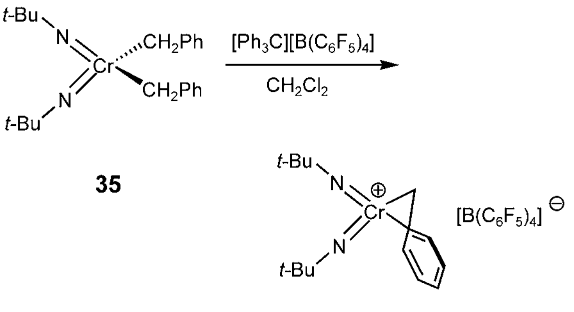
3.3 Group 6

Much of the work to date on group 6 imido olefin polymerisation catalysts has been carried out by Gibson and co-workers. Group 6 complexes in the +6 oxidation state require two dianionic supporting ligands in order to be isolobal with the group 4 bent metallocenes (*cf.* Figure 5). Bis(imido) complexes fulfil this criterion, and in 1994 Gibson et al. reported ethylene polymerisation catalysis by [Cr(N-*t*-Bu)$_2$Cl$_2$] with both Et_2AlCl and MAO activators.[63,64] Both activators gave low activities of 9.0 and 4.4 kg mol^{-1} h^{-1} bar^{-1} respectively. The molybdenum analogue [Mo(N-*t*-Bu)$_2$Cl$_2$] showed little activity, with a value of < 0.2 kg mol^{-1} h^{-1} bar^{-1} obtained with Et_2AlCl activator. Alkylation of [Cr(N-*t*-Bu)$_2$Cl$_2$] afforded [Cr(N-*t*-Bu)$_2$(CH$_2$Ph)$_2$] (**35**); the corresponding complexes [Cr(N-2,6-*i*-$Pr_2C_6H_3$)$_2$R$_2$] (R = CH_2Ph, Me) were also prepared.[64,81]

When activated with $B(C_6F_5)_3$ or [$PhNMe_2H$][$B(C_6F_5)_4$] these dialkyl compounds gave activities up to 66 kg mol^{-1} h^{-1} bar^{-1}. Treatment of [Cr(N-*t*-Bu)$_2$(CH$_2$Ph)$_2$] (**35**) with [Ph_3C][$B(C_6F_5)_4$] in CH_2Cl_2 [Equation (1)] gave [Cr(N-*t*-Bu)$_2$(η^2-CH$_2$Ph)][$B(C_6F_5)_4$] (**36**) which was studied by NMR spectroscopy. The chemical shift of the *ipso* carbon (128.8 ppm) along with the reduced value of the $^2J_{C,H}$ coupling constant for the methylene protons (5.3 Hz) were diagnostic of a η^2-bound benzyl ligand. The molybdenum alkyls [Mo(N-*t*-Bu)$_2$(CH$_2$Ph)$_2$] and [Mo(N-2,6-*i*-$Pr_2C_6H_3$)$_2$(CH$_2$Ph$_2$)$_2$] gave low activities of 3 and 4 kg mol^{-1} h^{-1} bar^{-1} when activated with [$PhNMe_2H$][$B(C_6F_5)_4$]. It is thought that the low activities for molybdenum complexes can be explained by their tendency to form dimeric imido-bridged species. The polymer produced by Gibson and co-workers' well-defined chromium systems was found to have a broad and often bimodal molecular weight distribution, possibly indicating the presence of multiple active sites.



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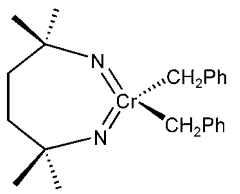
(1)

Chromium mono(imido) compounds of the type $[Cr(NR^1)Cl(X)_m(L)_n]$ {where R^1 = alkyl, aryl, SiR_3; X = halogen, OR [m = 2 (monoanionic), 1 (dianionic)]; L = neutral donor (n = 0, 1, 2, 3)} have recently been patented by Elenac GmbH.[82]



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Siemeling et al. have reported the application of Gibson's bis(imido)chromium compound **35** and some other related chromium and molybdenum bis(imido) chelate complexes (*ansa*-metallocene analogues) to the homo- and co-polymerisation of polar olefins.[83] Both **35** and the *ansa*-type compound $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (**37**) were shown to polymerise acrylonitrile and MMA in the absence of activators. Indeed, under the conditions used for ethylene polymerisation these compounds were inactive for the polymerisation of polar monomers. This indicates that the mechanism does not involve reactions of a cationic metal centre, the precise mechanism being unknown. The molybdenum analogue of **37** can also polymerise acrylonitrile and MMA, although with lower efficiency than the chromium complexes. The chromium compounds were also active in the co-polymerisation of acrylonitrile and MMA.

DFT studies by Jensen and Børve[84] on models of Gibson's chromium system **36** have revealed the possibility of chemically modified active species as a result of [2+2] cycloaddition of ethylene to a Cr=NR bond of a monoalkyl cation. These authors studied cations of the general formula $[Cr(NR')_2R]^+$, looking at monomer insertion by the Cossée–Arlman mechanism. DFT calculations were carried out for the case of a methyl cation, a propyl cation (i.e., the product of the first insertion and a model for a growing polymer chain) and a benzyl cation. Insertion following both frontside and backside approach of ethylene was calculated, the lowest energy pathway being frontside coordination followed by a frontside to backside rearrangement and backside insertion ($14\ kcal\ mol^{-1}$). A competing reaction of [2 + 2] cycloaddition of the frontside coordinated ethylene to one imido Cr=N bond had a barrier of only $3-6\ kcal\ mol^{-1}$ for different imido NR substituents.

The same researchers subsequently reported calculations on the [2 + 2] $Cr{=}NR/C_2H_4$ cycloaddition product,[85] where they had discovered a facile β-hydrogen transfer from the growing chain to the azachromacycle, resulting in an α-olefin coordinated to a Cr(IV) centre. The barrier of this reductive elimination was found to be comparable to the barriers for the insertions, but being an irreversible reaction, indicated that in Gibson's catalyst systems the chromium(VI) cations may be reduced rapidly following exposure to ethylene. Further modification could then be possible resulting in reduced active species. Although the barriers to insertion seem to be particularly high for chromium compared to Group 4 metallocenes (due to a high barrier to inversion around the metal centre), clearly these results may have implications for all transition metal imido olefin polymerisation catalysts. It should be mentioned that these DFT results did not take into account anion or solvent effects.

4 Summary and Outlook

During the past decade much progress has been made in the development of imido-supported non-metallocene olefin polymerisation catalysts. The isolobal relationship with cyclopentadienide has helped researchers design new catalysts reminiscent of the well-established group 4 metallocenes. The imido ligand has been found to be a useful supporting ligand in group 4–6 metal catalysts. Much of the early success in the area was confined to vanadium and chromium systems, although at best these were only moderately active on the "Gibson scale".[86] Only in the last couple of years have we seen the emergence of highly active imido catalysts, predominantly based on titanium(IV). Catalysts based on zirconium or hafnium imido compounds certainly appear to be a "missing link" in this area.

Certain research groups have shown (for a particular catalyst family) how activity can depend greatly on the imido NR substituent, possibly due to both electronic and steric factors. However, it appears that there is still a long way to go before one will be able to predict structure-activity relationships with any degree of accuracy. Computational studies have indicated that in some cases the M=N bond itself could play a role in the catalytic process, suggesting that one should hold questionable any assumption that the imido ligand is merely a spectator ligand in all of the systems described above. Clearly a future challenge is to investigate this possibility in more depth, both computationally and experimentally.

As yet, no imido-based Ziegler–Natta catalyst has proved capable of catalysing living olefin polymerisation or controlling polymer stereochemistry. Furthermore, few reports of the homo- or co-polymerisation of α-olefins have been published. These are also desirable goals for the future.

Acknowledgements

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