



1-hexenes & 1-octenes Industrial Catalysis for Polymerization: A Brief Literature Review

Connor Atkinson*

*Department of Science, University of Leeds, United Kingdom.

Abstract

1-hexenes and 1-octenes are in growing demand, for the production of LLDPE and LDPE. Selective 1-hexene and 1-octene production is assessed via the catalyst/ligand design of Bis(imino) pyridine-chromium(III) chloride and chromium-bis(diarylphosphino)amine catalyst systems. 1-butene, 1-hexene, 1-octene and Polyethylene yields are reported and compared. Proposing the relative stability of 5-, 7-, and 9-member rings and the relative rates of competing processes such as alkene insertion or β -H elimination, control selectivity, with catalyst selection and their conditions having a considerable effect on this. Changing catalyst conditions is even shown to switch catalyst selectivity.

Keywords: Ethene, 1-hexene, 1-octene, catalysis, Mechanism.

1. Introduction

1-alkenes in the 1-butene to 1-octadecene range, are normally intermediates during the manufacture of polymers, synthetic lubricants and other industrial hydrocarbons, seen in figure 1.¹ Preparation of Low-density polyethylene (LDPE) and Linear low-density polyethylene (LLDPE), typically utilise 1-hexene or 1-octene as these comonomers produce industrially desirable polyethylene products with decent density and molecular weight distributions.²⁻⁶ 1-butene to 1-octadecene comonomer selection results in good polymer backbone branching so the polymer chains are prevented from packing together tightly, lowering polymer density. 1-hexene and 1-octene comonomer's produce superior LLDPE, increasing the polymers impact and tear strength.

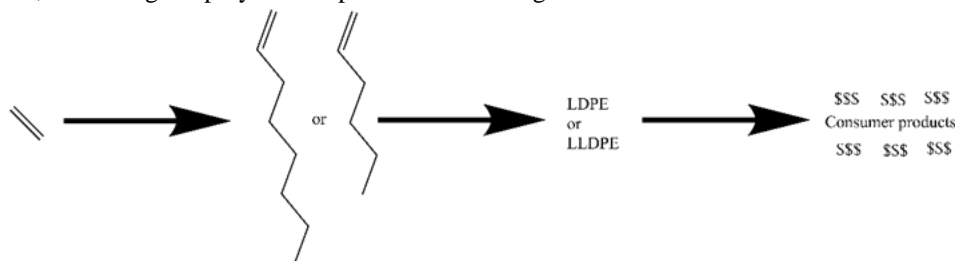


Figure 1: Ethene to consumer products steps, showing ethene to 1-alkene to polyethylene before finally being sold as consumer products.

As 1-hexene and 1-octene are superior comonomers during LLDPE and LDPE production, their demand has grown markedly. Substantial amounts of 1-Hexene currently being produced are used in polyethylene manufacture.⁴ Sasol,



Chevron Phillips, INEOS and Shell are currently the top producers of 1-hexene and 1-octene.¹ Some well known industrial examples of ethene oligomerization catalysts are nickel-based SHOP catalyst and Phillips catalyst, however both lack ideal 1-hexene or 1-octene selectivity.⁴ Catalysts capable of 1-hexene or 1-octene production with industrial selectivity and activity are thus in high demand. Bis(imino) pyridine-chromium(III) chloride and chromium-bis(diarylphosphino)amine complexes both show good selectivity for 1-hexene and 1-octene as well as some selectivity for 1-butene and polyethylene at respectable activity, basic structures shown in figure 2.

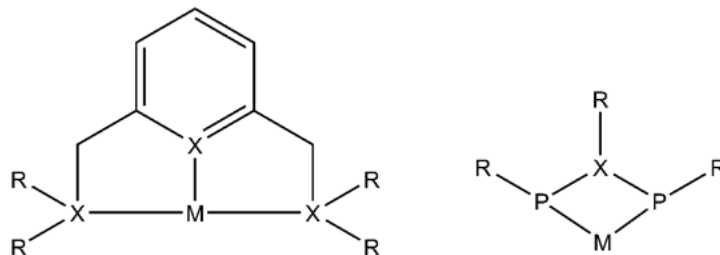


Figure 2: The basic skeletal structure of Bis(imino) pyridine-chromium(III) chloride, left, and chromium-bis(diarylphosphino)amine, right, complexes, when M is a transition metal, X is a donor atom and R is a functional group.

Selective 1-alkene production has been reported utilising transition metals titanium and tantalum but chromium is frequently reported as the most selective.⁷ Typically, catalyst systems utilise NNN pincer ligands with various substituents on the N donor atoms. More versatile ligands have also been reported employing S, N, P and C donor atoms in a diverse array such as SNS, NNN or PCP and functional groups typically alternate steric bulk, electron donation or withdrawing nature. The metal and ligand's electronic and steric effects, dictate catalyst selectivity and activity. Selective ethylene oligomerization has been shown to be more complicated than just catalyst selection however and selectivity is dependent on temperature, catalyst, activator, solvent, and ligand to metal ratio.^{1,5,8,9} Thus, chromium complexes with different ligands are screened for selective 1-alkene synthesis under various conditions. Chevron-Phillips being among the first to commercially implement chromiumpyrrolide catalyst.⁶ Generally, the simple and most widely accepted ethylene oligomerization mechanism, involves metallacyclic intermediates.^{2,5,8} Seen in figure 3.

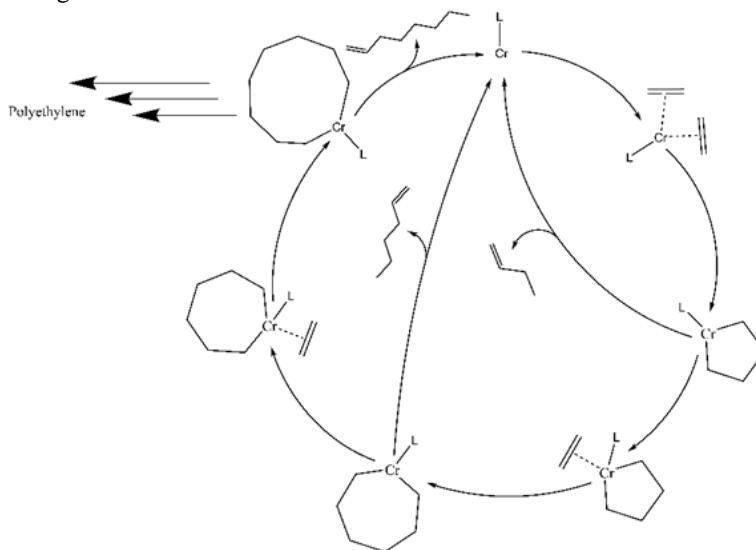


Figure 3: General simple mechanism for ethylene oligomerization, when L represents Ligand. The aim of this report is to assess the catalyst/ligand design of Bis(imino) pyridine-chromium(III) chloride and chromium-bis(diarylphosphino)amine catalyst systems as possible solutions to 1-hexenes and 1-octenes growing demand, for LLDPE and LDPE production.



2. Results and Discussion

Although most ethylene oligomerisation produces a mixture of 1-butene, 1-hexene, 1-octene and Polyethylene, Chromium catalyst systems show some of the highest selectivity, depending on the complex ligand substituents and its conditions. Ligand system for catalyst 1 showing one of the highest Butene selectivity's at >98 mol%, predominantly producing 1-Butene in ~99 mol%.⁹ Ligand system for catalyst 2 showing one of the highest Hexene selectivity's at 93 mol%, predominantly producing 1-Hexene in 99.8 mol%.⁴ Ligand system for catalyst 3 showing one of the highest Octene selectivity's at 72.7 mol%, predominantly producing 1-Octene in 98 mol%.⁵ Ligand system for catalyst 4 showing one of the lowest Polyethylene molecular weight distributions of 1.29.¹⁰ All catalysts seen in figure 4. The exact relationships between ligand functional groups, pressure, temperature, time and co-catalyst are extremely complicated and varied for each ligand, making it difficult to conduct any exact analysis however a few selectivity trends have generally been deduced.

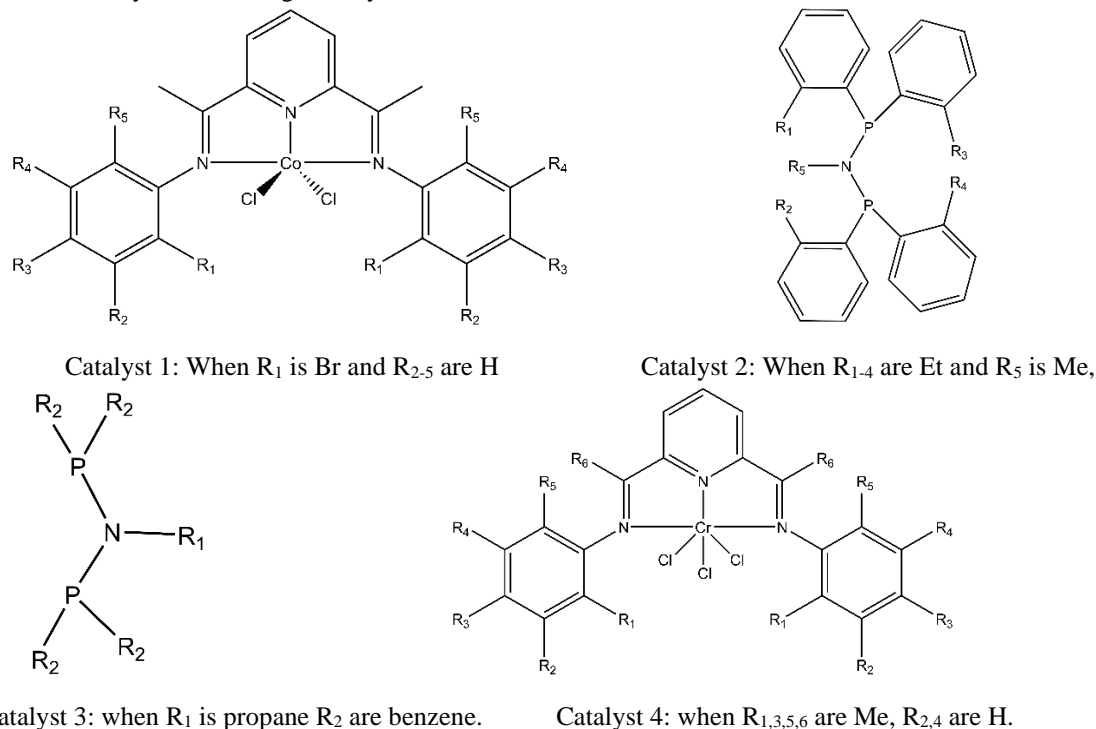


Figure 4: Catalysts 1-4 chemical structure.

1-Butene has mostly been selectively produced utilising NNN pincer complexes, the exact mechanism isn't well understood as it isn't as well reported as 1-hexene or 1-octene. Generally, ortho and para halogen substituted cobalt(II) complexes catalysts 1, 5 and 6 and mono-ortho alkyl substituted chromium(II) complexes catalysts 79, selectively produce 1-Butene.^{9,11} All catalysts seen in figure 5.

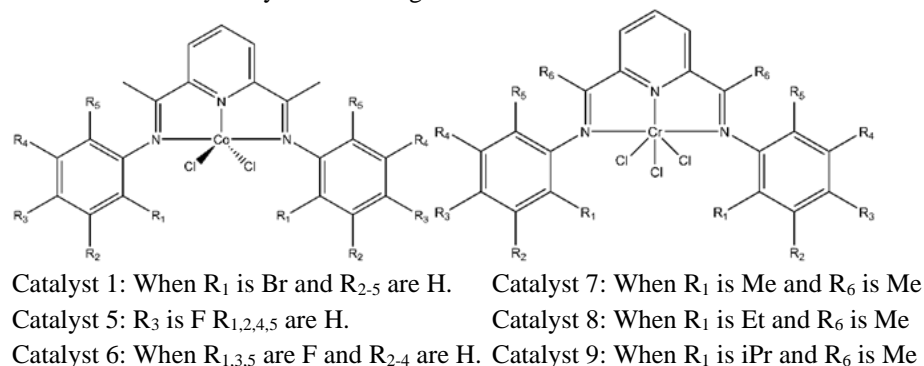


Figure 5: Catalysts 1, 5-9 chemical structure



1-Hexene is very well reported as being selectively produced utilising many chromium complexes and has been extensively studied. Generally, Bulky ortho substituted chromium(III) complexes catalysts 10-12 and ortho donating groups catalyst 13, increase 1-Hexene selectivity.^{2,3} All catalysts seen in figure 6.

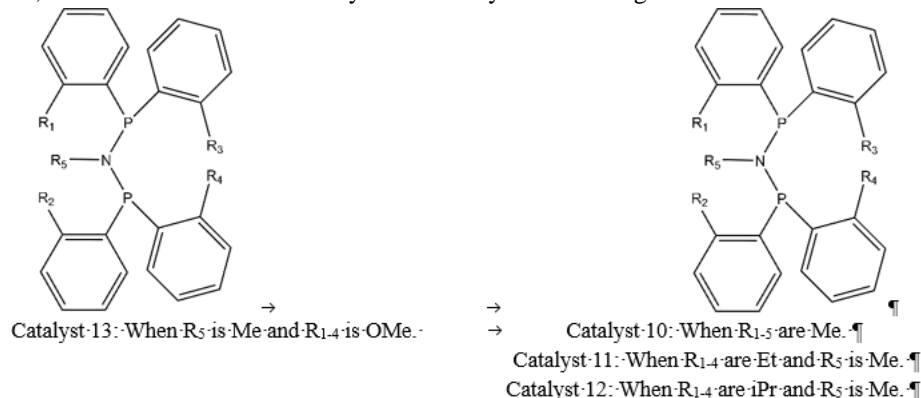


Figure 6: Catalysts 10-13 chemical structure

1-Octene is again very well reported as being selectively produced utilising many chromium complexes and has been extensively studied in the literature but slightly less so than 1-Hexene. Generally, altering co-catalyst catalyst 3 or increasing pressure and temperature catalyst 14 in addition to reducing the steric bulk/charge chromium(III) complexes 15, 16 will increase 1-Octene selectivity.^{2,5,12} All catalysts seen in figure 7.

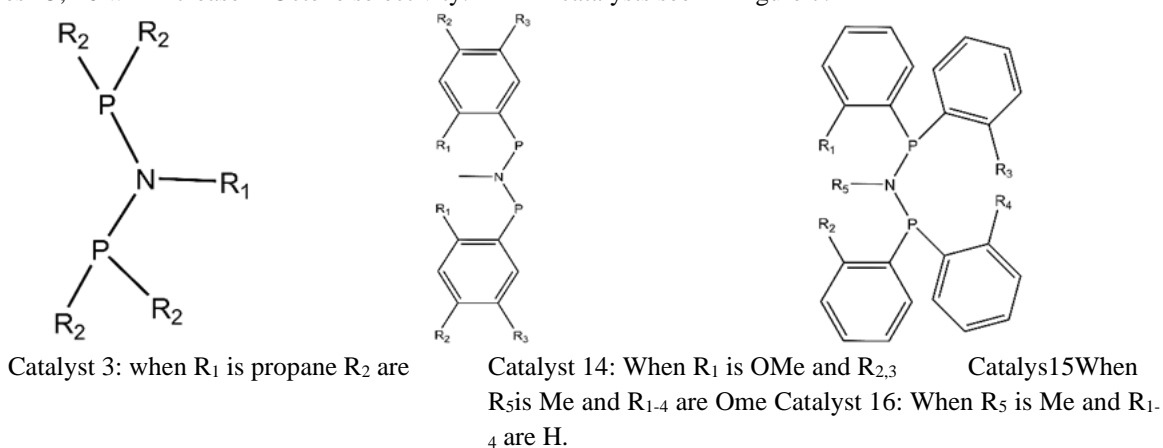


Figure 7: Catalysts 3, 14-16 chemical structure.

Polyethylene selective formation is somewhat well reported for NNN pincer chromium complexes. One of the highest activity and high molecular weight selective catalysts is ortho methyl substituted chromium(III) complex catalyst 4.^{9,10} It has also been indicated that comonomer polymerisation to branched waxes can be achieved complex 17 but most often long chain polyethylene is formed.¹¹ Polymerisation is also indicated to be cocatalyst sensitive complex 3.¹³ All catalysts seen in figure 8.

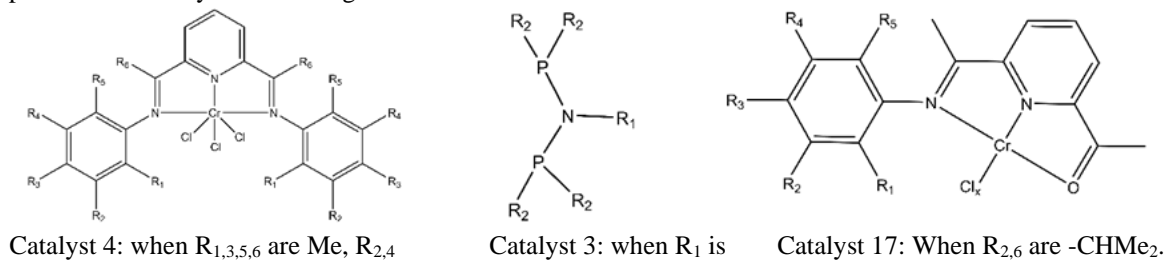


Figure 8: Catalysts 3, 4, 17 chemical structure

All selective ethylene oligomerization catalysts are dependent on cocatalyst selection, $\text{Al}(\text{OC}_6\text{F}_5)_3$ showing the highest 1-Hexene selectivity ~89.9 %, $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ with the highest 1-Octene selectivity ~72.7 % and $[\text{Ph}_3\text{C}][\text{CB}_{11}\text{H}_6\text{Br}_6]$ having the highest Polyethylene selectivity 45.9 %.¹³ Varying the cocatalyst ratio can have a profound effect on catalyst performance, further demonstrating the remarkable influence cocatalyst selection has over the catalyst system.

Obviously, the exact relationships between functional groups, pressure, temperature and co-catalyst are extremely complicated making exact mechanistic analysis and comparison limited. However, generally most suggested mechanisms involve the relative stability of 5-, 7-, and 9-member rings as well as the relative rates of competing processes such as alkene insertion or β -H elimination.⁶ It's proposed, two ethene undergoing oxidative coupling at the metal active site forming a metallacyclopentane, before either β -hydrogen elimination to 1-butene or ring expansion by ethylene insertion to form metallacycloheptane. Metallacycloheptane can then either undergo β -hydrogen elimination, leading to 1-hexene or ring expansion by ethylene insertion to form metallacyclononane, again either undergoing β -hydrogen elimination to 1-octene or further expanding.⁶ Further ring expansion by repeated ethylene insertion to form long chain metallacyclic intermediates can also occur past this point.

Thus, this general mechanism can mostly explain the trends across each catalyst system. Shorter 1-alkenes form selectively when β -hydrogen elimination is favoured, with steric bulk around the catalytic centre constraining the ring into a more favourable conformation for β -hydride transfer and electron donating substituents resulting in competitive coordination slowing the co-ordination and insertion of ethylene into the metallacycle.^{2,3} Longer 1-alkenes form selectively when ethylene insertion is favoured, increased pressure and certain cocatalysts favouring ethylene insertion for ring growth to selective ring length.^{5,6}

Although an obvious oversimplification, kinetic studies support this theory as mostly correct. Suggesting, upon each addition a new intermediate metal-alkyl species tipping point occurs where, ethylene insertion or beta-H elimination can occur.⁶ Trimerization mechanistic studies of 1,2-ethylene- D_2 indicate that reductive elimination is fast compared to 2,1-reinsertion, explaining why 1-alkene forms over 2-alkene. Observing a Shultz-Flory distribution, when there's no preference for β -H elimination. A comprehensive ethylene oligomerization scheme has also been proposed, seen in figure 9, involving additional ethylene insertions, hydride/alkyl reinsertion and R-olefin incorporation.

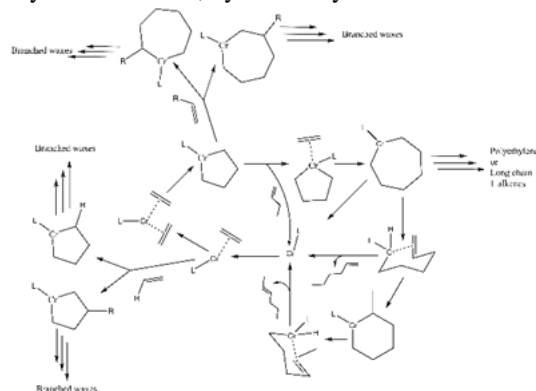


Figure 9: Comprehensive ethylene oligomerization scheme, showing most reported alternative processes. More recently research has focused on switching the catalyst selectivity by changing the systems conditions, catalyst seen in figure 9. Switching from ethylene trimerization to tetramerization has been illustrated by altering co-catalyst or pressure.⁸ MMAO favouring formation of 1-Octene and AlMe_3 favouring the formation of 1-Hexene. Theorised to result from competing mono- and bi-ethene insertion pathways, both having very similar energy barriers with only a calculated difference of $\Delta\Delta G = +0.1 \text{ kcal mol}^{-1}$, it seems feasible bis-ethene insertion pathway becomes dominant with elevated ethene pressures or altered co-catalyst.



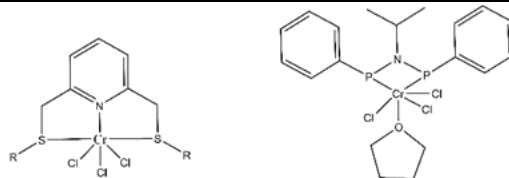


Figure 10: Catalyst capable of switching selectivity with conditions, left, ethylene trimerization to polymerization and, right, ethylene trimerization to tetramerization.

Switching from ethylene trimerization to polymerization has also been illustrated by increasing pressure, catalyst seen in figure 10.¹ Theorising, under increased pressure 1-Hexene release is disfavoured over further ring growth and formation of polyethylene. Given reports of comonomer branched wax formation, further investigation might develop a one pot LLDPE synthesis only changing system conditions. Although, branched 1-alkene insertion is ~20 times energetically disfavoured, supported by most reports forming linear Polyethylene, making this unlikely or also forming unwanted side products.^{6,7,10,11}

Conclusion

Bis(imino) pyridine-chromium(III) chloride and chromium-bis(diaryldiethylphosphino)amine catalysts 1-butene, 1-hexene, 1-octene and polyethylene selectivity and activity have been assessed. Finding that generally, catalyst selection and their conditions have considerable effects on selectivity and activity. 1-butene, 1-hexene, 1-octene and Polyethylene all reported in decent yields. Although, the exact relationships between ligand functional groups, pressure, temperature, time and co-catalyst are extremely complicated and varied for each catalyst, a few selectivity trends have generally been deduced. Mechanisms propose the relative stability of 5-, 7-, and 9-member rings and the relative rates of competing processes such as alkene insertion or β -H elimination, control selectivity. Shorter 1-alkenes form selectively when β -hydrogen elimination is favoured, via steric bulk or electron donating substituents around the catalytic centre and longer 1-alkenes form selectively when ethylene insertion is favoured via increased pressure or certain cocatalysts. Changing catalyst conditions is shown to switch catalyst selectivity. Theorised to result from competing pathways having similar energy barriers, each becoming dominant under a different condition. However as branched 1-alkene insertion is ~20 times energetically disfavoured, one pot LLDPE synthesis seems unlikely, supported by most reports forming linear Polyethylene. Bis(imino) pyridine-chromium(III) chloride and chromium-bis(diaryldiethylphosphino)amine catalysts have however been indicated as possible solutions to 1-hexenes and 1-octenes growing demand, for LLDPE and LDPE production.

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