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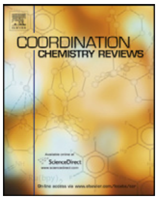

Review

Selective ethylene oligomerization: Recent advances in chromium catalysis and mechanistic investigations

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Contents

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Dedicated to Professor Harry Gray on the occasion of his 75th birthday. Thank you for your mentorship.

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ABSTRACT

Selective production of linear α-olefins is of significant commercial interest. Recently discovered catalytic systems based on titanium, tantalum, and chromium show remarkable selectivity and productivity for the oligomerization of ethylene to 1-hexene or 1-octene. Chromium-based catalysts are the most selective and active and show the highest structural diversity. This paper discusses the most recent advances in chromium chemistry related to selective olefin oligomerization. Aspects regarding ligand design, catalyst generation, selectivity for different products, and reaction mechanism are presented. Isotopic labeling protocols designed to distinguish between various mechanisms of catalysis are reviewed.

1. Introduction

Linear α-olefins are important commodity chemicals with a variety of applications including the copolymerization with ethylene and the generation of plasticizers, detergents, surfactants, and lubricants [1]. A significant part of the light fraction (C_4–C_8) is utilized as comonomer for the copolymerization with ethylene to generate Linear Low Density PolyEthylene (LLDPE). In this context, 1-hexene and 1-octene are particularly valuable, imparting polymers good tear resistance and other desirable properties [2]. For this application, very good purity of α-olefin is essential, because internal olefins are unreactive and thus build up in co-polymerizations. Currently, even carbon number α-olefins are generated industrially mostly via non-selective oligomerization of ethylene [1]. Starting with reports from 40 years ago indicating that non-statistical oligomerization of ethylene is possible, the field of selective oligomerization of olefins has developed significantly. Particularly over the last decade an abundance of studies has been reported from both industrial and academic laboratories. These recent reports describe the non-statistical oligomerization of ethylene to 1-hexene or mixtures of 1-hexene and 1-octene with good selectivities for the α-olefin [3–25]. In connection to these results, alternative strategies have been studied for the preparation of C_n olefins by the selective homo- and co-trimerization of α-olefins. Selective olefin trimerization or tetramerization has been reported for titanium [26–33], tantalum [34,35], and chromium systems, the last being the most selective and productive. Overviews of the selective olefin oligomerization field have been published: an extensive review of ethylene trimerization systems appeared in 2004 [3], followed by a discussion of the frontiers in this area of research in 2007 [4], and a review focused on dimerizations and industrial developments in 2009 [36]. The present paper focuses on mechanistic and structural aspects of the most recent catalyst systems displaying multidentate ligand architectures. The main classes of chromium complexes capable of supporting selective olefin oligomerization are discussed with emphasis on the features that control the observed selectivity and catalytic behavior. Earlier work has been thoroughly reviewed in a previous article and is mentioned here only briefly [3]. Reports regarding catalyst initiation, effect of activators, chromium oxidation states, and reaction mechanism are summarized. Computational results have contributed to the understanding of mechanistic aspects and are discussed under the corresponding topics. Experimental tests available for interrogating the mechanism of olefin oligomerization are delineated. A few non-selective chromium oligomerization catalysts are included, as they are proposed to function via a mechanism similar to the selective oligomerization of olefins.

2. Brief historical overview

Selective olefin oligomerization systems have been reported for chromium, titanium, and tantalum with the chromium based catalysts being the most numerous, active and selective. From a historical perspective, the chromium systems were reported first. Initial studies were related to the Phillips catalyst for olefin polymerization [37,38]. Early reports by Manyik using chromium 2-ethylhexanoate activated with hydrolyzed triisobutyl aluminum indicated the generation of 1-hexene as the major ethylene oligomer byproduct in the polymerization of ethylene [39,40]. Ethylene trimerization was implicated in the context of polyethylene formation based on the fact that the generated polymer displayed *n*-butyl branches, indicative of formation of 1-hexene in situ [39]. A follow-up study suggests distinct mechanisms for 1-hexene formation vs. polyethylene formation with these chromium/aluminum catalysts [40]. It also proposes that selective 1-hexene formation involves chromacyclopentane intermediates. A decade later, Briggs reported that optimization of this system by the addition of dimethoxyethane provides a catalyst selective for ethylene oligomerization to 1-hexene (74%) with polymer being the minor product [5]. A mechanism involving chromacyclopentane and chromacycloheptane intermediates was proposed and remains the accepted version of the mechanism of selective ethylene trimerization [5]. Reports from industrial laboratories, primarily published in patents, have uncovered a number of catalytic systems for the selective trimerization of ethylene with a variety of modifications [41–44]. A chromium-pyrrolide catalyst has been implemented commercially by the Chevron-Phillips Chemical Company [3,41,45]. Ligands capable of supporting selective olefin oligomerization include pyrrolides, maleimidyl, cyclopentadienyl, boratabenzene, phosphines, and phenoxides. These reports have been thoroughly reviewed previously and will not be discussed here [3].

Over the last decade, increased interest in the development of selective oligomerization catalysts has lead to a diverse array of catalytic systems based on titanium, tantalum, and chromium. The tantalum systems are considered ligand-less as they do not rely on added organic ligands for catalysis; the activators serve the role of converting the Ta^{V} precursor to Ta^{III} [34,35]. The initial titanium systems rely on ligands based on monocyclopentadienyl motifs linked to arenes that can act as labile ligands via the π-system

[26,27,30–32]. Variants of these catalysts with pendant thiophene or ether groups replacing the arene have also been reported [28,29]. More recently, a titanium catalyst based on phenoxy-imines with pendant ethers was shown to convert ethylene to 1-hexene selectively [33]. For chromium, the early catalytic systems rely on ligands such as pyrrolides and carboxylates, while the more recent ones are based on multidentate ligands displaying P, N, S, and O donors. The array of successful chromium catalysts based on multidentate ligands is diverse; they display donor combinations such as PP, PNP, SNS, NNN, NNS, and NNO. Synthetic, structural, spectroscopic, isotopic labeling and computational investigations have been performed to address structure–activity relationships, the nature of the active species, and details of the mechanism of catalysis.

3. Catalysts for selective ethylene oligomerization

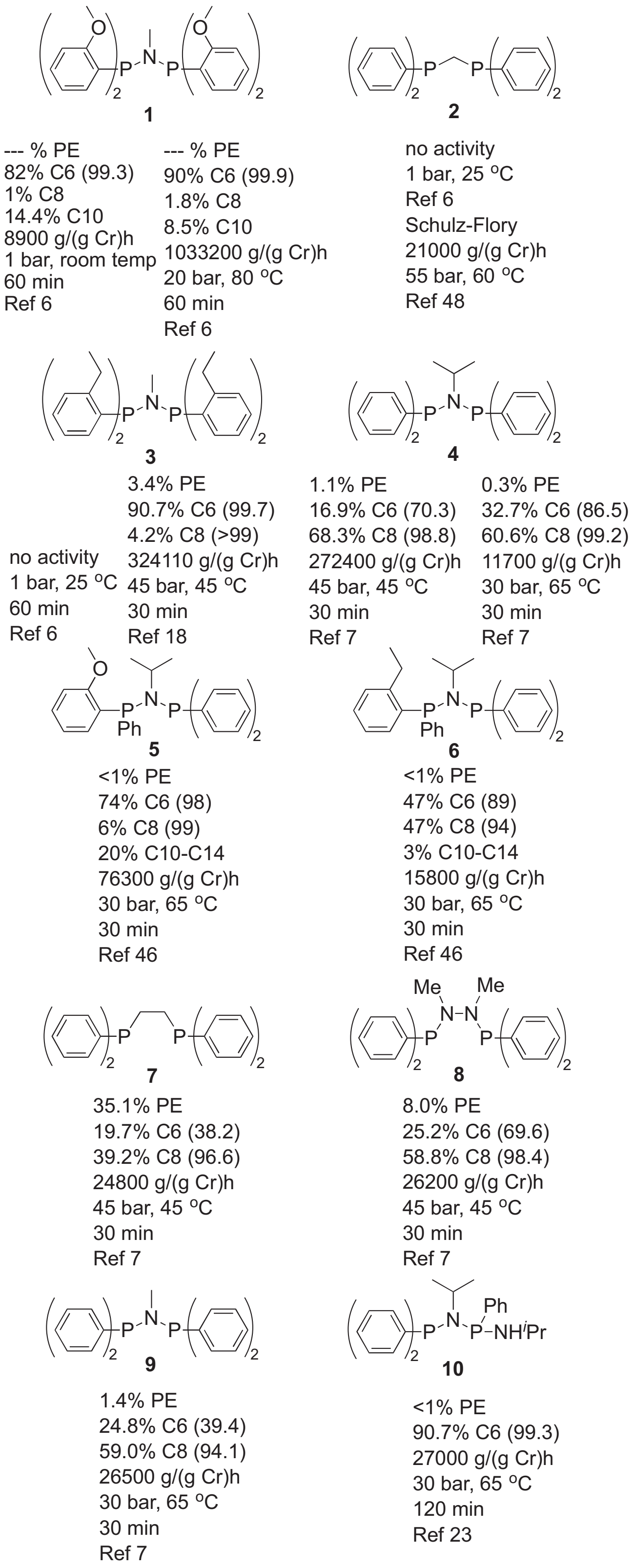
3.1. PNP systems

3.1.1. Versatility: from trimerization to tetramerization

In the context of ethylene oligomerization, the "PNP" (Fig. 1) ligand family was introduced in the early 2000s as a very successful architecture for the selective trimerization of ethylene to 1-hexene [6]. As with the majority of reported catalysts, the active system is generated in situ by mixing solutions of chromium precursor (Cr^{II} or Cr^{III} halide, for example) and phosphine, followed by activation with methyaluminumoxane (MAO) under ethylene (Scheme 1). The PNP^{O4} (**1**) system is very active, with a productivity of 1,033,200 g/g Cr/h (at 20 atm C_2H_4 and 80 °C) resulting in 90% C6 fraction with 99.9% 1-hexene. The main byproduct corresponds to the C10 fraction that is generated from the cotrimerization of one equivalent of 1-hexene with two equivalents of ethylene; hence the amount of 1-hexene produced by this catalyst system is actually higher than the reported yield, but part of it is consumed in the cotrimerization. Important for commercial applications, this system generates no polymer byproduct, a valuable feature in the context of maintaining polymerization reactors clean of solid material. The initial report emphasized two ligand features required for high activity and selectivity: the four ortho-OMe substituents on P-bound aryls and the PNP backbone. Replacing the PNP backbone with PCP (**2**) or changing to ethyl groups from methoxy (**3**) were reported to lead to a system with no catalytic activity under 1 atm of C_2H_4 [6]. Following this initial report several groups have studied extensively this family of ligands. Aspects related to ligand architecture, catalysis conditions, metal oxidation states, and mechanism of selectivity have been investigated. Tuning of the ligand structure has lead to systems that can generate 1-octene, another valuable α-olefin, as the major product [7]. The most selective ethylene tetramerization system, based on $Ph_2PN(^iPr)PPh_2$ (**4**), generates 1-octene and 1-hexene as the major products. While 1-octene is almost the exclusive C_8 product (68% yield at 98.8% selectivity in the C_8 fraction), 1-hexene constitutes only about 70% of the C_6 fraction; the main byproducts in the C_6 fraction are methylcyclopentane and methylenecyclopentane [7,9].

3.1.2. Effect of ortho-substituents

The PNP ligands have been systematically modified at every position: the substituents on the phosphine, the linker connecting the phosphines, and the nitrogen substituent. Generally, for aryl-substituted PNP phosphines, the presence of at least one MeO group ortho to the phosphine leads to selective formation of 1-hexene [46]. The yield of C6 products changes from over 90% with four ortho-OMe substituents to ~70% with only two or one ortho-OMe group (ligand **5**). The selectivity for 1-hexene in the C6 fraction remains high, at >98%. Upon complete removal of ortho donor groups (and other ortho substituents, *vide infra*), the yield for 1-



1

--- % PE
82% C6 (99.3)
1% C8
14.4% C10
8900 g/(g Cr)h
1 bar, room temp
60 min
Ref 6

--- % PE
90% C6 (99.9)
1.8% C8
8.5% C10
1033200 g/(g Cr)h
20 bar, 80 °C
60 min
Ref 6

2

no activity
1 bar, 25 °C
Ref 6
Schulz-Flory
21000 g/(g Cr)h
55 bar, 60 °C
Ref 48

3

no activity
1 bar, 25 °C
60 min
Ref 6

3.4% PE
90.7% C6 (99.7)
4.2% C8 (>99)
324110 g/(g Cr)h
45 bar, 45 °C
30 min
Ref 18

4

1.1% PE
16.9% C6 (70.3)
68.3% C8 (98.8)
272400 g/(g Cr)h
45 bar, 45 °C
30 min
Ref 7

0.3% PE
32.7% C6 (86.5)
60.6% C8 (99.2)
11700 g/(g Cr)h
30 bar, 65 °C
30 min
Ref 7

5

<1% PE
74% C6 (98)
6% C8 (99)
20% C10-C14
76300 g/(g Cr)h
30 bar, 65 °C
30 min
Ref 46

6

<1% PE
47% C6 (89)
47% C8 (94)
3% C10-C14
15800 g/(g Cr)h
30 bar, 65 °C
30 min
Ref 46

7

35.1% PE
19.7% C6 (38.2)
39.2% C8 (96.6)
24800 g/(g Cr)h
45 bar, 45 °C
30 min
Ref 7

8

8.0% PE
25.2% C6 (69.6)
58.8% C8 (98.4)
26200 g/(g Cr)h
45 bar, 45 °C
30 min
Ref 7

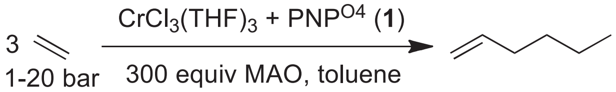
9

1.4% PE
24.8% C6 (39.4)
59.0% C8 (94.1)
26500 g/(g Cr)h
30 bar, 65 °C
30 min
Ref 7

10

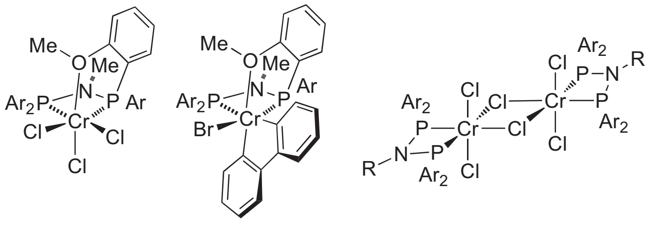
<1% PE
90.7% C6 (99.3)
27000 g/(g Cr)h
30 bar, 65 °C
120 min
Ref 23

Fig. 1. PNP and related phosphines and their performance for ethylene oligomerization. The numbers in parentheses represent the purity of α-olefin in the corresponding Cn fraction. Activators and chromium precursors vary (see references).



Scheme 1.

hexene drops to below 40% in most cases, with a selectivity of less than 90% (see **4**, for example). It is important to note that the outcome of the catalytic trials with these phophine variants is dependent on the reaction conditions, in particular on the pressure of ethylene. At higher pressures, the formation of 1-octene becomes dominant with ligands without ortho-OMe substituents. In studies aimed at determining the role of the ortho-OMe groups in terms of electronic effects vs. the availability of additional donors, phosphines bearing ortho-, meta-, or para-OMe have been compared [46]. High selectivity for 1-hexene was observed only for the variants displaying ortho-OMe groups. These studies all point to the coordinating ability of the ortho-subtituents as one of the determining factors for the selectivity for 1-hexene. Single crystal X-ray diffraction (XRD) studies of Cr(PNP) complexes provide detailed information regarding the ability of the pendant OMe groups to bind to chromium [13,17]. A series of $Cr^{III}(PNP^{O4})$ complexes with diverse ligands bound to chromium has been reported. In all these complexes the ancillary PNP^{O4} ligand displays a *fac*-k_3-(P,P,O) coordination mode (**11** and **12**, Fig. 2). The Cr–P bond lengths vary from 2.3855(7) Å to 2.6606(14) Å and Cr–O bond lengths vary from 2.1562(15) Å to 2.435(2) Å. The longer bond lengths were observed with strong trans influencing ligands. These parameters suggest that the PNP^{O4} ligand framework is quite adaptable to a number of structural variations; this adaptability was proposed to be important for the stabilization of intermediates along the catalytic cycle. Well-defined $Cr^{III}(PNP^{O4})$ complexes show catalytic activity for ethylene trimerization, lending support to mononuclear catalysts supported by coordination of both O and P donors. Variable temperature ^2H NMR spectroscopy studies of Cr^{III} complexes supported by an ortho-OCD_3 substituted PNP ligand show an exchange process involving the ether groups. For $Cr^{III}(PNP^{O4})Cl_3$, two peaks are observed in the ^2H NMR spectrum at −50 °C, one assigned to the metal-bound OCD_3 group (32 ppm) and one to the free OCD_3 groups (3.8 ppm). This spectrum is consistent with a solution structure similar to the solid-state one. Upon increasing the temperature, two coalescences are observed corresponding to exchange processes between the ligated and non-ligated pendant ethers. Ligand variants with donors other than ethers, such as amines and thioethers, have not been reported to lead to active ethylene oligomerization catalysts. In fact different types of ligations were observed for systems with pendant N or S in the ortho position. For example, a PNP^{S4} variant displays a *fac*-k_3-(P, S, S) coordination mode [17]. In the absence of ligating ortho-subtituents the sixth coordination site of chromium is occupied by a solvent molecule or dimerization. For the dinuclear species, two P donors, two terminal halides, and two bridging halides occupy the six coordination sites of chromium (**13**, Fig. 2).



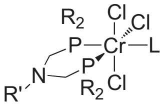
11 **12** **13**

Fig. 2. Well-defined chromium complexes supported by PNP ligands.

As discussed above, the ortho-OCH_3 groups of aryl substituted PNP phosphines coordinate to Cr^{III} and dramatically affect the selectivity of olefin oligomerizaton toward formation of 1-hexene. The possibility that the same outcome in selectivity could be achieved by increasing the steric bulk at the ortho position, without involving any coordinating groups has been investigated [18]. Initial reports from bp regarding PNP ligands with four ortho-(CH_2CH_3) substituents indicate no trimerization activity at room temperature and 1 atm of ethylene; more stringent conditions (45 atm and 45 °C), however, lead to ethylene trimerization (>85% C6 products with a selectivity for 1-hexene >99%). Substituting the ethyl groups for methyl or isopropyl preserve the high selectivity for 1-hexene. Removing the steric bulk generated by the ortho-alkyl substituents by replacing one, two, or three of these groups with hydrogen leads to a significant decrease in the selectivity for the C6 fraction and 1-hexene (47% C6 products with a selectivity for 1-hexene of 89%, see **6**, Fig. 1). This correlates with increased selectivity for the C8 fraction, containing more than 94% 1-octene. This behavior highlights the ability of the PNP ligand framework to tune catalysis for trimerization vs. tetramerization of ethylene based on sterics, in the absence of a labile coordinating group. The steric pressure of four alkyl ortho-subtituents is required to generate a similar selectivity for 1-hexene in the C6 fraction as from one ortho-OMe group. Notable, less polymer byproduct is observed in the presence of pendant ethers.

3.1.3. *Backbone effects*

Alteration of the PNP backbone has been studied to determine its effects on the electronics of the metal center and catalysis. Cr^0 tetracarbonyl complexes supported by PNP and PCP ligands without *o*-OMe groups show average CO stretching frequencies that are very similar [13]. On the other hand, Cr^0 tetracarbonyl complexes with and without *o*-OMe groups show a difference of about 10 cm^{-1}, with the more electron reach PNP^{O4} ligand displaying the lower stretching frequency. Hence, the PNP and PCP backbones are electronically very similar, at least as reflected in the CO stretching frequencies. A PCH_2CH_2P backbone (**7**) does not alter the average CO stretching frequency significantly either, but this ligand leads to a significantly less selective and less active catalyst [7,13]. Carbon bridged diphosphine ligands have been investigated for selective oligomerization of ethylene and generally were less selective than the PNP counterpart even though in some cases good activity and selectivity were observed [47,48]. A PN(Me)N(Me)P backbone (**8**), while leading to a tetramerization catalyst with 1-octene selectivity similar to the best observed for any system, still results in modest productivity. These observations reflect a role for the PN linkage beyond a structural effect (for instance by altering the P–Cr–P angle), since the presumed five- and four-member chromium chelates show higher selectivity for backbones containing PN moieties rather than the PC counterparts. A POP variant was studied in the context of ethylene tetramerization and did not show catalytic activity, again pointing to the importance of the PN moieties for catalysis [49]. The effect of the N-substituent on catalysis has been studied. Upon varying it from alkyls (Me, iPr, Cy), to aryls (2-naphthyl, 4-biphenyl) and to substituents with donors atoms ($(CH_2)_2OCH_3$), the selectivity for 1-octene in the C8 fraction generally stays high (above 90%), but the selectivity for 1-hexene in the C6 fraction (38–86%) and the productivity (8000–52000 g/g Cr/h) varies significantly (see **9** vs. **4**, Fig. 1, for example) [7,13,16,50]. The most selective systems for α-olefin are based on ligands with substituents carrying an α-branch (iPr and Cy) potentially suggesting a requirement for steric pressure around the metal center in order to achieve selectivity. The presence of pendant ethers on the N-substituent increases catalytic productivity by improving catalyst stability [16]. PNP variants with alkyl substituents on the phosphine and pendant ethers or thioethers connected at



14

R, R' = alkyl or Ph
L = THF

	R'=^{i}Pr, R=Cy **15**	R'=^{i}Pr, R=^{n}Bu **16**
--- % PE	97% C6 (95)	78% C6 (99)
	1% C8 (99)	21% C8 (98)
	4579 g/(g Cr)h	5127 g/(g Cr)h
	30 bar, 45 °C	30 bar, 45 °C
	30 min	30 min
	Ref 25	Ref 25

Fig. 3. Chromium complex supported by PCNCP ligand and catalytic performance for ethylene oligomerization. The numbers in parentheses represent the purity of α-olefin in the corresponding Cn fraction. See reference for further details on catalytic conditions.

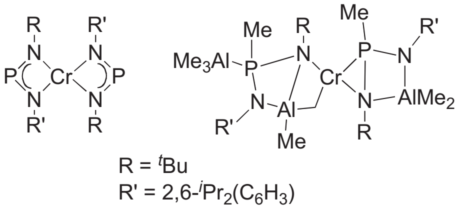
the nitrogen generate more than 96% 1-octene in the C8 fraction, albeit with lower overall selectivity [19]. It is not clear how the pendant donors exercise their effect since the crystal structures obtained for the corresponding chromium trihalide complexes do not show coordination of the pendant base to the metal center. Solid-state characterization shows a structure similar among PNP complexes without a ligating ortho-substituent: dinuclear comples with bridging halides to satisfy a coordination number of six for the metal center (**13**, Fig. 2) [7,16,51]. A number of Cr$^{\text{I}}$ tetracarbonyl complexes supported by a variety of phosphines was investigated by EPR and ENDOR spectroscopy to reveal spectral differences dependent on the ligand type [52]. These variations, however, did not follow a well-defined trend that could be correlated with the reported catalytic data.

3.1.4. *(PNP)N system*

A relative of the (Ar)$_2$PN(R)P(Ar)$_2$ ligands, Ph$_2$PN(^{i}Pr)P(Ph)(NHR) (**10**) is a catalyst for the trimerization of ethylene (90.7% C6 with 99.3% 1-hexene in the C6 fraction) [23,53,54]. The CrCl$_3$ complex of the above ligand shows k_2-(P,P) coordination similar to PNP ligands without pendant donors. Deprotonation of the pendant NH moiety was reported in the context of aluminum chemistry and one chromium complex supported by a Cp ligand, but not for catalytically relevant chromium precursor. It was proposed that in the presence of both Cr and Al, the ligand is deprotonated and generates a hetero-dinuclear species; this was assumed to be the active catalyst for ethylene trimerization. This proposal is supported by the observation that a ligand variant without an N–H group does not lead to an active catalyst. A close interaction between aluminum and the Cr–PNPNHR ligand may lead to a sterically and coordinatively congested active site that favors 1-hexene formation. This behavior parallels the characteristics of other PNP ligands—variants with bulky substituents or pendant donors favor the generation of 1-hexene instead of 1-octene.

3.2. *PCNCP system*

A class of bidentate ligands displaying the PCH$_2$N(R)CH$_2$P motif (**14**, Fig. 3) was recently reported to support selective ethylene trimerization catalysis [25]. While these frameworks have three potential coordination sites, structural characterization indicates that only the phosphines bind to chromium. These ligands are related structurally to some of the diphophines with carbon-only linkers studied for ethylene trimerization and tetramerization [47]. The carbon-only counterparts have a combined selectivity for 1-hexene and 1-octene of up to 81% [47], while **14** variants show combined selectivities of over 90% in the majority of systems studied (Fig. 3). As with the PNP frameworks (Fig. 1), the inclusion of a nitrogen in the three-atom linker makes a significant impact on the selectivity and productivity for 1-hexene. Notably, the less sterically hindered variants lead to a decrease in the selectivity for C6 products in favor of C8 products. Upon changing the phosphorous substituents from cyclohexyl to *n*-butyl, the selectivity shifts from 97% C6 products (with 95% 1-hexene) to 78% C6 (99% 1-hexene) and 21% C8 (98% 1-octene). This effect, of the sterics of the ligand, on the selectivity of ethylene oligomerization was also investigated by computation. It was found that bulkier ligands disfavor metallacycle growth from chromacycloheptane to chromacyclononane compared to 1-hexene formation by 3,7-H-shift.



R = ^{t}Bu
R' = 2,6-^{i}Pr$_2$(C$_6$H$_3$)

17 **18**

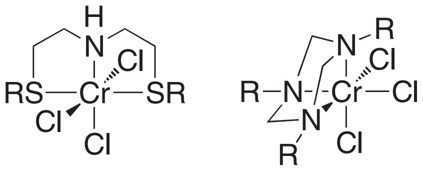
Fig. 4. Chromium complexes supported by ligands with NPN moieties.

3.3. *NPN system*

Expanding on the three atom PNP linkages (Fig. 1) successful for ethylene trimerization and tetramerization, a NPN variant (Fig. 4) generates a catalyst for the oligomerization of ethylene to 1-hexene [55]. This system leads to polymerization, selective trimerization, or non-selective oligomerization of ethylene depending on the activation protocol [55–57]. Treatment of the Cr(NPN)$_2$ precursor (**17**) with different aluminum alkyls has allowed for the isolation of heteromultinuclear species that differ in their catalytic capabilities. For example, the reaction of Cr(NPN)$_2$ with four equivalents of AlMe$_3$ leads to a Cr–3Al species (**18**) that constitutes a single component ethylene trimerization catalyst. Further activation of this species with excess MAO generates a non-selective oligomerization catalyst, while [Al(^{t}Bu)$_2$]$_2$O leads to a polymerization catalyst [55]. Notably, the structure of the initial NPN supporting ligand (**17**) is significantly changed in **18**, due to alkylation at phosphorous.

3.4. *Mer-coordinating tridentate ligands*

A variety of linear tridentate ligands (**19**, Figs. 5 and 6) are emerging as efficient frameworks for chromium-based ethylene trimerization [8,10,11,15,58]. When available, XRD of Cr$^{\text{III}}$ complexes supported by these ligands typically show meridional coordination (**19**, Fig. 5). Generally, these ligands have central nitrogen donors linked via hydrocarbon chains to soft donors such as phosphines or thioethers. One ligand variation displays secondary amines as central donors connected via ethylene linkers to phosphines or thioehers; these frameworks support selective ethylene trimerization (**21**–**24**, Fig. 6). These ligands are not locked in the geometry for meridional coordination and facial binding can be envisioned and in some cases has been observed (S–Cr–S angle of 98°) [58]. Typically, the active species are generated by treating the



19 **20**

Fig. 5. Chromium complexes supported by SNS and NNN ligands representing meridional and facial binding, respectively.

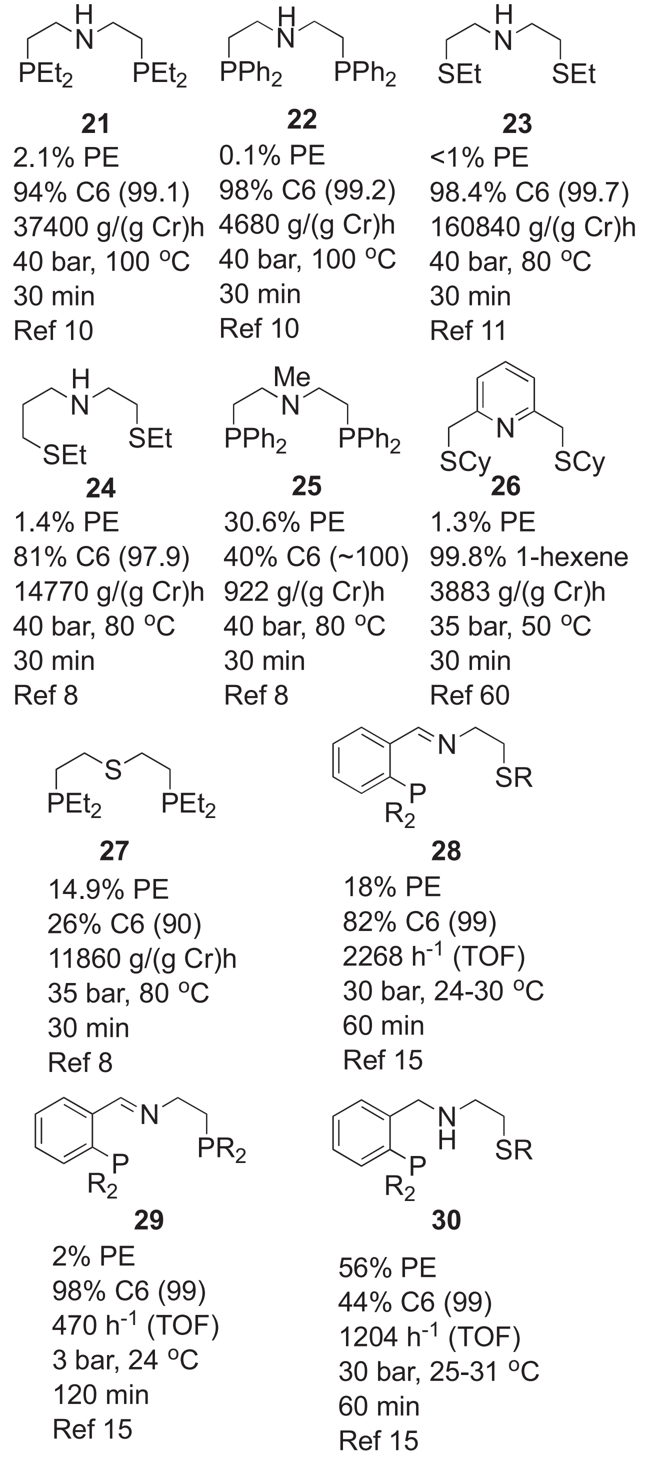


Fig. 6. Mer-coordinating ligands and their performance for ethylene oligomerization. The numbers in parentheses represent the purity of α-olefin in the corresponding Cn fraction. Activators and chromium precursors vary (see references).

preformed Cr^{III}-ligand complexes with MAO. The performance of the $R_2P(CH_2)_2NH(CH_2)_2PR_2$ (**21**, **22**) system varies with the nature of the phosphine substitutents [10]. Compared to cyclohexyl and phenyl, the ethyl variant is the most selective and productive (up to 98% C6 products with 99.2% 1-hexene selectivity and the best activity at 37,400 g/(g Cr) h) under the conditions reported (40 bar C_2H_4, 50–120 °C). Replacement of the phosphines with thioethers leads to a new family of trimerization catalysts (**23**, “SNS” systems) [11]. With little polyethylene produced (<1%), selectivity for hexenes of higher than 93% containing more than 99.3% 1-hexene, and productivity of up to 160,000 g/(g Cr) h (40 bar C_2H_4, 80 °C) these are very competitive ethylene trimerization catalysts. Variation of the external alkyl substitutent of the thioethers led to more active systems for the longer linear alkyl chains compared to shorter ones; this was speculated to be a consequence of the higher solubility of these variants [11]. Interestingly, the longer chain systems afforded viable catalysts at much lower MAO loading, an important feature from a commercial perspective. Structural characterization shows that Cr–S bond lengths vary significantly, from 2.4508(7) to 2.6854(12) Å, similar to the behavior of the PNP^{O4} system [13,58].

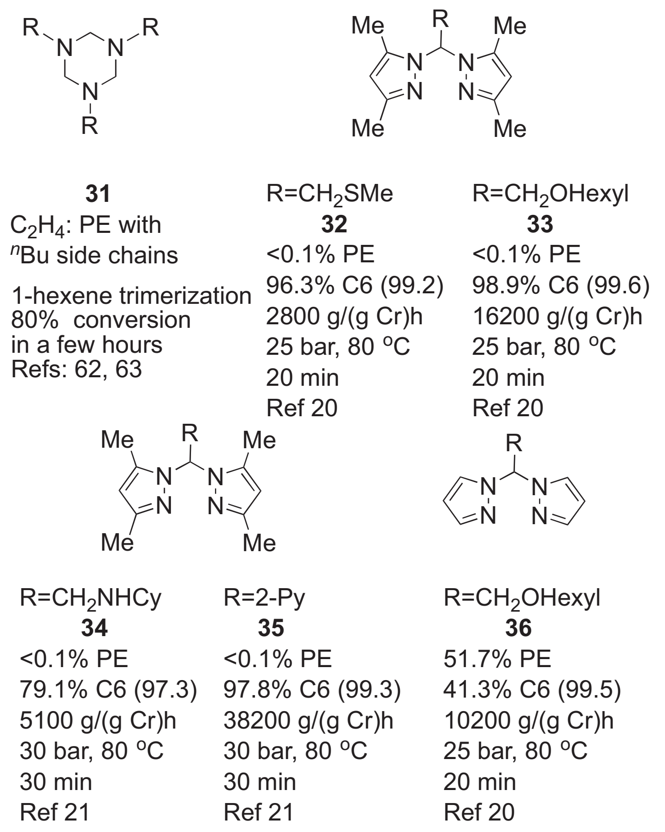
To further explore the ligand features important for catalytic activity several structural modification were investigated [8]. The size of the linker connecting the N and S donors was increased from two to three CH_2 groups (**24**) leading to a trimerization catalyst with lower activity and selectivity for C6 products. In a different variation, the secondary amine was replaced with a tertiary amine (**25**) to lead to a catalyst that generates significant amounts of polymer (>30%) and lower selectivity for the C6 fraction. The authors speculate that the N–H functionality is essential for high activity and selectivity, potentially allowing for deprotonation by aluminum activators [8]; subsequent reports however suggest that the N–H moiety remains intact with aluminum alkyls [59]. In a different report, a pyridine variant (**26**) of the present system trimerizes ethylene selectively despite not displaying an acidic proton [60]. The activities reported for the pyridine variant are lower than the ones for the SNS ligands with central donors based on secondary amine. PSP and SPS variants were studied as well [8]. Depending on the phosphine substituents, the PSP system generates either an unselective catalyst leading to a Schulz–Flory distribution of olefins or a mixture of active species leading to a Schultz–Flory distribution enriched in the C6 fraction (for **27**). The SPS-supported catalyst shows results similar to **27**. These results suggest that the PSP and SPS catalysts are capable of performing selective ethylene trimerization, but unselective oligomerization occurs at the same time. In a separate study, a tristhiolate variant ($S(CH_2CH_2SC_{10}H_{21})_2$) supports selective ethylene trimerization as well [61].

A class of related meridional ligands displays nitrogen central donors based on an imine moiety linked to phosphines, thioethers, ethers, or amines (**28**–**30**, Fig. 6) [15]. These systems generate significant amounts of polyethylene, however, under certain conditions, the PNS (**28**) and PNP (**29**) variants produce C6 products with greater than 82% selectivity and with >98% 1-hexene content. Notably, when the imine moiety is replaced with a secondary amine version (**30**), the catalyst generates primarily polyethylene and less than 44% C6 products.

3.5. *Fac-coordinating tridentate ligands*

3.5.1. *Triazacyclohexane*

Complexes of chromium supported by substituted triazacyclohexane (**31**, Fig. 7) show facial coordination of the three nitrogen donors (**20**, Fig. 5) [62–64]. These systems have high activity for the polymerization of ethylene upon activation with MAO and are considered homogeneous models for the Phillips catalyst [63]. The resulting polyethylene shows incorporation of 1-hexene indicating that the catalyst is also able to selectively trimerize ethylene. This catalyst selectively trimerizes α-olefins, such as propene, 1-hexene, and styrene [62,64,65]. The unique ability of this catalyst to trimerize α-olefins was explained in terms of an open metal center due to the small N–Cr–N angle enforced by the triazacyclohexane ligand. It is noteworthy that even though some of the phosphine-based catalysts capable of selective ethylene oligomerization are only bidentate and hence quite open, they have not been reported to trimerize α-olefins.



31
C_2H_4: PE with
^{n}Bu side chains
1-hexene trimerization
80% conversion
in a few hours
Refs: 62, 63

R=CH_2SMe
32
<0.1% PE
96.3% C6 (99.2)
2800 g/(g Cr)h
25 bar, 80 °C
20 min
Ref 20

R=CH_2OHexyl
33
<0.1% PE
98.9% C6 (99.6)
16200 g/(g Cr)h
25 bar, 80 °C
20 min
Ref 20

R=CH_2NHCy
34
<0.1% PE
79.1% C6 (97.3)
5100 g/(g Cr)h
30 bar, 80 °C
30 min
Ref 21

R=2-Py
35
<0.1% PE
97.8% C6 (99.3)
38200 g/(g Cr)h
30 bar, 80 °C
30 min
Ref 21

R=CH_2OHexyl
36
51.7% PE
41.3% C6 (99.5)
10200 g/(g Cr)h
25 bar, 80 °C
20 min
Ref 20

Fig. 7. Fac-coordinating ligands and their performance for ethylene oligomerization. The numbers in parentheses represent the purity of α-olefin in the corresponding Cn fraction. Activators and chromium precursors vary (see references).

3.5.2. [NNN], [NON] and [NSN] heteroscorpionates

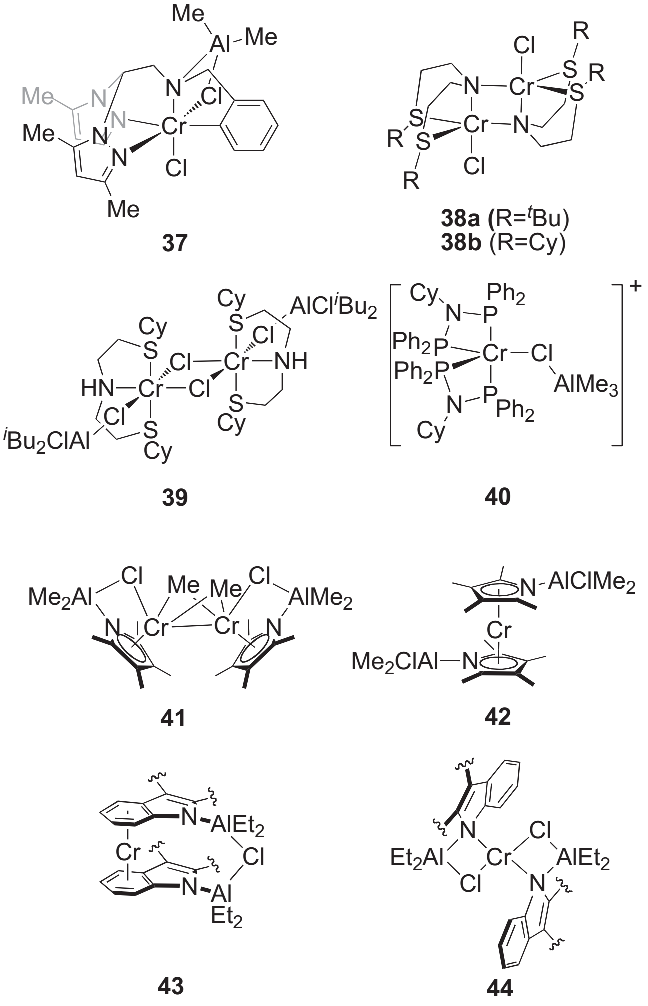
Heteroscorpionates provide a versatile family of facial ligands that allows for variations of the steric and electronic properties of the supporting framework as well as the nature of the donor atoms. The heteroscorpionates investigated for selective ethylene trimerization display two pyrazolyl arms and one arm displaying a N, O, or S donor (**32**–**36**, Fig. 7) [20,21,66]. Chromium complexes supported by heteroscorpinate ligands were activated with MAO to give a catalytic system selective for the generation of 1-hexene (selectivity for C6 larger than 94%, with more than 96% 1-hexene). The productivities of these systems range from 1000–21,000 g/(g Cr) h and the amount of polyethylene produced is less than 0.1%. The nature of the third donor of the heteroscorpionate ligand affects the selectivity and productivity of these catalysts. The ether based (**33**) catalysts are more productive than the thioether (**32**) ones, but they display similar selectivities for the C6 fraction and 1-hexene. For nitrogen-based donors, nitrogen heterocycles (**35**) are more active and selective than variants displaying alkyl amines (**34**, for example). Generally, the order of productivity for heteroscorpionate-based catalysts is [NNN(heterocyclic ring)] > [NNO] > [NNN(amine)] > [NNS]. Compared to the nature of the third arm of the heteroscorpionate ligand, the substitutents on the pyrazolyl arms have a larger effect on the amount of C6 products. Replacing the methyls with hydrogens (**36**) leads to a catalysts that makes primarily polymer. XRD analysis of Cr^{III} complexes supported by heteroscorpionate ligands show the expected facial binding mode. The increased steric requirements of these ligands compared to the triazacyclohexane system may explain the difference in reactivity, in particular their ability to trimerize ethylene, but not bulkier α-olefins.

4. Identifying the active species

4.1. Effect of cocatalyst

4.1.1. Cr–Al species

Generally, aluminum-based cocatalysts have been the most commonly employed activators for screening for catalytic activity in trimerization systems. Typically, a solution of ligand and chromium precursor ($Cr(acac)_3$, $CrCl_3(THF)_3$, $CrCl_2$, etc.) is treated with a solution of cocatalyst under ethylene. Methylaluminumoxane (MAO), modified MAO, isobutylaluminumoxane (iBAO), and other, better defined alkyl aluminum species have been utilized as activators. To determine the nature of the catalyst, numerous studies have focused on the reaction of chromium complexes with aluminum species. Heterodinuclear species containing chromium and aluminum have been suggested as potential active species in the trimerization of ethylene or precursors of the actual catalysts upon dissociation of the aluminum moiety. In some cases ligands with acidic protons can be deprotonated in the presence of aluminum alkyl reagents. For example, a tridentate heteroscopionate ligand displaying a secondary amine is deprotonated by $AlMe_3$ [67]. C–H activation of a pendant phenyl group is observed as well (**37**, Fig. 8) to lead to a heterobimetallic species with bridging chloride and amide ligands and a tetradentate ligand on chromium. Compound **37** is indeed active for ethylene trimerization upon treatment with excess MAO.



37

38a (R=^{t}Bu)
38b (R=Cy)

39

40

41

42

43

44

Fig. 8. Cr–Al complexes characterized by XRD.

The SNS family of ligands (Fig. 6) has been investigated extensively with respect to the effect of aluminum reagents and potential for deprotonation of the secondary amine. Deprotonation of a Cr(SNS) precursor can be performed with DABCO (1,4-diazabicyclo(2.2.2)octane) to lead to the isolation of a Cr^{II} dinuclear complex (**38a**, Fig. 8) with bridging amides [58]. The authors proposed similar deprotonating ability for aluminum alkyl reagents. Upon activation with MAO or a mixture of trialkylaluminum and $B(C_6F_5)_3$, the isolated dinuclear Cr^{II} species performs ethylene trimerization with activities comparable to mononuclear Cr^{III} precursors. Based on these results, the authors propose a catalytic cycle involving Cr^{II}/Cr^{IV} intermediates.

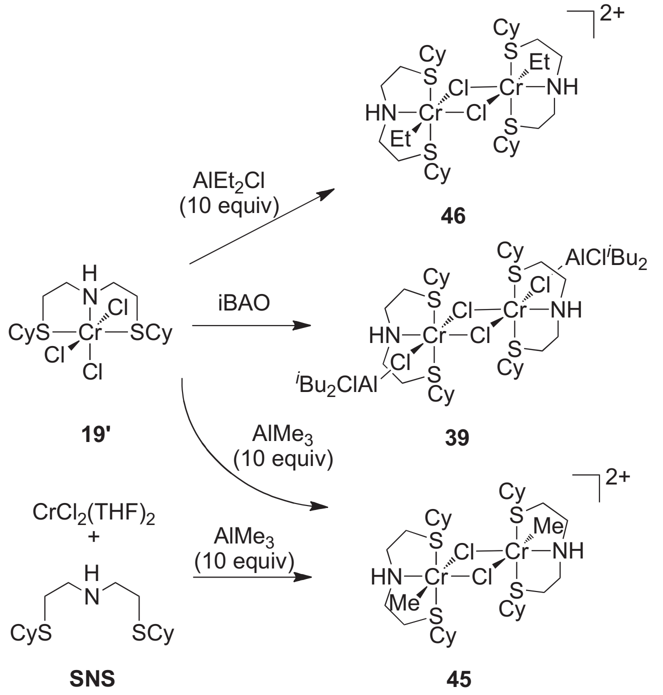
In contrast to the above results, in a separate study, deprotonation of the R_2NH groups was detrimental to trimerization activity [59]. A Cr^{II} dinuclear complex similar to **38a**, but with cyclohexyl thioether substituents (**38b**), is inactive for ethylene oligomerization. Importantly, treatment with some aluminum alkyl reagents does not lead to amine deprotonatin. Nevertheless, a heteromultinuclear Cr–Al species (**39**, Fig. 8) was isolated and characterized by XRD to reveal a Cr_2Cl_2 diamond core with bridging chlorides connecting to $AlCl(^i Bu)_2$ moieties. The active catalyst in this Cr(SNS) system, obtained upon additional treatment of **39** with MAO, was proposed to consist of a heteronuclear Cr–Al complex [59]. A subsequent report indicates that the behavior of this catalyst system is more nuanced, with catalytic activity increasing in the order $[Cr(SNS)Cl_3] < \{[Cr(SNS)MeCl]_2\}^{2+} < \{[Cr(SNS)EtCl]_2\}^{2+}$; this was suggested to reflect the ability of the dinuclear cationic species to dissociate and form an unsaturated and catalytically active mononuclear cationic species [68].

The PNP system (Fig. 1) active for ethylene tetramerization also supports a heterodinuclear Cr–Al complex (**40**, Fig. 8) in which Cr and Al atoms bridge via a chloride [69]. This complex forms by treating a Cr^{III} precursor with $AlMe_3$. Activation of **40** with MAO leads to catalytic trimerization and tetramerization of ethylene. The authors suggested that this species may be on the pathway leading to the formation of the active species upon activation with MAO. As discussed earlier, the NPN system (Fig. 4) also supports multinuclear complexes (**18**) capable of selective ethylene trimerization under certain conditions.

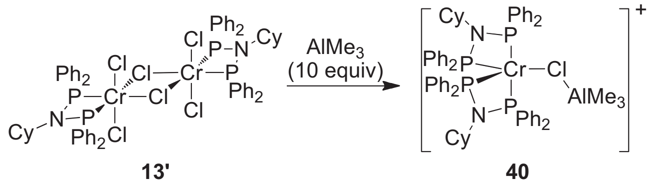
Pyrrolide ligands provide metal biding sites via the aromatic π-system and the nitrogen electron pair found in the plane of the ring. These features allow pyrrolides to bind two metal centers, to generate heteromultinuclear Cr–Al complexes (**41**–**44**) that are active for ethylene trimerization or polymerization depending on the structure of the multinuclear precursor [70,71]. Complexes **41** and **43** are single component catalysts for the trimerization of ethylene and complexes **42** and **44** catalyze the polymerization of ethylene. While the formation of multinuclear species has been confirmed by XRD studies in the discussed systems, the possibility of dissociation during catalysis to access mononuclear species is still open. In some cases related precursors with different structures (**38b** vs. **39**, **41** vs. **43**, **42** vs. **44**) have divergent catalytic behavior indicating that the differences in the precatalyst structures may be retained during catalysis.

4.1.2. Effect of aluminum activator on the oxidation state of chromium

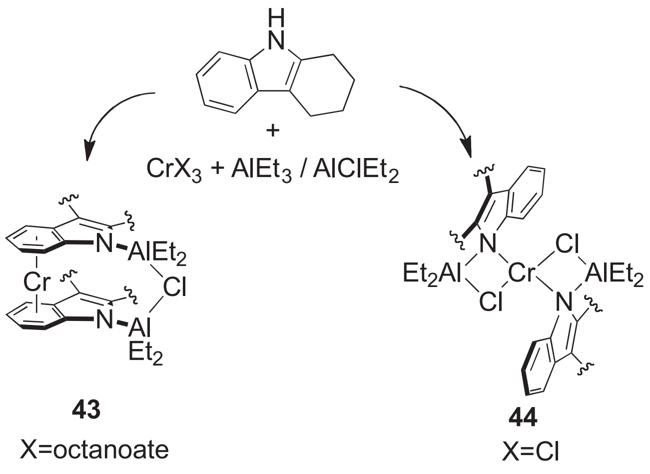
An important aspect for a variety of catalytic chromium systems activated by aluminum compounds is the ability of aluminum activators to facilitate oxidation state changes of chromium. The challenges in studying the effect of the activator on the precatalysts are highlighted by the diversity of multinuclear Cr–Al complexes generated (Fig. 8). The nature of the aluminum activator has a profound effect on the reaction with chromium precursors. For example, $CrCl_3(SNS)$ (**19′**, Scheme 2) reacts with $AlMe_3$ to generate a Cr^{III} species (**39**), while with iBAO it leads to a Cr^{II} species (**45**) [59,68]. This behavior was explained in terms of a higher propensity of $^i Bu$ vs. Me to lead to reductive elimination events, presumably by H-elimination followed by reductive elimination. Upon treatment of **19′** with $AlEt_2Cl$ a Cr^{III} complex (**46**) displaying a Cr-Et moiety was isolated and characterized by XRD. Given the presence of β-hydrogens, the isolation and stability of this species is remarkable. Even more intriguing is the fact that the Cr^{III} species **45** is also generated upon treating a mixture of $CrCl_2(THF)_2$ and SNS with $AlMe_3$. The apparent oxidation of the Cr^{II} precursor to Cr^{III} was explained by an $AlMe_3$-induced disproportionation to Cr^0 and Cr^{III}. These results suggest that the reduction of Cr^{III}–Cr^{II} is dependent on factors beyond the presence of β-hydrogens in the aluminum alkyl groups. The PNP catalyst system also undergoes redox chemistry upon treatment with alkyl aluminum species (Scheme 3) [69]. Upon treatment with excess $AlMe_3$, well-defined Cr(PNP) precursor **13′** generated a Cr^{II} species, **40** (Scheme 3). Species **40** can be prepared independently from $CrCl_2(THF)_2$ and $AlMe_3$. A system based on pyrrolide variants undergoes reduction with alkyl aluminum reagents as well (Scheme 4) [71]. Treatment of a Cr^{III} precursor with 2,3,4,5-tetrahydro-1H-carbazole and ethyl aluminum reagents leads to chromium products in different oxidation states depending on the nature of the chromium precursor. From a chloride precursor a Cr^{II} species is obtained (**44**), while from a carboxylate, a Cr^{I} species (**43**) is generated. These studies all highlight the propensity for oxidation state change upon treatment of chromium precursors with alkyl aluminum activators.



Scheme 2.



Scheme 3.



Scheme 4.

4.1.3. Catalyst activation without MAO

Cr^{II} or Cr^{III} species are the most common precursors for catalyst generation, upon activation with MAO. Several well-defined complexes that can be activated with stoichiometric reagents or that are single-component catalysts have been reported [12–14,17,55,70,71]. An alternative approach to a catalytically relevant Cr^{I} species starts from Cr^{0} carbonyl complexes. Chemical and electrochemical oxidation leads to $[Cr^{I}(PNP)(CO)_4]^+$ [49,72,73]. Treatment with excess triethyl aluminum (200–400 equiv. vs. Cr) is required for removal of the carbonyl groups, as evidenced by IR spectroscopy and generation of a competent catalyst. The use of non-coordinating anions such as $[B(C_6F_5)_4]^-$ and $\{Al[OC(CF_3)_3]_4\}^-$ rather than $[BF_4]^-$ and $[PF_6]^-$ is necessary for catalytic activity. This strategy for accessing an active trimerization catalyst starting with a Cr^{I} precursor adds support to the proposal that the catalysis occurs via a Cr^{I}–Cr^{III} cycle. Furthermore, it represents an alternative to utilizing MAO as cocatalyst. In efforts to optimize catalytic activity in the absence of MAO, a variety of activators were tested starting from Cr^{III} precursors. Noncoordinating perfluoroborates and fluorinated alkoxymetalates in close-to-stoichiometric amounts have been investigated as cocatalysts in conjunction with excess triethylaluminum. Treatment of a chromium/PNP ligand combination with a mixture of $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$ and excess $AlEt_3$ generates systems active for ethylene oligomerization. While the selectivity for α-olefin in the corresponding Cn fraction is similar to the results from MAO, the productivity and stability of the catalysts is lower and the amount of generated polyethylene is higher. During the course of these experiments it was found that excess $(Ph_3C)[B(C_6F_5)_4]$ leads to PNP ligand degradation resulting in non-selective oligomerization catalysis [51]. Furthermore, scrambling between the boron and aluminum substituents contributes to cocatalyst deactivation. Targeting more stable cocatalysts, fluorinated alkoxymetalates were explored and led to the observation that the nature of the anion has a large effect on the C6/C8 ratio (~25 with $Al(OC_6F_5)_3Et$ and ~0.5 with $\{Al[OC(CF_3)_3]_4\}^-$). This was interpreted as a consequence of the coordinating ability of the counteranion; a more coordinating anion interacts stronger with the metal center (either by coordination or by steric pressure) to make the system more similar (electronically or sterically) to a trimerization catalyst (with coordinating ortho-OMe groups or bulky but non-coordinating ortho-alkyl groups). Consequently, the less coordinating anions are more selective for tetramerization, with $(Ph_3C)\{Al[OC(CF_3)_3]_4\}$ being the most selective due to its stability and weak coordinating abilities. As with olefin polymerization with early metal catalysts, if the interaction between the cationic catalyst and the anion affects catalysis, the solvent can have a significant effect. Indeed using PhCl instead of toluene leads to a more stable and productive Cr(PNP) catalyst [16]. Other chlorinated additives affect catalyst selectivity and productivity as well [24,74]. A related Cr(PNP) catalyst decomposes in toluene by phosphine loss to generate a $[Cr^{I}(\eta^6\text{-arene})_2]^+$ species [75].

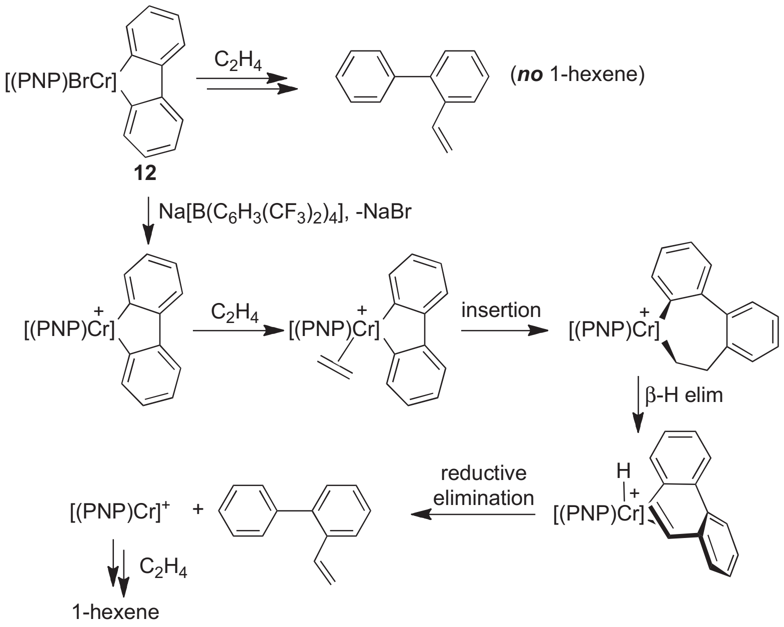
4.2. Oxidation state of active species

4.2.1. Precatalysts

Determining the oxidation states accessed during the selective olefin oligomerization has been an intense area of study. For a mononuclear species, the oxidation states M^n and M^{n+2} have to be accessible to allow for oxidative coupling and reductive eliminations. For chromium, mononuclear mechanisms involving Cr^{II}/Cr^{IV}, Cr^{I}/Cr^{III}, Cr^{III}/Cr^{V} have been proposed [12–14,17,58,59,68–70,76]. Active catalysts have been generated by activation of precursors displaying diverse oxidation states: Cr^{I} in $[Cr(PNP)(CO)_4]^+$, [49,73]. Cr^{II} in $[Cr(PNP)_2ClAlMe_3]^+$ (**40**) and $Cr(SNS)Cl_2$, [58,59]. Cr^{III} in a variety of systems including $Cr(PNP^{O4})Cl_3$ (**11**), $Cr(SNS)Cl_3$ (**19**), and $Cr(NNN)Cl_3$ (**20**) [11,13,62]. Given that aluminum alkyls can lead to oxidation state changes, the nature of the precursor may not be indicative of the active species generated upon treatment with aluminum activators. Hence, better defined systems have been targeted for study.

Chromacycles have been characterized structurally for the oxidation states Cr^{III} and Cr^{VI}, but primarily with ligands that do not support catalytic activity. Cr^{III}-alkanediyl species were isolated with an ancillary cyclopentadienyl ligand; thermolysis led to 1-hexene production from chromacycloheptane and 1-butene from chromacyclopentane. In this system, the chromacyclopentane is significantly less stable thermally than the chromacyclopentane [77]. A Cr^{VI}-xylenediyl moiety was isolated with two imide supporting ligands [76]. With supporting ligands relevant to catalytic oligomerization, a $Cr^{III}(PNP)Br(biphenyldiyl)$ complex (**12**) was isolated and characterized by XRD [12–14]. This complex produces vinylbiphenyl upon treatment with ethylene (Scheme 5). This suggests that some of the organometallic transformations proposed for the catalytic 1-hexene formation are feasible from the Cr^{III} oxidation state. Vinylbiphenyl generation likely involves ethylene coordination to Cr^{III} and insertion into a Cr^{III}–C bond, followed by β-H elimination and reductive elimination (or metal assisted β-H abstraction) to generate a Cr^{I} intermediate. Notably, no 1-hexene formation is observed from this neutral precursor. Halide abstraction followed by treatment with ethylene leads to vinylbiphenyl and catalytic 1-hexene generation. A related precatalyst, $Cr^{III}(PNP)Ph_3$, reacts with ethylene to form phenyl-terminated ethylene oligomers and benzene, but no 1-hexene [17]. 1-Hexene formation is observed upon protonation with $[H(Et_2O)][B(C_6H_3(CF_3)_2)_4]$ and treatment with ethylene (Scheme 6). Interestingly, biphenyl is not generated under these conditions, suggesting that ethylene first inserts into the Cr–Ph bond to then allow for β-H elimination (or abstraction) and reductive elimination to lead to a reduced chromium species. This behavior suggests a mechanism involving Cr^{III} metallacycles and Cr^{I} cationic species. The requirement for a cationic species was proposed to stem from a variety of reasons such as a more electrophilic metal center may be necessary for ethylene coordination and oxidative coupling to generate a new metallacyclopentane, an additional coordination site may be needed for this process, or the low-coordinate neutral chromium(I) species is more likely to deactivate by forming dimeric species via halide bridges [14].

Well-defined single component catalysts are of particular interest for studies related to the oxidation state of the active species. Complexes **18**, **41**, and **43** afford 1-hexene selectively upon treatment with ethylene, without the addition of activators [55,70,71].

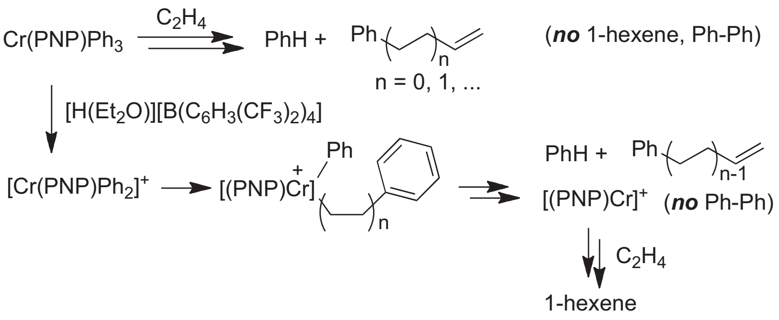


Scheme 5.

The oxidation states of the starting materials are Cr^{II} (**18** and **41**) and Cr^{I} (**43**) again suggesting that different redox cycles (Cr^{I}/Cr^{III} or Cr^{II}/Cr^{IV}) may be supported by different ligands. Even with these well-defined systems, redox chemistry and structural rearrangements could occur before entering the catalytic cycle. Addressing this, a number of studies describe the divergent catalytic reactivity of Cr/Al complexes supported by the same ancillary ligands but with different structures and/or chromium oxidation states [55–57,70,71]. For example, chromium-pyrrolide complexes **41** and **42** display the same oxidation state, Cr^{II}, but have a different number of supporting pyrrolides and aluminum moieties per chromium atom [70]. These chromium complexes lead to different catalytic outcomes upon treatment with ethylene. The trinuclear $CrAl_2$ complex **42** supported by two pyrrolides leads to ultrahigh molecular weight polyethylene, while the tetranuclear Cr_2Al_2 complex **41** performs ethylene trimerization. Importantly, aluminum or pyrrolide additives do not afford different catalytic outcomes of the two species above, indicating that they do not interconvert during catalysis. This observation may lend support to the hypothesis that the oxidation state of the starting material corresponds to species in the catalytic cycle, but computational investigations indicate that, in the presence of ethylene, complex **41** first disproportionates to generate a transient Cr^{I} species [70]. Additional information about the catalytically active species can be obtained from studies of the actual catalytic trials.

4.2.2. Spectroscopic studies under catalytic conditions

Determination of the oxidation state of the resting state of the catalyst was attempted via measurements of the solution magnetic moment using the Evans method, XPS, and EPR studies [62,75,78,79]. In the case of the Cr(NNN) system **20**, magnetic susceptibility measurements were performed on solutions at different points in the preparation of the catalyst and during catalysis [62]. The results ($\mu_{eff} = 3.1–4.1\ \mu_B$) were interpreted to support the presence of mononuclear and dinuclear Cr^{III} species in solution. A system based on tris-2-ethylhexanoatechromium precursor, a bulky monodentate phenol and triethyl aluminum was also investigated by magnetic susceptibility measurements under catalytic conditions [78]. The catalytic behavior was dependent on the nature of the aromatic solvent utilized, with anisole leading to a more productive and selective catalyst than xylene. The magnetic susceptibilities of solutions in the two solvents were different; the one in xylene ($\mu_{eff} = 5.17\ \mu_B$) was proposed to correspond to Cr^{II} and the one in anisole ($\mu_{eff} = 3.61\ \mu_B$) to either low spin Cr^{II} or a mixture of Cr^{II} and Cr^{III} [78]. XPS studies were performed with a chromium-pyrrolide catalyst to correlate the effect of exposure to air with oxidation state and catalytic behavior changes [79]. Samples not exposed to air gave higher productivity for C6 species and, in almost all cases, also higher selectivity for 1-hexene. These catalysts show a larger ratio of Cr^{III}–Cr^{VI} by XPS, hence the Cr^{III} oxidation state was implicated in the production of 1-hexene. EPR studies were performed with the PNP system (**4**) for ethylene tetrameriza-



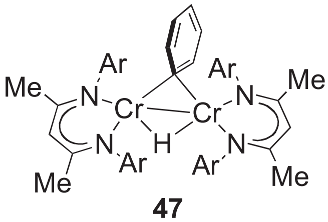
Scheme 6.

tion investigating the effect of Cr^{III} precursor and solvent on the nature of species generated upon activation with MMAO and reaction with ethylene [75]. A Cr^{I}(PNP) was observed by EPR, but this accounted for only a small part of the chromium species in solution. Nevertheless, the signal corresponding to this species broadens upon addition of ethylene, behavior interpreted as an indication of the fluctuation between Cr^{I} and Cr^{III} during catalysis. The authors proposed that the EPR silent species could consist of Cr^{II} complexes or Cr^{I} dimers. A $[Cr^{I}(\eta^6\text{-arene})_2]^+$ species was identified by spectroscopy indicating a route for catalyst deactivation by dissociation of the PNP ligand.

While the above experiments are performed under catalytic conditions, a situation in which the active species is in small concentration and not detectible cannot be discounted. Furthermore conclusions distilled from the oxidation state of the precatalysts suffer from problems derived from oxidation state changes occurring in the activation process. Some of these challenges have been tackled by the isolation and investigation of Cr–Al multinuclear species. Further careful studies regarding the effect of activators on the structure, oxidation state, and catalytic behavior of the active species are necessary. Valuable information about the oxidation states of chromium can be provided by computation. Computational studies suggest a Cr^{II}/Cr^{IV} cycle for the chromium-pyrrolide systems, Cr^{II}/Cr^{IV} and Cr^{I}/Cr^{III} cycles for chromium-dimethoxyethane-carboxylate systems, Cr^{II}/Cr^{IV} cycle for simple chloride ligands, Cr^{I}/Cr^{III} cycle for diphosphine systems based on PNP and **14** [25,80–83]. These studies suggest that the supporting ligand framework can modulate the oxidation states involved in the selective oligomerization of ethylene.

4.3. Chromium spin state

Beyond considerations of metal oxidation state, another aspect of redox catalysis with chromium is the spin state of the metal center. A point of interest is the ability of metal complexes in different spin states to perform various basic organometallic transformations. An example applicable in the context of selective olefin oligomerization is the reductive elimination of a C–H bond from a chromium alkyl hydride. Two isomeric dinuclear complexes of chromium differing by a C–H reductive elimination process have been isolated; one displays a $Cr^{II}_2(\mu\text{-Ph})(\mu\text{-H})$ (**47**) moiety while the other a $Cr^{I}_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-}C_6H_6)$ (**48**) moiety (Fig. 9) [84–86]. The spin states of the two complexes differ, the Cr^{II}_2 complex being S = 0 and the Cr^{I}_2 complex being S = 3. Surprisingly, compound **47** is stable with respect to reductive elimination up to 120 °C. An initial explanation of this behavior invoked the different spin states of the complexes as a factor increasing the kinetic barrier to conversion. Computation suggested that, in fact, the $Cr^{II}_2(\mu\text{-Ph})(\mu\text{-H})$ (**47**) isomer is more stable. Nevertheless, in the context of redox catalysis involving paramagnetic chromium complexes, the potential spin states of the intermediates and their effect on reactivity need to be carefully considered. Given the synthetic challenges represented by the isolation of catalytically relevant species in different oxidation states, this area has benefited from computational investigations [25,80–83,87]. For mechanisms computed with a Cr^{I}/Cr^{III} redox couple, the quartet states were generally calculated to be the most stable. For the Cr^{II}/Cr^{IV} mechanisms, the triplet states were calculated to be the most favorable.



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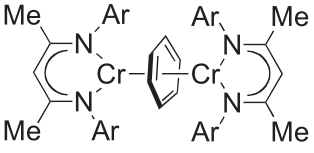

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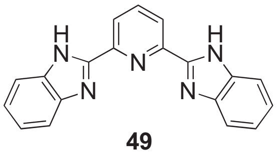
Fig. 9. Complexes investigated in the context of C–H bond reductive elimination.



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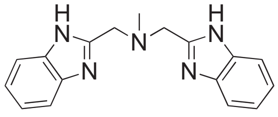

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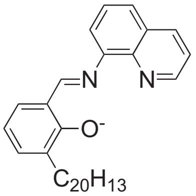

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Fig. 10. Supporting ligands for chromium-catalyzed non-selective ethylene oligomerization by a mechanism involving metallacycles.

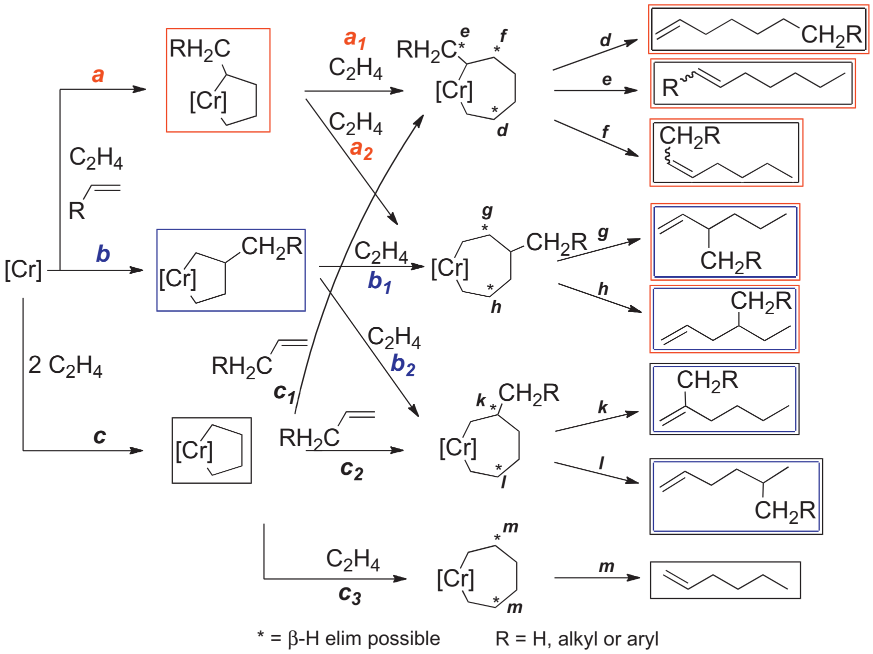
5. Catalysts for non-selective ethylene oligomerization by a metallacyclic mechanism

The ability of the discussed catalysts to effect the selective oligomerization of ethylene has been explained by the mechanism of reaction in those systems, involving metallacyclic intermediates. The relative stability of the 5-, 7-, and 9-member rings with respect to β-H elimination may explain the observed selectivities. In this context, it is of interest to discuss some systems that perform non-selective ethylene oligomerization and that have been studied in detail mechanistically. Chromium complexes displaying tridentate ligands such as **49**, **50** and **51** (Fig. 10) based on nitrogen, oxygen, or carbene donors are efficient catalysts for the linear oligomerization of ethylene [88–91]. These ligands are reminiscent of some PNP, SNS, SNP ligands that support chromium catalyzed selective ethylene trimerization [10,11,58]. Other chromium complexes supported by related, meridionally binding, NNN ligands give nonselective ethylene oligomerization catalysts [92–96]. Complex **49** shows classical Shultz–Flory distribution, while complexes **50** and **51** have more complicated product distributions due to chain transfer to aluminum and competing catalyst differentiated sites, respectively. In all cases, a nonselective distribution of α-olefins is observed. Unexpectedly, mechanistic investigations revealed that the oligomerization of a 1:1 mixture of C_2H_4 and C_2D_4 (*vide infra*) leads to an isotopolog distribution consistent with metallacyclic intermediates. This observation clearly shows that the metallacyclic pathway does not insure the selective formation of specific α-olefins. Questions regarding selectivity remain open. Why, in these systems, are the large metallacycles stable enough to allow for propagation rather than selective oligomerization? This is a problem well suited for computation.

6. Beyond ethylene tri(tetra)merization

6.1. Cotrimerizations

Having access to an expanding toolbox of catalysts for the trimerization and tetramerization of ethylene, an area of interest is the development of catalytic systems for new products derived from this methodology. The ability of a trimerization catalyst to incorporate monomers other than ethylene into the trimer is dependent on the relative rates of olefin oxidative coupling or insertion into the metallacyclopentane. Studies with a Cr-biphenyldiyl(PNP^{O4}) model (**12**) indicate that ethylene inserts 20–400 times faster than α-olefins, depending on the steric bulk



Scheme 7.

of the olefin, and more than 1000 times faster than internal olefins [14]. Hence, with the PNP ligand, the cotrimerization of ethylene with α-olefins was investigated. This process raises interesting questions of selectivity with respect to metallacycle formation and β-H elimination. Considering only the trimers stemming from the cotrimerization of one molecule of α-olefin with two of ethylene, the formation of the metallacyclopentane can involve one molecule of each olefin to give two possible regioisomers (Scheme 7, routes ***a*** and ***b***) or two molecules of ethylene (***c***). The α-olefin could insert into the unsubstituted metallacyclopentane in 1,2-(***c*₂**) or 2,1-fashion (***c*₁**), while ethylene could insert at the either end of the substituted metallacyclopentane (***a*₁** vs. ***a*₂** and ***b*₁** vs. ***b*₂**). These processes can lead to three substituted metallacycloheptane isomers. For each isomer, β-H elimination can occur from either end of the alkanediyl chain (***e***–***m***) to generate seven isomers (not counting *E*–*Z* isomers). Products of interest could be obtained if the selectivity of these processes could be controlled by catalyst design or reaction conditions. Selectivity studies performed with a model Cr-biphenyldiyl(PNP^{O4}) species indicate that α-olefin insertion occurs in a 1,2-fashion and that β-H elimination is favored from the endocyclic positions [14]. Consistent with these experiments, catalytic cotrimerizations of ethylene and propene did not show products stemming from 2,1-insertions of propene into the parent metallacyclopentane or β-H elimination from exocyclic positions. The observed selectivity, however, could be due in part to processes occurring prior to metallacycloheptane formation, such as the formation of metallacyclopentane, which were not addressed by experiments with the model Cr-biphenyldiyl species. In a separate study with a series of PNP-based catalysts, the cotrimerization of ethylene and styrene was investigated [97,98]. The product distribution varies depending on the steric demands of the ancillary ligand, with the bulkier systems favoring the linear vs. branched products. The predominant linear products stem from the 2,1-incorporation of styrene, but the step when styrene is incorporated (metallacyclopentane vs. metallacycloheptane) is not clear.

6.2. *α-Olefin and diene trimerization*

A different strategy to valuable products involves the selective homooligomerization of α-olefins. The trimerization of 1-decene and 1-dodecene with the chromium-triazacyclonone catalyst system (**20**), followed by hydrogenation, has been exploited for the synthesis of lubricants in the C30–C36 range [65]. This approach requires catalysts capable of trimerizing α-olefins, which are very rare [62,99]. As with the cotrimerization of ethylene and α-olefins, multiple isomers can be generated at each step of the mechanism and selective generation of specific products remains a challenge in catalyst design. In a related approach, the trimerization of dienes to linear products has been reported. Chromium catalysts supported by PNP ligands have been investigated for the oligomerization of isoprene [98,100,101]. Both linear and cyclic trimers are obtained, with the linear product being major for most ligands investigated.

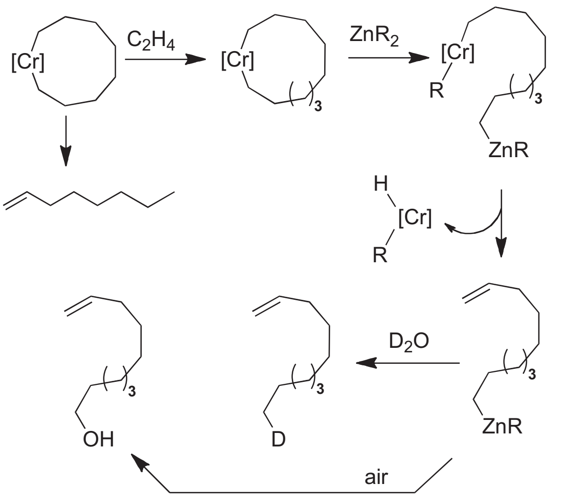
6.3. *Chain transfer and functionalization*

Aiming to expand the repertoire of products available from olefin trimerization, studies have been performed on the use of chain transfer agents during catalysis [102]. Zinc alkyls were used as transmetallating agents in conjunction with the ethylene oligomerization reaction catalyzed by the Cr(PNP) system (**4**) activated with MAO (200 psig C_2H_4, 25 or 45 °C). Under the conditions investigated, the quantity of polymer decreased in favor of C10–C22 oligomers upon adding transmetallating agents. Quenching with D_2O led to the formation of D-end-labeled α-olefins in the C10–C22 fraction, but not in the C_8 fraction. The authors explained this behavior in terms of chain transfer to zinc (Scheme 8) that is competitive with β-H elimination/alkene elimination for higher metallacycles, but not for metallacyclononane. The zinc bound alkyl can then be quenched with D_2O to lead to D-attachment. This result lends promise to the possibility of preparing end-functionalized olefins by this route. In fact, treatment with O_2 leads to the formation of terminal alcohols.

7. Labeling experiments to interrogate the mechanisms of olefin oligomerization

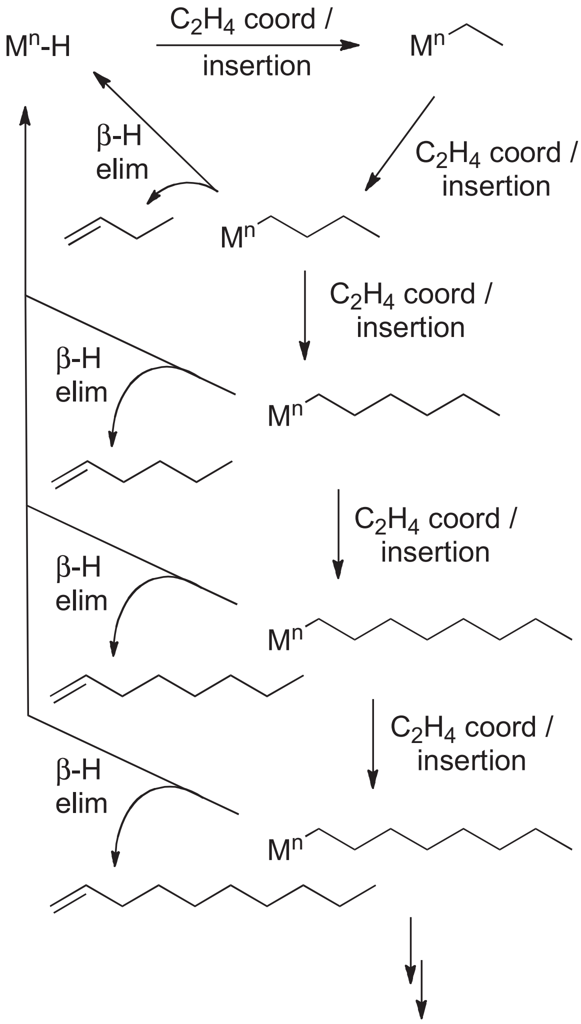
7.1. *General mechanistic aspects*

The oligomerization of olefins in a non-selective fashion is proposed to occur via a Cossee type mechanism involving inter-

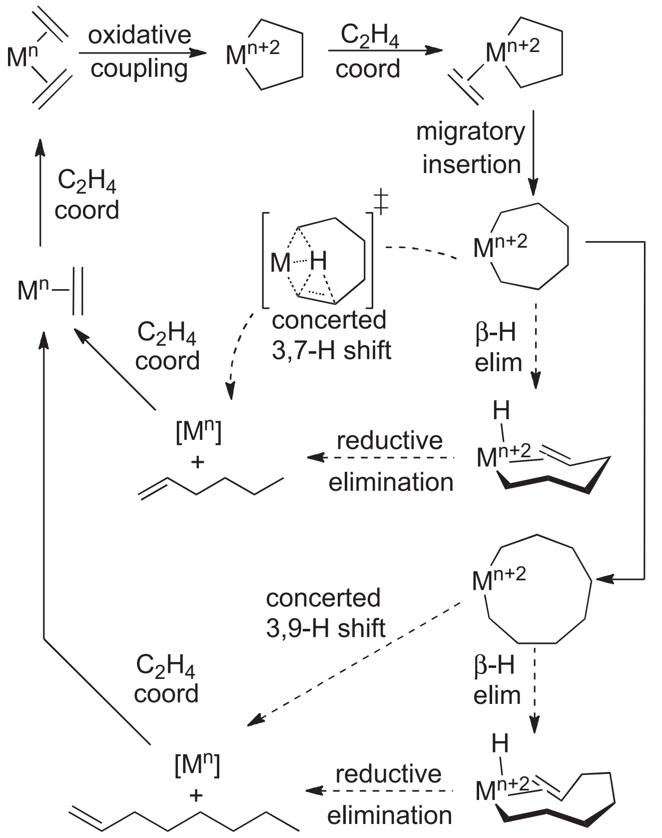


Scheme 8.

mediate linear alkyl chains which, upon β-H elimination, lead to the formation of α-olefins (Scheme 9) [103]. Based on this mechanism it is difficult to reconcile selective formation of single oligomers, rather than a Shultz–Flory distribution with formation of higher homologs [104–107]. Only recently was this mechanism demonstrated experimentally to be inconsistent with the selective formation of 1-hexene, under catalytic conditions [12,14]. The most popular proposed mechanism to account for the high selectivity involves metallacyclic intermediates (Scheme 10). Initial coordination of two equivalents of ethylene to a M^n species followed by oxidative coupling forms a metallacyclopentane of oxidation state M^{n+2}. The transition state for β-hydrogen elimination from the chromacyclopentane leading to 1-butene is expected to be rather strained; hence ring expansion by ethylene insertion dominates. The resulting metallacycloheptane is flexible enough to undergo rapid β-hydrogen elimination, giving a metal-alkenyl-hydride species that reductively eliminates 1-hexene to regenerate M^n and closes the catalytic cycle. In agreement, well characterized chromacyclopentane and chromacycloheptane complexes have been reported; the latter decomposes more readily (at 56 °C compared to 151 °C for the former) and yields 1-hexene [77]. The relative stability of metallacyclopentane vs. metallacycloheptane is also reflected in the rates of platinum(II) metallacycle decomposition: $1.7 \times 10^4\,s^{-1}$ at 60 °C (platinumcycloheptane) vs. $0.53 \times 10^4\,s^{-1}$ at 120 °C (platinumcyclopentane) [108]. It has been suggested, based on computational studies, that the release of 1-hexene from the metallacycloheptane intermediate proceeds via a concerted 3,7-hydrogen shift with formal 2-electron reduction of the metal, without metal hydride intermediates [25,80,81,109–116]. For the formation of 1-octene, the insertion of ethylene into the intermediate chromacycloheptane to extend the ring to a chromacyclononane was proposed to compete, in the more open PNP systems (Fig. 1), with β-H elimination (or 3,7-H-shift) from the chromacycloheptane (Scheme 10).

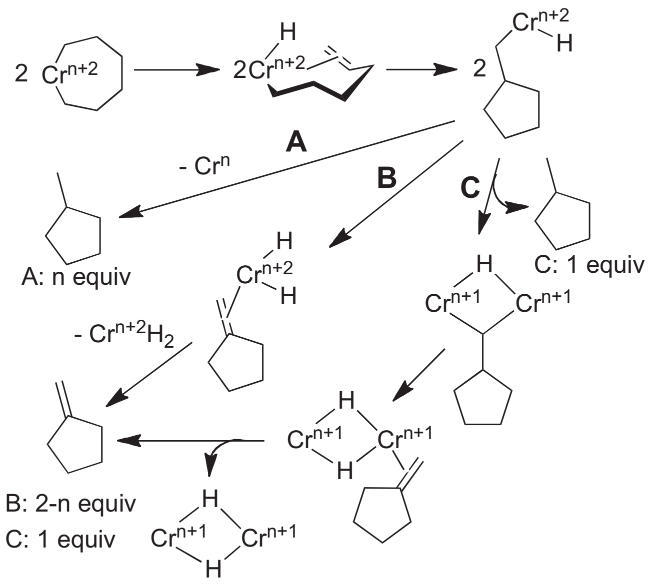


Scheme 9.



Scheme 10.

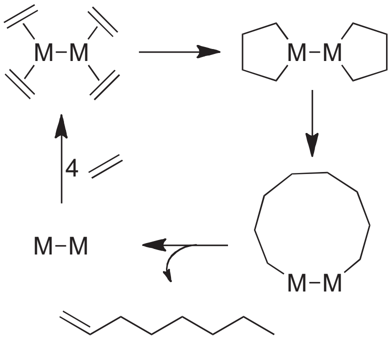
In contrast to computational studies that have indicated that the formation of olefin from metallacyclic intermediates does not involve metal-hydride intermediates, experimental evidence indicating the formation of metal-hydride species has been reported



Scheme 11.

for the Cr(PNP) system for ethylene tetramerization [9,16]. The formation of methylcyclopentane and methylenecyclopentane in a 1:1 ratio was reported in this system. An intermediate chromium-hexenyl-hydride species was proposed to account for the formation of these products (Scheme 11). The pendant olefin inserts into the Cr–C bond instead of the Cr–H bond to generate a chromium-methylenecyclopentane-hydride. This species could perform several transformations. Mechanistic possibilities involving mononuclear reductive elimination to give methylcyclopentane (path A) and β-H elimination (path B) to generate methylenecyclopentane have been proposed. These pathways do not explain the equimolar distribution of products, except for the case when the rates of reductive elimination and β-H elimination are identical; this special case is unlikely given that under a variety of conditions the 1:1 ratio was retained. The lack of effect of a hydrogen atom donor (triphenylmethane) on the ratio products was proposed to disprove a radical mechanism. A binuclear mechanism (path C) was proposed in order to explain the distribution of products. Reductive elimination of one equivalent of methylcyclohexane between two chromium species leads to a dinuclear chromium-alkyl-hydride in a process that reduces each metal center by one electron. Related species have been isolated for Cr^{II} and are stable with respect to reductive elimination [84,117] β-H elimination is proposed to occur instead, to produce one equivalent of methylenecyclohexene.

A recent alternate mechanistic proposal for the formation of 1-octene involves dinuclear chromium complexes (Scheme 12) [54]. This proposal is based on precedent for the involvement of dinuclear chromium complexes in the trimerization of acetylene and on the formation of small amounts of 1-octene upon thermal decomposition of tetralithium tetrabutanediyldichromate [54,118]. In this proposed catalytic cycle (Scheme 12), each metal center of the dinuclear complex supports a metallacyclopentane; reductive elimination of a C–C bond leads to the formation of a 1,2-dimetallacyclodecane that generates 1-octene by β-H elimination followed by reductive elimination. This mechanism avoids an intermediate metallacycloheptane that could lead to 1-hexene generation. Sterically more open PNP frameworks have been documented to support dinuclear complexes via five-member chelates and hence are proposed to be more likely to lead to 1-octene formation via this mechanism than the bulkier systems that lead to 1-hexene [119]. More structural information and characterization data is necessary in order to better understand how the structure of the active species affects the behavior of this catalyst.

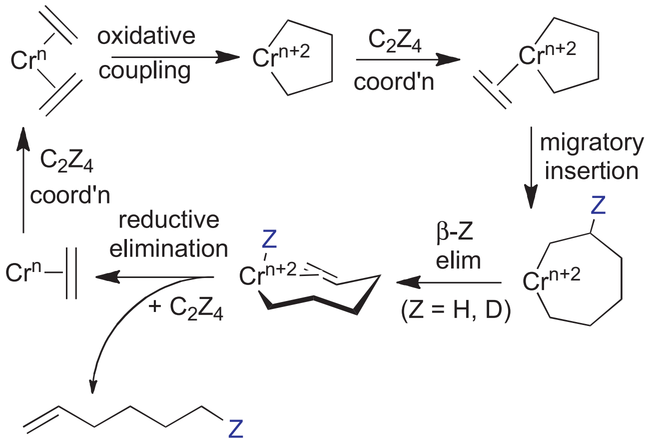


Scheme 12.

The monometallic metallacyclic mechanism provides a rational for the selective generation of 1-hexene in terms of the relative stability of metallacyclic intermediates. Similarly, the bimetallic mechanism provides a rational for the selective production of 1-octene. The metallacyclic mechanism, however, has been invoked for non-selective oligomerization catalysts as well (Fig. 10) [88–90]. Several computational studies have addressed, for monometallic mechanisms, the relative rates of metallacycle growth by ethylene insertion vs. collapse to α-olefin [25,81,87,109–111,113,114]. For the systems investigated, the collapse of metallacycloheptane to generate 1-hexene is, in general, energetically favored vs. ethylene insertion to produce metallacyclononane. The relative energy parameters for these processes depend significantly on the nature of the metal center and the ancillary ligand, indicating that metallacyclononanes and higher metallacycles can be energetically accessible.

7.2. *Reaction kinetics*

To detail the mechanism of selective ethylene trimerization and tetramerization, kinetics studies have been performed on several catalytic systems [6,17,22,24,27,40,53,62,120–123]. Chromium carboxylate and pyrrolide catalysts show second order dependence of 1-hexene yield with respect to ethylene concentration [40,122]. Similarly, the chromium-PNP^{O4} system (**1**, Fig. 1) displays second order dependence of productivity on ethylene pressure. Based on these observations it was proposed that the rate determining step is the oxidative coupling of two ethylene molecules to generate a metallacyclopentane. In contrast, ethylene trimerization catalysts based on chromium-(PNP)N (**10**, Fig. 1) and 1-hexene trimerization catalysts based on chromium-triazacyclohexane show first order dependence on monomer concentration. Titanium catalysts also display first order dependence on ethylene concentration [27,123]. This was interpreted to indicate that ethylene insertion into metallacyclopentane to generate the metallacycloheptane intermediate is the rate determining step. A different behavior is characteristic of variants of the chromium-PNP catalyst (**4**, Fig. 1) for the trimerization and tetramerization of ethylene; these show non-integer overall reaction order in ethylene (1.7 and 1.6 in two different studies) [120,121]. In one case the non-integer overall order was explained as a combination of two competing mechanisms leading to the two oligomers. 1-Hexene shows close to first (1.29 ± 0.15) order dependence while 1-octene second order dependence on ethylene concentration [121]. An alternate explanation of non-integer reaction orders for ethylene invokes rate determining metallacyclopentane formation with competitive incorporation of α-olefin products leading to a decrease in the expected second order dependence on ethylene concentration [120]. These results show that the kinetics of ethylene oligomerization are dependent on the nature of the catalyst and,

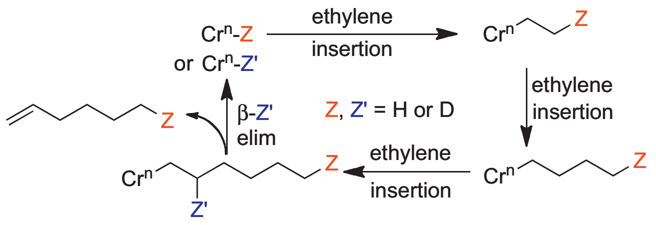


Expected distribution:

$C_6D_{12} + C_6D_8H_4 + C_6D_4H_8 + C_6H_{12}$

1 : 3 : 3 : 1

Scheme 13.



Expected distribution:

C_6H_{12}	**1**	$C_6D_7H_5$	**2**
C_6DH_{11}	**1**	$C_6D_8H_4$	**3**
$C_6D_3H_9$	**1**	$C_6D_9H_3$	**1**
$C_6D_4H_8$	**3**	$C_6D_{11}H$	**1**
$C_6D_5H_7$	**2**	C_6D_{12}	**1**

Scheme 14.

in addition, on parameters such as solvent, activator, temperature, and ligand to metal ratio. Kinetics measurements also reveal that the catalysts studied decompose over time. Catalyst decomposition is first order for chromium-PNP^{O4}, chromium-PNP, and chromium-triazacyclononane, and second order for titanium catalysts [17,62,120,123]. It is important to note that interpretation of the above kinetics experiments without knowledge of the resting state of the catalyst is difficult. With chromium complexes being paramagnetic, it is challenging to determine the nature of intermediates during catalysis. Further mechanistic insight requires detailed characterization of catalytically relevant species and study of their kinetic behavior with ethylene. Given the experimental challenges, aspects of the catalytic cycle have been studied by computation. Metallacycle growth was computed as rate determining for chromium pyrrolide and titanium catalysts [80,110,113,114]. In a different study of the titanium catalyst, ring opening of metallacycloheptane was computed as rate determining [111]. An analogous result was obtained for a hypothetical hafnium catalyst, but this study claims that for the titanium system, the rate determining step is ethylene insertion into metallacyclopentane [114].

7.3. Crossover experiments with C_2H_4 and C_2D_4

Utilization of mixtures of C_2H_4 and C_2D_4 was introduced as an experimental method for distinguishing between the mechanism involving metallacyclic intermediates and the Cosseee-type mechanism for the oligomerization of ethylene [12,14]. This test was first applied to the ethylene trimerization reaction, but subsequent studies have used it for the selective dimerization and tetramerization of ethylene, and for non-selective oligomerizations [9,12,14,88–90,124,125]. Several preparations of the chromium-PNP^{O4} catalyst system were utilized in the initial experiments with mixtures of C_2H_4 and C_2D_4. The formation of four 1-hexene isotopologs, C_6H_{12}, $C_6D_4H_8$, $C_6D_8H_4$, and C_6D_{12} in a 1:3:3:1 ratio was observed in all cases suggesting that the same mechanism occurs under different conditions tested [12,14].

Analysis of the two proposed mechanisms reveals differences in the expected distribution of 1-hexene isotopologs. The metallacyclic mechanism can generate intermediates with both hydrogen and deuterium in the β-position (Scheme 13). Hence β-Z (Z = H or D, blue) elimination would move either a hydrogen or a deuterium from the alkyl chain to the chromium center. However, in the subsequent reductive elimination step the transferred Z atom would be returned to the same alkenyl chain. The net effect involves no hydrogen/deuterium scrambling between different molecules of 1-hexene. The alternative mechanism, concerted 3,7-H shift with loss of 1-hexene, effects the same transformation. As a consequence of either mechanism, only isotopologs bearing even numbers of deuteriums and hydrogens are expected from the metallacyclic mechanism. Taking into account the possible routes to access each of the isotopologs, we find that the distribution corresponds to the binomial expansion coefficients—for the trimerization reaction the calculated ratio is 1:3:3:1. Hence, the metallacyclic mechanism is consistent with the experimental results for the chromium-PNP^{O4} catalyst.

The Cossee type mechanism also involves hydride or deuteride intermediates. Upon ethylene insertion the initial Z (Z = H or D) moves from the metal center, to the end of the linear alkyl chain (Scheme 14). Two further ethylene insertions ensue, but unlike the metallacyclic mechanism, the atom (Z′, Z′ = H or D) abstracted in the metal-hexyl species to give 1-hexene is not the same as the initially metal bound one (Z). As a consequence, scrambling of deuterium and hydrogen between $[C_2Y_4]_3$ (Y = H, D) units may occur. Hence, isotopologs bearing odd numbers of hydrogens and deuteriums are expected for the Cossee-type mechanism. The various possibilities to access 1-hexene isotopologs by this mechanism lead to a much broader distribution—ten isotopologs can be formed theoretically, with six of them containing odd numbers of hydrogens and deuteriums. This is not observed experimentally for the chromium-PNP^{O4} catalyst, result inconsistent with the Cossee-type mechanism. The difference in the outcome of these crossover experiments between the proposed mechanisms is graphically compelling when the simulated mass spectra of the isotopologs of 1-hexene for the two different cases are plotted together (Fig. 11). For accuracy, the natural abundance of ^{13}C and ^2H, and the isotopic purity of C_2D_4 should be taken into account.

Similar studies have been performed on a variety of ethylene oligomerization systems. A study of the chromium-PNP catalyst based on ligand **4** leading to a mixture of ethylene trimer and tetramer revealed that the distribution of isotopologs in both oligomers is consistent with a metallacyclic mechanims [9]. The ratio of C_2H_4 and C_2D_4 does not have to be 1:1 for this mechanistic

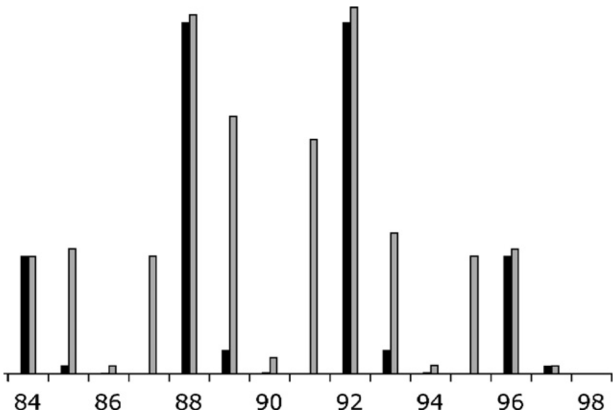
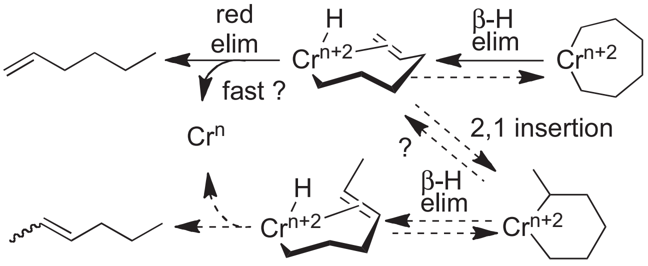
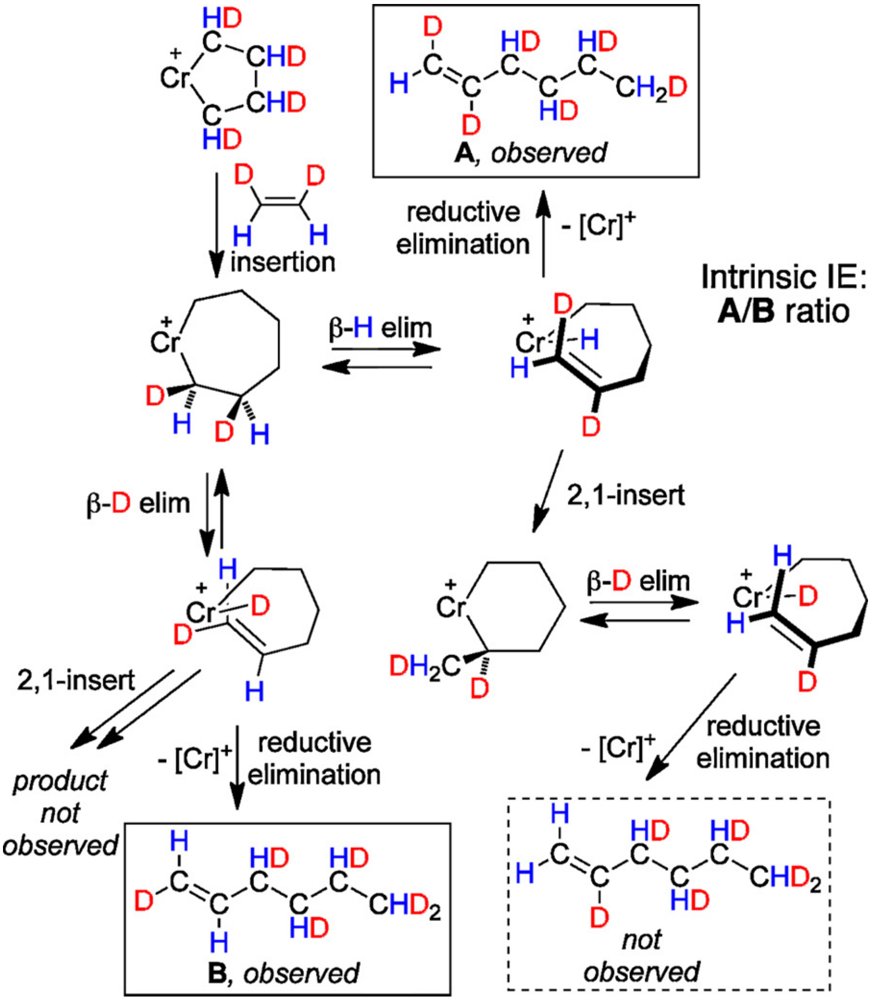


Fig. 11. Black—simulated isotopolog distribution in 1-hexene for a mechanism involving metallacyclic intermediates. Gray—simulated isotopolog distribution for a Cossee-type mechanism. All intensities are normalized to same value at $m/z = 84$. Adapted from Ref. [14].



Scheme 15.

test, but the predicted isotopolog distribution needs to be adjusted accordingly. A tungsten-based ethylene dimerization catalyst investigated with the crossover experiment shows a distribution consistent with the Cossee mechanism [124,125]. For chromium-based non-selective catalysts (**49**–**51**), analysis of the isotopolog distribution is consistent with a metallacyclic mechanism [88–91]. Investigations of non-selective ethylene oligomerizations catalyzed by Co and Fe 2,6-bis(imino)pyridine complexes and by the SHOP catalyst, $Ni(Ph_2PCH_2COO)(PPh_3)(Ph)$ [126], show an isotopolog distribution consistent with the Cossee mechanism [14,90]. The catalytic systems leading to a mixture of oligomers reveal an interesting effect: the higher molecular weight fractions show a higher incorporation of the heavy isotopolog (C_2D_4) [9,14,90]. For the catalytic system generating 1-hexene and 1-octene, the proposed explanation involved a secondary isotope effect for the formation of metallacyclopentane by oxidative coupling [9]. A subsequent proposal explains this effect for both metallacyclic growth and Cossee mechanisms [14,90]. When multiple oligomers are formed, there is a branching point for each intermediate metal-alkyl species (Scheme 10): ethylene insertion can occur to increase the carbon number or β-H elimination (followed by reductive elimination) can occur to generate the corresponding α-olefin. While ethylene insertion is expected to have a small, secondary



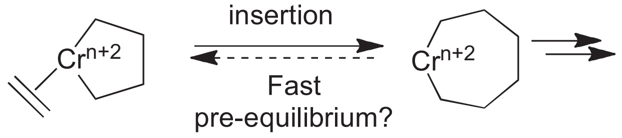
Scheme 16.

isotope effect, the β-H elimination will have a larger, primary isotope effect; the latter will be the main contributor to the isotope effects on the isotopolog distributions. Every time the last inserted ethylene is C_2D_4, the metal alkyl will have a slower rate of β-Z elimination leading to a higher probability for insertion of another monomer with the net effect that higher olefins carry more deuterons. This isotope effect on the isotopolog distribution cannot occur if only one oligomer is formed, as in the selective formation of 1-hexene because there are no branching points with respect to β-H elimination vs. additional ethylene insertion (metallacyclopentane is slow with respect to β-H elimination). Simulations of isotopolog distributions need to take into account isotope effects for accuracy [88,90]. For the Cossee mechanism, ethylene can insert into M–H or M–D bonds and deinsert from the resulting M-ethyl species before ethylene insertion into the M-ethyl bond. If this process is fast compared to oligomerization, then complete H/D scrambling into ethylene is expected. This results in isotopolog mixtures described by the formula $C_{2n}H_mD_{(4n-m)}$ (n = degree of polymerization and m = 0, 1,. . ., 4n) with a binomial distribution [90]. The studies discussed above highlight the versatility of the crossover experiment for interrogating the mechanism of olefin oligomerization.

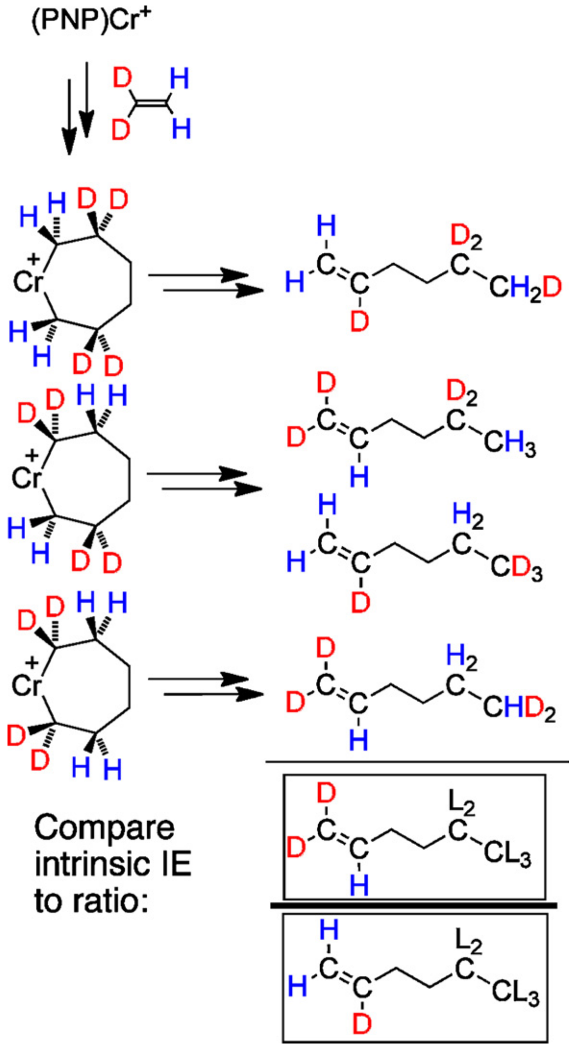
7.4. Testing for reversible olefin reinsertion: reactions with 1,2-dideuteroethylene

Trimerization of partially deuterated ethylene can provide further insight into the mechanism of formation of 1-hexene and answer questions regarding the steps that control the selectivity for α-olefin vs. internal olefin [12,14]. The competition between 2,1-insertion vs. reductive elimination from the intermediate metal-alkenyl-hydride complex (Scheme 15) can be investigated by performing the trimerization of *cis*- or *trans*-ethylene-d_2. The cationic biphenyldiyl chromium precursor (**12**) was utilized for these experiments. The products were analyzed by ^{1}H NMR spectroscopy to reveal two types of isotopomers with respect to the substituents on the olefin: two hydrogens or two deuteriums at the 1 and 2 positions of 1-hexene, both with a [=CDH] terminal methylene group. Due to the cis stereochemistry for both insertion of ethylene into chromiun-carbon bond of the metallacyclopentane and β-H elimination (or the 3,7-H shift alternative), upon conversion of ethylene to 1-hexene the geometry around the double bond is inverted (Scheme 16). For example, *cis*-ethylene-d_2 leads to the formation of 1-hexene that has the two deuteriums or hydrogens trans to each other. The ratio of the two observed isotopomers can be measured by integrating the ^{1}H NMR spectra and was determined to range from 3.1(1) to 4.1(1) depending on the temperature and the ethylene isotopomer used.

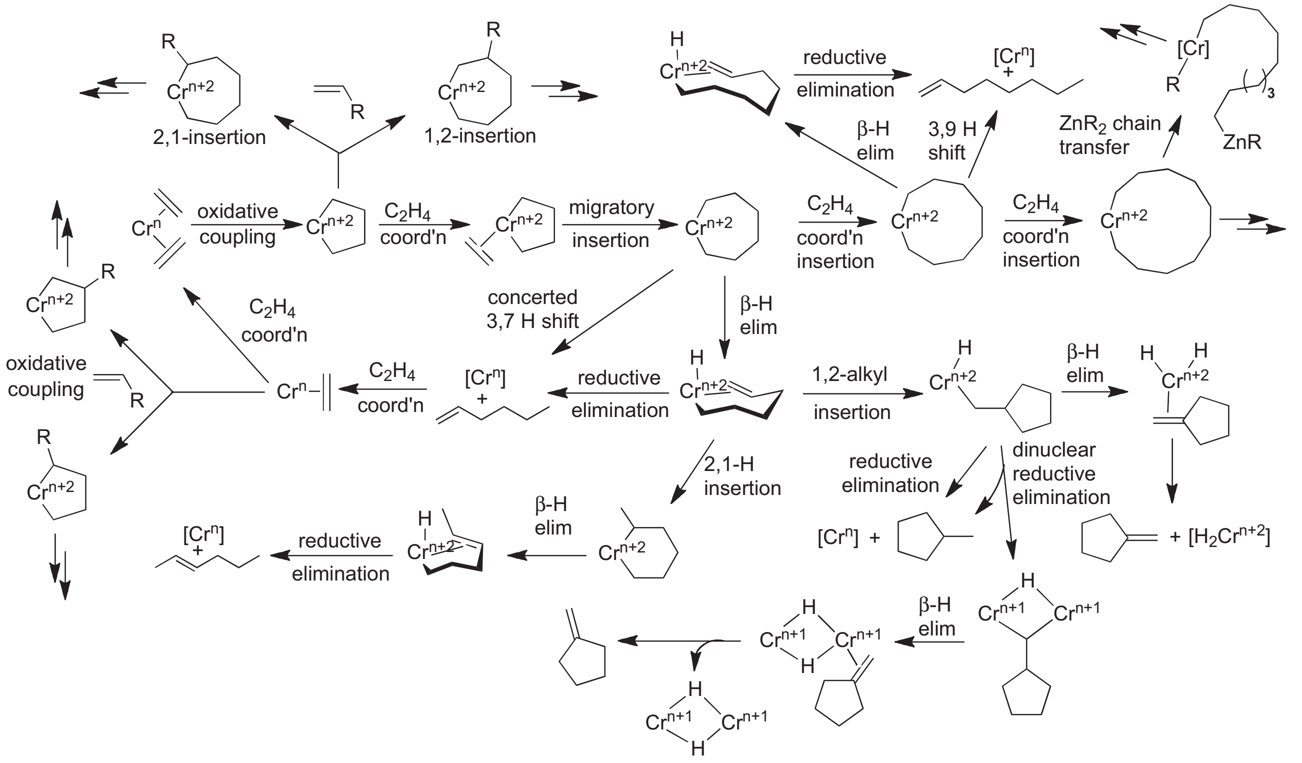
Analysis of the metallacyclic mechanism in the context of the trimerization of 1,2-ethylene-d_2 indicates that the steps leading to the formation of the chromacycloheptane should not be affected significantly compared to non-deuterated ethylene—only small, secondary isotope effects are expected. The chromacycloheptane intermediate so generated has one hydrogen and one deuterium on each carbon in the ring when it reaches the branching point between β-H and β-D eliminations (Scheme 15). These two pathways are completely analogous; only one will be described in detail. Upon β-H elimination, a chromium-alkenyl-hydride species is formed which can undergo reductive elimination to generate a 1-hexene isotopomer with a [=CDH] end group. Alternatively, the chromium-alkenyl-hydride species could perform a 2,1 reinsertion into the [Cr–H] bond to lead to the formation of a methyl-chromacyclohexane. From this intermediate, β-D elimination from the exo position generates a chromium-alkenyl-hydride species. Reductive elimination leads to a 1-hexene isotopomer with a [=CH_2] end group. Experimentally, only 1-hexene isotopomers with a [=CDH] end groups are observed, without any detectable isotopomers with [=CH_2] or [=CD_2] end groups. The ratio of the two observed isotopomers corresponds to the intrinsic isotope effect for the conversion of metallacycloheptane to 1-hexene; this isotope effect can be a composite of elementary step isotope effects depending on the processes involved in this transformation [14]. The results of the trimerization of 1,2-ethylene-d_2 in the chromium PNP system indicate that the reductive elimination from chromium-alkenyl-hydride (or the concerted 3,7-H transfer) is (are) fast compared to 2,1 reinsertion into the [Cr–H] bond (Scheme 14). This has important consequences on the purity of the resulting trimerization product. If 2,1-H insertion were a competitive process then the resulting chromacyclohexane could conceivably undergo β-H elimination from intracyclic CH bonds, followed by reductive elimination, leading to the formation of 2-hexene, an undesired byproduct.



Scheme 17.



Scheme 18.



Scheme 19.

An alternative explanation for the selective formation of the observed isotopomers of 1-hexene in the trimerization of 1,2-ethylene-d_2 involves concerted 3,7-H (or D) shifts instead of stepwise β-H (or D) elimination followed by reductive elimination (Scheme 10) [80,109–111,113,114,116]. If a true chromium hydride is not formed, as in the 3,7-H shift mechanism, then no selectivity issues remain relative to olefin reinsertion. A number of computational studies have indicated that the 3,7-H shift is more energetically favorable than a stepwise mechanism for titanium, tantalum, and chromium ethylene trimerization systems [80,109–111,113–116]. Catalytic systems closely related to the PNP^{O4} system generate byproducts that likely arise via intermediate β-H elimination steps, however [7,9,16]. The isotope labeling experiments using *cis*- or *trans*-ethylene-d_2 cannot distinguish between the 3,7-H (or D) shifts and stepwise β-H (or D) elimination followed by reductive elimination.

Interestingly, the PNP^{O4} framework with at least one *ortho*-ether group or four bulky *ortho*-alkyl substituents is capable of rendering the reaction very selective for the formation of 1-hexene in the C6 fraction, with essentially no isomerization coming from chain walking or insertions of the pendant olefin. Two explanations were proposed [12,14]. One possibility invokes the steric bulk of the ligand favoring the transition state for 3,7-H shift over β-H elimination. Conversely, if β-H elimination does occur, reductive elimination is very fast compared to isomerization. Again, the sterics of the ligand (or the ability of pendant donors to compete for coordination sites) would slow the coordination of the pendant olefin and the hydride reinsertion.

7.5. Testing for reversibility of metallacycle formation: reactions with 1,1-dideuteroethylene

The trimerization of *gem*-ethylene-d_2 has been used to investigate the reversibility of the formation of chromacycloheptane [12,14]. In the context of the metallacyclic mechanism, the reverse process would involve an elimination of ethylene to generate a chromacyclopentane–ethylene species (Scheme 17). Upon utilizing the cationic biphenyldiyl chromium precursor (**12**) as catalyst for these experiments, the formation of two types of olefin isotopomers of 1-hexene was observed, depending on the terminal methylene group, [=CD_2] or [=CH_2]. The integrals corresponding to the peaks for the vinyllic protons were used to determine the ratio between the two possible double bond isotopomers. Three chromacycloheptane isotopomers are expected from *gem*-ethylene-d_2 (Scheme 18). If the formation of the chromacycloheptane is reversible and fast compared to subsequent steps, then the various chromacyloheptane isotopomers can interconvert rapidly; this will lead to a distribution of 1-hexene isotopomers according to the intrinsic isotope effect for the conversion of chromacycloheptane to 1-hexene which is measurable in the trimerization of *cis*- or *trans*-ethylene-d_2. A ratio of product isotopomers different from the intrinsic IE indicates that the mechanism does not involve a reversible formation of metallacycloheptane. In the Cr(PNP^{O4}) system, the observed isotope effect for the trimerization of *gem*-ethylene-d_2 (IE = 1.3(1)) was indicative of irreversible metallacycloheptane formation. While this labeling experiment could be used to determine the symmetry of the two end of the metallacycloheptane with respect to β-H elimination (or 3,7-H shift), the IE in the Cr(PNP^{O4}) system is not conclusive [12,14].

8. Summary and outlook

The field of selective olefin oligomerization has developed tremendously since selective ethylene trimerization was reported more than four decades ago. A combination of studies involving new ligand design, organometallic synthesis, structural characterizations, isotope labeling, activator optimization, and computational studies have provided access to catalysts of excellent selectivity and productivity, and have afforded detailed mechanistic information. Isotope labeling experiments are consistent with a mechanism involving metallacyclic intermediates and do not support a Cossee mechanism. Even considering only metallacyclic intermediates, potential reaction pathways lead to a very complex mechanistic picture (Scheme 19) with many possible products. Aspects related to the ability of intermediates to take different mechanistic branches have been investigated. For instance, a metallacycloheptane could lead to 1-hexene via 3,7-H shift or β-H elimination followed by reductive elimination. These two processes compete with additional ethylene insertion to lead to a metallacyclononane. Additionally, chain transfer could occur (not shown) in the presence of appropriate chain transfer agents. In the presence of in situ generated or added α-olefins, the formation of substituted metallacycles is possible, further complicating the distribution of products. For any generated metal-hydride-alkenyls, in addition to reductive elimination, several reaction pathways involving insertions can lead to a variety of products. Products resulting from many of the above processes have been observed. Given the complexity of these reactions, the selectivity observed for some of the reported catalysts is impressive. Determining the structure activity relationship for these catalysts has been a very active area of research.

With a diversity of catalysts for selective ethylene oligomerization available, a research direction apparent in several recent reports is to apply this methodology to the synthesis of other useful products. Potential valuable products include cotrimers of ethylene with other olefins, homotrimers of α-olefins, and functionalized alkanes and alkenes. Some of these processes require the development of novel catalysts selective for the specific product of interest. Improvement of catalyst performance with respect to life-time, activity and selectivity, all important for commercial applications, has been an area of interest. The effect of supporting ligand, solvent and activator on catalyst life-time and activity have already been studied in several systems. Catalysts that are self-activating or use only small amounts of activator have also been studied given the potential advantages for commercial applications. Determining the nature of the active catalyst is an area of continued interest as well. Considering the significant advances over the last decade in understanding the effect of catalyst structure on the outcome of catalysis, the design of catalysts suitable of specific applications remains a stimulating and rich area of research. Designing appropriate mechanistic test experiments and using computation to answer questions regarding mechanistic aspects of selective olefin oligomerization have complemented advances in catalysis and are expected to continue to provide valuable support for new catalyst development and investigation.

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Note: After the submission of this manuscript a review that covers processes for the production of 1-octene, including the selective tetramerization of ethylene, appeared in press [127].

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