# Recent advances in homogeneous chromium catalyst design for ethylene tri-, tetra-, oligo- and polymerization

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*Dedicated to Professor Armando J.L. Pombeiro for his outstanding achievements in Coordination Chemistry and Catalysis*

**Abstract**

This review focuses on recent progress made using well-defined molecular chromium complexes that, upon suitable activation, can catalyze the tri-, tetra, oligo- and/or polymerization of ethylene. In particular, emphasis will be placed on the tuning of the performance characteristics of these homogeneous catalysts through structural modifications made to the multidentate ligand manifold (*e.g.*, donor atoms, charge, backbone and strain) and the effects these changes have on the resulting ethylene derivatives. While the ability of these catalysts to mediate the formation of high molecular weight linear polyethylene continues to see many developments, their capacity to form polyethylene waxes and oligomers has witnessed some major advances. Moreover, the impressive selectivity of some chromium systems to generate commercially important 1-hexene and more recently 1-octene has seen the implementation of this technology at the industrial level. The types of precatalysts to be discussed will be divided broadly on the basis of their ability to generate either polymers/oligomers or short chain α-olefins; the effects of co-catalyst and reaction conditions (*e.g.*, temperature, pressure, solvent) on catalytic activity and selectivity, will be also developed. In addition, current proposals as to the mechanistic details displayed by these versatile chromium catalysts will be highlighted.

**Keywords**: Chromium precatalyst; Ethylene oligomerization; Ethylene polymerization; Ligand modification; Catalytic mechanism; Polyethylene microstructure.

**Contents**

## 1. Introduction

The application of chromium as a metal center in olefin polymerization has a long and illustrious track record. Since the discovery by Hogan and Banks at Phillips Petroleum Company in the early 1950s that chromium oxide supported on silica ($CrO_3/SiO_2$) could serve as a highly active polymerization catalyst forming high density polyethylene (HDPE), new developments in the field have continued apace to this day. Staggeringly, this heterogeneous Phillips process, which was licensed in less than 4 years, nowadays produces around 40 - 50% of HDPE produced globally [1].

Driven originally by a desire to shed some light on the mechanistic pathway and active species operating in heterogeneous chromium catalysts, many types of homogeneous variants have been disclosed. While revealing in many cases, these studies have curiously led to a wide variety of proposals as to the formal oxidation state of the catalytically-active chromium species. Nonetheless, some of the resulting molecular catalysts have proved highly active in their own right for not only olefin polymerization but also oligomerization and perhaps most significantly selective α-olefin formation. Given this outstanding versatility and with a view to designing more advanced homogeneous catalysts

2

based on chromium, a raft of different ligand frames has been studied. Many of the early developments focused on $\eta^5$-cyclopentadienyl ligands with a view to modelling the Union Carbide catalyst (Cp$_2$Cr/SiO$_2$) [2-4], some examples include cyclopentadienyl-amine [5-8], cyclopentadienyl-phosphine [9,10], cyclopentadienyl-amido [11] and pentamethylcyclopentadienyl [12,13]. Indeed, the most productive of these chromium catalysts is bound by a cyclopentadienyl-amine ligand and delivers activities as high as ~$10^4$ kg PE (mol Cr)$^{-1}$ h$^{-1}$ [6]. Several review articles have been concerned with covering these developments [14-17].

Notwithstanding these major advances involving cyclopentadienyl chemistry, other ligand systems including those based on monodentate (*e.g*, NR) [18-21], bidentate (*e.g.*, N^N, N^O, N^P, P^P; see sections 2 and 3), tridentate (*e.g.*, N^N^N, S^P^S, S^N^S, P^N^P and P^P^O; see sections 2 and 3) and tetradentate (*e.g.*, N^N^N^N; see section 2) frameworks have emerged and moreover proved their suitability as supports for homogeneous chromium catalysts. Through variation in the donor atom, charge on the ligand manifold, bite angle, steric and electronic properties and more recently ligand strain, a rich toolbox of soluble chromium catalysts are now available to the chemist. Most importantly, many of these non-cyclopentadienyl chromium complexes are highly active and can produce a broad range of commercially important materials from high molecular weight polymers through to linear $\alpha$-olefins (LAO's) [5,22-25]. Significantly, some catalysts can show remarkable selectivities for short chain LAO's such as 1-hexene or 1-octene, something that it is not achievable with conventional SHOP or Ziegler-type approaches which form statistical product distributions [26-34]. As a consequence, these short chain LAO's can be used directly as co-monomers in the manufacture of linear low-density polyethylene (LLDPE) eliminating the need for prior purification/separation. Unsurprisingly, the chromium-based trimerization technology used to form 1-hexene has been the subject of much industrial interest with disclosures made by Union Carbide [2-4], Chevron-Phillips [6,35-37] and BP [7]. More

recently, Sasol has commissioned the first process to form 1-octene using ethylene tetramerization technology based on a molecular chromium catalyst [38-45].

In this review, we focus on the various developments that have occurred in primarily the last ten years involving chromium precatalysts based on non-cyclopentadienyl ligands. For earlier accounts, the reader is directed towards a number of key review articles [46-55]. The discussion of the types of precatalyst will be divided into two main sections based on the selectivity of the catalyst towards either oligomers/polymers or short chain LAO's. The performance characteristics of each precatalyst will be further discussed in terms of the ligand type, co-catalyst and operating conditions. A final section will be dedicated to the current understanding of reaction mechanism.

## 2. Chromium precatalysts for ethylene oligo-/polymerization

Herein we document key examples of homogeneous chromium catalysts that show good performance for ethylene oligomerization, polymerization or both. The nature of the chelating ligand is used to sub-divide the section with catalysts based on i) N^N^N, N^N^N^N, ii) fused-N^N^N, iii) N^N^O, N^O^N, N^O and iv) N^N, N^P ligands described accordingly; other multidentate ligand frames with different donor atom combinations have also been reported but are considered beyond the scope of this article [56,57].

*2.1. N^N^N and N^N^N^N ligands and their Cr precatalysts*

Esteruelas *et al.* first reported in 2003 symmetrical bis(imino)pyridine-chromium(III) chloride complexes **1a - 1j** and their role as precatalysts for ethylene polymerization (Figure 1); unsymmetrical examples containing two different aryl groups were also reported [22]. The catalytic activities of **1a – 1j** were investigated using a variety of activators including MAO, TIBA or TIBAO. With regard to the MAO activation, cyclohexyl-containing **1a** showed only low activity. By contrast, those with N-aryl

groups, **1b** – **1j**, containing at least one substituent at their *ortho* positions showed much higher activities operating most effectively at 70 °C (between $1.25 \times 10^5$ and $4.14 \times 10^7$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$). Indeed, the highest activity was achieved for 2,4,6-trimethylphenyl-containing **1g** highlighting the beneficial effect of a *para*-methyl group. In terms of steric properties, the size of the *ortho*-substituents is crucial with too much bulk (*e.g.*, $^t$Bu in **1h**) rendering the catalyst inactive. Notably, changing the imine-carbon methyl in **1g** for a phenyl group had little or no effect on the activity. On the other hand, the presence of donor groups, such as methoxy, in the *ortho* or *para* positions of the N-aryl groups (*e.g.*, **1i** and **1j**) resulted in the catalysts being inactive. It should be noted that the good thermal stability of these systems (optimum performances between 60 – 70 °C) contrasts with the lower optimal temperatures observed for iron and cobalt catalysts with the same ligands [58-61]. The molecular weight of the polyethylene obtained using the *ortho*-$^t$Bu-containing **1h** was the highest of the series reaching a $M_w$ of 257500 g mol$^{-1}$. All the other catalysts, incorporating less sterically bulky N-aryl groups, gave linear polyethylene of lower molecular weight with $M_w$'s between 1630 and 35900 g mol$^{-1}$ and in most cases containing some content of waxes.



**1b:** R$^1$ = R$^2$ = Et, R$^3$ = H; **1c:** R$^1$ = CF$_3$, R$^2$ = R$^3$ = H
**1d:** R$^1$ = $^i$Pr, R$^2$ = Me, R$^3$ = H; **1e:** R$^1$ = R$^2$ = $^i$Pr, R$^3$ = H
**1f:** R$^1$ = R$^2$ = Me, R$^3$ = H; **1g:** R$^1$ = R$^2$ = R$^3$ = Me
**1h:** R$^1$ = $^t$Bu, R$^2$ = R$^3$ = H; **1i:** R$^1$ = OMe, R$^2$ = Me, R$^3$ = H
**1j:** R$^1$ = R$^3$ = OMe, R$^2$ = H

**2a:** R$_1$ = R$_2$ = R$_3$ = R$_4$ = R$_5$ = H
**2b:** R$_1$ = Me, R$_2$ = R$_3$ = R$_4$ = H, R$_5$ = naphthyl
**2c:** R$_1$ = R$_5$ = F, R$_2$ = R$_3$ = R$_4$ = H
**2d:** R$_1$ = R$_5$ = Br, R$_2$ = R$_3$ = R$_4$ = H
**2e:** R$_1$ = R$_2$ = R$_3$ = R$_4$ = R$_5$ = F

**3a:** R$_1$ = R$_2$ = H.
**3b:** R$_1$ = R$_2$ = 2-Me
**3c:** R$_1$ = R$_2$ = 2-Et
**3d:** R$_1$ = R$_2$ = 2-$^i$Pr
**3e:** R$_1$ = R$_2$ = 2-$^t$Bu

**3f:** R$_1$ = R$_2$ = 2,6-Me$_2$
**3g:** R$_1$ = R$_2$ = 2,5-$^t$Bu$_2$
**3h:** R$_1$ = 2,4,6-Me$_3$, R$^2$ = 4-$^t$Bu
**3i:** R$_1$ = 2,4,6-Me$_3$, R$^2$ = 2-Me
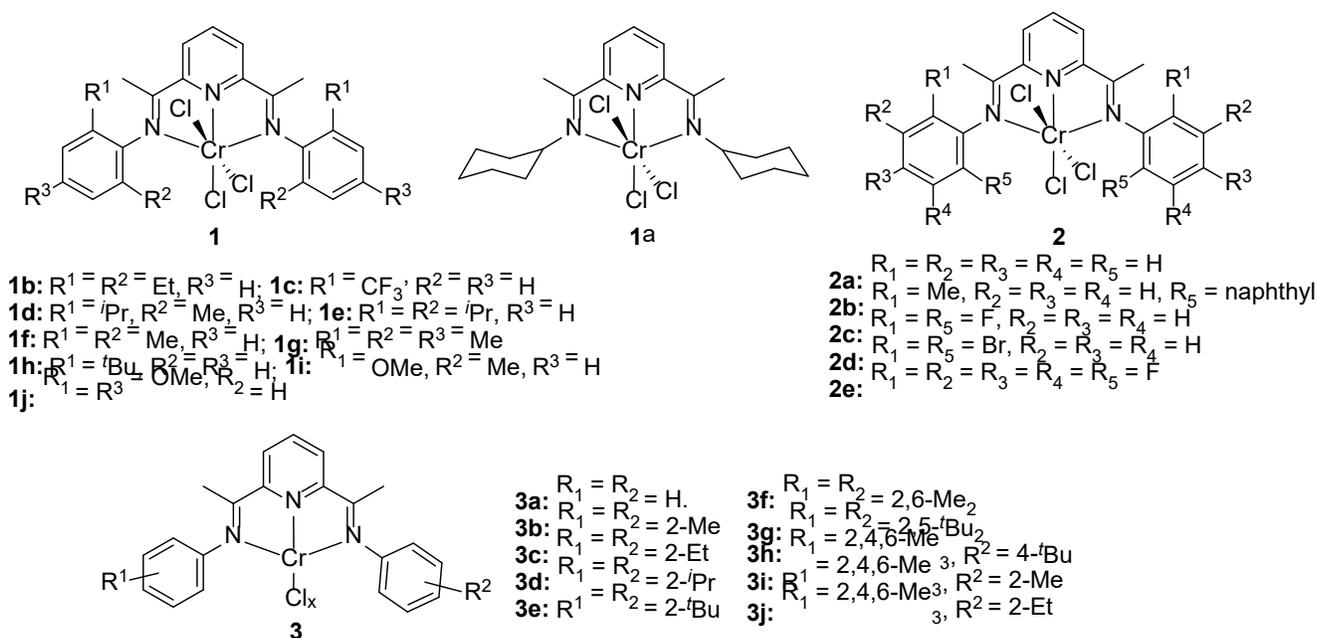**3j:** R$_1$ = 2,4,6-Me$_3$, R$^2$ = 2-Et

**Figure 1.** First generation bis(imino)pyridine-chromium precatalysts **1** - **3** [22-24,62]

Shiono and co-workers also investigated the polymerization performance of the chromium(III) chloride complexes **1a**, **1b** and **1e** - **1f** and in addition reported **2a** - **2k** which contain either unsubstituted N-aryl groups or aryl groups possessing naphthyl and halide (F and Br) substituents (Figure 1) [62]. The catalytic evaluation revealed MMAO to be a more effective co-catalyst than TMA, DEAC, TIBA and MAO. High productivities for polyethylene were again observed for **1a**, **1b** and **1d** - **1f**, while **2a** – **2k** were much less active than complexes containing just two alkyl substituents in the *ortho* positions of the N-aryl groups. In the case of **2a**, which contains an unsubstituted N-phenyl group, significant ethylene uptake and reaction exotherm was observed with low polyethylene yield. Complexes **1b**, **1d** - **1f** and **2j** showed high activity $(1.79 – 3.40 \times 10^5$ g $(mol\ Cr)^{-1}\ h^{-1})$ at an Al/Cr molar ratio of 500 and gave highly linear polymer. Intriguingly, complex **2k** possessing N-pentafluorophenyl groups was found to promote ethylene homo-polymerization leading to branched polyethylene containing mostly ethyl branches with moderate activity $(4.38 \times 10^4$ g $(mol\ Cr)^{-1}\ h^{-1})$.

In 2009 Semikolenova *et al.* compared the ethylene polymerization performance of bis(arylimino)pyridine-iron, cobalt, vanadium and chromium complexes (Figure 1) [23]. In case of the bis(arylimino)pyridine-chromium(III) chloride **1f**, this was screened with MAO at a relatively low Al/Cr molar ratio of between 100 and 200. The polymerization was shown to commence immediately affording high activity $(4.0 \times 10^5$ $(mol\ Cr)^{-1}\ bar^{-1})$, providing higher yields of polyethylene when compared with the system employed without preactivation $(1.4 \times 10^5$ g $(mol\ of\ Cr)^{-1}\ bar^{-1}\ min^{-1})$. The data also showed that the preactivated systems $((LCrCl_3/MAO) + TIBA)$ were highly active at increased polymerization temperature. For example, the yield of the polyethylene obtained in the polymerization run at 70 $^oC$ $(12400$ kg $(mol\ Cr)^{-1}\ bar^{-1})$ was nearly 1.3 times higher than that obtained at 35 $^oC$ $(9920$ kg $(mol\ Cr)^{-1}$ $bar^{-1})$ which highlights the appreciable thermal stability of the catalyst. The polymers produced were highly linear with a narrow dispersity $(M_w/M_n = 1.7 – 1.9)$ with similar $M_w$ values $(1.2 – 1.5 \times 10^3$ g mol$^{-1})$.

Several chromium(II) and chromium(III) chloride complexes, **3a** – **3j**, supported by symmetrical and unsymmetrical tridentate bis(imino)pyridines have been reported by Small *et al.* (Figure 1) [24]; monoimine N^N^O ligand systems were also disclosed (see **22** in Figure 6). The work focused on the chromium(III) complexes, as the chromium(II) species proved more air sensitive and more difficult to obtain analytically pure. Nevertheless, both Cr(II) and Cr(III) complexes (**3a** – **3j**) were active for ethylene oligomerization and polymerization. Indeed, **3a** – **3f** on activation with MMAO were able to dimerize and oligomerize ethylene under 1 bar $C_2H_4$, Al/Cr = 500, Temp = 25 – 35 °C, generating 2-butene, 1-butene and polyethylene waxes. For **3a** - **3d**, the catalytic activity was increased by raising the temperature from room temperature to 35 °C affording predominantly high purity 1-butene (>99%) with trace amounts of hexene and octene. By contrast, **3e** and **3f** containing 2-$^tBu$ and 2,6-dimethyl groups produced waxes and polyethylene with $M_w$'s of $0.72 – 0.83 \times 10^3$ g mol$^{-1}$ for the solid fractions. On the other hand, **3g** containing 2,5-substituted *tert*-butyl substituents showed a high activity of $1.15 \times 10^4$ g (g Cr)$^{-1}$ at 100 °C forming polyethylene. In the case of **3i** and **3j**, productivities of between $1.13 – 1.75 \times 10^4$ g (g Cr)$^{-1}$ were achieved affording linear α-olefins with $K$ values of between 0.60 and 0.65 [$K$ represents the probability of chain propagation ($K$ = rate of propagation / ((rate of propagation) + (rate of chain transfer)) = (moles of $C_{n+2}$) /(moles of $C_n$)] [24,25,44,49,55].



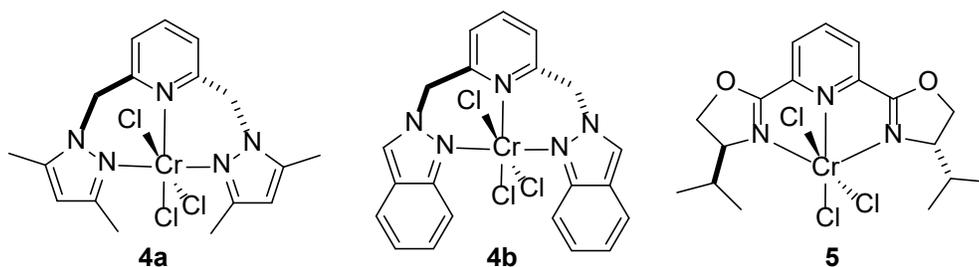**Figure 2.** N^N^N-chromium precatalysts, **4** and **5** [63,64]

Valderrama and co-workers explored the use of 2,6-bis(azolylmethyl)pyridine-chromium(III) chlorides **4a** and **4b** for the polymerization of ethylene (Figure 2) [63]. Both complexes, on activation with MAO, gave activities as high as $1.15 – 1.52 \times 10^5$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$ and formed polymers with

molecular weights of between 78.2 and 126.9 kg mol$^{-1}$ with narrow dispersities ($M_w/M_n$ = 1.74 – 2.15). In comparison, chromium complexes bearing bis(imino)pyridine ligands (*e.g.*, **1g**) are more active catalysts for ethylene polymerization, showing activities of up to 4.14 × 10$^6$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$ [22]. Comparing **4b** with **4a**, reveals the former to give higher activity which has been accredited to the more extended conjugation of the indazole rings making the metal center more electron deficient and in turn promoting the coordination and insertion of ethylene.

Chromium complex **5**, ligated by a 2,6-bis[(4S)-isopropyl-2-oxazolin-2-yl]pyridine, has been investigated by the Esteruelas group as a precatalyst for the ethylene homo- and co-polymerization of ethylene and ethylene/1-hexene, respectively (Figure 2) [64]. The polymerization was performed using MAO as co-catalyst in a saturated solution of ethylene in heptane under 4 bar C$_2$H$_4$ which was continuously supplied. At room temperature, **5**/MAO displayed an activity of 1.27 × 10$^3$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$ while on increasing the temperature to 45 °C, the activity increased to 6.29 × 10$^3$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$. The resulting polyethylene displayed high molecular weight ($M_w$ = 699700 g mol$^{-1}$) but with a very broad dispersity ($M_w/M_n$ = 86.7). Co-polymerization of ethylene with 1-hexene using **5**/MAO rendered a branched polyethylene with a slight decrease in activity (5.17 × 10$^3$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$) when compared with that achieved during the homo-polymerization. Specifically, at 45 °C and in the presence of 15 mL of 1-hexene, **5**/MAO generated 1.8 g of a branched polyethylene with 1.20 mol% incorporation of 1-hexene.
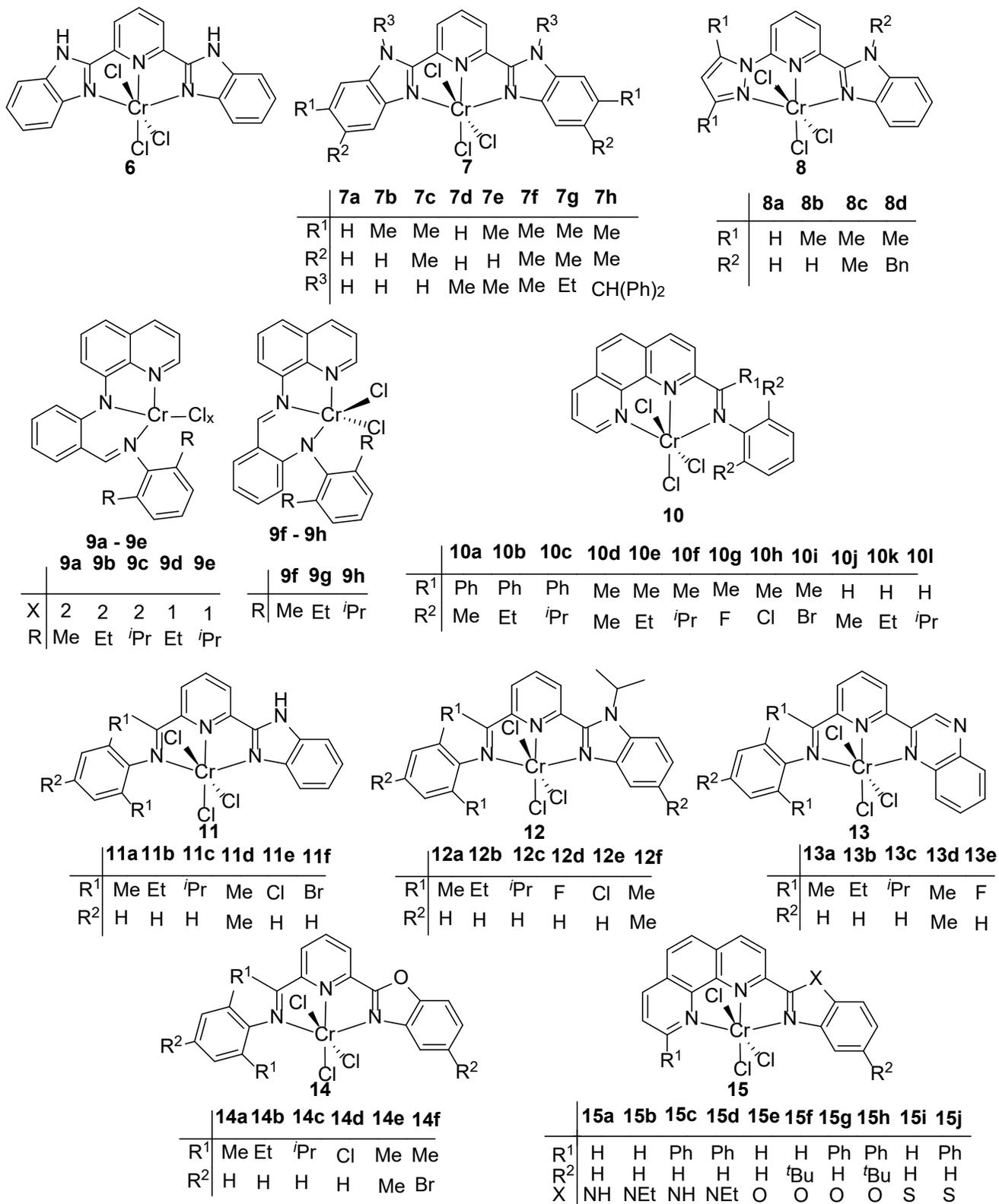
**Figure 3.** Various N^N^N-chromium precatalysts, **6 - 15** [65 - 73, 78]

| | 7a | 7b | 7c | 7d | 7e | 7f | 7g | 7h |
|---|---|---|---|---|---|---|---|---|
| R$^1$ | H | Me | Me | H | Me | Me | Me | Me |
| R$^2$ | H | H | Me | H | H | Me | Me | Me |
| R$^3$ | H | H | H | Me | Me | Me | Et | CH(Ph)$_2$ |

| | 8a | 8b | 8c | 8d |
|---|---|---|---|---|
| R$^1$ | H | Me | Me | Me |
| R$^2$ | H | H | Me | Bn |

| | 9a | 9b | 9c | 9d | 9e |
|---|---|---|---|---|---|
| X | 2 | 2 | 2 | 1 | 1 |
| R | Me | Et | $^i$Pr | Et | $^i$Pr |

| | 9f | 9g | 9h |
|---|---|---|---|
| R | Me | Et | $^i$Pr |

| | 10a | 10b | 10c | 10d | 10e | 10f | 10g | 10h | 10i | 10j | 10k | 10l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R$^1$ | Ph | Ph | Ph | Me | Me | Me | Me | Me | Me | H | H | H |
| R$^2$ | Me | Et | $^i$Pr | Me | Et | $^i$Pr | F | Cl | Br | Me | Et | $^i$Pr |

| | 11a | 11b | 11c | 11d | 11e | 11f |
|---|---|---|---|---|---|---|
| R$^1$ | Me | Et | $^i$Pr | Me | Cl | Br |
| R$^2$ | H | H | H | Me | H | H |

| | 12a | 12b | 12c | 12d | 12e | 12f |
|---|---|---|---|---|---|---|
| R$^1$ | Me | Et | $^i$Pr | F | Cl | Me |
| R$^2$ | H | H | H | H | H | Me |

| | 13a | 13b | 13c | 13d | 13e |
|---|---|---|---|---|---|
| R$^1$ | Me | Et | $^i$Pr | Me | F |
| R$^2$ | H | H | H | Me | H |

| | 14a | 14b | 14c | 14d | 14e | 14f |
|---|---|---|---|---|---|---|
| R$^1$ | Me | Et | $^i$Pr | Cl | Me | Me |
| R$^2$ | H | H | H | H | Me | Br |

| | 15a | 15b | 15c | 15d | 15e | 15f | 15g | 15h | 15i | 15j |
|---|---|---|---|---|---|---|---|---|---|---|
| R$^1$ | H | H | Ph | Ph | H | H | Ph | Ph | H | Ph |
| R$^2$ | H | H | H | H | H | $^t$Bu | H | $^t$Bu | H | H |
| X | NH | NEt | NH | NEt | O | O | O | O | S | S |

The 2,6-bis(2-benzimidazolyl)pyridine-chromium(III) complex **6**, first disclosed by Castillo-Blum in 2000 [65], was used by the Gibson group in 2005 as a precatalyst for ethylene oligomerization (Figure 3) [66]. On activation with MAO, **6** afforded moderate activity ($3.06 - 5.35 \times 10^3$ g (mol Cr)$^{-1}$ bar$^{-1}$ h$^{-1}$) generating a distribution of α-olefins. When the reaction temperature was raised from 32 to 75 $^{\circ}$C, the α-olefin selectivity dropped from 98.5% to 85.7%.

Our group has studied the catalytic behavior of a range of N^N^N-chromium(III) chloride complexes including those based on bis(benzimidazolyl)pyridine [67], 2-imino-1,10-phenanthroline [68], 2-benzazole-1,10-phenanthroline [69], 2-(1H-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine [70], 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine [71], 2-quinoxalinyl-6-iminopyridine [72] and 2-benzoxazolyl-6-arylimino-pyridine [73], for both ethylene oligomerization and polymerization. Generally, these N^N^N-coordinated chromium complexes show catalytic activities that range from good to high. For example, the substituted bis(benzimidazolyl)pyridine-chromium(III) chlorides **7a - 7h**, showed in the presence of MAO at 1 atm C$_2$H$_4$, moderate catalytic activities ($0.43 - 2.8 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$) for ethylene oligomerization forming mainly oligomers in the C$_4$ - C$_8$ range [Al/Cr = 500, Temp = 20 $^{\circ}$C] [67] (Figure 3). The activities depended directly on the environment imparted by the ligand with the values decreasing in the order, **7a** > 7b > 7g > 7c > 7d > 7h > 7f > 7e, which indicates that the more substituted the fused phenyl group, the lower the ethylene reactivity. This finding was attributed to the increasing nucleophilicity of the metal center on account of the greater number of methyl groups on the phenyl ring, leading to a weaker interaction between the chromium center and the π-electrons of the ethylene monomer and in turn decreasing the rate of ethylene insertion in the chain-growth step. On the other hand, the incorporation of an *N*-alkyl group to the imidazole unit (**7d - 7h**) led to a dramatic decrease in ethylene reactivity and greatly affected the distribution of the oligomers. On increasing the temperature from 0 to 60 $^{\circ}$C, the productivity increased for both oligomer and polymer. However, with the reaction temperature further increased to 80 $^{\circ}$C, the activity sharply decreased due to deactivation of the active species. Increasing the temperature also influenced the α-

olefin selectivity with this parameter decreasing with elevated temperature. With the pressure increased to 10 atm $C_2H_4$, a remarkably high catalytic activity ($0.56 - 23.7 \times 10^6$ g mol $Cr^{-1}$ $h^{-1}$) for ethylene polymerization was achieved (Al/Cr = 1000, Temp = 40 °C). The molecular weight of the polyethylene showed some differences with bimodal and multimodal distributions apparent which were dependent on the ligand environment. For example, **7a** ($R^1 = R^2 = R^3 = H$), **7b** ($R^1 = Me$, $R^1 = R^2 = H$), **7c** ($R^1 = R^2 = Me$, $R^3 = H$) and **7d** ($R^1 = R^2 = H$, $R^3 = Me$) gave values of $M_w$ ranging from 927 to 1657 g $mol^{-1}$ affording mainly wax-like polyethylenes. Conversely, **7e - 7h** containing sterically bulky substituents produced high molecular weight polymer (from 6.0 to $14.5 \times 10^4$ g $mol^{-1}$) along with a low molecular weight fraction.

A series of chromium(III) chlorides bearing 2-benzimidazol-6-pyrazol-pyridines, **8a - 8d** (Figure 3), displayed high activities for both ethylene oligomerization ($2.17 \times 10^6$ g (mol $Cr)^{-1}$ $h^-$) and polymerization ($6.78 \times 10^5$ g (mol $Cr)^{-1}$ $h^{-1}$) when treated with MAO [74]. Moreover, the resultant oligomers showed high selectivity for α-olefins (>99%). Elsewhere, the Mu group disclosed a family of chromium complexes **9a - 9h** supported by N^N^N-tridentate quinolinylanilidoimine ligands (Figure 3) [75]. Notably, the Cr(III)-containing **9a - 9c** and **9f - 9h** exhibited moderate activities ranging from 50 to 218 kg (mol $Cr)^{-1}$ $h^{-1}$, while the Cr(II) complexes, **9d** and **9e**, were inert under the same conditions.

The 2-imino-1,10-phenanthroline-chromium(III) chlorides **10a - 10l**, on activation with MAO and at 10 atm $C_2H_4$, exhibited high catalytic activities (from 0.46 to $11.5 \times 10^6$ g (mol $Cr)^{-1}$ $h^{-1}$) for ethylene oligomerization generating oligomers in the range $C_4 - C_{28}$ with the predominant component being 1-hexenes (up to $4.5 \times 10^5$ g (mol $Cr)^{-1}$ $h^{-1}$) (Figure 3) [68]. As the temperature was raised from 20 to 80 °C, the ethylene reactivity increased while the selectivity for α-olefins decreased as a result of the faster rate of chain isomerization. Changes to the ligand environment made by modifying the imine-carbon substituent with Ph (**10a - 10c**), Me (**10d - 10i**) and H (**10j - 10l**) revealed the methyl-ketimine systems to be less productive than the phenyl-ketimine and the aldimine counterparts. Indeed, the phenyl-ketimines, **10a – 10c**, displayed the highest catalytic activity ($1.15 \times 10^7$ g (mol $Cr)^{-1}$ $h^{-1}$) followed by

the aldimine catalysts ($2.73 – 5.00 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$). At either ambient or high pressure of ethylene, the influence of the N-aryl group on the oligomerization showed similar behavior. Phenyl-ketimine **10b** possessing 2,6-diethyl groups showed the highest oligomerization activity. The electron withdrawing 2,6-halide substituents on the methyl-ketimine, **10f** – **10i**, resulted in little influence on the catalytic activity but gave the higher $K$ values and lower α-olefin selectivity.

The 2-benzimidazolyl-6-(1-(arylimino)ethyl)pyridine-chromium(III) chlorides **11a** - **11f** were employed as precatalysts for ethylene oligomerization and polymerization (Figure 3) [70]. At 1 atm C$_2$H$_4$ and 20 $^o$C, the best oligomerization activity of $1.06 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ was observed affording 97.5% selectivity for α-olefins while for polymerization a value of $2.0 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ was recorded. On raising the pressure to 10 atm C$_2$H$_4$, the activities for oligomerization and polymerization both increased to $1.86 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ and $2.37 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$, respectively; again a high α-olefin selectivity was a feature of the oligomerization. With regard to the 2,6-dialkyl-substituted precatalysts **11a** – **11c**, a somewhat reduced catalytic activity was observed for **11c** which was attributed to the bulkier isopropyl group preventing the ethylene coordination step. Complexes **11e** and **11f**, containing electron withdrawing 2,6-dihalide substituents, exhibited relatively higher oligomerization activities ($1.39 – 1.86 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$) than seen for **11a** – **11d** ($0.58 – 1.08 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$). Higher catalytic activities along with longer chain oligomers in the range of C$_4$ – C$_{36}$ could be obtained with increased ethylene pressure.

The chromium(III) complexes **12a** - **12f**, bearing 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridines, displayed moderate to high activity, with MMAO as co-catalyst, generating both oligomers and polymers (Figure 3) [71]. Indeed, at 10 atm C$_2$H$_4$ these MMAO-promoted oligo-/polymerizations were between 12 - 20 times ($2.26 – 27.0 \times 10^4$ g(PE) (mol Cr)$^{-1}$ h$^{-1}$ and $6.76 – 114.5 \times 10^4$ g(oligomers) (mol Cr)$^{-1}$ h$^{-1}$) more active than using MAO. In the main, long chain olefins were produced in the ethylene oligomerizations ($\geq$C$_{10}$). However, the yield of 1-hexene was unusually low (C$_4$, 26.6 wt%; C$_6$, 4.4 wt%; C$_8$, 19.1 wt%), indicating that these chromium catalysts showed much lower

activity for ethylene trimerization as compared to other types of oligomerizations [76–78]. All these chromium complexes promoted high selectivities for α-olefins during the oligomerizations. In particular, **12d** and **12e** containing electron withdrawing 2,6-dihalide substituents showed 97.5 – 99.6% selectivity for α-olefins. On comparison of the 2,6-dialkyl-substituted **12a** - **12c** (with Me, Et, $^{i}$Pr), an increase in the steric properties of these groups generates a less active catalyst. Generally, the less bulky and electron withdrawing substituents produce a positive influence by increasing the catalytic activity. The polymerizations performed at 10 atm $C_2H_4$ showed high activities of between 0.57 and 3.95 × $10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ for ethylene oligomerization with high α-olefin selectivities of between 96.1 and 100%. The resulting polymers showed broad molecular weight distributions while the proportion of polyethylene decreased at higher temperature due to an increased rate of β-elimination relative to the rate of propagation at elevated temperature [60–61, 79].
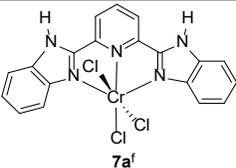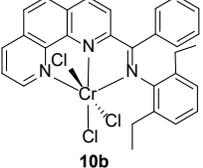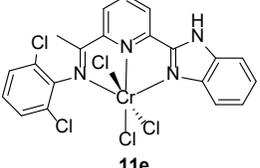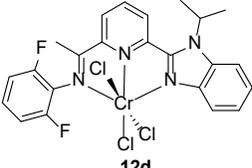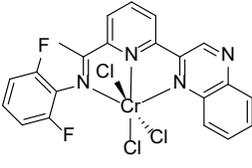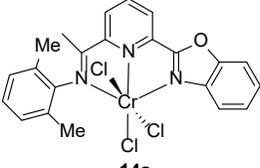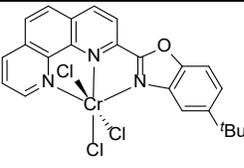
The 2-quinoxalinyl-6-iminopyridine-chromium complexes **13a** - **13e** showed, on activation with MAO, high activities for ethylene oligomerization and moderate activities for ethylene polymerization (Figure 3) [72]. At 1 and 10 atm $C_2H_4$, **13b** showed activities of between 12.6 – 110.7 × $10^4$ g (mol Cr)$^{-1}$ h$^{-1}$) for ethylene oligomerization and between 5.6 – 40.2 × $10^4$ g (mol Cr)$^{-1}$ h$^{-1}$ for ethylene polymerization, with the predominant product being butenes. Under optimal conditions (Al/Cr = 1000, Temp = 20 ºC and 1 atm $C_2H_4$), **13a** - **13e** showed moderate activities of 1.07 – 2.36 × $10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ forming oligomers with a high selectivity for α-olefins (83 – 94%). Complex **13e**, containing an electron withdrawing *ortho*-fluoro substituents, showed much higher oligomerization activity than that seen with the *ortho*-alkyl **13a** – **13d**. At 10 atm $C_2H_4$, all the chromium complexes exhibited high catalytic activities in the range 1.15 – 3.50 × $10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ for oligomerization and moderate activities of 0.29 – 6.71 × $10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ for polymerization with a high selectivity for α-olefins ranging from 91 to 98%. Interestingly, the chromium complexes bearing alkyl substituents generated much higher polymerization activity than those with halides. Furthermore, the complexes containing fluoride substituents gave lower *K* values and lower α-olefin selectivity.

The chromium trichloride complexes **14a** - **14f**, bearing 2-benzoxazolyl-6-arylimino-pyridines, showed high productivities for ethylene oligomerization and polymerization on activation with either MMAO or MAO (Figure 3) [73]. 2,6-Dimethyl-containing **14a** was evaluated with MMAO and showed activities for oligomerization of between $1.56 – 6.44 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ and polymerization of between $0.17 – 5.20 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$. By contrast, with Et$_2$AlCl lower activity for ethylene oligomerization was observed affording trace amounts of oligomers, but good activity for ethylene polymerization ($1.70 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$). On elevating the reaction temperature from 20 to 60 ºC, the formation of oligomers markedly increased (from trace amounts to $9.19 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$). Conversely, the ethylene polymerization activity first increased then decreased with the best activity of $1.14 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ observed at 40 ºC. Further increasing the reaction temperature to 70 ºC, both the level of oligomerization and polymerization decreased. This finding has been attributed to the decomposition of the active species and lower ethylene solubility at higher temperature [60–61, 79]. Moreover, the selectivity for α-olefins decreased as the reaction temperature was raised from 20 to 70 ºC which was credited to faster chain transfer or isomerization at higher temperature. Of the three 2,6-dialkyl-containing chromium complexes **14a** – **14c**, **14c** showed the lowest activity which has been attributed to the bulkier isopropyl substituents slowing down ethylene coordination and hence hindering chain propagation. Furthermore, **14d** bearing 2,6-substituted chlorides showed lower activity as well as lower α-olefin selectivity affording a higher proportion of the C$_4$ fraction. It was suggested that the electron-withdrawing substituents may increase the positive charge on the metal center, thereby enhancing the M–R bond strength and making the insertion of ethylene more difficult, resulting in lower catalytic activity [72]. In addition, complexes **14e** and **14f** possessing *para*-substituents (Me, Br) exhibited much lower activity and produced a lower polymer content than that seen with **14a**. On comparison of the activators, MMAO gave higher activities for ethylene oligomerization than with MAO (up to $5.09 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ MMAO *vs*. $1.56 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ for MAO). By contrast, the activities for ethylene

polymerization with MAO were more than 10 times higher than seen with MMAO ($5.20 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ $vs.$ $5.31 \times 10^4$ g (mol Cr)$^{-1}$ h$^{-1}$) under similar conditions.

The chromium(III) complexes, **15a - 15j**, bearing 1,10-phenanthrolines substituted at their 2-positions by benzimadazole (**15a** – **15d**), benzoxazole (**15e** – **15g**) and benzothiazole (**15i, 15j**) have been explored for their ethylene reactivity (Figure 3) [69]. For example, benzoxazole-containing **15f** on activation with MMAO showed high catalytic activity for ethylene oligomerization and polymerization and produced oligomers in the $C_4$ - $C_{24}$ range; activation with Et$_2$AlCl and MAO proved less active. At 1 atm $C_2H_4$, peak activities of $2.31 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$ for ethylene oligomerization and $2.21 \times 10^5$ g (mol Cr)$^{-1}$h$^{-1}$ for ethylene polymerization were achieved. On raising the pressure to 10 atm $C_2H_4$, higher catalytic activity was observed for all precatalysts, with the topmost oligomerization activity being $7.36 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$, affording a broad oligomer distribution from $C_4$ to $C_{24}$ and a polymerization activity of up to $1.28 \times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$. For benzimidazole-containing **15a** – **15d**, the presence of the NEt group was detrimental to the performance in both the oligomerization (from $10.1 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ to trace) and polymerization (from $9.13 \times 10^4$ g (mol Cr)$^{-1}$ h$^{-1}$ to trace). Indeed NH-containing **15a** and **15c** showed higher activities and α-olefin selectivities than their $N$-alkylated analogues **15b** and **15d**. The benzoxazole-containing complexes incorporating a $^t$Bu at the 4-position (**15, 15h**) of the fused benzene ring caused higher activities for oligomerization and polymerization. Overall, the influence of heteroatoms belonging to the benzene-fused five-membered rings on the catalytic activity followed the order: O > N > S. In general, our N^N^N-chromium(III) chloride complexes showed high activities toward ethylene oligomerization and polymerization, and selected precatalysts were listed in Table 1.

**Table 1.** Catalytic performance data for selected N^N^N-chromium(III) chloride precatalysts[a]

| Precatalyst (5 μmol) | Co-catalyst (Al/Cr molar ratio) | Oligomers | | | Polyethylene | Ref. |
|---|---|---|---|---|---|---|
| | | Activity[b] | $K$[c] | % α-olefin[d] | Activity[e] | |
| 7a[f] | MAO (1000) | 23.7 | - | >95 | | [67] |
| 10b | MAO (1000) | 11.5 | 0.48 | >87 | 4.1 | [68] |
| 11e | MMAO (1500) | 1.5 | - | 96.9 | 20.1 | [70] |
| 12d | MMAO (1500) | 3.95 | - | 99.2 | | [71] |
| 13e | MAO (1000) | 3.5 | 0.27 | >91 | 0.29 | [72] |
| 14a | MMAO (1000) | 9.19 | - | 99.6 | 0.18 | [73] |
| 15f | MMAO (1500) | 7.36 | 0.60 | >94 | 12.8 | [69] |

[a] General conditions: temperature = 20 - 80 °C, time = 20 - 60 min, 100 mL toluene and 10 atm $C_2H_4$;
[b] Activity for oligomers: $\times 10^6$ g (mol Cr)$^{-1}$ h$^{-1}$;
[c] $K$ = probability of propagation;
[d] α-Olefin percentage, determined by GC and GC-MS;
[e] Activity polyethylene (wax): $\times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$;
[f] 2 μmol.

A family of chromium complexes containing bis(benzimidazolemethyl)-amine ligands proved extremely active towards ethylene oligomerization (Figure 4) [80]. For example, up to 100000 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ was achieved using **16b** in combination with MAO as co-catalyst. However, their analogues bearing bulkier substituents on the central nitrogen (**16c - 16j**) showed only low activities. Elsewhere, the Gibson group studied the chromium bis(benzimidazolyl)amine complexes **17a – 17c** as ethylene oligomerization catalysts (Figure 4) [76]. Upon activation with MAO, **17a** was exceptionally active (1.00 – 1.07 × 10$^5$ g (mol Cr)$^{-1}$ h$^{-1}$) for ethylene oligomerization with high α-olefin selectivity (≥99%) and it was noted that nanomolar catalyst loadings were needed to avoid excessive exotherms. At 4 atm C$_2$H$_4$, activities in excess of 8.0 × 10$^6$ g (mol Cr)$^{-1}$h$^{-1}$ were attained using **17a**/MAO. Similarly, the salts **17b** and **17c** displayed very high activities (0.15 – 0.21 × 10$^5$ g (mol Cr)$^{-1}$ h$^{-1}$) but somewhat lower than that seen for **17a**, which was attributed to the presence of oxygen donor residues arising from the THF and acac ligands.
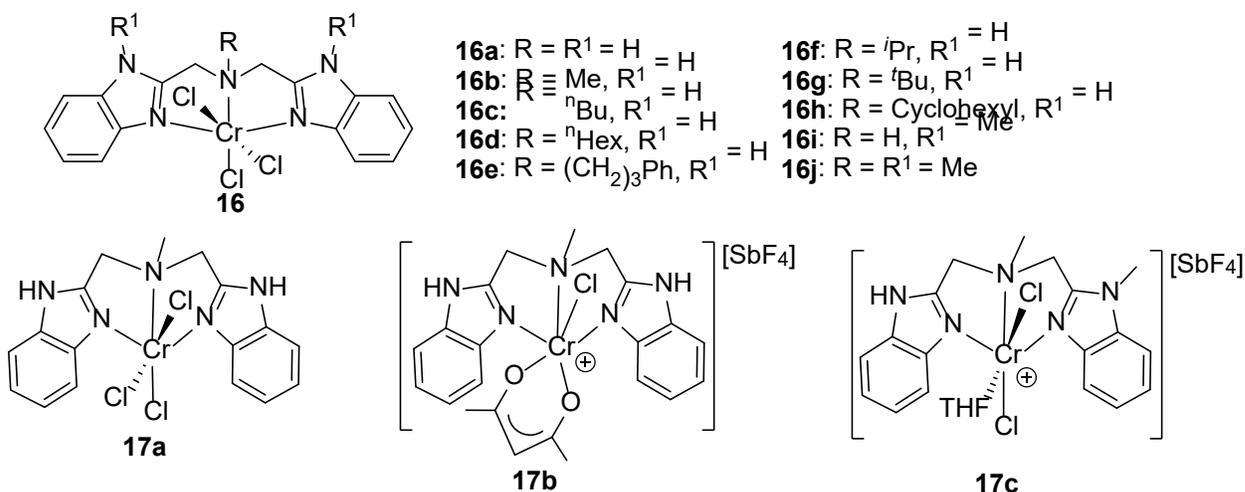


16a: R = R$^1$ = H
16b: R = Me, R$^1$ = H
16c: R = $^n$Bu, R$^1$ = H
16d: R = $^n$Hex, R$^1$ = H
16e: R = (CH$_2$)$_3$Ph, R$^1$ = H
16f: R = $^i$Pr, R$^1$ = H
16g: R = $^t$Bu, R$^1$ = H
16h: R = Cyclohexyl, R$^1$ = H
16i: R = H, R$^1$ = Me
16j: R = R$^1$ = Me

**Figure 4.** Chromium(III) precatalysts bearing bis(benzimidazoly)amines, **16** and **17** [76, 80]

Köhn *et al.* explored 1,3,5-triazacyclohexane complexes of chromium(III), **18a – 18d**, containing N-alkyl groups of various chain lengths and screened these precatalysts using MAO or [PhMe$_2$NH][B(C$_6$F$_5$)$_4$]/$^i$Bu$_3$Al as the co-catalyst (Figure 5) [81]. Indeed, **18**/MAO all showed high activity for ethylene polymerization (455 – 717 kg (mol Cr)$^{-1}$ h$^{-1}$) and the resultant polymer showed

molecular weights of around $M_w$ = 40000 g mol$^{-1}$ with $M_w/M_n$ = 2 - 4 [81]. The use of *fac* and *mer* derivatives of the bis(2-pyridylmethyl)alkylamine-chromium(III) complexes **19a** – **19d** for ethylene polymerization was investigated by Carney and co-workers (Figure 5) [82]. The screening of **19a** – **19d** with MAO as co-catalyst was conducted in either dichloromethane or dichloroethane owing to their poor solubility in toluene. It was found that the molecular weight of the polymer formed in dichloromethane was more uniform than that produced in dichloroethane. Notably, *fac* **19a** and **19b** displayed higher activity (1.4 – 2.0 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$) than that observed for *mer* **19c** and **19d** (4.0 – 6.0 × 10$^2$ g (mol Cr)$^{-1}$ h$^{-1}$). Relatively low molecular weights (33200 – 74100 g mol$^{-1}$) for the polymers were seen using **19a** and **19b** when performed in dichloroethane. By contrast with dichloromethane as the solvent, higher molecular weights for the polymers were observed (110000 – 147000 g mol$^{-1}$) for all precatalysts [83]. Generally, the *fac* isomers yielded higher activity than their *mer* counterparts [84,85].

The polymerization behavior of a series chromium(II) and chromium(III) complexes ligated by the tetradentate tripodal tris(pyridylmethyl)amine were also investigated by Carney *et al.* (Figure 5) [86]. On activation with MAO, chromium precatalysts **20a** - **20g** proved moderately active for ethylene polymerization (10 - 20 g of PE (mmol of Cr)$^{-1}$ h$^{-1}$ atm$^{-1}$). The melting point data for the polymers were consistent with the formation of low to moderate molecular weight high density polyethylene. Polymers produced in dichloromethane typically possessed lower molecular weight than those produced in chlorobenzene suggesting that dichloromethane acts as an effective chain termination agent. In addition, the chromium complexes, **21a** and **21b**, bearing pyrrolide-imine-amine ligands (Figure 5) [87], upon activation with MAO, exhibited good activities for ethylene oligomerization with TOFs in the range 47.0 – 73.5 × 10$^3$ (mol ethylene) (mol Cr)$^{-1}$ h$^{-1}$.
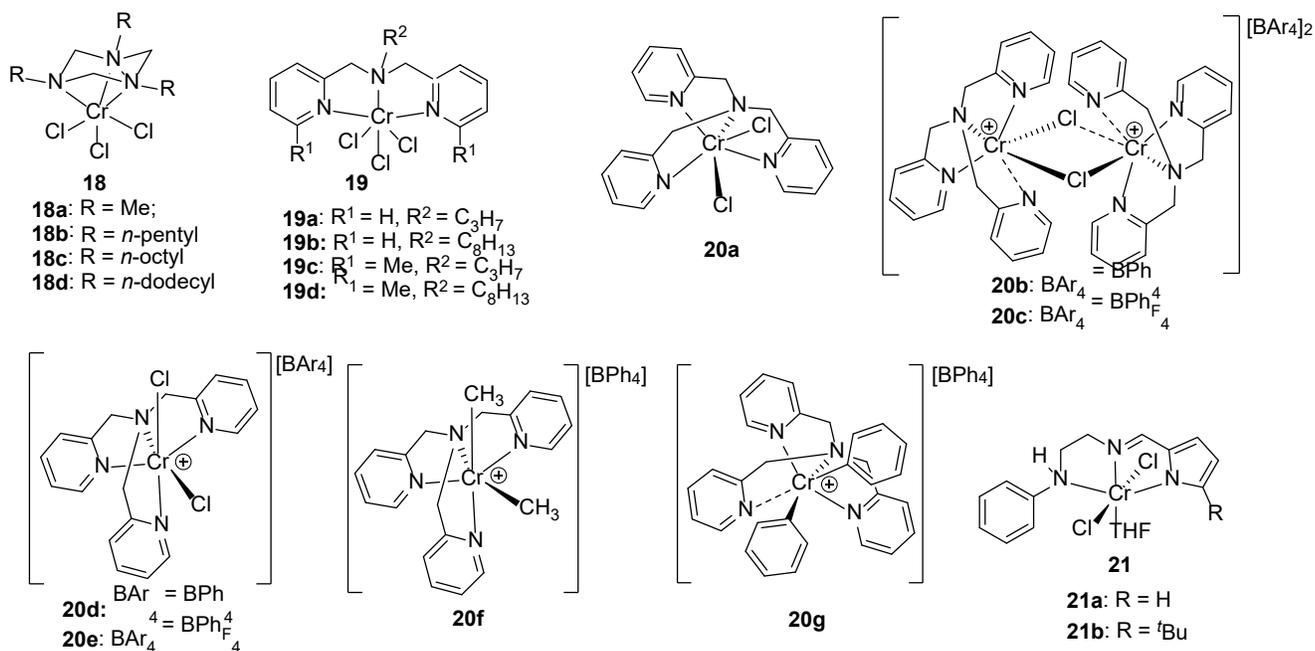
**Figure 5.** Chromium(III) precatalysts bearing distinct N^N^N and N^N^N^N ligand frameworks, **18 - 21** [81,82,86,87]

## 2.2. Cycloalkyl-fused bis(arylimino)pyridines and their Cr precatalysts

During the last five years or so, our group has been interested in developing bis(arylimino)pyridines (**A**, Figure 6) fused with cycloalkyl groups with a view to forming new chelating N^N^N-ligands incorporating various degrees of ring tension depending on the size of the fused ring (**B** and **C**, Figure 6) [88-103]. Indeed, we have reported a variety of iron and cobalt precatalysts based on these cycloalkyl-fused ligands which have displayed excellent performance characteristics and produced oligomeric and polymeric materials displaying a range of properties that can be quite different to that observed using parent **A** [104]. In this section, we focus on chromium precatalysts bearing **B** and **C** and show how the fusion of the cycloalkyl groups affects catalytic performance, thermal stability and the selectivity towards oligomers and polymers [88-91].
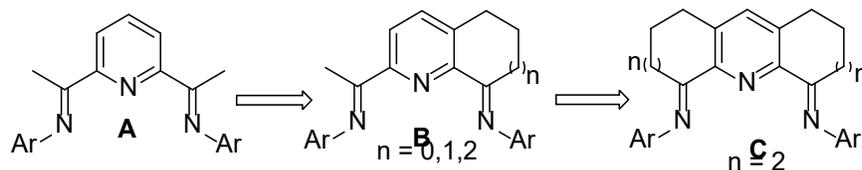


**Figure 6.** Ligand frameworks derived from bis(imino)pyridine **A**, through the fusion of cycloalkyl groups

Initially, we investigated the chromium(III) complexes, **22a** - **22e**, containing cyclopentyl fused 2-(1-aryliminoethyl)-7-arylimino-6,6-dimethylcyclopenta[*b*]pyridines for ethylene polymerization (Figure 7) [88]. On activation with MMAO, **22a** – **22c** exhibited good activities at 30 °C of up to $4.44 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ forming strictly linear polyethylenes of high molecular weight (*ca.* $6.48 \times 10^5$ g mol$^{-1}$). On the other hand, using EASC as the co-catalyst, the resulting catalysts were less active (up to $3.24 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$) and generated lower molecular weight polymer (*ca.* $4.77 \times 10^5$ g mol$^{-1}$). In comparison with bis(imino)pyridine-containing **1** (Figure 1), these chromium catalysts showed their optimal performance at a lower temperature. In terms of the relative performance, their activities followed the order: **22d** [2,4,6-tri(Me)] > **22e** [2,6-di(Et)-4-Me] > **22c** [2,6-di($^i$Pr)] > **22b** [2,6-di(Et)] > **22a** [2,6-di(Me)]. The higher activities displayed by **22d** and **22e** have been ascribed to the better solubility due to the presence of the *para*-methyl group [103,105]. In addition, the chromium precatalysts containing the bulkier *ortho*-substituents, have shown a propensity towards higher catalytic activity which has been attributed to steric protection afforded to the active site [70,72 - 74].
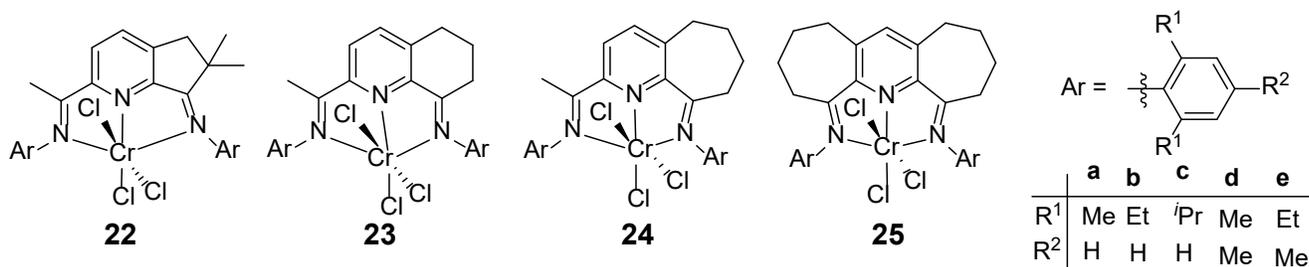


**Figure 7**. Cycloalkyl-fused bis(arylimino)pyridine-chromium precatalysts, **22 - 25** [88 - 91]

Complexes **23** and **24**, containing cyclohexyl- and cycloheptyl-fused groups, showed high activities ($1.44 – 1.59 \times 10^7$ g (mol Cr)$^{-1}$ h$^{-1}$) on activation with MAO with **24b** and **24a** the most active and formed polyethylene waxes ($M_w \sim 10^3$ g mol$^{-1}$) with narrow dispersities ($M_w/M_n$ = 1.1 - 1.9) (Figure 7) [89,90]. Furthermore, by comparison with **22**, these catalysts were not only more active but also more thermally stable, operating most effectively at 80 °C [89]. It is worthy of note that such narrowly disperse waxes are of interest for applications such as long-chain branched copolymers, functional polymers and as well

as coating materials [88]. Elsewhere, a kinetic study was conducted using precatalyst **23d** [106], and when compared to the corresponding iron and cobalt complexes, the chromium catalyst exhibited a superior thermostability and formed polymers of low molecular weight with narrow distribution.

The doubly fused chromium(III) complexes **25**, bearing α,α'-bis(arylimino)-2,3:5,6-bis(pentamethylene)pyridines, were also investigated for ethylene polymerization with either MMAO or Et$_2$AlCl as co-catalyst (Figure 7) [90]. In the case of Et$_2$AlCl, good activity was observed at 20 $^o$C (up to $4.13 \times 10^5$ g (mol Cr)$^{-1}$ h$^{-1}$) and produced highly linear polyethylene of high molecular weight and broad molecular weight distribution. By contrast, polymerization with MMAO resulted in higher activities (up to $1.60 \times 10^7$ g (mol Cr)$^{-1}$ h$^{-1}$) and what is more, the catalysts displayed greater thermal stability by operating most effectively as 80 $^o$C. Furthermore, the molecular weight of the materials was quite different with low molecular weight linear polyethylene waxes with vinyl end-groups being generated in this case.

*2.3. N^N^O, N^O^N and N^O-ligands and their Cr precatalysts*

Small *et al.* studied the N^N^O-chromium(III) complexes **26a – 26j**, bearing 2-acetyl-6-iminopyridines for the polymerization of ethylene (Figure 8) [24]. In case of **26h** (2,5-di-*tert*-butyl substituted) with MAO as co-catalyst (Al/Cr = 100 - 800), the activity of the catalyst was less ($7.8 – 10.8 \times 10^2$ g (mol Cr)$^{-1}$ h$^{-1}$) than that observed by the corresponding bis(imino)pyridine-containing **3g** ($1.14 \times 10^4$ g (mol Cr)$^{-1}$ h$^{-1}$) and formed polyethylene of moderate molecular weight (32200 - 55000 g mol$^{-1}$) that was dependent on the Al/Cr molar ratio. As with **26h**, the other N^N^O-coordinated catalysts of this series displayed lower catalytic activity than that observed with their bis(imino)pyridine-containing counterparts [97,98,103,107,108].
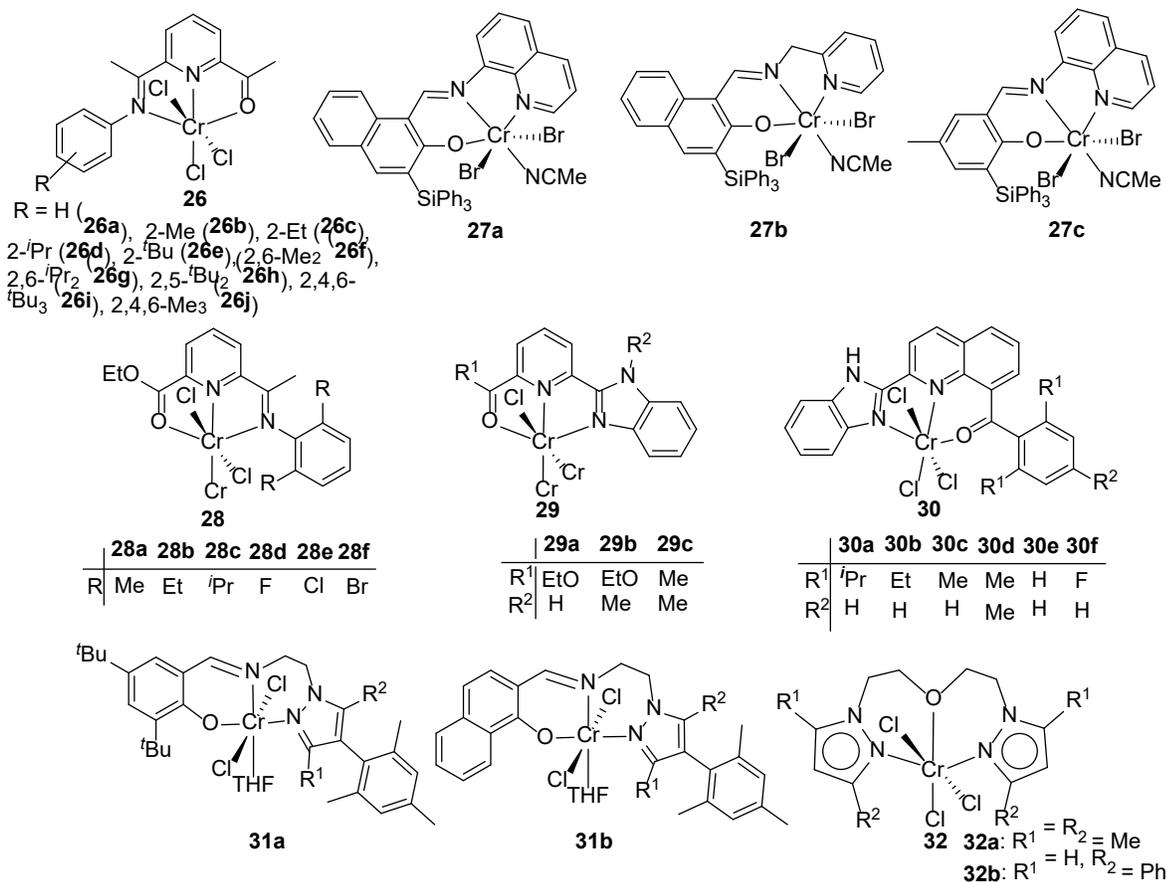
**Figure 8.** N^N^O- or N^O^N-chromium precatalysts **26** - **32** [24,109 - 113]

Chromium(III) complexes **27a** - **27c** bound by phenolate-imine-quinolines/pyridines have been studied as precatalysts for ethylene oligomerization by Kirillov *et al.* (Figure 8) [110]. Complexes **27a** and **27b**, on activation with MAO (Al/Cr = 500 - 800), afforded stable and productive catalytic systems with activities of between 14160 and 12600 kg (mol Cr)$^{-1}$ h$^{-1}$ under 6 atm $C_2H_4$ and at 50 °C. Running the reaction by using **27a** at room temperature over a shorter run time gave a very high activity of 23730 kg (mol Cr$^{-1}$) h$^{-1}$. Complex **27c**, based on a triphenylsilyl-substituted phenolate-imine-quinoline was two times less active (6680 kg (mol Cr)$^{-1}$ h$^{-1}$) than **27a** and **27b**. High exothermicity was a feature of all these oligomerizations even with low catalyst loadings making the temperature difficult to control. $^1$H and $^{13}$C NMR spectroscopy revealed the ethylene oligomers to comprise a high percentage of vinyl end-groups (90%). Typically, the products of the oligomerizations were linear α-olefins (89 - 96% vinyl-end; $M_n$ = 600 -1450 g mol$^{-1}$, $M_w/M_n$ = 1.9 - 2.3).

Our group has reported several chromium(III) complexes supported by N^N^O ligands of the type 2-carbethoxy-6-iminopyridine [109], 2-benzimidazolyl-6-acetyl-pyridine [112] and 2-benzimidazolyl-N-phenylquinoline-8-carboxamide (Figure 8) [113]. In 2007, the 2-carbethoxy-6-iminopyridine-chromium(III) complexes, **28a** - **28f**, were screened for ethylene polymerization using EtAlCl$_2$ as co-catalyst [109]. Moderate to good catalytic activities were observed at pressures of 1 and 10 atm C$_2$H$_4$ at 25 °C. At the lower pressure, the activities for the precatalysts were found to fall in the order, Br > Cl > $^i$Pr > F > Et > Me (from 3.69 to 7.40 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$), with the highest activity seen for bromo-containing **28f**. At the higher pressure, the activities were found to be higher (range: 1.47 – 2.33 × 10$^5$ g (mol Cr)$^{-1}$ h$^{-1}$) displaying a range of molecular weights (0.9 – 12.0 × 10$^4$ g mol$^{-1}$) and dispersities for the polymers ($M_w/M_n$ = 1.91 – 15.92).

The 2-benzimidazolyl-6-acetyl-pyridine-chromium(III) complexes **29a** - **29c** were screened for ethylene oligomerization and polymerization (Figure 8) [112]. On activation with MAO, all three complexes showed higher catalytic activity (8.70 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$) than the systems activated by MMAO or Et$_2$AlCl (5.63 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$ and 6.71 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$) forming both oligomers (in the C$_4$ – C$_{20}$ range) and wax-like polyethylene products in all cases. The structural features of the ligand were influential on the catalytic activity (3.41 – 5.63 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$) and shown to fall in the order: **29a** > **29b** > **29c**. Similarly, the 2-benzimidazolyl-N-phenylquinoline-8-carboxamide-chromium(III) complexes, **30a** – **30f**, in the presence of either MAO or MMAO at 1 atm C$_2$H$_4$ and at 20 °C, formed both oligomers and polymers with high selectivity for α-olefins displayed by the oligomeric fraction (>99%) (Figure 8) [113]; high catalytic activity of up to 3.05 × 10$^6$ g (mol Cr)$^{-1}$ h$^{-1}$ was observed for both activators. This distribution of oligomers was found to closely resemble Schulz–Flory with $K$ = 0.70 - 074 as determined for the molar ratio of the C$_{12}$ and C$_{14}$ components [114-116]. On increasing the temperature, the activity was found to drop from 2.62 × 10$^6$ g (mol Cr)$^{-1}$ h$^{-1}$ at 30 °C to 1.97 × 10$^6$ g (mol Cr)$^{-1}$ h$^{-1}$ at 40 °C. At 10 atm C$_2$H$_4$, the catalytic activity significantly increased with the highest activity

reaching $1.91 \times 10^7$ g (mol Cr)$^{-1}$ h$^{-1}$. In comparison with the results obtained at lower pressure, the amount of polyethylene wax increased from 32.8 to 38.5%. As a general observation, the 2,6-dialkyl substituted systems were more active than the 2,6-difluoride while the least hindered 2,6-dialkyl was the most active highlighting the combined roles of electronic and steric effects.

Casagrande Jr. *et al.* reported a pair of chromium(III) complexes {N^N^O}CrCl$_2$(THF) (**31a** and **31b**, N^N^O = pyrazolyl-imine-phenoxy, Figure 8) [117] that, upon activation with MAO, showed moderate activity in ethylene reactivity with TOFs between 6.8 and $14.5 \times 10^3$ (mol ethylene) (mol Cr)$^{-1}$·h$^{-1}$ at 80 °C; in general, mixtures of oligomers and polymers were produced.

The (N^O^N)CrCl$_3$ complexes, **32a** and **32b**, were also investigated as oligomerization precatalysts in which the tridentate ligand was composed of a central oxygen donor and two variable pyrazolyl exterior donors (Figure 8); the corresponding complexes with the central O donor replaced by NR or S were also reported [111]. On activation with MAO, **32a** and **32b** displayed relatively high TOFs in the range 13700 - 69600 h$^{-1}$ for ethylene oligomerization. For **32a**, increasing the Al/Cr molar ratio from 100 to 1000, led to the TOFs rapidly increasing from 3400 to 69600 h$^{-1}$. By comparison the bulkier phenyl-substituted **32b** was more productive than methyl-substituted **32a** (**32a**: TOF = 47400 h$^{-1}$, **32b**: 26700 h$^{-1}$). Nevertheless, both the chromium complexes produced oligomers with distributions ranging from C$_4$ − C$_{14+}$ with high selectivities for α-olefins. In addition, the central donor atom of the ligand (O *vs.* NR or S) was found to be influential on the catalytic activity and product distribution.
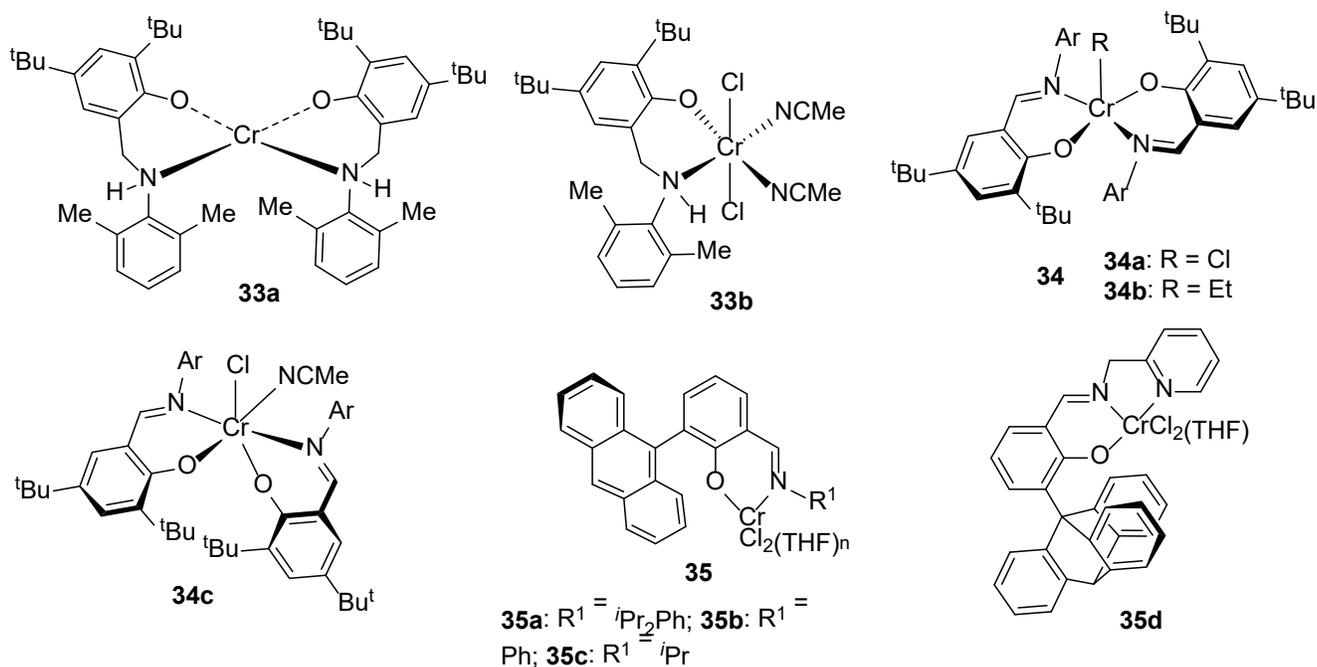
**Figure 9.** N^O- and N^N^O-chromium precatalysts **33** - **35** [118 - 120]

The Gibson group has investigated a wide range of chromium complexes ligated by N^O-ligands for ethylene oligomerization and polymerization (Figure 9) [118 - 124]. For example, **33a** and **33b**, based on bulky monoanionic reduced Schiff-base N^O chelating ligands, displayed reasonable activity for ethylene polymerization and formed high molecular weight linear polymer [118]. The highest activity of 130 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ was observed using **33b** with Et$_2$AlCl as the co-catalyst; under related conditions *bis*-chelated **33a** showed around half the activity. Similarly, the five-coordinate *bis*-salicylaldiminato-chromium(III) complex, **34a**, displayed on activation with DEAC a peak in activity of 96 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ at 35 °C and 10 atm C$_2$H$_4$ [119]. When the reaction temperature was raised to 75 °C, the catalyst system became almost inactive. Replacing DEAC with DMAC as co-catalyst with the temperature at 35 °C, the catalytic activity of **34a** dropped to 84 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$. Under similar conditions, **34b** and **34c** showed lower catalytic activities of between 50 and 66 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ forming solid polymer with very high molecular weight (1420000 – 1762000 g mol$^{-1}$), moderate dispersities ($M_w/M_n$ = 3.6 – 5.1) and virtually no branching. Notably, the polymer produced using

**34c**/DEAC was shown to contain vinyl end-groups by IR spectroscopy highlighting the importance of β-hydrogen elimination as a termination pathway in these polymerizations.

The chromium complexes **35a** – **35c** containing a single salicylaldiminate ligand appended with a bulky polycyclic *ortho*-substituent were also investigated by Gibson and co-workers for ethylene polymerization (Figure 9) [120]. In particular, anthracenyl and triptycenyl-containing **35a** – **35d** were the subject of a high throughput screening using MAO as the co-catalyst. Notably, 2,6-diisopropylphenyl-substituted **35a** on activation with MAO showed low activity of < 40 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ while the introduction of less sterically bulky N-R$^1$ substituents (R$^1$ = Ph **35b**, $^i$Pr **35c**) led to significant increases in activities from 95 to 1760 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$. Moreover, **35d** bearing a tridentate N^N^O ligand containing a bulky triptycenyl group on the phenolate moiety achieved an activity of 6970 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ which is by far the highest for this class of N^O-containing chromium catalyst. While the molecular weight of the polymer generated using **35d** was low ($M_w$ = 1200), that formed by **35a** – **35c** was high to very high molecular weight.
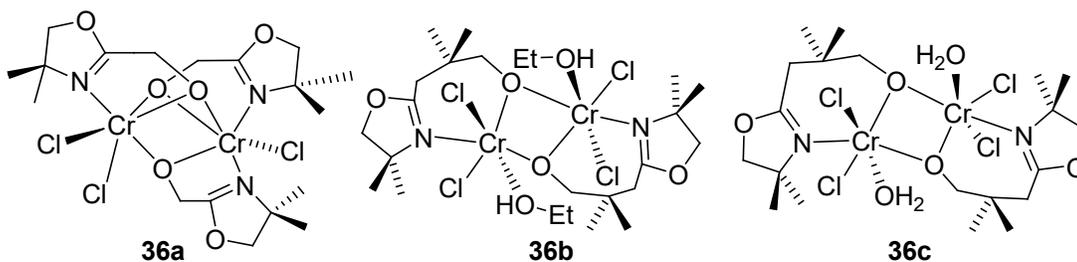


**Figure 10.** Dinuclear N^O-chelated chromium precatalysts **36** [125]

Braunstein *et al.* investigated the use of the dinuclear chromium(III) complexes **36a** - **36c**, which contain monoanionic N^O-oxazoline-alcoholate ligands, for ethylene oligomerization and polymerization with MMAO as co-catalyst at 1 atm C$_2$H$_4$ (Figure 10) [125]. All these precatalysts showed moderate activity from 2.36 to 3.79 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$ at 0 °C for polymerization and were less active for oligomerization (1.63–1.95 × 10$^4$ g (mol Cr)$^{-1}$ h$^{-1}$). The polymerizations were performed

at low temperature as these temperatures favored chain propagation. On the other hand, when the temperature was increased from 0 to 40 °C, the level of oligomerization activity gradually went up while the level of polymerization greatly decreased. However, at 60 °C, the amount of both oligomers and polymers were both found to decline. At 10 atm $C_2H_4$, **36a** – **36c** showed good activity in the range 1.4 – 6.2 × $10^5$ g (mol Cr)$^{-1}$ h$^{-1}$ for ethylene polymerization forming mainly linear polyethylene while the activities for ethylene oligomerization were markedly less falling between 2.37 – 3.60 × $10^4$ g (mol Cr)$^{-1}$ h$^{-1}$. Of the three complexes, **36a** showed the highest activity of 6.2 × $10^5$ g (mol Cr)$^{-1}$ h$^{-1}$.

*2.4. N^N and N^P-ligands and their Cr precatalysts*

Rüther *et al.* investigated the chromium(III) complexes **37a** - **37c**, **38a**, **38b**, **39a** and **39b** bearing imidazole-based chelating ligands there were modified by the inclusion of a Y group that could act as a tridentate tripodal ligand or as a bidentate ligand (Figure 11) [126]. Exposure of toluene solutions of **37**/MMAO and **39**/MMAO to 40 bar of ethylene resulted in the formation of linear α-olefins in the range of $C_4$ - $C_{30}$ (maximum at $C_8$) with high selectivities. In general, tripodal **37** were more active than the bidentate counterparts **39**. Indeed, the maximum activity of 208 g (mol Cr)$^{-1}$ h$^{-1}$ was shown by **37a** generating α-olefins as the predominant product (79%) along with 9% isoalkenes and 12% alkanes.



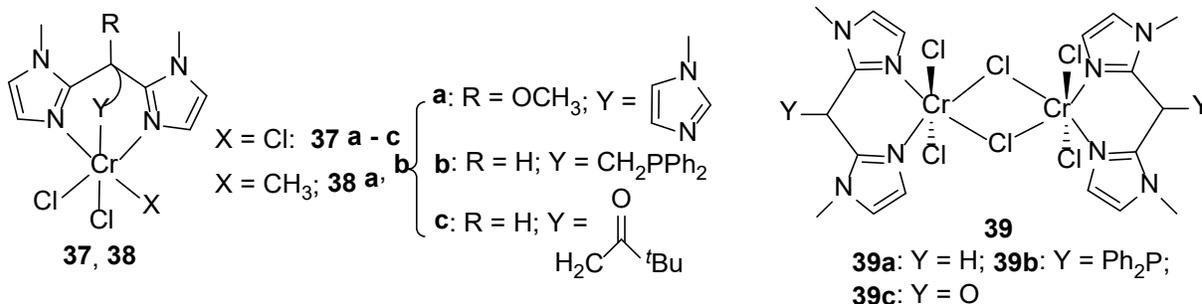**Figure 11.** N^N^Y and N^N-chelated chromium precatalysts, **37 - 39** [126]

The Gibson group also explored chromium(II) and (III) complexes containing a variety of N^N-ligands including the monoanionic β-diketimate ('NacNac') [122] and pyrrolide-imine [127] ligands for ethylene polymerization. For example, pyrrolide-imine-containing **40** – **42**, were evaluated using either

MAO, Et$_2$AlCl or Me$_2$AlCl as co-catalysts (Figure 12) [127]. The effect of the co-catalyst on the activity was pronounced with MAO showing much lower activity than with Et$_2$AlCl or Me$_2$AlCl. The highest catalytic activities were revealed by **41** and **42b** of around 120 g (mmol Cr)$^{-1}$ h$^{-1}$ bar$^{-1}$ with the polymers displaying high molecular weight of between 293000 and 1958000 g mol$^{-1}$ and dispersities in the range 2.2 - 53.1. It is noteworthy that the control polymerization tests undertaken using the low valent chromium precursors, CrCl$_3$·3THF and CrCl$_2$·THF, gave only trace amounts of polyethylene.



**Figure 12.** N^N-chelated chromium precatalysts, **40 - 42** [127]

The chromium complexes **43a - 43c**, bearing bis(iminophosphoranyl)methanido ligands, were investigated by Floch *et al.* for ethylene oligomerization with MAO as co-catalyst (Figure 13) [128]. The products of the catalytic conversions were oligomers with mainly linear α-olefins as detected by GC. The productivity increased significantly when the oligomerizations were carried out at lower temperatures. This effect was most noticeable for isopropyl-containing **43a**, for which the TON increased from 18421 to 19789 mol(C$_2$H$_4$) (mol Cr)$^{-1}$ as the temperature was reduced from 45 °C to 20 °C, respectively. Interestingly, all the catalysts exhibited two distinct product distributions in the liquid phase with one centered around 1-hexene and a second narrow distribution in the C$_{14}$ – C$_{24}$ range.
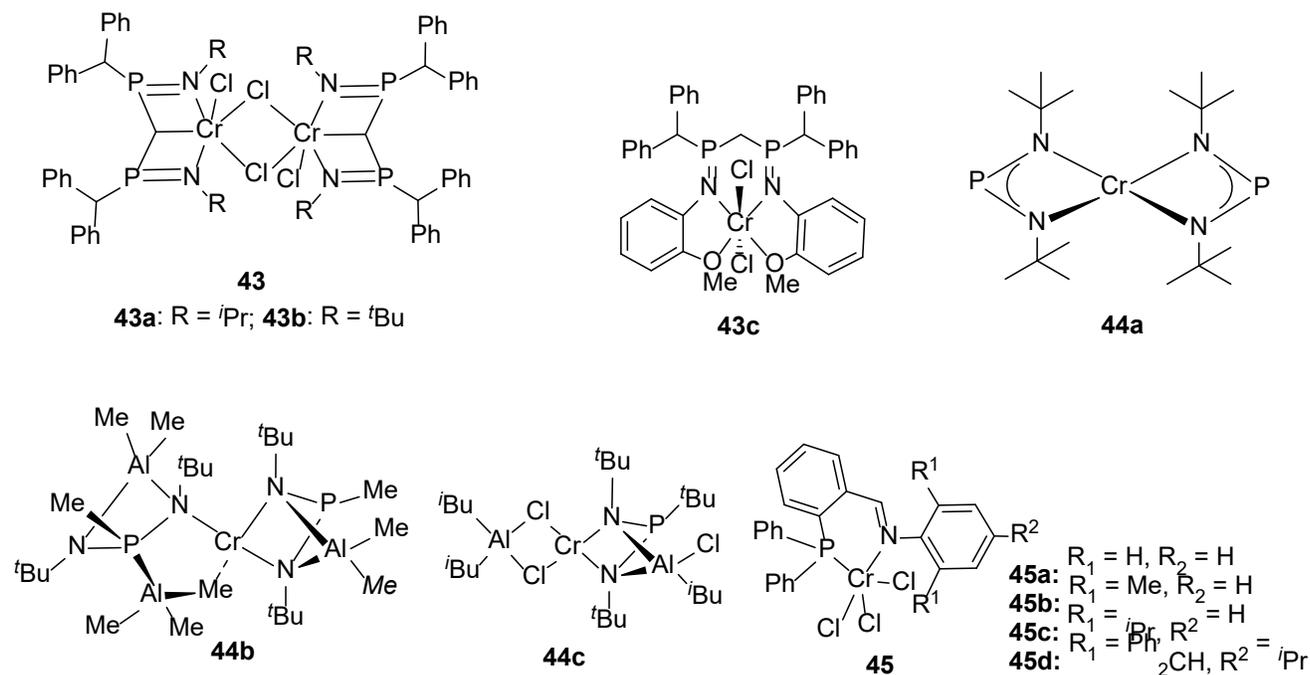
**Figure 13.** N^N and N^P-chelated chromium precatalysts, **43** - **45** [128 - 130]

Duchateau and Gambarotta employed the *bis*-chelated chromium complex, **44a** as a precursor to **44b** and **44c** (Figure 13) [129]. When activated with MAO, **44a** yielded a statistical distribution of ethylene oligomers (including waxes) with very high activity. Indeed, it proved difficult to control the reaction temperature with catalyst concentrations as low as 5 μM. Moreover, the catalyst was found to be thermally robust, as tests performed at higher catalyst loading maintained high activities at temperatures up to 110 °C for prolonged periods of time. Furthermore, the catalytic activity gradually rose with an increased Al/Cr molar ratio but this did not, however, affect the product distribution. For **44a**/MAO, the best activity of 23600 g (mol Cr)$^{-1}$ h$^{-1}$ was observed at an Al/Cr ratio of 2000, while at 500 the activity rapidly reduced to 400 g (mol Cr)$^{-1}$ h$^{-1}$. Using **44b** gave similar results to **44a** with **44b**/MAO showing its highest activity of 18800 g (mol Cr)$^{-1}$ h$^{-1}$ at an Al/Cr molar ratio of 2000 whereas at 1000 the activity was 18000 g (mol Cr)$^{-1}$ h$^{-1}$. Conversely, **44c**/MAO showed its peak activity of 34000 g (mol Cr)$^{-1}$ h$^{-1}$ at an Al/Cr molar ratio of 2000. On reducing the Al/Cr molar ratio to 1000, the drop in activity to 27600 g (mol Cr)$^{-1}$ h$^{-1}$ was less pronounced. All the products were composed of predominatly 1-hexene in the range 35.5 to >85%. Interestingly, **44a**, on activation with ($^i$Bu$_2$Al)$_2$(μ-O), behaved as

an ethylene oligomerization catalyst displaying high activity in the range 24400 – 32800 g (mol Cr)$^{-1}$ h$^{-1}$ with an Al/Cr = 500 - 1000. By contrast, when ($^i$Bu$_2$Al)$_2$(μ-O) was employed as the activator with **44b** and **44c** the activity was less than that seen with **44a**. All the materials generated were of low molecular weight with narrow dispersities ($M_w/M_n$ = 1.2 – 4.3). Moreover, on activation with Al$^i$Bu$_3$ (Al/Cr = 500 – 10000), **44a** gave 1-hexene with excellent selectivity (>99.9%). The chromium complexes **45a** - **45d** (Figure 13) bearing phosphino–imine P^N bidentate ligands [130], in the presence of MAO, exhibited moderate to high activities of between 64 – 314 kg(PE) (mol Cr)$^{-1}$ h$^{-1}$. Complex **45d**, containing the most steric hindered group, produced only low activity but afforded the highest molecular weight polyethylene (68.3 × 10$^4$ g mol$^{-1}$); for comparison **45a** possessing the least sterically N-aryl group generated the lowest molecular weight polyethylene of 9.5 × 10$^4$ g mol$^{-1}$.

## 3. Chromium catalysts for selective ethylene trimerization and tetramerization

While homogeneous chromium catalysts have shown their importance in oligomerization and polymerization of ethylene (see section 2), they have also emerged as effective catalysts for the selective trimerization and more recently tetramerization of ethylene. Moreover, the products, 1-hexene and 1-octene are in high demand due to their use as comonomers for the production of linear low-density polyethylene (LLDPE) [38,40,48,81,131-147]. In this section, we again use the type of multidentate ligand to divide the sections with catalysts based on N^N^N discussed first before moving on to P^P, S^P^S, S^N^S, P^N^P and P^P^O systems.

### 3.1. Tridentate ligands based on N-donors and their Cr precatalysts

As noted in section 2, Köhn *et al.* found that 1,3,5-triazacyclohexane-chromium complexes **18a** - **18d** (Figures 4 and 14) on activation with MAO, could polymerize ethylene with activities up to 717 kg (mol Cr)$^{-1}$ h$^{-1}$ [148]. Interestingly, and analogous to observations made with the heterogeneous Phillips catalyst (CrO$_3$/SiO$_2$), 1-hexene and decenes as 'co-trimers' of 1-hexene and ethylene could be found in

solutions of these polymerization reactions. In addition to this, $^{13}$C NMR spectroscopic analysis revealed the presence of butyl side chains in the polyethylene, indicative of 1-hexene incorporation during polymerization. Subsequently the same group found that **18c**/MAO or **18d**/MAO were also effective catalysts for the trimerization of higher α-olefins such as propene, 1-hexene and styrene [81]. At ambient temperature, these catalysts showed high conversions for trimerization of about 80% which could be increased by running the reactions at 0 °C.
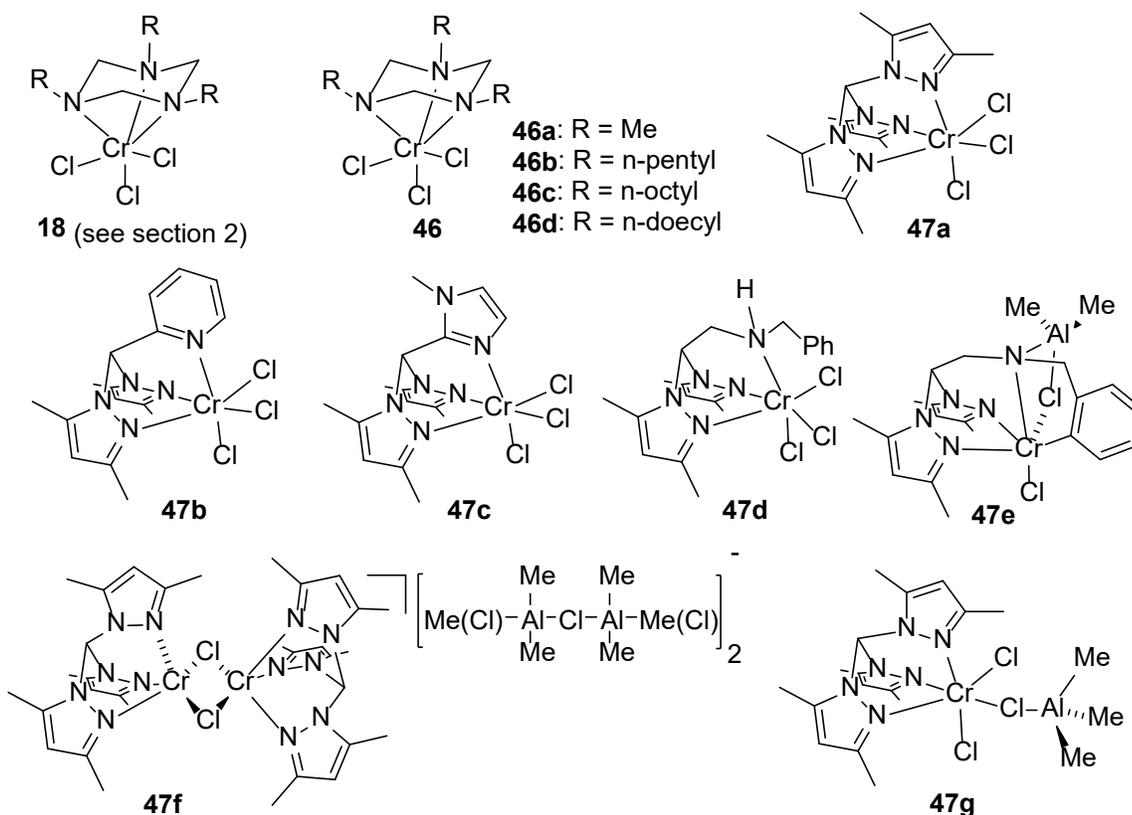


**Figure 14.** N^N^N-chelated chromium precatalysts for ethylene trimerization, **18**, **46**, **47** [135,148,149]

As an extension to their work with **18a – 18d**, Köhn and Wasserscheid used the triazacyclohexane-chromium(III) complexes **46a - 46e**, containing a range of linear and branched N-alkyl substituents, for the trimerization of 1-decene and 1-dodecene (Figure 14) [149]. The 2-ethylhexyl-containing **46d**, on activation with MAO was able to selectively trimerize 1-dodecene with a conversion of 80.5% yielding 93% $C_{36}$, 7% internal $C_{12}$ with a TON of 1026. Some control of the performance could be introduced by the changing the triazacyclohexane N-R substituents. For example, **46a** gave conversions of up to 97.7%

but the amount of $C_{36}$ was decreased (81%) whereas the undesired isomer formation increased by up to 19%.

The Hor group studied the pyrazolyl-containing chromium complexes **47a** - **47g** as precatalysts for ethylene trimerization (Figure 14) [134]. By conducting the reactions at 80 °C and 30 atm $C_2H_4$, with MAO as co-catalyst, **47a** – **47g** displayed good activities of between 32400 and 53000 g (g Cr)$^{-1}$ h$^{-1}$ and high selectivities for α-olefins (92.1 - 98.7%) with the predominant product being 1-hexene (98.3 - 99.3%). The highest activity was obtained by **47c** (53000 g (g Cr)$^{-1}$ h$^{-1}$) which contains a bound imidazolyl group (Table 2). Complex **47d**, incorporating an amino group, exhibited less activity and less selectivity than those bearing bound heterocyclic groups (**47a** - **47c**).

### 3.2. Bi- and tridentate ligands based on P- and S-donors and their Cr precatalyts

Wass and co-workers at BP investigated a series of neutral $Ar_2PN(Me)PAr_2$ (PNP) ligands **48a** - **48g** as supports for chromium complexes with a view to exploring their potential as catalysts for the trimerization of ethylene (Figure 15) [48,150]. Initial screening of *ortho*-methoxy **48a** in the presence of $CrCl_3(THF)_3$ with MAO at 1 atm $C_2H_4$ saw a large exotherm. Under these conditions moderate activities of between 4610 – 9500 g (g Cr)$^{-1}$ h$^{-1}$ were observed with high selectivities for α-olefins (64.1 – 91.5%) for ethylene trimers along with lesser amounts of $C_8$ and $C_{10}$ (shown by GC). When the ethylene pressure was raised to 4, 8 and then 20 atm, the activity observed using **48a** steadily increased with a remarkably high value of 1033200 g (g Cr)$^{-1}$ h$^{-1}$ with a selectivity for 1-hexene of >99.9% (Table 2). It is noteworthy that the selectivity for 1-hexene improved with a higher pressure of ethylene. By contrast, use of ligands **48b** and **48c**, which contain *ortho*-ethyl and *para*-methoxy substituents, respectively, proved inactive at 1 atm $C_2H_4$ and ambient temperature. Likewise, **48f** and **48g** which contain dissimilar ligand backbones but incorporate *ortho*-methoxy groups, were also inactive under the same reaction conditions. On the other hand, 2,5-dimethoxy-containing **48d** and 2-methoxy-3-fluoro **48e** were active for ethylene trimerization.
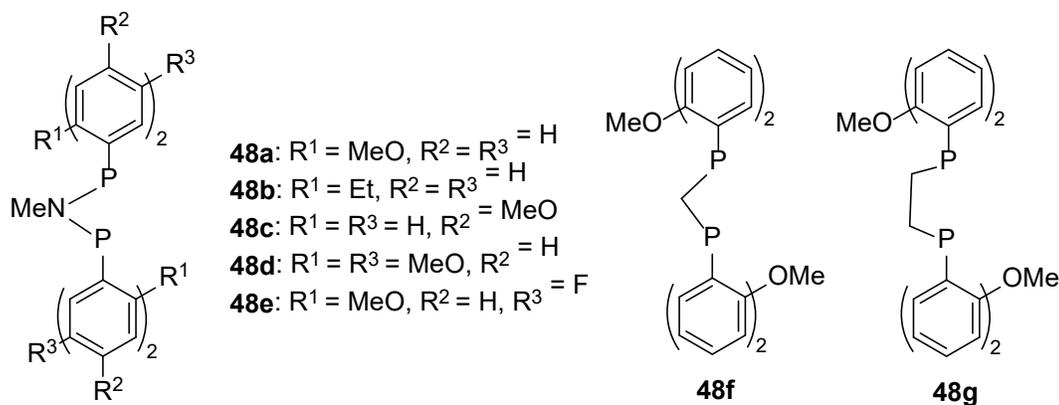
**Figure 15.** P^P ligands **48** used for chromium mediated ethylene trimerization [48]

In a series of publications, McGuinness *et al.* evaluated a variety of chromium(III) complexes, and in some cases chromium(II), bearing combinations of P^N^P, P^S^P and S^N^S chelating ligands, for the trimerization of ethylene (Figure 16) [135,136,138]. Initially, their studies focused on P^N^P-containing **49a** – **49c** and showed that on activation with MAO (Al/Cr = 850), the maximum activity was obtained using **49c** of 37400 g (g Cr)$^{-1}$ h$^{-1}$ [135]. With the exception of **49b**, the other two complexes performed effectively for the trimerization of ethylene with selectivities for 1-hexene between 98.9 and 99.3%. By contrast, cyclohexyl-containing **49b**/MAO generated polyethylene as the main product (85.7%) along with 14% hexenes with only 80% 1-hexene selectivity. However, despite the high activities and good selectivities, the sensitivity, cost and toxicity associated with the secondary alkyl phosphine precursors makes these ligand types less attractive and has led to other donor sets being sought. Indeed in a follow-up study, **49a** – **49c** were again investigated and this study was extended to cover S^N^S **49d** – **49g**, P^N^P **49h**, **49i**, P^S^P **49k**, **49l**, S^P^S **49m** and S^N^S **49j** with the aim to explore the effect of P, S and N donor substitution and chelate ring size (Figure 16) [136]. Both the P^N^P and S^N^S systems generated high selectivities for 1-hexene with the highest values being over 97%. Indeed, the S^N^S system was optimized more extensively and displayed TOFs of up to 260000 h$^{-1}$. The optimal temperature was shown to be between 80 - 100 °C with lower temperatures resulting in

lower activities and the noticeable formation of polymer. While at temperatures >100 °C, catalyst deactivation occurred along with the observation of higher oligomers. By comparison of **49e** with **49g**, which differ in the chain length of the alkyl substituent, longer alkyl chain derivative **49g** led to significantly higher catalytic activity. In particular, **49g** displayed a TOF of 153482 h$^{-1}$ in the presence of a very low loading of MAO. In the case of P^N^P **49h** and **49i**, which contain N-alkyl groups, lower activity and polymer formation was observed. The TOF of unsymmetrical S^N^S **49j** is similar to that seen with symmetric S^N^S **49e** with values around 27380 h$^{-1}$. Nevertheless, the activity of **49j** is less than half the activity displayed by symmetrical **49e**. P^S^P-containing **49l** gave predominantly 1-hexene, although the results were less impressive than that obtained with the S^N^S and P^N^P systems.
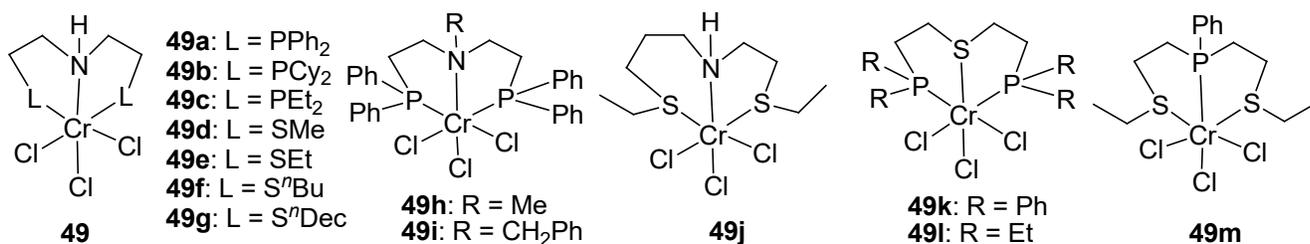


**Figure 16.** P^N^P-, S^N^S-, P^S^P-chelated chromium precatalysts, **49**, for ethylene trimerization [135,136, 138]

The Bluhm group have been interested in Cr(III) complexes bearing an assortment of mixed donor tridentate ligands as ethylene trimerization catalysts (Figure 17) [131]. In particular, imine **50a**, **50b**, **50e**, **50f**, **50g** and amine **51a"**, **51b"** were the most active for the trimerization with excellent selectivity (82 - 98%) for 1-hexene while **50c**, **50h**, **50i**, **50j**, **50k** and **51c"** produced polyethylene. The S^N^S and N^O-containing systems displayed lower activity than the P^N^P catalysts with the rate of polymer formation increasing. The reaction temperature and ethylene pressure strongly influenced the product distribution: for example, at temperatures of between 70 and 85 °C and 30 bar $C_2H_4$, the formation of polymer was found to increase. When the reaction ethylene pressure was reduced the activity decreased. In addition, higher olefins have been observed using catalysts based on larger amounts of MAO.
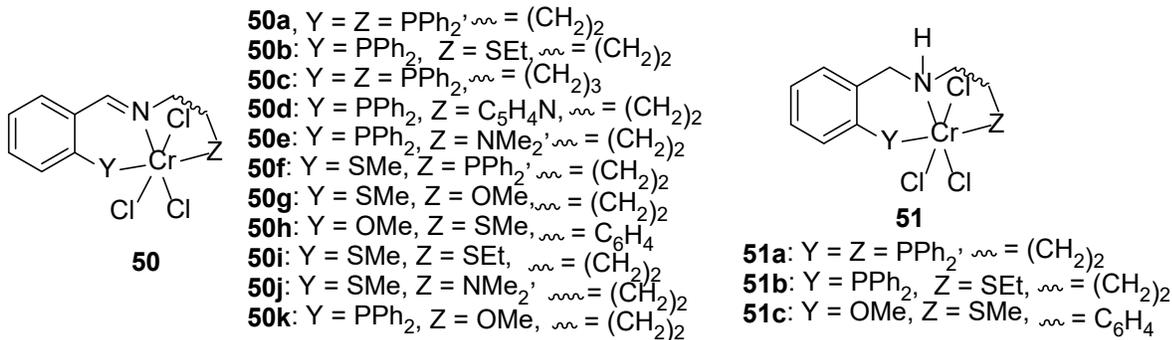
**50a**, Y = Z = PPh$_2$, $\sim$ = (CH$_2$)$_2$
**50b**: Y = PPh$_2$, Z = SEt, $\sim$ = (CH$_2$)$_2$
**50c**: Y = Z = PPh$_2$, $\sim$ = (CH$_2$)$_3$
**50d**: Y = PPh$_2$, Z = C$_5$H$_4$N, $\sim$ = (CH$_2$)$_2$
**50e**: Y = PPh$_2$, Z = NMe$_2$, $\sim$ = (CH$_2$)$_2$
**50f**: Y = SMe, Z = PPh$_2$, $\sim$ = (CH$_2$)$_2$
**50g**: Y = SMe, Z = OMe, $\sim$ = (CH$_2$)$_2$
**50h**: Y = OMe, Z = SMe, $\sim$ = C$_6$H$_4$
**50i**: Y = SMe, Z = SEt, $\sim$ = (CH$_2$)$_2$
**50j**: Y = SMe, Z = NMe$_2$, $\sim$ = (CH$_2$)$_2$
**50k**: Y = PPh$_2$, Z = OMe, $\sim$ = (CH$_2$)$_2$

**51a**: Y = Z = PPh$_2$, $\sim$ = (CH$_2$)$_2$
**51b**: Y = PPh$_2$, Z = SEt, $\sim$ = (CH$_2$)$_2$
**51c**: Y = OMe, Z = SMe, $\sim$ = C$_6$H$_4$

**Figure 17.** Various P^S^P-, S^P^S-, P^N^P-, S^P^N-, S^N^O- and P^N^O-chelated chromium precatalysts for ethylene trimerization, **50** and **51** [131]

The Cr(III) and Cr(II) complexes **52a** - **52d** and **52a'** - **52b'** containing S^N^S ligands incorporating a central pyridine donor have been the subject of a study by Duchateau and Gamborotta (Figure 18) [139]. Complexes **52a** and **52b** were exceptionally selective for the production of 1-hexene (>99%) in the presence of MAO. By contrast, **52b** displayed lower activity with no change in the selectivity for 1-hexene with polyethylene formed under conditions of increased loading of MAO. At an ethylene pressure of 10 bar the activity was lower (781 g (g Cr)$^{-1}$ h$^{-1}$) than that at the higher pressure of 35 bar (5177 g (g Cr)$^{-1}$ h$^{-1}$), while when the reaction was run at room temperature, the activity dropped to 301 g (g Cr)$^{-1}$ h$^{-1}$. Complexes **52a'** - **52b'** and **52d** on activation with MAO [Al/Cr = 1000], gave C$_6$ as the major product in 49.5 - 57.8%. On the other hand, using Al/Cr = 100, 51.2 - 83.4% of C$_4$ - C$_{16}$ was formed. Notably, **52b'** formed only two reaction products with the predominant one being C$_6$ (83.4%) and the minor one C$_4$ (16.6%). In the case of **52d**, this generated a higher amount of 1-hexene (49.5%) and 1-octene (20.4%) when compared with other oligomers. Unfortunately, **52c** could not be isolated in an analytically pure form to allow its catalytic evaluation.
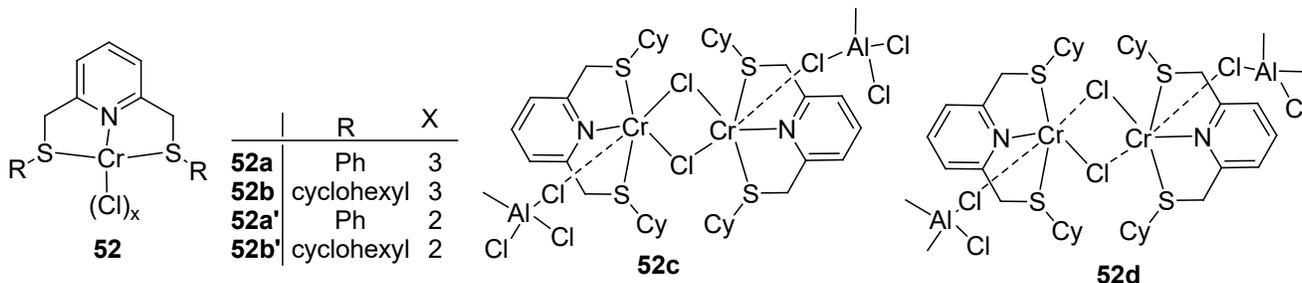
**Figure 18.** Various S^N^S -chelated chromium precatalysts for ethylene trimerization, **52** [139]

Braunstein *et al.* prepared the Cr(III) complexes, **53a - 53h**, bearing N^O^N and N^S^N heteroscorpionate ligands derived from bis(pyrazol-1-yl)methane, for use in ethylene trimerization (Figure 19) [140]. The catalytic performance of the thioether complexes **53a - 53c** with MAO were highly selective for 1-hexene with a total $C_6$ selectivity of >94.7% and 1-hexene >96.1% with activities of between 1050 - 3900 g (g Cr)$^{-1}$ h$^{-1}$. The ether analogue **53d** was more active (1-hexene 97.1% and 5400 g (g Cr)$^{-1}$ h$^{-1}$) than its thioether analogues. Complexes **53d - 53g** gave remarkable selectivity for 1-hexene ~ 96.1 - 98.9% with the optimal conditions established as 80 °C, 25 bar $C_2H_4$ and 200 equivalents of MAO. The topmost activity was 16200 g (g Cr)$^{-1}$ h$^{-1}$ identified using **53f**. By comparison, the S^N^S-chromium system reported by the Sasol, [CrCl_3{HN(CH_2CH_2-S^ndecyl)_2}] (**49g**, Figure 16) was more active [132]. Over a longer reaction time of 1 hour, **53f** showed reduced activity which highlights the shorter lifetime of this catalyst.
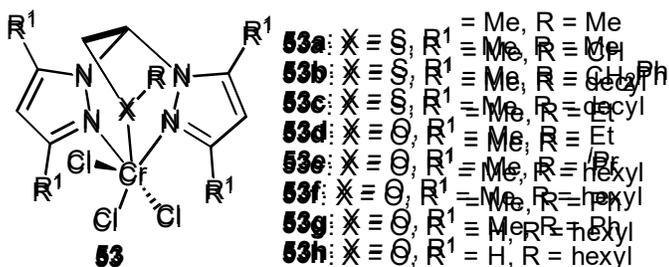


**Figure 19.** Various N^O^N- and N^S^N-chelated chromium precatalysts, **53**, for ethylene trimerization [140]

The cationic S^N^S-organochromium(III) species, **54a**, **54b**, **55a – 55e** and neutral **55f**, **55g** have also been reported by Duchateau and Gambarotta (Figure 20) [141,142]. By employing **54a** and **54b** in

the presence of MAO (50 °C, 35 bar $C_2H_4$, 1 hour of reaction time and Al/Cr = 1000) activities in the range 6903 - 9383 g (g Cr)$^{-1}$ h$^{-1}$ were observed with high selectivities for 1-hexene (98%). Similarly, **55a** and **55b** at low Al/Cr molar ratios [500 - 1000] afforded high activities (2200 - 8024 g (g Cr)$^{-1}$ h$^{-1}$) and high selectivity for $C_6$ (>98%) on activation with MAO. Conversely, when the Al/Cr molar ratio was increased to 2000, the catalytic activity of **55a** and **55b** and selectivity for $C_6$ dropped reaching values of 1510 - 1941 g (g Cr)$^{-1}$ h$^{-1}$ and ~32 - 97%, respectively. A similar detrimental effect on $C_6$ selectivity (lowering to 70.8 - 53.4%) was observed using **55e** in the presence of 2000 equivalents MAO. By way of contrast, neutral **55f** showed both low activity and low selectivity for $C_6$ while **55g** did not produce any oligomer.
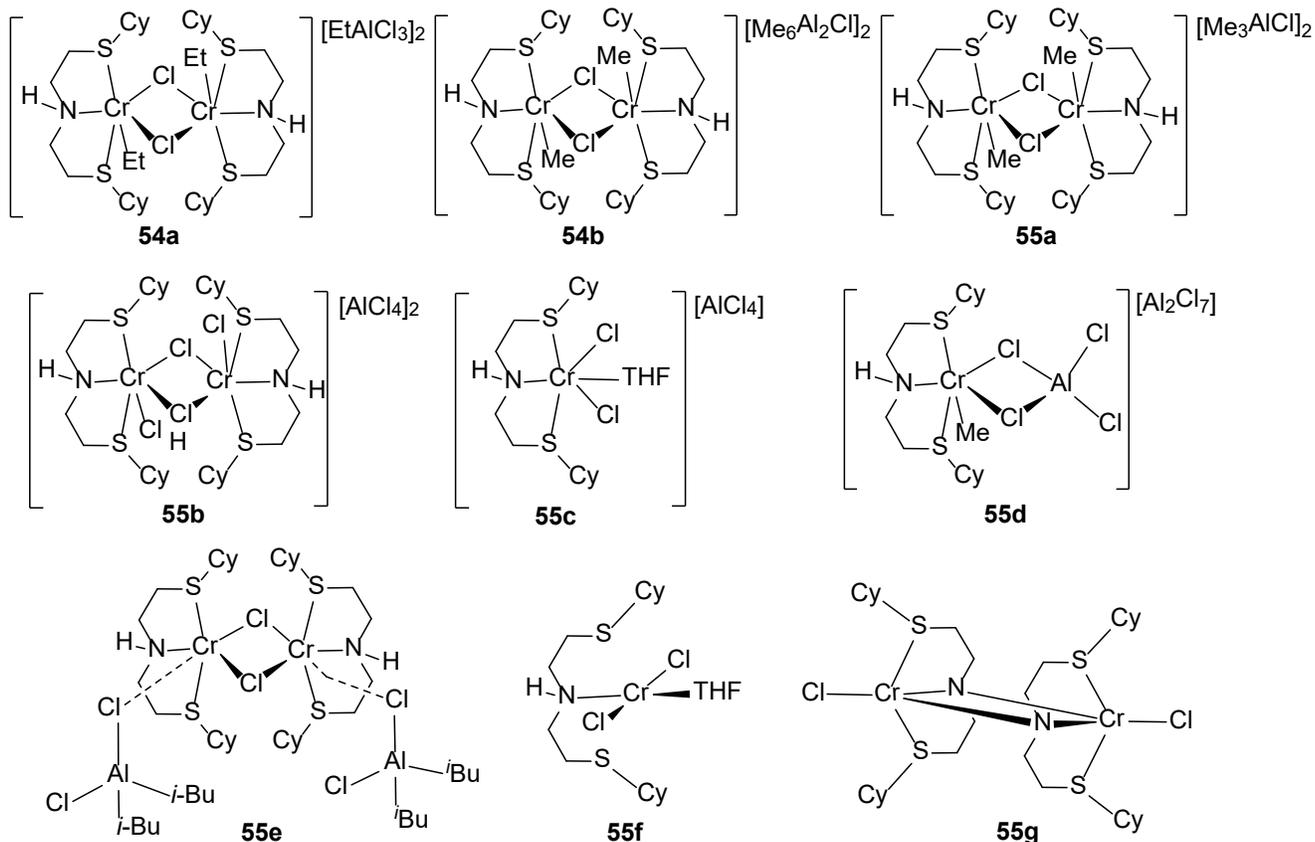


**Figure 20.** Various S^N^S-chelated chromium precatalysts for ethylene trimerization, **54** and **55** [141, 142]

**Table 2.** Catalytic performance data for chromium trimerization catalysts generated either using a precatalyst/activator system or made *in-situ* from ligand/chromium precursor/activator

| Ligand or precatalyst | Activator or Cr precursor/Activator | Reaction conditions | Conversion to $C_6$ (%) | 1-Hexene selectivity (%) | Activity [g (g Cr)$^{-1}$ h$^{-1}$] | Ref. |
|---|---|---|---|---|---|---|
| **48a** | Cr(THF)$_3$Cl$_3$ /MAO | 80 °C, 20 bar | 90.0% | 99.9% | 1033200 | [150] |
| | Cr(THF)$_3$Cl$_3$ /MAO | 45 °C, 45 bar | 82% | >99% | 159600 | [40] |
| **48b** | CrCl$_3$(THF)$_3$/MAO | 45 °C, 45 bar | 93.0% | 99.8% | 161660 | [137] |
| **49e** | MAO | 90 °C, 30 bar | 98.4% | 99.7% | 160840 | [136] |
| **49g** | MAO | 80 °C, 45 bar | 98.7 | 99.8 | 85950 | [132] |
| **49c** | MAO | 80 °C, 40 bar | 97.0 | 99.3 | TOF = 39890 h$^{-1}$ | [135] |
| **47b** | MAO | 80 °C, 30 bar | 97.8 | 99.3 | 38200 | [134] |

While catalysts capable of ethylene trimerization are now well-documented, the emergence of chromium complexes that can mediate ethylene tetramerization with high selectivities was first reported only in 2004 (Table 3). Bollmann *et al.* at Sasol re-explored the use of diphosphinoamino ligands, $((R_2)_2P)_2NR_1$, this time with a range of different substitution patterns on the P and N atoms (**56a** – **56i**). In the presence of a suitable chromium precursor and aluminoxane, **56a** – **56i** gave selectivities of up to 70% for 1-octene (Figure 21) [38]. The highest α-selectivity of 68.3% for $C_8$ was obtained using N-isopropyl/P-phenyl **56d**, with the major side products being 1-hexene, methylcyclopentane and methylene cyclopentane (Table 3). Ligands with bulkier aromatic substituents such as biphenyl and naphthyl groups (**56f**, **56g**), gave between 54 - 56% $C_8$ products at 65 °C and 30 bar. Unexpectedly,

ligands containing heteroaromatic substituents such as the thiophenyl groups in **56h** yielded in excess of 60% $C_8$ products at 45 °C and 45 bar. Even the use of ligands containing alkyl substituents, such as ethyl (**56i**) furnished more than 45% $C_8$ products at 45 - 65 °C and 30 - 45 bar.
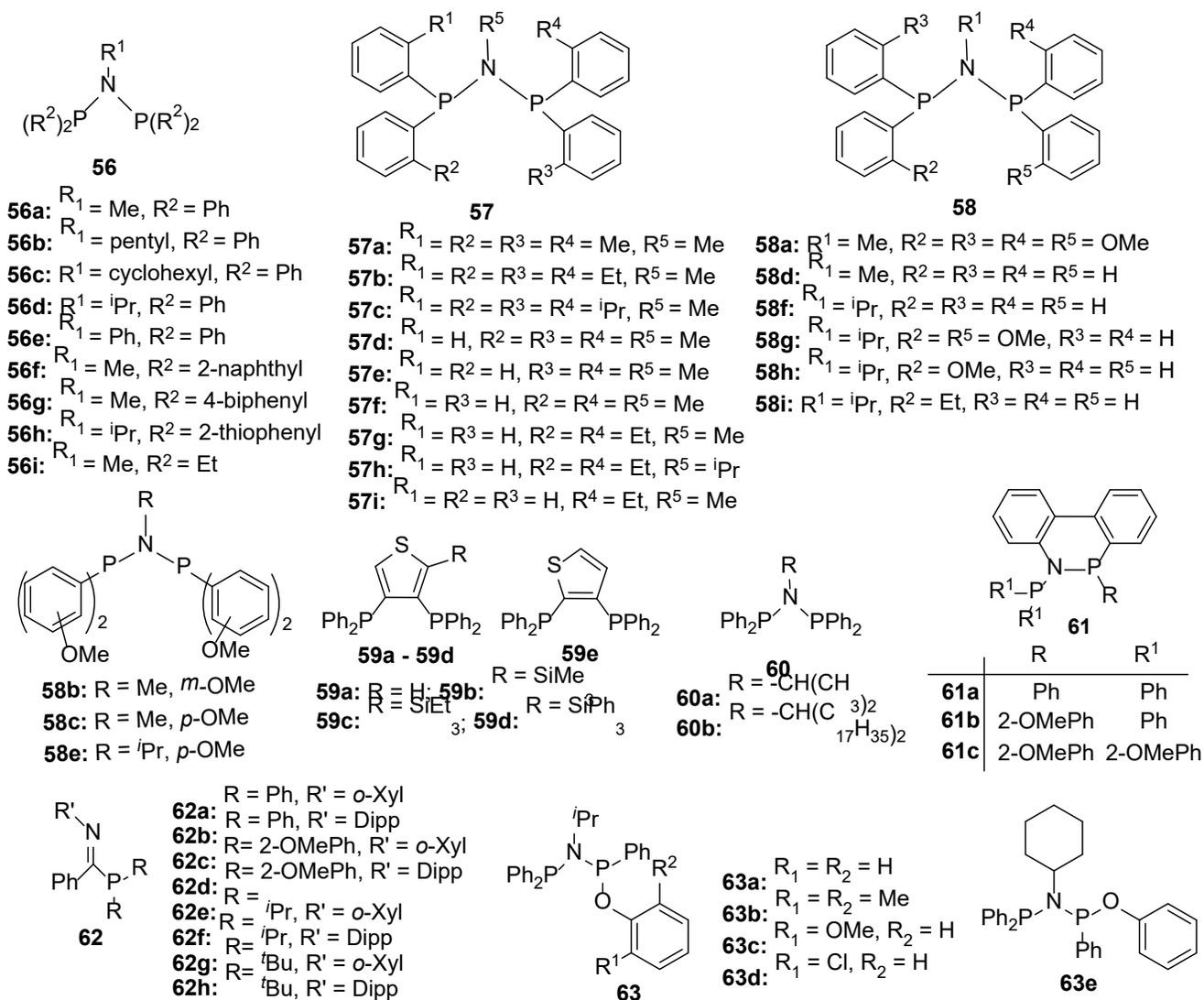


**56**

**56a:** $R^1$ = Me, $R^2$ = Ph
**56b:** $R^1$ = pentyl, $R^2$ = Ph
**56c:** $R^1$ = cyclohexyl, $R^2$ = Ph
**56d:** $R^1$ = $^i$Pr, $R^2$ = Ph
**56e:** $R^1$ = Ph, $R^2$ = Ph
**56f:** $R^1$ = Me, $R^2$ = 2-naphthyl
**56g:** $R^1$ = Me, $R^2$ = 4-biphenyl
**56h:** $R^1$ = $^i$Pr, $R^2$ = 2-thiophenyl
**56i:** $R^1$ = Me, $R^2$ = Et

**57**

**57a:** $R^1$ = $R^2$ = $R^3$ = $R^4$ = Me, $R^5$ = Me
**57b:** $R^1$ = $R^2$ = $R^3$ = $R^4$ = Et, $R^5$ = Me
**57c:** $R^1$ = $R^2$ = $R^3$ = $R^4$ = $^i$Pr, $R^5$ = Me
**57d:** $R^1$ = H, $R^2$ = $R^3$ = $R^4$ = $R^5$ = Me
**57e:** $R^1$ = $R^2$ = H, $R^3$ = $R^4$ = $R^5$ = Me
**57f:** $R^1$ = $R^3$ = H, $R^2$ = $R^4$ = $R^5$ = Me
**57g:** $R^1$ = $R^3$ = H, $R^2$ = $R^4$ = Et, $R^5$ = Me
**57h:** $R^1$ = $R^3$ = H, $R^2$ = $R^4$ = Et, $R^5$ = $^i$Pr
**57i:** $R^1$ = $R^2$ = $R^3$ = H, $R^4$ = Et, $R^5$ = Me

**58**

**58a:** $R^1$ = Me, $R^2$ = $R^3$ = $R^4$ = $R^5$ = OMe
**58d:** $R^1$ = Me, $R^2$ = $R^3$ = $R^4$ = $R^5$ = H
**58f:** $R^1$ = $^i$Pr, $R^2$ = $R^3$ = $R^4$ = $R^5$ = H
**58g:** $R^1$ = $^i$Pr, $R^2$ = $R^5$ = OMe, $R^3$ = $R^4$ = H
**58h:** $R^1$ = $^i$Pr, $R^2$ = OMe, $R^3$ = $R^4$ = $R^5$ = H
**58i:** $R^1$ = $^i$Pr, $R^2$ = Et, $R^3$ = $R^4$ = $R^5$ = H

**58b:** R = Me, $m$-OMe
**58c:** R = Me, $p$-OMe
**58e:** R = $^i$Pr, $p$-OMe

**59a - 59d**
**59a:** R = H; **59b:** R = SiMe$_3$; **59d:** R = SiPh$_3$
**59c:** R = SiEt$_3$

**59e**
**60a:** R = -CH(CH$_3$)$_2$
**60b:** R = -CH(C$_{17}$H$_{35}$)$_2$

**61**

| | R | R$^1$ |
|---|---|---|
| **61a** | Ph | Ph |
| **61b** | 2-OMePh | Ph |
| **61c** | 2-OMePh | 2-OMePh |

**62**
**62a:** R = Ph, R' = $o$-Xyl
**62b:** R = Ph, R' = Dipp
**62c:** R= 2-OMePh, R' = $o$-Xyl
**62d:** R= 2-OMePh, R' = Dipp
**62e:** R = $^i$Pr, R' = $o$-Xyl
**62f:** R = $^i$Pr, R' = Dipp
**62g:** R= $^t$Bu, R' = $o$-Xyl
**62h:** R= $^t$Bu, R' = Dipp

**63**
**63a:** $R_1$ = $R_2$ = H
**63b:** $R_1$ = $R_2$ = Me
**63c:** $R_1$ = OMe, $R_2$ = H
**63d:** $R_1$ = Cl, $R_2$ = H

**63e**

**Figure 21.** Various P^P, P^N and P^O-containing ligands **56 – 63** for use in chromium-mediated ethylene tri-/tetramerization [38,40,137,143]
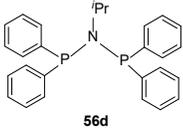
Overett and Blann also investigated the use of diphosphinoamine ligands (**57**, Figure 21) as supports for chromium catalysts for ethylene tri-/tetramerization [40,137]. In particular, they observed selectivity for either trimerization or tetramerization of ethylene, depending on the position and number of substituents on the aryl rings. The sterically encumbered *ortho*-alkyl substituent derivatives **57a** - **57i**

proved highly activity and selective towards ethylene trimerization. The maximum productivity of $298800 - 324110$ g (g Cr)$^{-1}$ h$^{-1}$ was obtained using **57a** and **57b** with MMAO as activator. Conversely, the best selectivity for 1-hexene was shown by *ortho*-ethyl **57b** and *ortho*-isopropyl **57c** which increased to ~93%. On the other hand, the unsubstituted diphosphinoamines (*e.g.*, **58f/56d**) yielded predominantly 1-octene [38]. To explore the effect of partial substitution of *ortho* groups, **57d** – **57i** were also tested. Removal of only one *ortho*-methyl group caused a dramatic shift in product selectivity (**57d**) with the $C_8$ selectivity increasing to 42% and the $C_6$ fraction decreasing to 42%. The selectivity to 1-hexene in the $C_6$ fraction was concomitantly reduced to 82%. Ligands with only two *ortho*-methyl substituents such as the unsymmetrical **57e** and its symmetrical counterpart **57f**, both afforded catalysts favoring the formation of 1-octene. Likewise for ligand **57g**, the *ortho*-ethyl substituted analogue of **57f**, a similar tendency was observed. However, on exchanging the N-methyl group for an N-isopropyl moiety (**57h**) a change in selectivity back towards 1-hexene was apparent. This was observation was attributed to a steric effect of the ethyl substituents, caused by the greater bulk of the isopropyl group. An N-isopropyl ligand with one *ortho*-ethyl group (**57i**) gave a $C_8$-selective catalyst, in accord with its reduced steric properties.

The same group also explored chromium(III) complexes bearing the methoxy-substituted diphosphinoamines **58a** - **58i** as catalysts for ethylene tri-/tetramerization (Figure 21) [40]. Two different sets of reaction conditions were explored namely, 30 bar $C_2H_4$/65 ºC and 45 bar $C_2H_4$/45 ºC; both employing MMAO or MAO as activators. Higher activity was observed at 45 bar/45 ºC which has been attributed to higher ethylene pressure producing higher activity and reduced catalyst deactivation at lower temperatures. The best tetramerization activity was obtained with **58e**, containing a *para*-methoxy substituent, showing 68% selectivity of $C_8$ with an activity of 112700 g (g Cr)$^{-1}$ h$^{-1}$. Changing the pattern of the aryl substitution progressively from *ortho* (**58a**) to *meta* (**58b**) to *para* (**58c**) changes the selectivity of the catalyst from selective trimerization to predominantly tetramerization (50% $C_8$ with **58c**). The unsubstituted derivatives **58d** and **58f** gave $C_8$ with selectivities of between 59 and 68% which is similar

to that seen for *para*-methoxy **58e** (68%). Interestingly, only a small shift in selectivity towards $C_8$ is observed on reducing the number of *ortho*-methoxy substituents. Complexes **58a**, **58g** and **58h** remain predominantly selective for trimerization (48 - 91%) with a maximum of 17% $C_8$ observed. By comparison, the sterically similar *ortho*-ethyl substituted ligand **58i** resulted in a $C_8$ selectivity of 63% under similar conditions.

**Table 3.** Selected catalytic performance data using chromium tetramerization catalysts generated either using **56d**/Cr precursor/activator

| Ligand | Cr precursor/Activator | Reaction conditions | Conversion to $C_8$ (%) | 1-Octene selectivity (%) | Activity (g (g Cr)$^{-1}$ h$^{-1}$) | Refs |
|---|---|---|---|---|---|---|
| | $Cr(THF)_3Cl_3$ /MAO | 65 °C, 45 bar | 72.2% | 99% | 125600 | [42] |
| **56d** | $Cr(acac)_3$/MAO | 45 °C, 45 bar | 68.3% | 99% | 272400 | [40] |
| | $Cr(THF)_3Cl_3$/AlEt$_3$/B(C$_6$F$_5$)$_3$ | 45 °C, 50 bar | 67.0% | 99% | 7110 | [44] |
| | $Cr(THF)_3Cl_3$/ MAO | 65 °C, 30 bar | 60.6% | 99.2% | 11700 | [38] |

Elsewhere, Cr(III) complexes coordinated by the diphosphinothiophenes **59a** - **59e** (Figure 21) have shown good performance characteristics for ethylene tri-/tetramerization. In particular, using **59b** the highest activity of 686.0 kg (g Cr)$^{-1}$ h$^{-1}$ was observed with a selectivity of 69.0% toward 1-hexene (29.5%) and 1-octene (39.5%) [143]. Well-defined cationic chromium(III) complexes, $[(\mathbf{60a})CrCl_2(NCCH_3)_2]^+[B(C_6F_5)_4]^-$ and $[(\mathbf{60b})CrCl_2(NCCH_3)_2]^+[B(C_6F_5)_4]^-$ bearing diphosphinoamine ligands **60a** and **60b** (Figure 21), showed moderate activities toward ethylene tetramerization in chlorobenzene when activated with the trialkylaluminum reagents Et$_3$Al and $^i$Bu$_3$Al [144]. Churakov and co-workers successfully designed the P(N)P ligands, 5,6-dihydrodibenzo-[c,e]-[1,2]-azophosphinine that could undergo coordination to Cr(CO)$_4$ [145] but the resultant precatalysts proved inactive for ethylene oligomerization. On the other hand, **61a** - **61c** (Figure 21) when reacted with Cr(acac)$_3$ formed precatalysts that displayed TOFs of between 126900 and 312500 h$^{-1}$ for ethylene oligomerization with **61c** producing 1-hexene and 1-octene in a 2:1 ratio along with some polymer. The

1-phosphanyl methanimine P^N-ligands, **62a - 62h** (Figure 21) have also emerged as compatible supports for chromium ethylene tri-/tetramerization catalysts [146] as have the phosphazane ligands **63a - 63e** (Figure 21) [147]. For example, the chromium catalyst derived from N-cyclohexyl-containing **63e** displayed a high activity of 316.7 kg (g Cr)$^{-1}$ h$^{-1}$ along with a high total selectivity of 85.1% towards 1-hexene (45.7%) and 1-octene (39.4%). On the other hand, its analogue containing **63a** generated a higher 1-octene selectivity (54.0%) but with a lower activity of 73.3 kg (g Cr)$^{-1}$ h$^{-1}$.

## 4. Mechanistic understanding

### 4.1. Oligo-/polymerization of ethylene

The oligo-/polymerization of ethylene in a non-selective manner as described in section 2 is proposed to occur by a Cossee-Alrman mechanism in which chain propagation involves a series of sequential steps based on ethylene coordination and migratory insertion before chain transfer terminates the reaction (Scheme 1). Typically, this termination occurs *via* β-H elimination (or transfer to monomer) forming α-olefins/polymers regenerating a common active chromium-hydride species [46]. Based on this mechanism, either a Schulz–Flory distribution of even-numbered α-olefins would result with a range of chain lengths or higher molecular weight linear polymer displaying various dispersities and alkyl/vinyl end-groups would be afforded [46]. Alternatively, the alkyl aluminum activator (*e.g.*, MAO and the AlMe$_3$ present within) can participate in chain transfer resulting in an aluminum-polymer species and the generation of an active methyl-chromium complex that can re-commence the propagation steps. Hydrolysis of the aluminum-polymer can then take place to give fully saturated polymers. In general, β-hydride elimination is the key pathway in homogeneous chromium catalysis with chain transfer to aluminum becoming competitive with large amounts of alkyl-aluminum (the effect of temperature has also been shown to be important) [22,75,90].
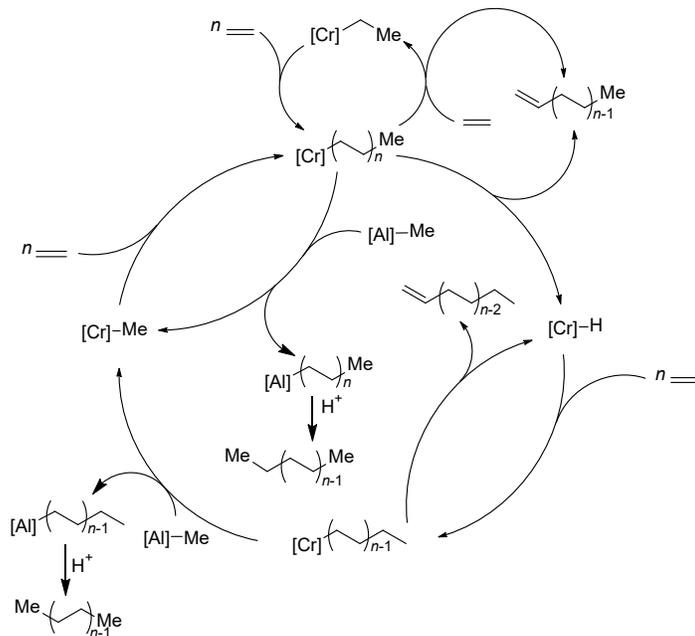
**Scheme 1.** Chain-propagation and chain-termination pathways for ethylene oligo-/polymerization; where [Al]-Me represents AlMe$_3$ or its derivatives present with in MAO
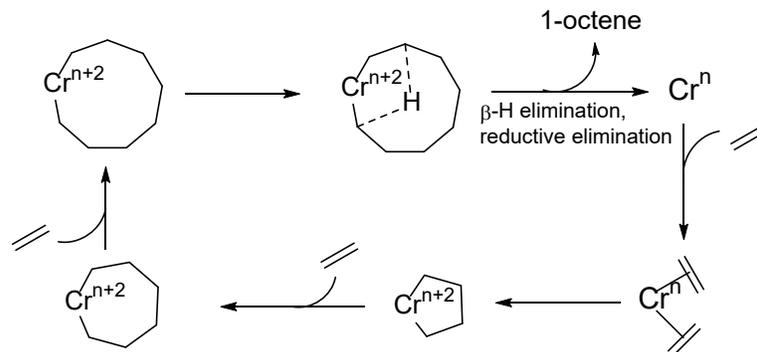
## 4.2. Tri-/tetramerization of ethylene

The origin of the selectivity towards ethylene trimerization shown with a number of chromium catalysts (see section 3) is considered to take place by metallacyclic-based mechanism, as initially proposed by Manyik [151], later modified by Briggs [152] and by a number of subsequent studies (Scheme 2) [153-155]. The first step of the catalytic cycle is to *cis*-coordinate two ethylene molecules to the metal center, which then undergoes oxidative cyclization to form a chromacyclopentane. The oxidative cyclization step is assumed to be essentially irreversible and thermodynamically driven due to the breaking of two π-bonds and the formation of two σ-bonds [133]. Due to the conformation of the metallacyclopentane an agostic interaction between the metal and the β-H is inhibited thereby preventing the release of 1-butene. In the next step, this metallacyclopentane coordinates another ethylene molecule. The coordinated ethylene molecule then undergoes a migratory insertion to expand the metallacyclopentane to metallacycloheptane. The release of 1-hexene from the metallacycloheptane intermediate is considered to occur by a two-step pathway involving β-H elimination and reductive elimination; a

concerted 3,7-H shift pathway has also been postulated. Some support for β-H elimination has been provided by the observation of methylcyclopentane and methylenecyclopentane as well as cyclopentyl end groups in the polymer chains, which highlights the involvement of alkenyl hydride intermediate [156].
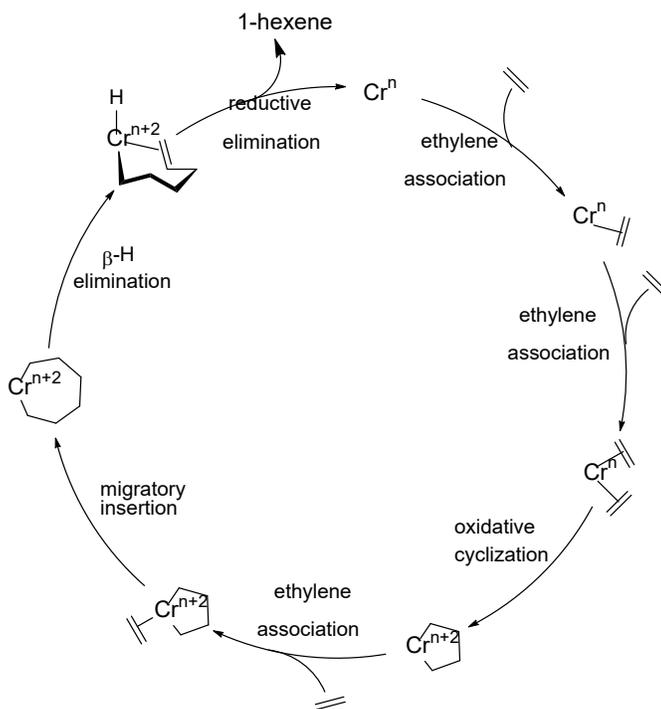


**Scheme 2.** Postulated mechanism for ethylene trimerization

The mechanism of tetramerization has also been the subject of a number of studies [5,45,48, 137,149,150,157-159]. The conclusion of many of these works is that a modified metallacyclic mechanism is operational in which chromacycloheptane species is now stable relative to 1-hexene elimination that occurs in the trimerization cycle, with the result that the larger 9-membered ring is now obtainable (Scheme 3). This chromacyclononane can then undergo β-H elimination to form 1-octene and regenerate the active species. Hence, it would appear the selectivity for trimerization or tetramerization is controlled by the relative stability of the different sized metallacycles.

**Scheme 3.** Postulated mechanism for ethylene tetramerization

Given the expected instability of nine-membered chromacyclononane intermediate, alternative tetramerization mechanisms have been postulated some of which involve a binuclear active species [160,161]. For example, Fritz *et al.* came up with a mechanism involving a dual-core low-valent chromium center (Scheme 4) [161]. In this mechanism, the two metal centers coordinate the ethylene molecules separately to form two metallacyclopentenes which then couple to form bimetallic ten-membered ring, reductive elimination ensues to from 1-octene.
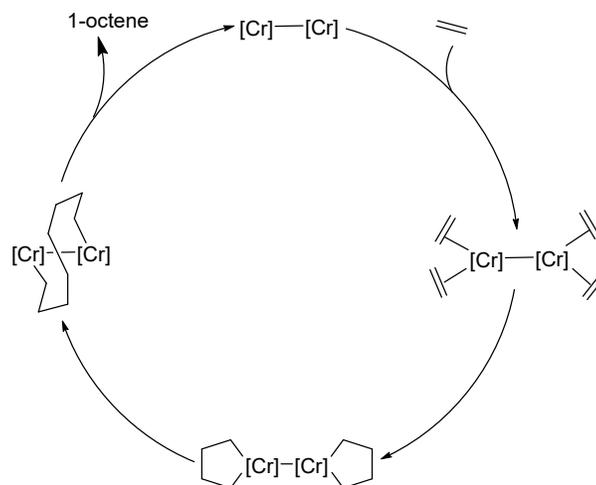


**Scheme 4.** Proposed binuclear mechanism for the selective ethylene tetramerization

To support the various proposals for the mechanism of oligo-/polymerization and selective oligomerization of ethylene, several researchers have employed density functional theory (DFT) to investigate the metal valence, active intermediate structure and the transition state of ethylene insertion

[162-171]. With regard to the selective ethylene tri- and tetramerization, the operational details of Cr-PNP (PNP = diphosphinoamine, *e.g.*, ligands **48**, **56 - 58**) catalysts have been subject of a series of computational studies by Britovsek and McGuinness [162-164]. For two representative ligand structures, $Ph_2PN(Me)PPh_2$ (**58d**) and (*o*-$OMeC_6H_4)_2PN(Me)P(o$-$OMeC_6H_4)_2$ (**48a/58a**), the results using **58d** reveal how a combination of single and double ethylene insertion mechanisms may lead to 1-octene, 1-hexene and the major side products (cyclopentanes and n-alkanes). For **48a/58a**, the *o*-methoxy substitutions lead to a more sterically congested active species and suppress the available pathways to generate 1-octene and side-products [163]. Moreover, for $Ph_2PN(^iPr)PPh_2$ (**58f**), a double-coordination mechanism with a bis(ethylene) chromacyclopentane intermediate seems to be responsible for 1-octene formation and other side-products that have a greater than first-order response to ethylene.

Liu and Eisen reported an unusual chromium(II) triphenylsiloxy complex, $[(Ph_3SiO)Cr(THF)]_2(\mu$-$OSiPh_3)_2$, that undergoes switching from ethylene polymerization to non-selective oligomerization [165]. The results of a combined experimental and DFT calculation investigation indicate that the chain propagation and chain transfer processes undergo a Cossee-Arlman mechanism and β-hydrogen transfer to the chromium center. Moreover, the trivalent cationic species, $[(Ph_3SiO)Cr^{III}Me]^+$ and $[(\eta^6$-toluene)$Cr^{III}Me_2]^+$, formed by a disproportionation reaction, are the most plausible active species for ethylene polymerization, while the divalent cationic model $[(\eta^6$-toluene)$Cr^{II}Me]^+$ could be responsible for ethylene non-selective oligomerization.

Elsewhere, a number of computational investigations have been performed to shed light on the valence state of the active chromium species [132,164,168-171]. Indeed, Cr(II)/Cr(IV) and Cr(I)/Cr(III) redox processes have been proposed for selective oligomerization which are largely dependent on the ligand structure. Indeed, for the Cr/PNP selective tri-/tetramerization catalytic systems both Cr(II)/Cr(IV) and Cr(I)/Cr(III) have been suggested highlighting the uncertainty that remains for this fundamental process [156].

## 5. Conclusions and outlook

The capacity of chromium complexes to mediate not only ethylene oligo-/polymerization but also the selective trimerization and tetramerization of ethylene has been reviewed and highlights the considerable versatility of these homogeneous catalysts. While research in this field was originally directed towards modelling the mechanistic events taking place in a heterogeneous polymerization process, developments in ligand design have allowed new types of catalysts to be unearthed that have shown unparalleled selectivities in ethylene reactivity. In particular, the implementation of soluble chromium catalysts into several industrial processes for converting ethylene to either 1-hexene or 1-octene underline the impact of such homogeneous technologies. While concepts based on steric and electronic properties of the chelating ligand type continue to be the subject of many developments, the importance of bite angle, backbone type, donor atoms and more recently ring strain have been identified as further influential factors. Indeed, our group has shown how the degree of ring strain within a tridentate nitrogen donor ligand can affect the activity and thermal stability of a chromium catalyst whilst also influencing the molecular weight, dispersity and selectivity towards polymer or oligomer.

While the industrially used Phillips catalyst generates HDPE that typically exhibits a broad molecular weight distribution, homogeneous chromium catalysts show great promise for producing HDPE with narrow dispersity. Moreover, considerable control of the molecular weight is now possible using such molecular catalysts, with linear polyethylene waxes through to high molecular weight polyethylenes all accessible. In terms of end use, the resulting high molecular weight linear polyethylenes are highly prized due to their excellent properties such as high rigidity and abrasive resistance as well as their good mechanical strength. Likewise linear polyethylene waxes are required in a variety of applications including as lubricants in plastics processing. In addition, the 1-hexene and 1-octene obtainable with certain selective chromium catalysts highlight the great potential for integrating such technology into processes for forming LLDPE. Furthermore, chromium catalysts that can promote

ethylene oligomerization with statistical distributions of alpha-olefins have in their own right a wide range of potential industrial uses. Meanwhile, it is worth emphasizing the importance of the aluminum activator, reaction solvent, temperature and pressure, all which have their role in affecting catalytic performance and hence warrant further study. Overall, it is our view that there are many discoveries still to be made in this field which can be arrived at through skillful and imaginative ligand design, in-depth catalytic screening and supported by state-of-the-art computational resource.

## 6. Acknowledgements

## 7. Glossary

| | |
|---|---|
| acac | Acetylacetonate |
| $BPh^F_4$ | Tetrakis(3,5-bis(trifluoromethyl)phenyl)borate |
| Cp | Cyclopentadienyl |
| Cy | Cyclohexyl |
| DEAC | Diethylaluminum chloride ($Et_2AlCl$) |
| DMAC | Dimethylaluminum chloride |
| DFT | Density Functional theory |
| EASC | Ethylaluminum sesquichloride |
| FT-IR | Fourier-transform infrared spectroscopy |
| GC-MS | Gas chromatography-mass spectrometry |
| $g\ (mol\ Cr)^{-1}\ h^{-1}$ | Grams of polyethylene per mole of metal precatalyst per hour |
| HDPE | High density polyethylene |
| *K* value | The probability of propagation |
| LAO | Linear alpha olefin |
| LLDPE | Linear low density polyethylene |
| $M_w$ | Weight averaged molecular weight |
| $M_n$ | Number averaged molecular weight |
| $M_w/M_n$ | Polydispersity index (PDI or MWD) |
| MAO | Methylaluminoxane |
| MMAO | Modified methylaluminoxane |
| NMR | Nuclear magnetic resonance |
| PNP | Diphosphinoamine |
| THF | Tetrahydrofuran |

| | |
|---|---|
| TIBA | Triisobutylaluminum |
| TIBAO | Triisobutylaluminoxane |
| TMA | Trimethylaluminum |
| TON | Turnover number = moles of ethylene per mole of precatalyst |
| TOF | Turnover frequency = moles of ethylene per mole of precatalyst per unit time |

## 8. References

1. B.C. Gates, H. Knözinger, Adv. Catal. (2012) 128–137.

2. G.L. Kaparinka, Union Carbide Corp., Ger offen. D. E., 1808388, 1970.

3. K.J. Karol, G.L. Karapinka, C. Wu, A.W. Dow, R.N. Johnson, W.L. Carrick, J. Polym, Sci., Part A-1. 10 (1972) 2621–2637.

4. G.L. Kaparinka, US Patent 3,709,853, Union Carbide Corp., 1973.

5. R. Emrich, O. Heinemann, P.W. Jolly, C. Krüger, J. Verhownik, Organometallics 16 (1997) 1511–1513.

6. A. Döhring, J. Göhre, P.W. Jolly, B. Kryger, J. Rust, G.P.J. Verhownik, Organometallics 19 (2000) 388–402.

7. V.R. Jensen, K. Angermund, P.W. Jolly, K.J. Børve, Organometallics 19 (2000) 403–410.

8. M. Enders, P. Fernández, G. Ludwig, H. Pritzkow, Organometallics 20 (2001) 5005–5007.

9. A. Döhring, V.R. Jensen, P.W. Jolly, W. Thiel, J.C. Weber, In Organometallic Catalysts and Olefin Polymerization; R. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes, Springer-Verlag: Berlin. (2001) 127.

10. A. Döhring, V.R. Jensen, P.W. Jolly, W. Thiel, J.C. Weber, Organometallics 20 (2001) 2234–2245.

11. Y. Liang, G.P.A. Yap, A.L. Rheingold, K.H. Theopold, Organometallics 15 (1996) 5284–5286.

12. B.J. Thomas, S.K. Noh, G.K. Schulte, S.C. Sendlinger, K.H. Theopold, J. Am. Chem. Soc. 113 (1991) 893–902.

13. G. Bhandari, Y. Kim, J.M. McFarland, A.L. Rheingold, K.H. Theopold, Organometallics 14 (1995) 738–745.

14. K.H. Theopold, Eur. J. Inorg. Chem. (1998) 15–24.

15. K.H. Theopold, Chemtech. 27 (1997) 26–32.

16. V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–315.

17. H. Tsurugi, K. Yamamoto, R. Rochat, K. Mashima, Polym. J. 47 (2015) 2–17.

18. K.C. Chew, W. Clegg, M.P. Coles, M.R.J. Elsegood, A.J.P. White, D.J. Williams, J. Chem. Soc. Dalton Trans. (1999) 2633–2639.

19. M.P. Coles, V.C. Gibson, W. Clegg, M.R.J. Elsegood, Polyhedron 15 (1998) 2483–2489.

20. M.P. Coles, C.I. Dalby, V.C. Gibson, W. Clegg, M.R.J. Elsegood, Polyhedron 14 (1995) 2455–2459.

21. A.A. Danopoulos, G. Wilkinson, T.K.N. Sweet, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1995) 2111–2123.

22. M.A. Esteruelas, A.M. López, L. Méndez, M. Olivián, E. Oñate, Organometallics 22 (2003) 395–406.

23. N.V. Semikolenova, V.A. Zakharov, L.G. Echevskaja, M.A. Matsko, K.P. Bryliakov, E. P. Talsi. Catal. Today 144 (2009) 334–340.

24. B.L. Small, M.J. Carney, D.M. Holman, C.E. O'Rourke, J.A. Halfen, Macromolecules 37 (2004) 4375–4386.

25. D.S. McGuinness, V.C. Gibson, D.F. Wass, J.W. Steed, J. Am. Chem. Soc. 125 (2003) 12716–12717.

26. R.F. Mason, Shell Oil Co., United States Patent. 3 676 523, 1972.

27. R.F. Mason, Shell Oil Co., United States Patent. 3 686 351, 1972.

28. P. Kuhn, D. Semeril, D.  Matt, M.J. Chetcuti, P. Lutz, Dalton Trans. (2007) 515–528.

29. A. Kermagoret, P. Braunstein, Dalton Trans. (2008) 822–831.

30. L.L. Böhm, Angew. Chem. Int. Ed. 42 (2003) 5010–5030.

31. K. Ziegler, Belgian Patent 533,362, 1954.

32. K. Ziegler, E. Holzkamp, H. Martin, H. Breil, Angew. Chem. 67 (1955) 541–547.

33. G. Natta, J. Polym. Sci. 16 (1955) 143–154.

34. G. Natta, Angew. Chem. 68 (1956) 393–403.

35. J.P. Hogan, Polym. Sci., Part A-1. 8 (1970) 2637–2652.

36. M.P. McDaniel, Adv. Catal. 33 (1985) 47–98.

37. A. Clark, Catal. Rev. 3 (1969), 145–173.

38. A. Bollmann, K. Blann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, A. Nveling, S. Otto, M. Overett, A.M.Z. Slawin, P. Wasserscheid, S. Kuhlmann, J. Am. Chem. Soc. 126 (2004) 14712–14713.

39. A.J. Rucklidge, D.S. McGuinness, R.P. Tooze, A.M.Z. Slawin, J.D.A. Pelletier, M.J. Hanton, P.B. Webb, Organometallics 26 (2007) 2782–2787.

40. M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, F. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, Chem. Commun. (2005) 622–624.

41. A. Jabri, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, Organometallics 25 (2006) 715–718.

42. D.S. McGuinness, A.J. Rucklidge, R.P. Tooze, A.M.Z. Slawin, Organometallics 26 (2007) 2561–2569.

43. L.E. Bowen, M.F. Haddow, A.G. Orpen, D.F. Wass, Dalton Trans. (2007) 1160–1168.

44. D.S. McGuinness, M. Overett, R.P. Tooze, K. Blann. J.T. Dixon, A.M.Z. Slawin, Organometallics 26 (2007) 1108–1111.

45. M.J. Overett, K. Blann, A. Bollmann, J.T. Dixon, D. Haasbroek, E. Killian, H. Maumela, D.S. McGuinness, D.H. Morgan, J. Am. Chem. Soc. 127 (2005) 10723–10730.

46. T. Agapie, Coord. Chem. Rev. 255 (2011) 861–880.

47. J.T. Dixon, M.J. Green, F.M. Hess, D.H. Morgan, J. Organomet. Chem. 689 (2004) 3641–3668.

48. D.F. Wass, Dalton Trans. (2007) 816–819.

49. D.S. Guinness, Chem. Rev. 111 (2011) 2321–2341.

50. K.A. Alferov, G.P. Belov, Y. Meng, Appl. Cat. A: Gen. 542 (2017) 71–124.

51. A. Otero, J. Fernández-Baeza, A. Lara-Sánchez, L.F. Sánchez-Barba, Coord. Chem. Rev. 257 (2013) 1806–1868.

52. C. Fliedel, A. Ghiosolfi, P. Braunstein, Chem. Rev. 116 (2016) 9237–9304.

53. P.W.N.M. van Leeuwen, N.D. Clément, M.J.-L. Tschan, Coord. Chem. Rev. 255 (2011) 1499−1517.

54. K.A. Alferov, I.A. Babenko, G.P. Belov, Pet. Chem. 57 (2012), 1−30.

55. D. Peng, X. Yan, C. Yu, S. Zhang, X. Li, Polym. Chem. 7 (2016) 2601−2634.

56. V.C. Gibson, C. Redshaw, W. Clegg, M.R.J. Elsegood, Chem. Commun. (1997) 1605−1606.

57. C. Redshaw, D. Homden, D.L. Hughes, J.A. Wright, M.R.J. Elsegood, Dalton Trans. (2009) 1231–1242.

58. B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 4049–4050.

59. G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849–850.

60. G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Strömberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728–8740.

61. G.J.P. Britovsek, S. Mastroianni, G.A. Solan, S.P.D. Baugh, C. Redshaw, V.C. Gibson, A.J.P. White, D.J. Williams, M.R. J. Elsegood, Chem. Eur. J. 6 (2000) 2221–2231.

62. Y. Nakayama, K. Sogo, H. Yasuda, T. Shiono, J. Polym. Sci. Part A: Polym. Chem. 43 (2005) 3368–3376.

63. J. Hurtao, D.M-L. Carey, A. Muñoz-Castro, R. Arratia-Pérez, R. Quijada, G. Wu, R. Rojas, M. Valderrama, J. Organomet. Chem. 694 (2009) 2636–2641.

64. M.A. Esteruelas, A.M. López, L. Méndez, M. Oliván, E. Oñate, New J. Chem. 26 (2002) 1542–1544.

65. A.E. Ceniceros-Gómez, N. Barba-Behrens, M.E. Quiroz-Castro, S. Bernès, H. Nöth, S.E. Castillo-Blum, Polyhedron 19 (2000) 1821–1827.

66. A.K. Tomov, J.J. Chirinos, D.J. Jones, R.J. Long, V.C. Gibson, J. Am. Soc. Chem. 127 (2005) 10166–10167.

67. W. Zhang, W.-H. Sun, S. Zhang, J. Hou, K. Wedeking, S. Schultz, R. Frölich, H. Song, Organometallics 25 (2006) 1961–1969.

68. S. Zhang, S. Jie, Q. Shi, W.-H. Sun, J. Mol. Catal. A: Chem. 276 (2007) 174–183.

69. M. Zhang, K. Wang, W.-H. Sun, Dalton Trans. (2009) 6354–6363.

70. L. Xiao, M. Zhang, W.-H. Sun, Polyhedron 29 (2010) 142–147.

71. Y. Chen, W. Zuo, P. Hao, S. Zhang, K. Gao  W.-H. Sun, J. Organomet. Chem. 693 (2008) 750–762.

72. S.A. Amolegbe, M. Asma, M. Zhang, G. Li, W.-H. Sun, Aust. J. Chem. 61 (2008) 397–403.

73. R. Gao, T. Liang, F. Wang, W.-H. Sun, J. Organomet. Chem. 694 (2009) 3701–3707.

74. W. Luo, A. Li, S. Liu, H. Ye, Z. Li, Organometallics 35 (2016) 3045–3050.

75. Z. Hao, B. Xu, W. Gao, Y. Han, G. Zeng, J. Zhang, Guanghua Li, Ying Mu, Organometallics 34 (2015) 2783–2790.

76. A.K. Tomov, J.J. Chirinos, R.J. Long, V.C. Gibson, M.R.J. Elsegood, J. Am. Chem. Soc. 128 (2006) 7704–7705.

77. M. Zhang, K. Wang, W.-H. Sun, Dalton Trans. (2009) 6354–6363.

78. L. Xiao, M. Zhang, W.-H. Sun, Polyhedron 29 (2010) 142–147.

79. S.A. Svejda, M. Brookhart, Organometallics 18 (1999) 65–74.

80. A.K. Tomov, J.D. Nobbs, J.J. Chirinos, P.K. Saini, R. Malinowski, S.K.Y. Ho, C.T. Young, D.S. McGuinness, A.J.P. White, M.R.J. Elsegood, G.J.P. Britovsek, Organometallics 36 (2017) 510–522.

81. R.D. Köhn, M. Haufe, S. Mihan, D. Lilge, Chem. Commun. (2000) 1927–1928.

82. M.J. Carney, N.J. Robertson, J.A. Halfen, L.N. Zakharov, A.L. Rheingold, Organometallics 23 (2004) 6184–6190.

83. F.-J. Wu, US 5811618, EP 0622347B1, (1998) Amoco.

84. E.L. Dias, M. Brookhart, P.S. White, Organometallics 19 (2000) 4995–5004.

85. L. Wang, T.C. Flood, J. Am. Chem. Soc. 114 (1992) 3169–3170.

86. N.J. Robertson, M.J. Carney, J.A. Halfen, Inorg. Chem. 42 (2003) 6876–6885.

87. A.C. Pinheiro, T. Roisnel, E. Kirillov, J.-F. Carpentier, O.L. Casagrande Jr., Dalton Trans. 44 (2015) 16073–16080.

88. Y. Zhang, C. Huang, X. Hao, X. Hu, W.-H. Sun, RSC Adv. 6 (2016) 91401–91408.

89. C. Huang, Y. Zhang, G.A. Solan, Y. Ma, X. Hu, Y. Sun, W.-H. Sun, Eur. J. Inorg. Chem. (2017) 4158–4166.

90. C. Huang, Y. Huang, Y. Ma, G.A. Solan, Y. Sun, X. Hu, W.-H. Sun, Dalton Trans. 47 (2018) 13487–13497.

91. C. Huang, S. Du, G.A. Solan, Y. Sun, W.-H. Sun, Dalton Trans. 46 (2017) 6948–6957.

92. V.K. Appukuttan, Y. Liu, B.C. Son, C.-S. Ha, H. Suh, I. Kim, Organometallics 30 (2011) 2285–2294.

93. W. Zhang, W. Chai, W.-H. Sun, X. Hu, C. Redshaw, X. Hao, Organometallics 31 (2012) 5039–5048.

94. W.-H. Sun, S. Kong, W. Chai, T. Shiono, C. Redshaw, X. Hu, C. Guo, X. Hao, Appl. Catal. A. 447–448 (2012) 67–73.

95. F. Huang, Q. Xing, T. Liang, Z. Flisak, B. Ye, X. Hu, W. Yang, W.-H. Sun, Dalton Trans. 43 (2014) 16818–16829.

96. F. Huang, W. Zhang, E. Yue, T. Liang, X. Hu, W.-H. Sun, Dalton Trans. 45 (2016) 657–666.

97. S. Du, X. Wang, W. Zhang, Z. Flisak, Y. Sun, W.-H. Sun, Polym. Chem. 7 (2016) 4188–4197.

98. S. Du, W. Zhang, E. Yue, F. Huang, T. Liang, W.-H. Sun, Eur. J. Inorg. Chem. (2016) 1748–1755.

99. F. Huang, W. Zhang, Y. Sun, X. Hu, G.A. Solan, W.-H. Sun, New J. Chem. 40 (2016) 8012–8023.

100. Y. Zhang, H. Suo, F. Huang, T. Liang, X. Hu, W.-H. Sun, J. Polym. Sci, Part A: Polym. Chem. 55 (2017) 830–842.

101. Z. Wang, G. A. Solan, Q. Mahmood, Q. Liu, Y. Ma, X. Hao, W.-H. Sun, Organometallics 37 (2018) 380–389.

102. J. Ba, S. Du, E. Yue, X. Hu, Z. Flisak, W.-H. Sun, RSC Adv. 5 (2015) 32720–32729.

103. C. Bariashir, Z. Wang, S. Du, G.A. Solan, C. Huang, T. Liang, W.-H. Sun, J. Polym. Sci. A Polym. Chem. 55 (2017) 3980–3989.

104. Z. Wang, G. A. Solan, W. Zhang, W.-H. Sun, Coord. Chem. Rev. 363 (2018) 92–108.

105. J.-Y. Liu, Y. Zheng, Y.-G. Li, L. Pan, Y.-S. Li, N.-H. Hu, J. Organomet. Chem. 690 (2005), 1233–1239.

106. C. Huang, V.A. Zakharov, N.V. Semikolenova, M.A. Matsko, G.A. Solan, W.-H. Sun, J. Catal. 369 (2019) 1–9.

107. V.C. Gibson, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Organometallics 26 (2007) 5119–5123.

108. W.-H. Sun, X. Tang, T. Gao, B. Wu, W. Zhang, H. Ma, Organometallics 23 (2004) 5037–5047.

109. W. Zhang, W.-H. Sun, X. Tang, T. Gao, S. Zhang, P. Hao, J. Chen, J. Mol. Catal. A: Chem. 265 (2007) 159–166.

110. E. Krilikov, T. Roisnel, A. Razavi, J.F. Carpentier, Organometallics 28 (2009) 2401–2409.

111. F. Junges, M.C.A. Kuhn, A.H.D.P. dos Santos, C.R.K. Rabello, C.M. Thomas, J.- F. Carpentier, O.L. Casagrade, Organometallics 26 (2007) 4010–4014.

112. J.A. Obaleye, S.A. Amolegbe, S. Adewuyi, W.-H. Sun, M.D. Oshodi, J. Chem. Chem. Eng. 4 (2010) 23–31.

113. D. Wang, S. Liu, Y. Zheng, W.-H. Sun, C. Redshaw, Organometallics 30 (2011) 3001–3009.

114. G.V.Z Schulz, Phys. Chem. Abt. B. 30 (1935) 379–398.

115. G.V.Z Schulz, Phys. Chem. Abt. B. 43 (1939) 25–46.

116. F.J. Flory, J. Am. Chem. Soc. 62 (1940) 1561–1565.

117. A.L. Bergamo, H.K.D. Cas, R.S. Rambo, C.S. Schwalm, A.C.A. Casagrande, R. Stieler, O.L. Casagrande Jr. Catal. Commun. 86 (2016) 77–81.

118. V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans. (1999) 827–829.

119. V.C. Gibson, S. Mastroianni, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D. J. Williams, J. Chem. Soc., Dalton Trans. (2000) 1969–1971.

120. D.J. Jones, V.C. Gibson, S.M. Green, P.J. Maddox, Chem. Commun. (2002) 1038–1039.

121. V.C. Gibson, C. Newton, Claire, G.A. Solan, PCT Int. Appl. (1999), WO 9919335 A1 19990422.

122. V.C. Gibson, P.J. Maddox, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 1651–1652.

123. V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, Dalton Trans. (2003) 4612–4617.

124. D.J. Jones, V.C. Gibson, S.M. Green, P.J. Maddox, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 127 (2005) 11037–11046.

125. S. Jie, R. Pattacini, G. Rogez, C. Loose, J. Kortus, P. Braunstein, Dalton Trans. (2009) 97–105.

126. T. Ruther, N. Braussaud, K.J. Cavell, Organometallics 20 (2001) 1247–1250.

127. V.C. Gibson, C. Newton, C. Redshaw, G.A. Solan, A.J.P. White, D.J. Williams, J. Chem. Dalton Trans. (2002) 4017–4023.

128. C. Klemps, A. Buchard, R. Houdard, A. Auffrant, N. Mézailles, X.F.L. Goff, L. Ricard, L. Saussine, L. Magna, P. L. Floch, New. J. Chem. 33 (2009) 1748–1752.

129. K. Albahily, E. Koç, D. Al-Baldawi, D. Savard, S. Gambarotta, T.J. Burchell, R. Duchatreau, Angew. Chem. Int. Ed. 47 (2008) 5816–5819.

130. Q. Zheng, D. Zheng, B. Han, S. Liu, Z. Li, Dalton Trans. 47 (2018) 13459–13465.

131. M.E. Bluhm, O. Walter, M. Döring, J. Organomet. Chem. 690 (2005) 713–721.

132. D.S. McGuinness, P. Wasserscheid, W. Keim, D. Morgan, J.T. Dixon, A. Bollmann, H. Maumela, F. Hess, U. Englert, J. Am. Chem. Soc. 125 (2003) 5272–5273.

133. R.D. Köhn, M. Haufe, G. Kociok-Köhn, S. Grimm, P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 4337–4339.

134. J. Zhang, A. Li, T.S.A. Hor, Organometallics 28 (2009) 2935–2937.

135. D.S. McGuinness, P. Wasserchied, W. Keim, C. Hu, U. Englert, J.T. Dixon, C. Grove, Chem. Commun. (2003) 334–335.

136. D.S. McGuinness, P. Wasserchied, D.H. Morgan, J.T. Dixon, Organometallics 24 (2005) 552–556.

137. K. Blann, A. Bollmann, J.T. Dixon, F.M. Hess, E. Killian, H. Maumela, D.H. Morgan, A. Neveling, S. Otto, M.J. Overett, Chem. Commun. (2005) 620–621.

138. D.S. McGuinness, D.B. Brown, R.T. Tooze, F.M. Hess, J.T. Dixon, A.M.Z. Slawn, Organometallics 25 (2006) 3605–3610.

139. C.N. Temple, S. Gambarotta, I. Korobkov, R. Duchateau, Organometallics 26 (2007) 4598–4603.

140. J. Zhang, P. Braunstein, T.S.A. Hor, Organometallics 27 (2008) 4277–4279.

141. C. Temple, A. Jabri, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, Angew. Int. Ed. 45 (2006) 7050–7053.

142. A. Jabri, C. Temple, P. Crewdson, S. Gambarotta, I. Korobkov, R. Duchateau, J. Am. Chem. Soc. 128 (2006) 9238–9247.

143. C. Zhang, L. Song, H. Wu, X. Ji, J. Jiao, J. Zhang, Dalton Trans. 46 (2017) 8399–8404.

144. E.H. Kim, H.M. Lee, M.S. Jeong, J.Y. Ryu, J. Lee, B.Y. Lee, ACS Omega 2 (2017) 765–773.

145. I.E. Nifant'ev, A.A. Vinogradov, A.A. Vinogradov, V.A. Roznyatovsky, Y.K. Grishin, A.V. Ivanyuk, I.V. Sedov, A.V. Churakov, P.V. Ivchenko, Organometallics 37 (2018) 2660–2664.

146. J.E. Radcliffe, A.S. Batsanov, D.M. Smith, J.A. Scott, P.W. Dyer, M.J. Hanton, ACS Catal. 5 (2015) 7095–7098.

147. Y. Zhou, H. Wu, S. Xu, X. Zhang, M. Shi, J. Zhang, Dalton Trans. 44 (2015) 9545–9550.

148. R.D. Kohn, G. Köciok–Köhn, Angew. Chem. Int. Ed. 33 (1994) 1877–1878.

149. P. Wasserschied, S. Grimm, R.D. Köhn, M. Haufe, Adv. Synth. Catal. 343 (2001) 814–818.

150. R.J. Baker, P.G. Edwards, J. Chem. Soc. Dalton Trans. (2002) 2960–2965.

151. R.M. Manyik, W.E. Walker, T.P. Wilson, J. Catal. 47 (1977) 197–209.

152. J.R. Briggs, J. Chem. Soc. Chem. Commun. (1989) 674–675.

153. T. Agapie, S.J. Schofer, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 1304–1305.

154. T. Agapie, J.A. Labinger, J.E. Bercaw, J. Am. Chem. Soc. 129 (2007) 14281–14295.

155. T. Gunasekara, J. Kim, A. Preston, D.K. Steelman, G.A. Medvedev, W.N. Delgass, O.L. Sydora, J.M. Caruthers, M.M. Abu-Omar, ACS Catal. 8 (2018) 6810–6819.

156. C. Song, G. Mao, Z. Liu, Y. Ning, T. Jiang, Chin. J. Org. Chem. 36 (2016) 2105–2120.

157. S. Kuhlmann, J.T. Dixon, M. Haumann, D.H. Morgan, J. Ofili, O. Spuhl, N. Taccardi, P. Wasserscheid, Adv. Synth. Catal. 348 (2006) 1200–1206.

158. P.W.N.M. van Leeuwen, N.D. Clément, M.J.-L. Tschan, Coord. Chem. Rev. 255 (2011) 1499–1517.

159. J.D. Nobbs, A.K. Tomov, C.T. Young, A.J.P. White, G.J.P. Britovsek, Catal. Sci. Technol. 8 (2018) 1314–1321.

160. S. Peitz, B.R. Aluri, N. Peulecke, B.H. Müller, A. Wöhl, W. Müller, M.H. Al-Hazmi, F.M. Mosa, U. Rosenthal, Chem. Eur. J. 16 (2010) 7670–7676.

161. P.M. Fritz, H. Bölt, A. Wöhl, W. Müller, F. Winkler, A. Wellenhofer, U. Rosenthal, M. Hapke, N. Peulecke, B.H. Müller, M. H. AlHazmi, V.O. Aliyev, F.M. Mosa (Linde AG/SABIC), WO 2009/068157, 2009.

162. D.S. McGuinness, B. Chan, G.J.P. Britovsek, B.F. Yates, Aust. J. Chem. 67 (2014) 1481–1490.

163. G.J.P. Britovsek, D.S. McGuinness, Chem. Eur. J. 22 (2016) 16891–16896.

164. G.J.P. Britovsek, D.S. McGuinness, T.S. Wierenga, C.T. Young, ACS Catal. 5 (2015) 4152–4166.

165. J. Zhang, P. Qiu, Z. Liu, B. Liu, R.J. Batrice, M. Botoshansky, M.S. Eisen, ACS Catal. 5 (2015) 3562–3574.

166. W.H. Monillas, G. Yap, K.H. Theopold, Angew. Chem. Int. Ed. 46 (2007) 6692–6694.

167. R.D. Köhn, Angew. Chem. Int. Ed. 47 (2008) 245–247.

168. C. Klemps, E. Payet, L. Magna, L. Saussine, X.F.L. Goff, P.L. Floch, Chem. Eur. J. 15 (2009) 8259–8268.

169. Y. Yang, Z. Liu, L. Zhong, P. Qiu, Q. Dong, R. Cheng, J. Vanderbilt, B. Liu, Organometallics 30 (2011) 5297–5302.

170. S. Bhaduri, S. Mukhopadhyay, S.A. Kulkarni, J. Organomet. Chem. 694 (2009) 1297–1307.

171. W.J. van Rensburg, J. van den Berg, P.J. Steynberg, Organometallics 26 (2007) 1000–1013.