# Chromium complex pre-catalysts in ethylene oligomerization/Polymerization

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**Abstract**: Recent progress of chromium complex pre-catalysts in ethylene oligomerization and polymerization is reviewed herein. As well as the well-established trimerization of ethylene by chromium catalytic systems, such pre-catalysts have more generally been explored for ethylene oligomerization. Furthermore, chromium complex pre-catalysts have been found to exhibit high activities during ethylene polymerization. The catalytic activities can be influenced by the nature of ligands present, which can provide useful knowledge in determining structure-activity relationships. This review provides collective references concerned with the design of complex pre-catalysts with a view to ethylene reactivity.

## INTRODUCTION

Chromium, the 22nd most abundant element on Earth, has been employed in metal alloys for over 2,000 years by the Chinese as verified by the discovery of the Terra Cotta figures from the Qin Dynasty, which exhibited the properties of resistant-tarnishing and high melting points as known in the current steel industry. The chromium-based Phillips catalyst has maintained its important role in the petrochemical industry[1] despite the increasing importance of Ziegler-Natta,[2] metallocene[3] and new late-transition metal pre-catalyst systems.[4-6] Single-site complex pre-catalysts are in demand given their ease of preparation, high activity, low co-catalyst loadings as well as their effective co-polymerization behavior. During our studies, chromium(III) complexes have been found to exhibit high activity during ethylene oligomerization and polymerization.[7,8] Both the electronic and steric effects of the ancillary ligands in the complex pre-catalysts were found to play significant roles in tuning the properties of the resulting active species. Although chromium possesses various oxidation states, chromium(III) complexes have been extensively explored and found to exhibit promising results. Herein, recent progress on chromium(III) complex pre-catalysts bearing tridentate ligands for use in ethylene oligomerization and polymerization is discussed.

2. Tridentate Chromium based Pre-catalysts:

Given the demand for 1-hexene by the industry sector, the process of ethylene trimerization has been an active topic for some time.[9] Chromium(III) complexes containing tridentate ligand sets such as those coordinated via N^N^N fashion[10] as well as other different combinations of neutral donors such as N^P^N[11], P^P^P,[12] S^N^S,[13] C^N^C,[14] N^N^O,[15] N^S^N,[16] P^N^P,[17] have also been investigated, and can be activated using co-catalysts such as MAO, MMAO, $Et_3Al$ or $Et_2AlCl$.

3. Design of Chromium (III) complexes based on N^N^N ligands:

Non-metallocene based oligomerization catalysts have been studied for over a decade, with much of the recent work centering on the use of bis(imino)pyridine complexes.[18,19] Following on from this, there has been significant focus on the development of alternatives/ variations of the bis(imino)pyridine framework and some notable successes have been achieved for ethylene oligomerization and polymerization.[20] Tenza *et al*. have reported a new class of bis(imino)thiazole chromium(III) metal complexes **1-2** (Scheme 1) by replacement of the central pyridine ring, which are active in the presence of the co-catalysts MMAO and $Et_3Al/[Ph_3C][Al(O^tBu^F)_4]$. The complex **1** has shown a distribution of higher α-olefin products at 20 °C with the co-catalyst MMAO and moderate activities obtained when using the co-catalyst $Et_3Al/[Ph_3C][Al(O^tBu^F)_4]$ at the same temperature. When under high concentrated conditions and a higher temperature (30 °C), there is a shift toward polymerization and higher productivity and longer catalyst life times are even possible, however with lower activity than observed previously. The complex **1** exhibited a normal Schulz-Flory distribution of oligomers in both cases; for MMAO and $Et_3Al/[Ph_3C][Al(O^tBu^F)_4]$, $k_{C6-C20}$=0.63 and 0.73, respectively within the liquid fraction. Catalysis using **1** activated with $Et_3Al/[Ph_3C][Al(O^tBu^F)_4]$ gave a catalyst with the same lifetime as and very similar productivity to, that when activated with MMAO. Catalytic results for complex **2** revealed high polymerization activity when compared to complex **1,** which was thought to be due the presence of the bulky 2,6-diisopropylphenyl groups.[21]
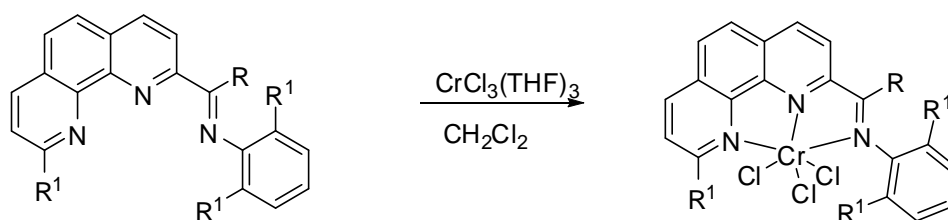
Scheme 1: Chromium (III) complexes bearing bis(imino)thiazole N^N^N Tridentate ligands **1-2**.



1 (R= Ph), 2 (R= Dipp)
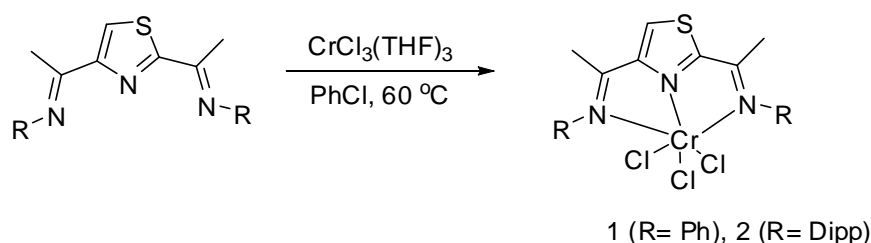
Our research group has also investigated chromium complexes bearing various N^N^N ligands and their catalytic behavior in the presence of different co-catalysts. Chromium complexes bearing tridentate 2-imino-1,10-phenanthroline ligands **3-14** are depicted in Scheme 2. All such complexes **(3-14)** exhibited high activities for ethylene oligomerization and moderate activities for polymerization in the presence of methylalumioxane (MAO). Among these complexes, **4** (R = Ph, $R^1$ = Et), **6** (R = Me, $R^1$ = Me) and **14** (R=H, $R^1$ = $i$-Pr) exhibited the highest activities for ethylene oligomerization (up to $1.15 \times 10^7$ g mol$^{-1}$ (Cr) h$^{-1}$) and moderate activities for ethylene polymerization on combination with MAO. The catalytic system **4** produced only butenes with low oligomerization activity on combination with either Et$_3$Al or Et$_2$AlCl as co-catalyst. By contrast, the aldmine (R=H) and phenylketamine (R=Ph) complexes showed higher activities than did the corresponding methylketimine (R=Me) complexes for **6-11**. The phenyl-ketimine complex **4** bearing 2,6-diethyl groups and the aldimine complex **14** bearing 2,6-diisopropyl groups exhibited higher oligomerization activity than did their corresponding analogues which?. The aldimine complexes exhibited higher oligomerization activities which varied in the order of (**12** $R^1$= Me < **13** $R^1$= Et < **14** $R^1$= i-Pr), which was different to that observed for the ketimine complexes. This was thought to be due to the presence of the less bulky hydrogen on the imino-C. The change of ligand environments in the [2-(ArN = CR)-1,10-phen] catalytic system led to different behavior. Changing the substituents on the imine functional group from ketimine (R = Ph, **3-5**; R = Me, **6-11**) to aldimine (R = H, **12-14**) resulted in differences in the productivity, K value and α-olefin selectivity.

The phenyl-ketimine and aldimine catalysts exhibited higher productivity than did the methyl-ketimine catalysts. The phenyl-ketimine complex **4** exhibited the highest activity at $1.15 \times 10^{7}$ g mol$^{-1}$ (Cr) h$^{-1}$ (larger K value), the aldimines **12 -14** displayed activities in the range $(2.73–5.00) \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$ and the methyl ketimines **6 - 11** (smaller K value) exhibited higher α-olefin selectivity. These complexes **3 - 14** produced α-olefin products varying from oligomers and polymers, and the distribution of oligomers resembled the Schultz–Flory rule.[20]

Scheme 2: Chromium(III) complexes bearing 2-benzazole-1,10-phenanthrolines **3-14**.
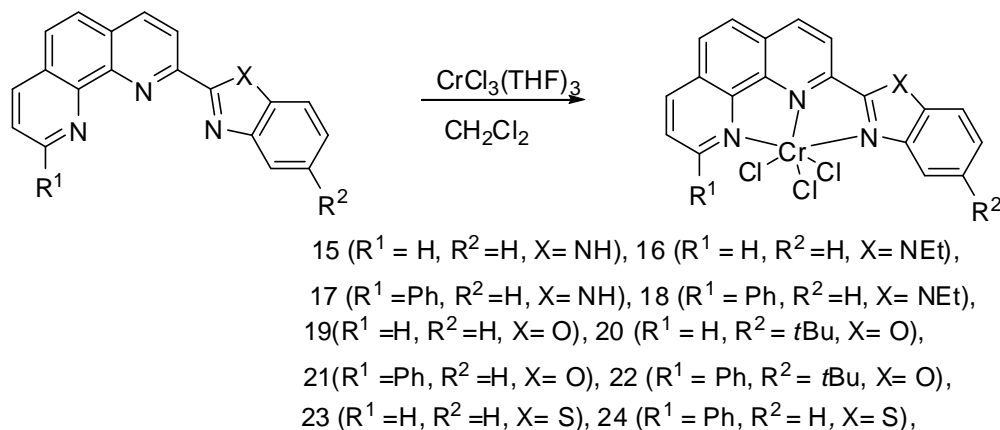


3 (R = Ph, $R^1$ =Me), 4 (R = Ph, $R^1$ =Et), 5 (R = Ph, $R^1$ =i-Pr),
6 (R = Me, $R^1$ =Me), 7 (R = Me, $R^1$ =Et), 8 (R = Me, $R^1$ =i-Pr),
9 (R = Me, $R^1$ =F), 10 (R = Me, $R^1$ =Cl),11 (R = Me, $R^1$ =Br),
12 (R = H, $R^1$ =Me),13 (R = H, $R^1$ =Et), 14 (R = Me, $R^1$ =i-Pr)

The synthesis of a new class of chromium(III) complexes bearing tridentate 2-benzazole-1,10-phenanthrolines ligands **15 - 24** (Scheme 3) was developed and the pre-catalysts were found to exhibit high activities for ethylene oligomerization (up to $7.36 \times 10^6$ g mol$^{-1}$ (Cr) h$^{-1}$) and ethylene polymerization (up to $1.28 \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$) upon activation with modified methylaluminoxane (MMAO). The effect of the reaction conditions for complex **20,** allowed for the production of butenes and hexanes, but with low activity, on combination with Et$_2$AlCl at ambient pressure. However, when activated with MAO, a species was generated that was capable of catalyzing the conversion of ethylene in both an oligomerization and a polymerization process. Increased catalytic activity for ethylene oligomerization and polymerization coupled with the production of longer chain oligomers was the result of using MMAO as the activator. On varying the Al/Cr ratio for complex **20**, the catalytic activity increased for Al/Cr ratios up to 1500:1, but then decreased on increasing the Al/Cr ratio to 1800:1. The temperature also affected the complexes, for example for the complex **20** the combined productivity increased for oligomerization/polymerization on going from 20 to 60 °C. Furthermore, the selectivity for α-olefins decreased from 93 to 82 % on increasing the temperature from 60 to 80 °C. The nature of the ligands also affected the complexes **15** and **17** bearing an N-H group, which exhibited higher activity and selectivity for α-olefins than did their *N*-alkylated analogues (**16** and **18).** The heteroatom (X = N, O and S) bearing benzoxazole complexes **15** ($R^1$ =H, $R^2$ =H, X=NH), **19** ($R^1$ =H, $R^2$ =H, X=O) and **23** ($R^1$ =H, $R^2$ =H, X=S) revealed differing catalytic activities in the order **19>15>23** or **O>N>S**. Among these complexes, **20** and **22** exhibited impressive results for catalytic activity due to the presence of a *t*-Bu group incorporated at the 4-position of the benzoxazole

ring. Indeed, the bulky substituent protects the active site and enhances the catalytic activities for ethylene oligomerization/polymerization.[6]

Scheme 3: Chromium(III) complexes bearing 2-benzazole-1,10-phenanthrolines **15-23**.



15 (R$^1$ = H, R$^2$=H, X= NH), 16 (R$^1$ = H, R$^2$=H, X= NEt),
17 (R$^1$ =Ph, R$^2$=H, X= NH), 18 (R$^1$ = Ph, R$^2$=H, X= NEt),
19(R$^1$ =H, R$^2$=H, X= O), 20 (R$^1$ = H, R$^2$= $t$Bu, X= O),
21(R$^1$ =Ph, R$^2$ =H, X= O), 22 (R$^1$ = Ph, R$^2$= $t$Bu, X= O),
23 (R$^1$ =H, R$^2$ =H, X= S), 24 (R$^1$ = Ph, R$^2$ = H, X= S),

Chromium(III) complexes **25-30** ligated by a 2-benzoxazolyl-6-arylimino-pyridine are shown in Scheme 4. These complexes exhibited high activities for ethylene oligomerization (up to $9.19 \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$) when using MMAO as a co-catalyst. Meanwhile, good activities for ethylene polymerization were achieved (up to $5.20 \times 10^5$ g mol$^{-1}$(Cr) h$^{-1}$) when using MAO as a co-catalyst.[23] The ligand environment can play an important role in these complexes too, for example, the complexes **25-27** with bulky substituents at the *ortho* position of the aryl rings exhibited lower activity most likely due to the bulkier substituent's slowing down the ethylene coordination and hindering chain propagation. Furthermore, those bearing electron-withdrawing groups will increase the positive charge of the center metal, enhance the M–R bond strength and thereby make the insertion of ethylene harder, which for example results in **30** exhibiting lower activity. In addition, complexes **29-30** bearing substituent's at the *para* position of the imino aryl ring produced much lower activity thought to be the result of the complexes solubility in toluene.

Scheme 4: Chromium(III) complexes bearing 2-benzoxazolyl-6-aryliminopyridines **25-30**.
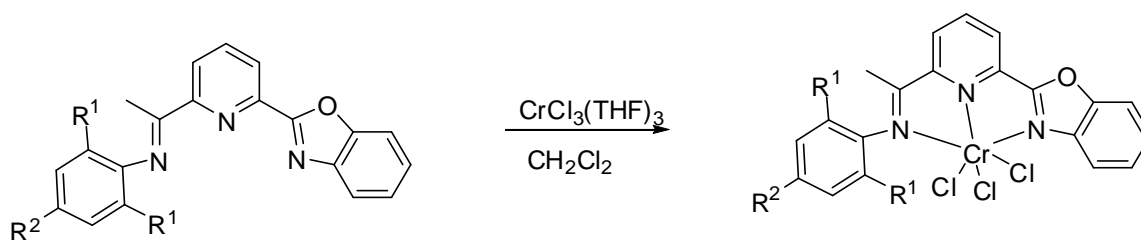


25 ($R^1$ = Me, $R^2$ =H), 26 ($R^1$ = Et, $R^2$ =H)
27 ($R^1$ = $i$-Pr, $R^2$ =H), 28 ($R^1$ = Cl, $R^2$ =H)
29 ($R^1$ = Me, $R^2$ =Me), 30 ($R^1$ = Me, $R^2$ =Br)

The 2-quinoxalinyl-6-iminopyridine chromium(III) chloride complexes **31-35** (Scheme 5) exhibited high activities for ethylene oligomerization (up to $3.50 \times 10^6$ g mol$^{-1}$Cr h$^{-1}$) and polymerization on combination with the co-catalyst MAO and the distribution of oligomers followed a Schulz–Flory distribution with a high selectivity for α-olefins.[24] The co-catalyst employed influences the behavior of complex **32**, for example, in the presence of Et$_2$AlCl only butenes were formed in low yield, whereas with MMAO, longer chain olefins were produced at ambient pressure. The catalytic activities were affected by the substituents on the imino aryl ring, and typically the complexes **31-34** bearing bulky groups produced more polymers but possessed lower activities than the complex **35** bearing a fluorine substituent (lower k values and lower α-olefin selectivity).

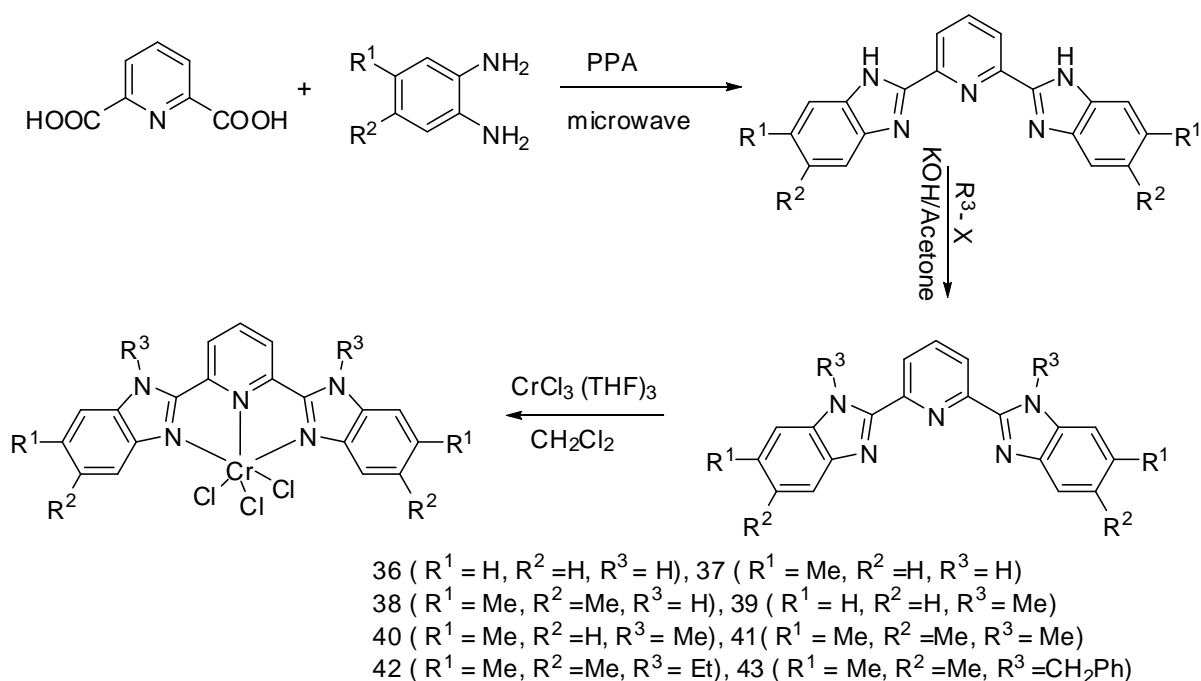Scheme 5: 2-Quinoxalinyl-6-iminopyridine Chromium (III) Chloride complexes **31-35**.
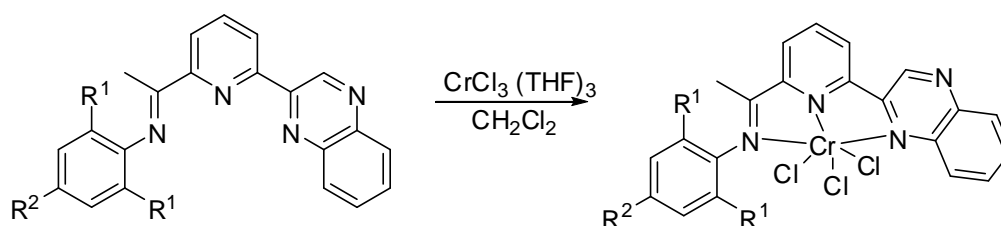


31 ( $R^1$ = Me, $R^2$ =H),
32 ( $R^1$ = Et, $R^2$ =H)
33 ( $R^1$ = $i$-Pr, $R^2$ =H),
34 ( $R^1$ = Me, $R^2$ =Me)
35 ( $R^1$ = F, $R^2$ =H),

Complexes of the type **36-43**, *ie* [2,6-bis(2-benzimidazolyl)pyridyl]chromium chloride complexes (Scheme 6), were found to be highly effective in ethylene oligomerization/polymerization in the presence of MAO and exhibited moderate activity for

ethylene polymerization when using diethylaluminum chloride (Et$_2$AlCl) as co-catalyst.[25] The products produced using MAO at 10 bar ethylene were polyethylenes of broad molecular weight distribution. The ligand environment could affect the performance of such complexes and **36-39** produced oligomers (wax-like polyethylene) with a distribution that closely resembles the Schulz-Flory rule. However, complexes **40-43** produced butenes and trace amounts of polymer. The productivity of these complexes **(36-43)** followed the order **36>37>38** and **39>40,** which indicated that a more substituted phenyl group produced lower ethylene activity. Interestingly, the incorporation of an alkyl group at the N atom of the imidazole ring resulted in metal complexes with lower activity and also with differing oligomer distributions.
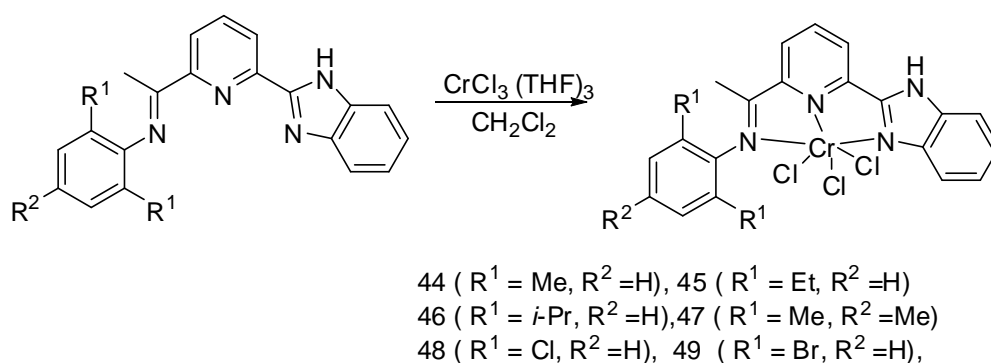
Scheme 6: [2,6-Bis(2-benzimidazolyl)pyridyl]chromium (III) Chlorides **36-43**.



36 ( R$^1$ = H, R$^2$ =H, R$^3$ = H), 37 ( R$^1$ = Me, R$^2$ =H, R$^3$ = H)
38 ( R$^1$ = Me, R$^2$ =Me, R$^3$ = H), 39 ( R$^1$ = H, R$^2$ =H, R$^3$ = Me)
40 ( R$^1$ = Me, R$^2$ =H, R$^3$ = Me), 41( R$^1$ = Me, R$^2$ =Me, R$^3$ = Me)
42 ( R$^1$ = Me, R$^2$ =Me, R$^3$ = Et), 43 ( R$^1$ = Me, R$^2$ =Me, R$^3$ =CH$_2$Ph)

In another study, chromium(III) ligated by tridentate 2-(1H-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine (see complexes **44-49**, Scheme 7) was found to exhibit high activities for ethylene oligomerization (up to $1.50 \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$) and polymerization (up to $2.06 \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$) at 10 atm ethylene pressure on treatment with modified methylaluminoxane (MMAO).[26] The Al/Cr molar ratio and the reaction temperature were found to affect the ethylene reactivity of complex **44**/MMAO. On increasing the Al/Cr ratio from 500:1 to 1500:1, the activity increased, but on further increasing the Al/Cr ratio to 2000:1, the observed activity decreased. The oligomeric distribution of the products from complex **44** did not follow the Schulz-Flory or Poisson rules; there was a small amount of C$_6$
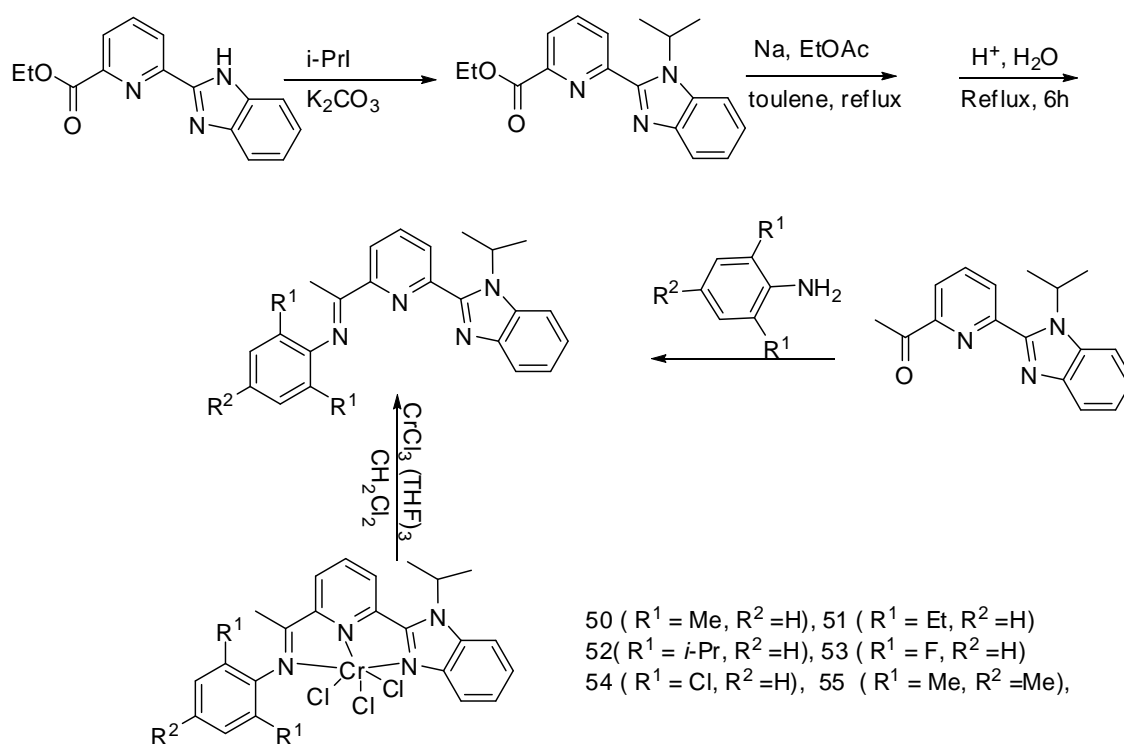
present. However, complex **44** exhibited high activities for both oligomerization/polymerization at temperature from 20 to 60 °C, but this increase of temperature led to decreases for the α- olefin selectivity from 97.5 to 88.7 %. For complexes **44-46**, the activities were lower due to the bulky substituents present at the *ortho* position of the imino aryl ring. Further, the complexes bearing a 2,6-dihalogen substitution pattern (**48** and **49**) exhibited higher productivity than the analogues containing a 2,6-dialkyl pattern (**44**, **45** and **46**).

Scheme 7: 2-(1H-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridylchromium chlorides **44-49**.



44 ( $R^1$ = Me, $R^2$ =H), 45 ( $R^1$ = Et, $R^2$ =H)
46 ( $R^1$ = *i*-Pr, $R^2$ =H),47 ( $R^1$ = Me, $R^2$ =Me)
48 ( $R^1$ = Cl, $R^2$ =H),  49  ( $R^1$ = Br, $R^2$ =H),

The 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino)ethyl)pyridine chromium complexes **50-55** (scheme 8) were found to exhibit good to high activities (up to $3.95 \times 10^6$ g mol$^{-1}$(Cr) h$^{-1}$) for ethylene oligomerization/polymerization on activation with MMAO.[27] On increasing the temperature from 20 to 80 °C,  there was a decrease of α-olefin selectivity from 93.5 to 80.2 %. In general, the complexes produced high activity and good selectivity for α- olefins at 20 °C. The catalyst life time is one of the main factors to be considered for industrial application. The complex **50** produced an optimum activity over a reaction time of 60 min. The sterics of the ligand play a role in complex **50**, and it was found to exhibit higher activity than did the complexes **51** & **52** due to the less bulky groups present on the iminoaryl ring. These complexes produced oligomers whose distributions did not follow the Schulz-Flory or Poisson rules, and low yields of hexanes were formed.

Scheme 8: Chromium(III) complexes ligated by 2-(1-isopropyl-2-benzimidazolyl)-6-(1-(arylimino) ethyl)pyridines **50-55**.

50 ( $R^1$ = Me, $R^2$ =H), 51 ( $R^1$ = Et, $R^2$ =H)
52( $R^1$ = *i*-Pr, $R^2$ =H), 53 ( $R^1$ = F, $R^2$ =H)
54 ( $R^1$ = Cl, $R^2$ =H),  55  ( $R^1$ = Me, $R^2$ =Me),

## 4.  Design of chromium(III) complex containing different combination of ligands for ethylene oligomerization/polymerization:

### 4.1. Design of chromium(III) complex based on N^P^N ligand:

Chromium(III) complexes bearing N^P^N tridentate ligands have been found to exhibit high selectivity for ethylene oligomerization/polymerization. In addition, chromium complexes have gained increasing significance for use in oligomerization systems,[28] particularly for ethylene trimerization[29] and tetramerization.[30] With this in mind, recently developed chromium(III) catalysts based on an N^P^N ligand have been screened for selectivity in ethylene oligomerization.[31] The Cr(III) complex *fac*-[Cr(NPN)Cl]  **56** (NPN = bis(2-picolyl)phenylphosphine) on reaction with MAO led to partial methylation affording the mononuclear complex *fac*-[Cr(NPN)Cl$_{2.23}$Me$_{0.77}$] **57**. By contrast, reaction with AlMe$_3$ in toluene led to partial halide abstraction and produced the dinuclear, chloride bridged dicationic complex [{*fac*-Cr(NPN)Me(μ-Cl)}$_2$][AlMe$_x$Cl$_{4-x}$]$_2$ **58**. A rare example of a Cr(III)-Et function was found in the complex *fac*-[Cr(NPN)Cl$_2$Et] **59**, which was isolated in high yield from the reaction of **56** with AlEt$_3$. Upon treatment of **56** with EtAlCl$_2$, the dinuclear Cr(III) complex [{*fac*-Cr(NPN)}$_2$(μ-Cl)$_3$][AlCl$_4$]$_3$(**60**.[AlCl$_4$]$_3$) was obtained,

which contains three bridging chlorides. These catalyst systems **56-60** (Scheme 9) on activation with MAO under comparable conditions, afforded similar activities between 2700 and 2800 g of $C_2H_4$/((g of Cr) h), but **59** complex produced mostly oligomers of 1-decene in the presence of MAO. At room temperature, the Cr(III) complex *fac*-[Cr(NPN)Cl] **56** (NPN = bis(2-picolyl)phenylphosphine) with MAO exhibited only moderate activity of up to 840 g $Cr^{-1}h^{-1}$ and mostly polymers were obtained. When high temperatures were employed (80 $^\circ$C), not only the activity (2900 g (g of Cr)$^{-1}h^{-1}$) increased but also the selectivity for α-olefins. Complex **1** produced only polyethylenes without any significant detection of oligomers in the presence of the co-catalyst $EtAlCl_2$.

Scheme 9. Chromium (III) complex bearing tridentate N^P^N ligands **56-60**.
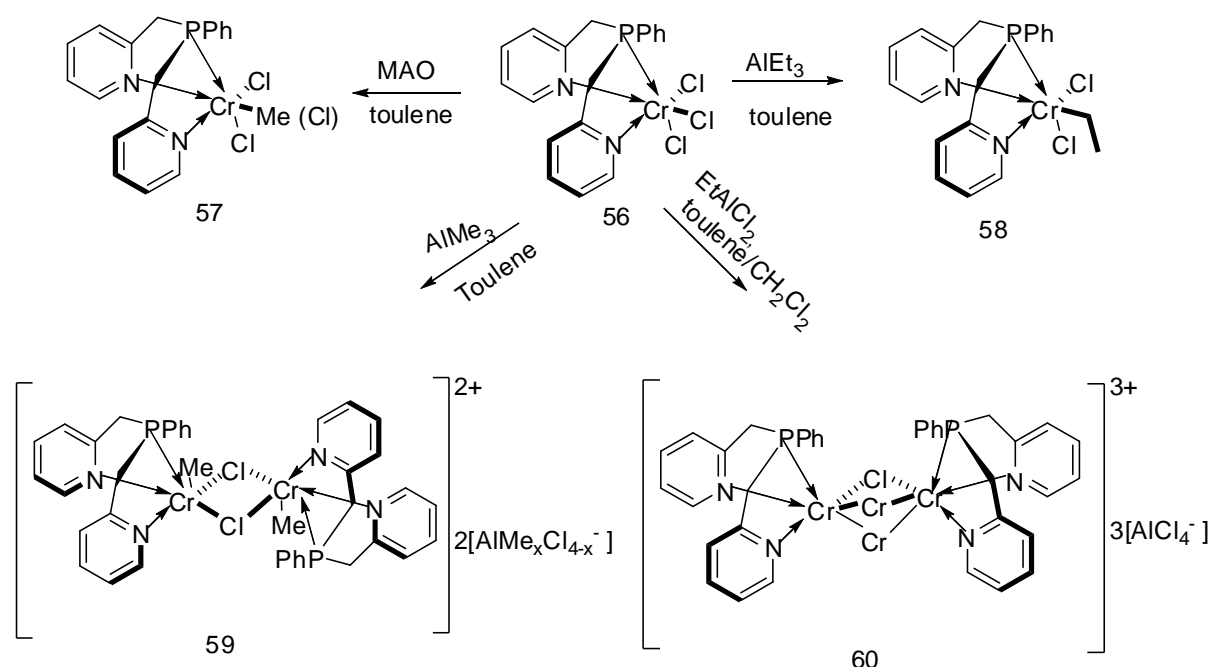


4.2. Design of Chromium (III) complex based on P^P^P Ligands:

Edwards[12] has reported chromium(III) complexes of a triphosphorus macrocycle 1,5,9-triethyl-1,5,9-triphosphacyclododecane ($P_3Et_3$) **61**, and related derivatives ($P_3R_3$, R=Ph, $C_3H_6Et_3$) and the catalytic activities thereof towards ethylene and propylene. The [12]ane$P_3Et_3MCl_3$ produced very high molecular weight polymers and displayed moderate catalytic activity in the homogeneous polymerization of ethylene on combination with alkyl aluminum co-catalysts. The difference in polymerization *versus* oligomerization behavior between metal complexes with *facially* capping phosphines compared to the *meridonally* coordinating phosphine may be due to the lack of axial steric protection from the linear phosphine which has been shown to be important in regulating the molecular weight of

polymers produced from late transition metals.[32] The complex **62** containing the ligand $Me_2P(CH_2)_aP(Ph)(CH_2)_bPMe_2(a = 3, b = 2)$ afforded a productivity of 48700 g × g $(Cr)^{-1}$× $h^{-1}$ and a selectivity for 1-hexene of 99.0 % in the presence of butylaluminoxane at 35 bar ethylene. The complexes **61** and **62** are depicted in figure 1.
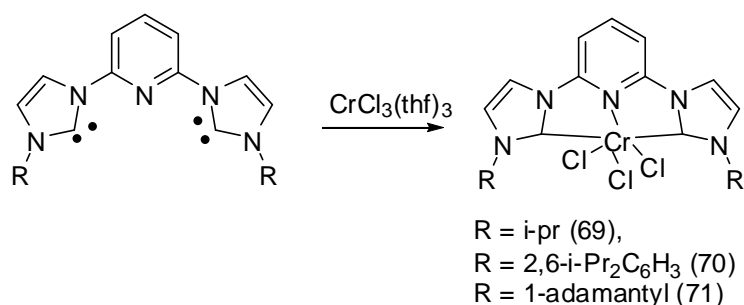
Figure 1: The chromium (III) complexes containing tridentate P^P^P ligands **61-62**.



**61**          **62**
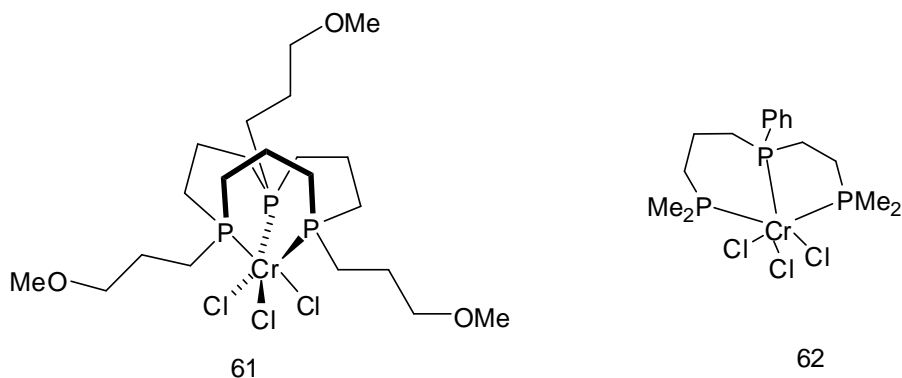
4.3. Design of chromium(III) complexes based on S^N^S ligands:

A few highly selective catalytic systems have led to the trimerization of ethylene to 1-hexene,[33] one such example is the class of Cr(III) complexes containing thioether bonding.[34] McGuinness *et al*. have studied Cr(III)-SNS complexes **63-66** (Scheme 10), which were found to be highly efficient catalysts for the trimerization of ethylene to 1-hexene.[35] Methyl **63** and ethyl **64** substituted complexes gave similar activities and selectivities. In contrast, the complex **65** was significantly more active than **63** and **64**, which was thought to be due to the shorter alkyl chain. Among these complexes, **66** gave the better results under similar conditions, which is likely due to it being more soluble and this system could achieve high catalyst activity in the presence of a very low amount of MAO. Use of a sterically compact and basic sulfur group lead to the highest activity and selectivity, while a secondary amine central donor was crucial for high activity, which raised the possibility that deprotonation of this group was occurring during catalyst formation. Sasol's system ($CySCH_2CH_2N(H)-CH_2CH_2SCy$) is one of the most important for chromium complexes bearing SNS ligands with its excellent selectivity for polyolefins.[36] The chromium(III) complexes bearing the tridentate pyridine SNS ($(2,6-CH_2SR)_2C_5H_5N(R=t$-Bu **67**, n-decyl **68**) ligands were synthesized[37] and screened for their catalytic activity in the presence of MAO. These complexes selectively afforded 1-hexene of very high purity, when compared to the corresponding Ph- and Cy-substituted derivatives $[(2,6-CH_2SR)_2C_5H_5N]CrCl_3$ (R = Ph, Cy).[38] Chromium(III) tridentate bearing S^N^S ligands are presented in scheme 11.

R= Me (63),
R= Et (64,
R= nBu (65),
R = ndecy (66)



R = t-Bu (67)
R= n-decyl (68)
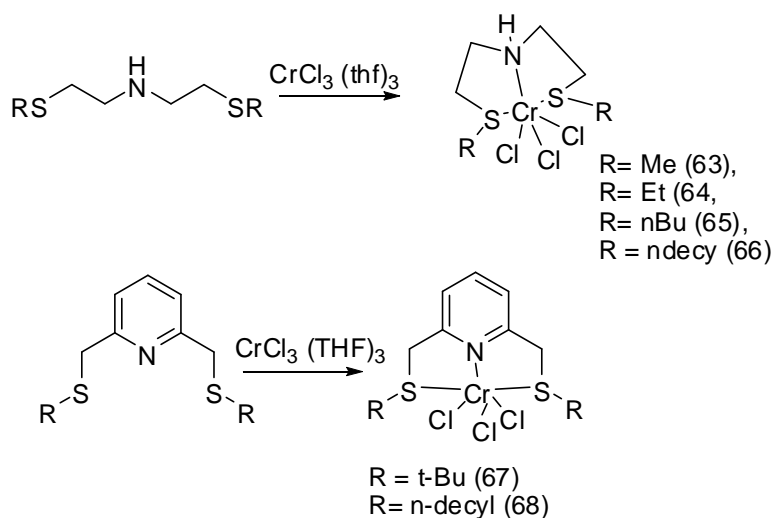
## 4.4. Design of chromium(III) complex based on C^N^C ligands:

Only a few reports are available on the topic of Cr(III) complexes bearing C^N^C type ligands. A new class of Cr(III) catalysts for the production of α-olefins based on tridentate pincer ligands containing heterocyclic carbene donors such as pyridine-2,6-bis(3-imidazoline) substitutions have been reported.[39] The complexes **69-71** (Scheme 12) were screened for ethylene oligomerization/polymerization in the presence of co-catalysts such as MAO, $Et_3Al$, triisobutyl aluminum and triethyl-$B(C_6H_5)_3$. Exceptionally active catalysts for ethylene oligomerization were produced in the presence of MAO, whilst <mark>the</mark> other co-catalysts were found to be inferior to MAO. The complexes **69, 70** very highly active and the products followed the Schulz-Flory distribution of α-olefins. For complex **71**, containing the adamantyl substituent, moderate activity and mainly polymer with only trace oligomers was produced. Complex **70**, at ambient temperature, afforded an activity as high as *ca* 40,000 g $mmol^{-1}$ $bar^{-1}h^{-1}$ for ethylene oligomerization, in the presence of triisobutyl aluminum as a scavenger and MAO as the co-catalyst.[40]

Scheme 12. The chromium (III) complexes containing tridentate C^N^C ligands **69-71**.



R = i-pr (69),
R = 2,6-i-$Pr_2C_6H_3$ (70)
R = 1-adamantyl (71)

4.5. Design of chromium(III) complex based on N^N^O ligands:

The Small group has developed a family of chromium complexes containing tridentate pyridine-based N^N^O ligands (Scheme 13), which were found to be highly active pre-catalysts for the oligomerization of ethylene/polymerization on combination with MAO.[41] The Cr(III) complexes based on the N^N^O ligands **72-82** such as **72** (R= H), **73** (R = 2-Me), **74** (R= 2-Et), **75** (R= 2-*i*Pr), **76** (R= 2-*t*Bu), **77** (R = 2,6-Me$_2$), **78** (R = 2,5-*t*Bu$_2$), **79** (2,6-*i*Pr$_2$), **80** (R = 2-*t*Bu), **81** (R= 2,4,6-Me) and **82** (R= 2,6-*i*Pr$_2$) were synthesized, and these complexes produced waxes and polyethylene in the presence of MAO. The butane producing catalysts could achieve a 1-butene purity of 99.5%, whilst the catalysts affording waxes produced highly linear to moderately branched waxes, depending on the presence of an α- olefin comonomer. Recently, our research group[13] has reported chromium(III) complexes ligated by 2-carbethoxy-6-iminopyridines **83-88** (Scheme 14) and examined their catalytic activities for ethylene polymerization in the presence of the co-catalyst ethylaluminum dichloride (EtAlCl$_2$). Of the complexes **83** (R = Me), **84** (R = Et), **85** (R= *i*-Pr), **86** (R = F), **87** (R= Cl) and **88** (R=Br), complex **88** exhibited the highest productivity of up to $2.33 \times 10^5$g mol$^{-1}$(Cr) h$^{-1}$ at 10 atm. These complexes exhibited notable catalytic activities for ethylene polymerization in the presence of the co-catalyst EtAlCl$_2$ and the resulting polyethylenes were obtained with different molecular weights ($(0.9–12) \times 10^4$) and broad distributions (1.91–15.92).

Scheme 13 & 14. The chromium (III) complexes containing tridentate N^N^O ligands **72-82 & 83-88**.
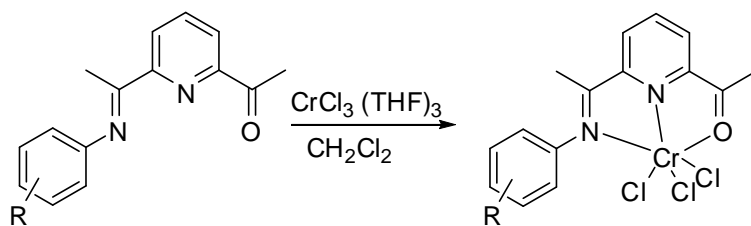
72 (R= H), 73(R = 2-Me), 74 (R= 2-Et),
75 (R= 2-iPr), 76 (R= 2-tBu), 77 (R = 2,6-Me$_2$),
78 (R = 2,5-tBu$_2$), 79 (2,6-iPr$_2$), 80 (R = 2-tBu),
81 (R= 2,4,6-Me), 82 (R= 2,6-iPr$_2$)
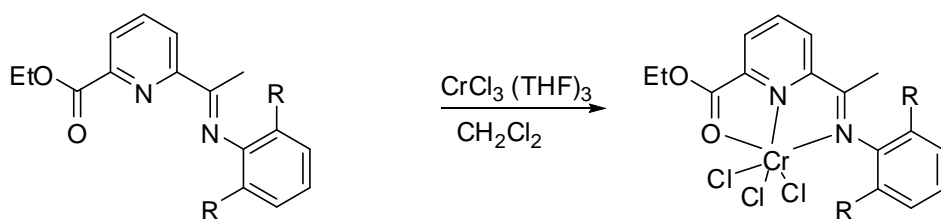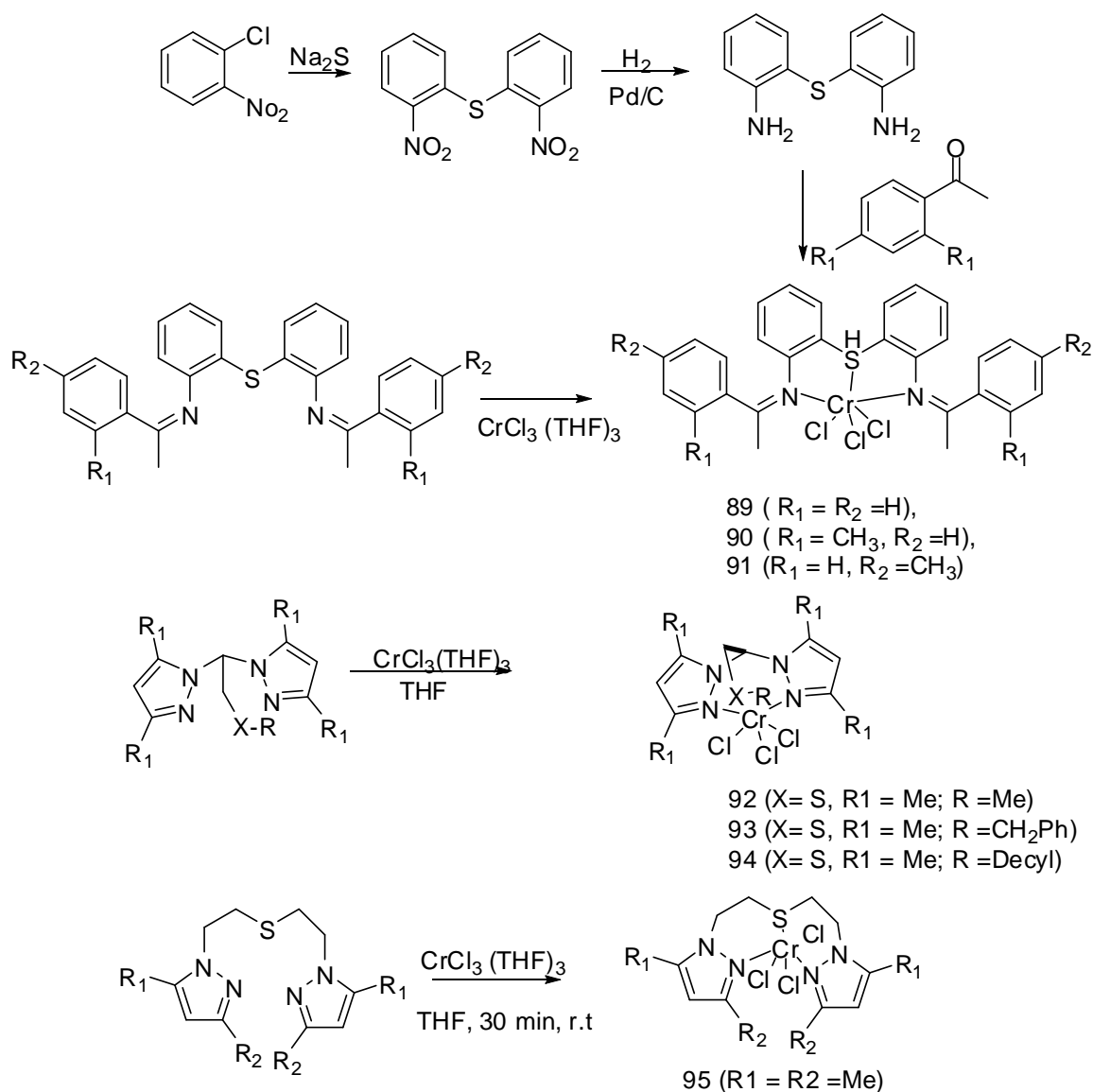
83 (R= Me), 84 (R= Et)
85 (R= i-Pr), 86 (R= F),
87(R= Cl),    88 (R=Br)

## 4.6. Design of chromium(III) complex based on N^S^N ligands:

Other types of NSN-Cr catalytic systems are important for ethylene oligomerization /polymerization. For example, a series of chromium(III) complexes **89-91** bearing chelating 2,2$^1$-iminodiphenylsulfide ligands [L = (2-ArMeCNAr)$_2$S] (Scheme 15) produced highly linear polyethylenes with broad molecular weight distribution and displayed moderate activity during the ethylene oligomerization.[18] Activity trials of **89-91** revealed that these complexes, in absence of co-catalysts, were unsuccessful in ethylene oligomerization. In the presence of MMAO, these complexes displayed ethylene polymerization (activity > 70 kg PE/mol$_{Cr}$•h) and converted ethylene into highly linear polyethylene. The catalytic activity order observed was **90**>**91**>**89**, which is likely due to the steric protection of the metal center, which is a crucial factor for controlling the chain transfer reaction. In general for chromium complexes, the catalytic activities towards ethylene polymerization increases gradually to a maximum value and then decreases gradually on increasing the temperature.[26,27] The Hor group reported the bis(pyrazol-1-yl)methane chromium(III) complexes **91-94** (Scheme 16), [42] which were utilized for the trimerization of 1-hexene. These pre-catalysts were highly selective toward trimerization (total C$_6$ selectivities > 94.7 %) to 1-hexene (> 96.1 %) with activities in the range 1050-3900 g/((g of Cr) h) in the presence of MAO. The Cr(III) pyrazolyl complexes were prepared by the reaction of CrCl$_3$(THF)$_3$ with 1.1 equiv of

tridentate nitrogen-, oxygen-, or sulfur bridged bis(pyrazoly) ligands (NZN).[41] In this way, Carpentier and Casagrande *et al.* have synthesized Cr(III) pyrazolyl complexes such as the pre-catalyst **95** (Scheme 17), which in the presence of MAO afforded a TOF = $131.0 \times 10^3$ h$^{-1}$ and selectivity for α-olefins of 89-97 %.[43]

Scheme 15, 16 & 17. The chromium (III) complexes containing tridentate N^S^N ligands **89-91, 92-94 & 95**.



89 ( R$_1$ = R$_2$ =H),
90 ( R$_1$ = CH$_3$, R$_2$ =H),
91 (R$_1$ = H, R$_2$ =CH$_3$)

92 (X= S, R1 = Me; R =Me)
93 (X= S, R1 = Me; R =CH$_2$Ph)
94 (X= S, R1 = Me; R =Decyl)

95 (R1 = R2 =Me)

## 4.7. Design of chromium(III) complex based on P^N^P ligands:

McGuinness, Wasserscheid *et al.* have reported MAO activation of the tridentate P^N^P chromium(III) complexes **96-98** (96, L=PPh$_2$; 97, L=PCy$_2$; 98, L= PEt$_2$) for the selective ethylene trimerization to 1-hexene (Scheme 18).[38] Upon activation with 120 equiv of MAO, the complex **96** was moderately active and exhibited excellent selectivity towards 1-hexene. When the bulky dicyclohexylphosphino ligand **97** was introduced, the activity

decreased and the main product formed was polyethylene. However, the diethylphosphino substituted complex **96** had an activity double that of catalyst **98**, and a high selectivity for 1-hexene. The combination of N and P donor ligand systems gave promising results in ethylene oligomerization.[44] Recently, the Gambarotta group reported polymer-free ethylene oligomerization using a pyridine based pincer PNP-type of ligand in the complex [2,6-$(Ph_2PCH_2)_2C_5H_3N]CrCl_3$.[43] It produced only oligomers with good activity and without visible polymeric material in the presence of MAO at a temperature of 80 °C or higher. The chromium(III) complexes bearing tridentate P^N^P ligands **96-98** are depicted in scheme 18.

Scheme 18. The chromium (III) complexes containing tridentate P^N^Pligands **96-98.**



96 (R= PPh$_2$),  97 (L= PCy$_2$), 98  (L= PEt$_2$)
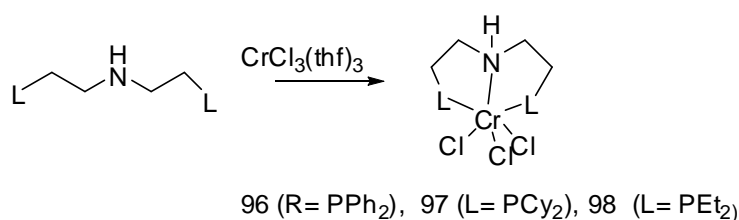
5**.** Conclusion

In recent years, catalysts for ethylene oligomerization/polymerization have attracted special attention, and in particular the ability of Cr(III) complexes to be tuned, *viz* oligomerization *versus* polymerization. This activity has been brought about by the very real need of the chemical industry for more efficient routes to 'polyethylene monomers', in particular ethylene trimerization to 1-hexene. Upon activation with MAO, tridentate N^N^N bearing Cr(III) complexes are highly selective for ethylene oligomerization and moderately active for polymerization. These areas need improvement in both selectivity and activity; the selection of the co-catalyst, the modification of the ligands, and the reaction conditions are all controllable and essential features of such systems. Further investigations are on-going to improve productivity/selectivity/activity of both the oligomeric and the polymeric products.

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