Chapter 1

Introduction

1.1 IMPORTANCE OF CATALYSIS

The global chemical industry of today is driven by catalysis to such an extent that one cannot underestimate the importance of catalytic processes to the wealth creation of any country. For example, it has been estimated that around 20% of the entire US Gross National Product is generated through the use of catalytic processes. These are instrumental in fields that include, but are not limited to, the production of fuels, petrochemicals, pharmaceuticals, polymers and agrichemicals, as well as environmentally favourable technologies such as catalytic converters [1].

1.2 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Within catalytic research there are two main different types of catalytic processes that are utilised and investigated, namely homogeneous and heterogeneous catalysis.

In homogeneous catalysis the reactions occur at metal centres and the metal complex catalysts, promoters, reagents and products are all soluble in the reaction medium. Conversely, heterogeneous catalytic reactions occur on a surface with many metal centres and the reagents (normally in the liquid or gas phase) are led over or through the catalyst, which in fact aids the separation of products from the reaction process [2].

Both processes have various advantages and disadvantages depending on what product or process is required. For instance, it has been said that the first response of an industrialist is to heterogenise a catalyst since this leads to a potentially simpler process, but that the academic often makes the case for the homogeneous catalyst since it is potentially easier to study and is more easily modified [1]. This is of course to some extent a generalisation as many industrial catalytic processes are in fact homogeneous, but is remains a fact that to a large degree these are easier to study than their heterogeneous counterparts. This particular study is based on homogeneity as the potential catalytic reactions involved in this project are of a homogeneous nature.

1.3 CATALYSIS AND TRANSITION METALS

Transition metals and homogeneous catalysis go hand in hand. This is due to certain favourable properties that transition metals possess [2]:

1. Bonding ability – Ability to form both sigma and pi bonds which is an essential factor in imparting catalytic properties to the transition metals and their complexes.
2. Extensive choice of ligands – Transition metals readily form linkages with the majority of other elements in the periodic table and with almost any organic molecule. It is this property that results in transition metals having such rich coordination chemistry relevant to their role as catalysts.
3. Ligand effects – The ability of transition metal catalysts to accommodate both participative and non-participative ligands within their coordination sphere offers us the possibility of being able to direct the course of the reaction between participative ligands by modifying the structural/electronic properties of the non–participative ligands.
4. Variability of oxidation states – Having access to a wide range of oxidation states helps transition metals to form complexes with a wide range of other elements and compounds. More important than access is the ability to interchange readily between oxidation states during the course of a catalytic cycle.
5. Variability of coordination number – The dissociation of ligands to create vacant coordination sites is associated with changes in the molecular structure of the catalyst.

1.4 CATALYTIC STEPS

All catalytic processes proceed via a number of interlinked steps [1]:

1. activation of the metal centre or generation of the active catalyst
2. movement of the reactants to the active centre and their binding and activation
3. making and breaking of the reactant bonds to generate new intermediate species
4. liberation of these intermediate species as products, with the return of the catalyst to a state where it is ready to begin the cycle again.

Incorporated within these standard catalytic steps are a number of key reactions. Each catalytic process makes use of some, and at times all, of these reactions:

1. Ligand substitution
2. Oxidative addition
3. Migratory insertion
4. Nucleophilic attack
5. Reductive elimination
6. β–elimination
7. α–elimination

1.5 OVERVIEW OF CATALYTIC DESIGN

Before detailing and discussing specific catalytic processes, it is important for one to appreciate that the study of any catalyst is driven by a number of key elements than can be traced back to a specific market need. This is illustrated in the Figure 1.1.

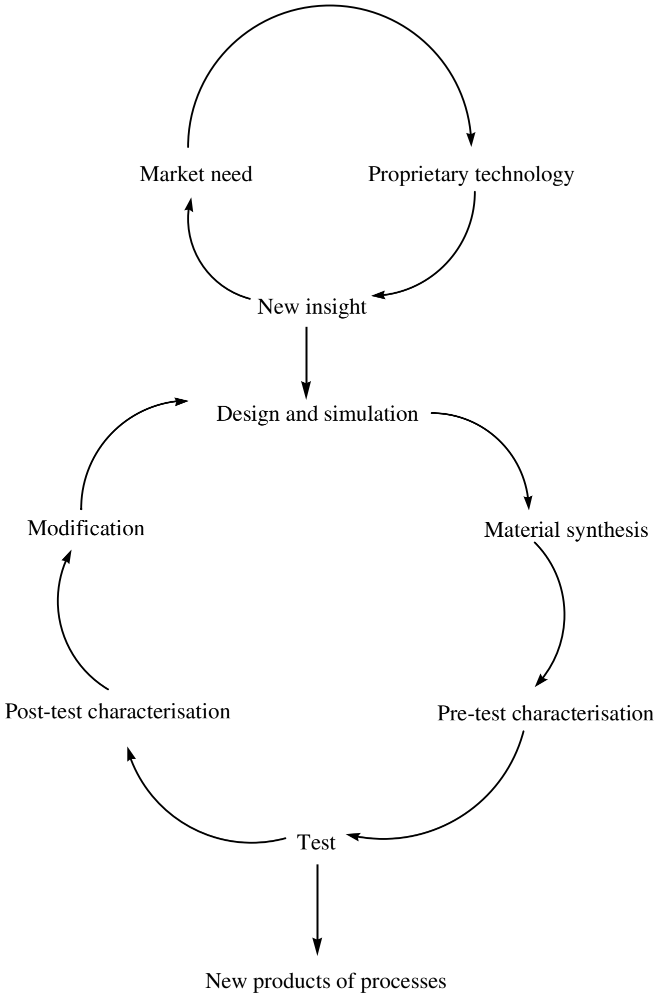


Figure 1.1 **Typical key steps in the study of many catalytic systems [3]**

Prime examples of where these steps would have been considered are given in the following section which provides a summary of the chemistry that has led to the fundamental catalytic precursor investigations undertaken in this study.

1.6 ETHYLENE OLIGOMERISATIONS

Selective trimerisation and tetramerisation of ethylene are the preferred on-purpose routes to the formation of the LAOs, namely 1–hexene and 1–octene respectively. They are useful intermediates in the production of co–polymers, detergents, synthetic lubricants and plasticiser alcohols [4].

1.6.1 1–HEXENE

It is widely agreed that the formation of both 1–hexene and 1–octene takes place via reactive metallacycles. Figure 1.2 shows the formation of 1-hexene [5]; the formation of 1–octene will be discussed with Figure 1.9. The formation of a five–membered metal ring system (metallocyclopentane) is achieved via the coordination of two ethene molecules, followed by oxidative coupling. Coordination of a further ethene molecule, along with olefin insertion, leads to a metallacycloheptane system. At this stage β–hydrogen elimination and then reductive elimination lead to the production of 1–hexene [5].

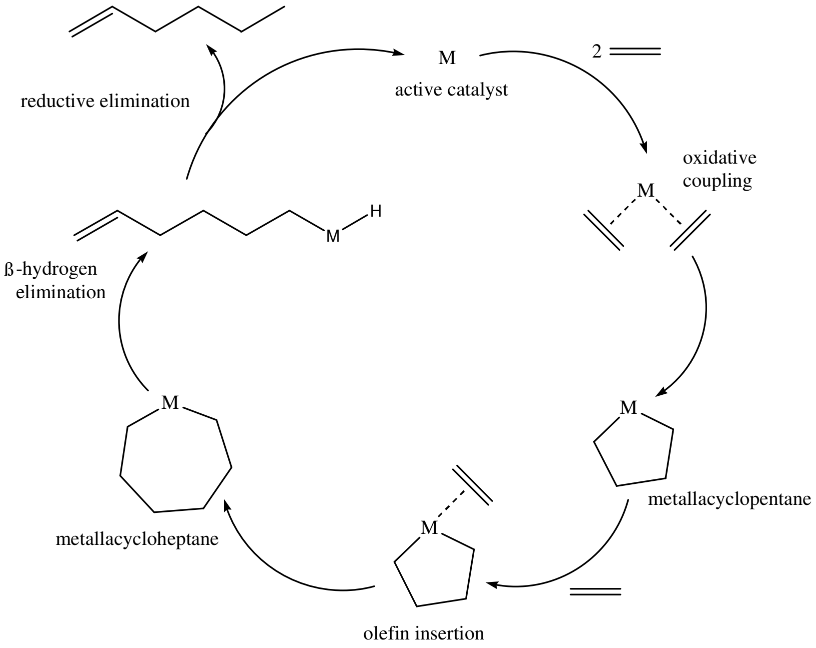


Figure 1.2 **Formation of 1-hexene via a metallacycle**

The first commercially productive trimerisation system was created in the late 1980s; this was the Phillips petroleum catalyst system based on chromium pyrrolyl compounds [6, 7]. However, it must be noted that this work was based on earlier research carried out by Manyik [8, 9].

Since the success of the Phillips system, a great deal of research has gone into modifying the pre–catalytic compounds and the catalytic conditions (i.e. activators, pressure, temperature, etc). While of course varying the catalytic conditions plays a significant role in optimising the production of 1–hexene and 1–octene, this can be done only once a good catalytic precursor has been designed.

Variations in the pre–catalytic compounds can be achieved by varying both the metal centre and the coordinated ligands. The search for metals other than chromium (Phillips system) revolved around environmental concerns, as well as the aim of enhancing catalytic performance. The metals studied included zirconium [10, 11], vanadium [12], tantalum [13, 14] and titanium [15, 16]. However, due to a combination of low activity, high costs and other practical problems, these metals have not been as successful as chromium [4]. The ligands studied included pyrrolyl derivatives with common steric and electronic properties.

The following discussion gives a brief insight into some of the major core ligand frameworks that have evolved in the search for more active and selective ethylene catalytic systems. Although not specifically mentioned, the frameworks have included various substituents with different steric and electronic properties. In 1997 the Tosoh Corporation developed a catalyst based on chromium and maleimidyl ligands. [17]. However, the 1–hexene selectivity was 12 to 15% lower than that of the Phillips catalyst and therefore not an economically viable option. Other similar ligands over the years have included cyclopentadienyl [18, 19], boratabenzenyl [20] and aryloxide [21, 22, 23, 24] ligands, all with varying degrees of success. Although these catalysts were noteworthy equivalents to the Phillips system, their lower selectivity towards 1-hexene made them less desirable from an economic viewpoint. Further ligand development began to focus on multidentate heteroatomic ligands, namely bidentate and tridentate ligands associated with nitrogen, phosphorous, sulphur and mixtures thereof.

With this in mind an advance worthy of mention was the Kohn system (Figure 1.3) which was originally developed as a homogeneous analogue of the Phillips CrO_3/SiO_2 polymerisation catalyst [25]. It entailed a tridentate nitrogen–based donor ligand (N–alkyl triazocyclohexane) that complexed with $[CrCl_3(thf)_3]$ to yield 1–hexene (as well as higher olefins). The selectivity towards 1–hexene under certain conditions was impressive, with >90% conversion. [26]. In fact this system was also used in the selective trimerisation of 1–decene and 1–dodecene [27].

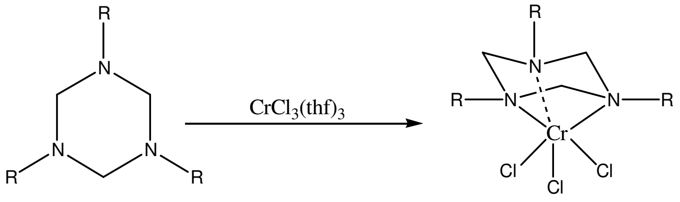


Figure 1.3 **The Kohn catalyst**

The Wass system (Figure 1.4) was built on the tridentate theme of Kohn but incorporated a combination of both nitrogen and phosphorous donor atoms in the ligand. More specifically, the system was based on bis(diarylphosphino)amine ligands coordinated with pendant methoxy groups that were thought to stabilise the coordinatively unsaturated intermediates proposed during the catalytic cycle, and were crucial to obtaining active systems [28]. This linked with work carried out by Bercaw and co–workers in which PNP ligands with ortho–methoxyaryl and ortho–thiomethoxy substituents were investigated [29, 30]. The selectivity of the Wass system was around 90%.

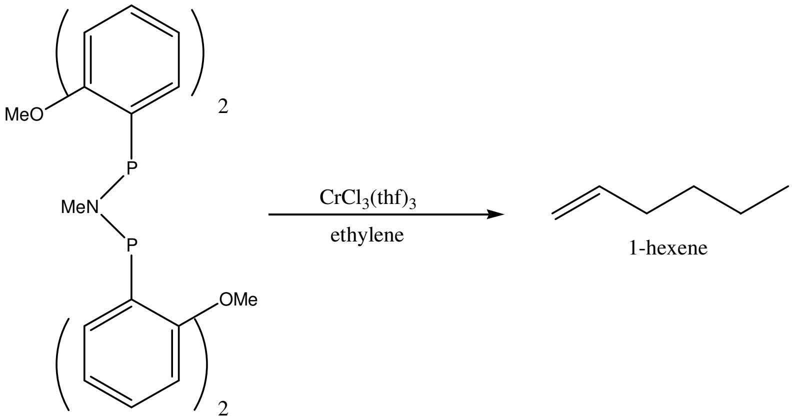


Figure 1.4 **The Wass catalyst**

In 2003 McGuinness and co–workers varied the Wass ligand system, as illustrated in Figure 1.5, and obtained a highly active system that was selective to 1–hexene. Of particular interest was that a crystal structure was obtained of the catalytic precursor and an octahedral geometry with a *mer* arrangement of ligands was seen [31]. Also to be noted is that, compared with the Wass system, it was more selective to 1–hexene but less active and stable.

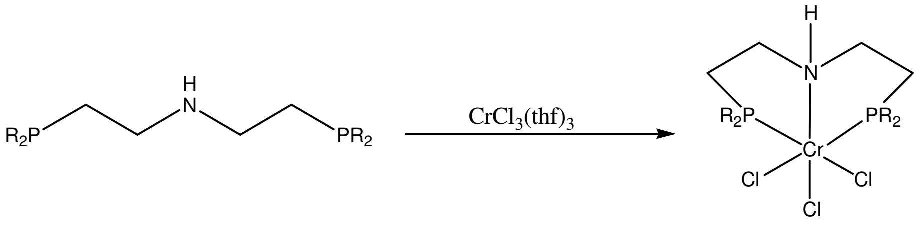


Figure 1.5 **Variation of the Wass catalyst by McGuinness [31]**

Although the PNP tridentate catalyst was highly selective towards 1–hexene, there were certain drawbacks. The toxicity of phosphines, their sensitivity to oxidation and the high cost of secondary alkyl phosphine precursors all contributed to the search for other catalysts that possessed the positive attributes of PNP but without the drawbacks. As a result the analogous SNS tridentate system, using both sulphur- and nitrogen-containing ligands came about [32].

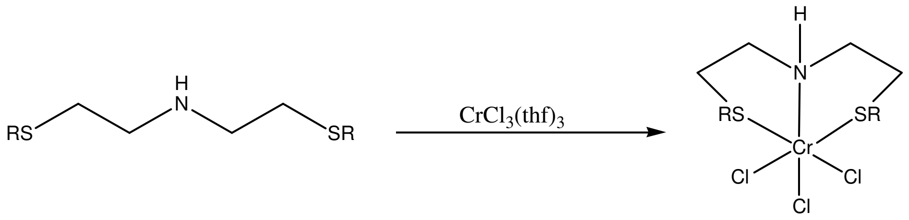


Figure 1.6 **Formation of the SNS complex**

Its attractiveness lay in its low cost, ease of synthesis and similar donor properties to PNP, while maintaining high activity and 1–hexene selectivity.

Due to the success of both the PNP and SNS systems, it was logical then to develop mixed-donor ligands which include SPS, PSP and PPP combinations. Also varied was the length of the N–S spacer to give asymmetrical SNS ligands. However, results have shown that these manipulations did not give the same high levels of activity or selectivity towards 1–hexene formation [33].

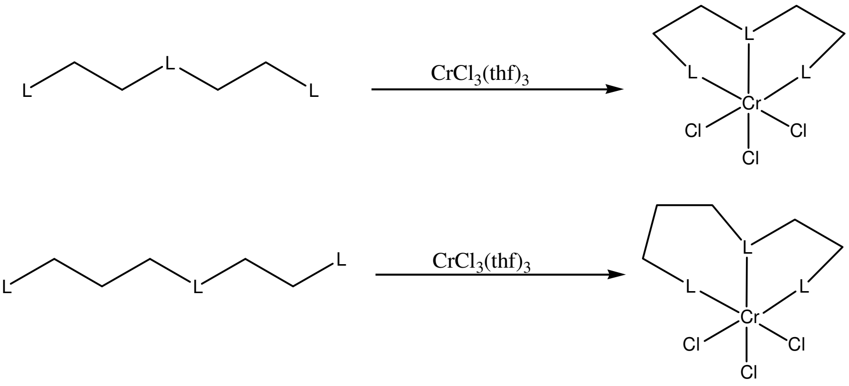


Figure 1.7 **Variation in spacer length of tridentate ligands**

1.6.2 1-OCTENE

All of the above systems have to a greater or lesser extent been useful as ethylene trimerisation catalysts. However, although the production of 1–octene via tetramerisation was also desirable, it had long been thought that this would be improbable as the metallocycle depicted in Figure 1.2 would have to extend to a nine–membered ring. This was said to be unlikely as the further ethylene insertion to give the metallanonane would compete with 1-hexene elimination. However, this was indeed achieved by the South African chemical company SASOL with essentially a modified bis(diarylphosphinoamine) Wass-type catalyst [34].

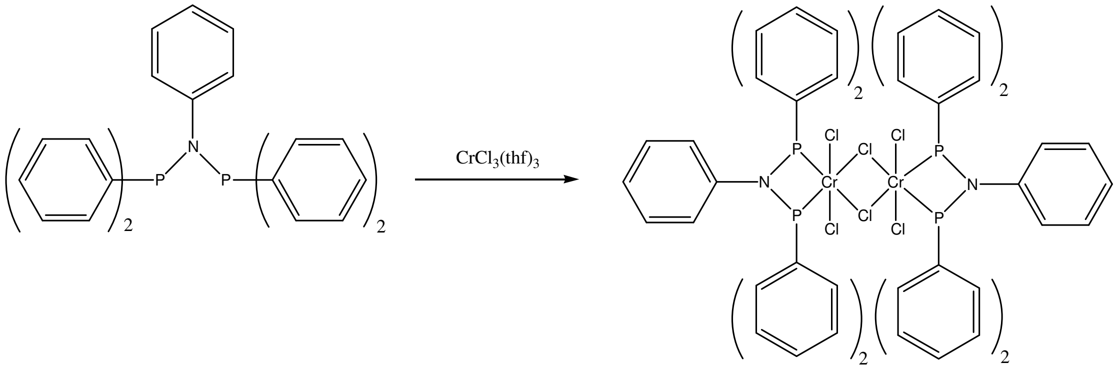


Figure 1.8 **The first tetramerisation catalyst**

As can be seen from Figure 1.8, this system was found to be based on a dimeric form for the active catalyst. As a result of the success of this catalyst, the metallacycle was studied in depth and it is now suggested that the production of 1–octene can occur via one of two pathways, as depicted in Figure 1.9 [5].

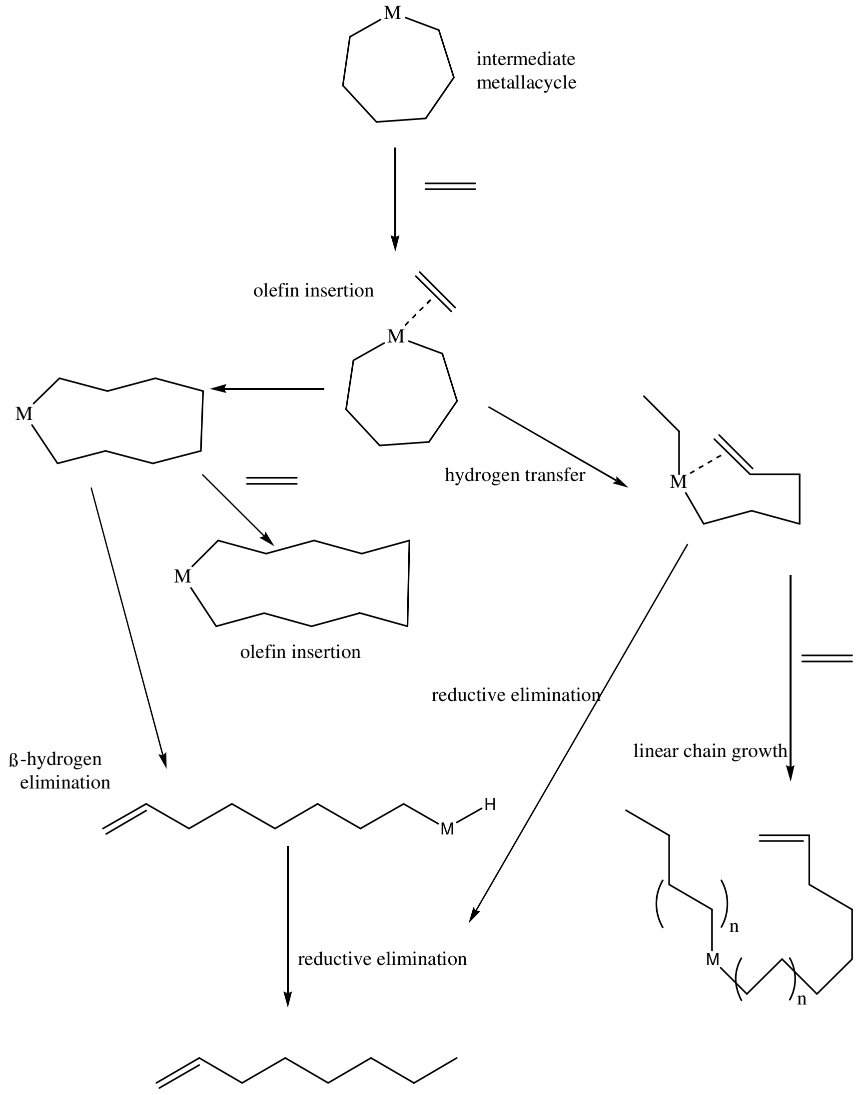


Figure 1.9 **Pathways to 1–octene formation**

1.7 PROJECT OUTLINE

Even with the great deal of research carried out to date on ethylene tri- and tetramerisation reactions, there remain a number of outstanding issues. One such issue is that of identifying the catalytically active species. This involves the complex composition, the mode of activation and the metal redox couple responsible for the olefin coordination and carbon–carbon coupling reactions during the chain growth [4, 35, 36].

With this in mind the aim of this project was to identify and study the fundamental chemistry behind potentially active novel chromium-based systems as these concepts can be applied to the chemistry of existing successful systems. This was to be achieved by making use of a variety of spectroscopic and structural techniques. Of these techniques, IR and Raman spectroscopy, in particular, have to an extent been underutilised as a means of investigating catalytic precursor chemistry. Emphasis is placed on the comparisons that can be drawn between the techniques, which results in well-characterised compounds in addition to a number of novel and interesting insights. Such insights refer to, among others, the monomeric and dimeric state of these systems. The following subsections (1.7.1 to 1.7.3.5) discuss the details of the project and include: the relevance of the monomeric and dimeric states, the selection of ligands and the characterisation techniques used.

1.7.1 MONOMERIC AND DIMERIC STATES

The conditions under which monomeric and dimeric states are formed are of interest. The catalytic precursors were synthesised via straightforward ligand substitution reactions to yield the monomer. However, it is generally believed that the co–catalyst acts upon the chromium precursor to give a cationic catalytically active intermediate [29, 25, 35, 36]. Also generally accepted is the role of dimeric chloro–bridged intermediates, the existence of which has been postulated or indicated by solid–state structures (as mentioned above) [34, 37, 38]. Isolated dimers show catalytic activity [38] and recently Jabri, Duchateau and co–workers isolated a dinuclear chloro-bridged chromium(III) complex after activation with excess $AlEt_2Cl$ [39, 40]. The stabilisation of vacant coordination sites is essential in a pre–catalytic stage to facilitate the coordination of ethylene at a later stage. Displacement of the weakly coordinated thf by bridging chloro ligands is assumed to be a way of reserving vacant coordination sites for attack by the co–catalyst, and eventual reaction with ethylene. In this study the focus was on the formation and cleaving of some dichromium(III) compounds containing bridging chloro ligands. The formation of such a dimer after the thermal decomposition of $[Cr(bipy)Cl_4]^-$ has been postulated and reported [41].

Figure1.10 shows that these dimers could be cleaved in a symmetrical (**A**) or asymmetrical (**B**) fashion with the choice of ligands discussed in detail in Subsection 1.8.3. The latter lead to the formation of cationic and anionic intermediates. This is, according to current thinking, more appropriate for the situation pertaining to the generation of the active catalyst for the tri– and tetramerisation of ethylene.

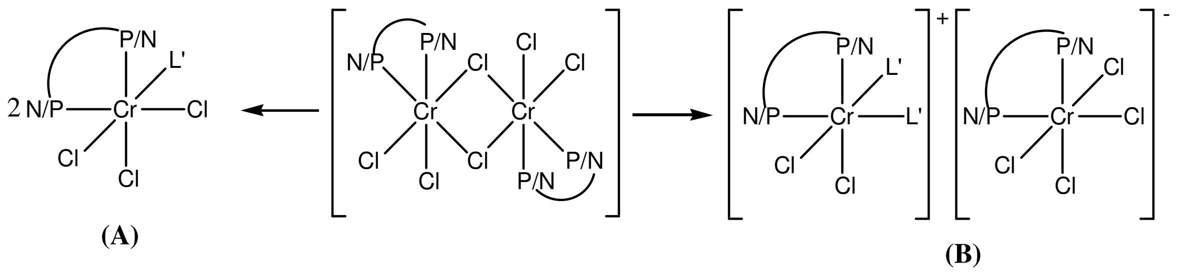


Figure 1.10 **Symmetrically (A) and asymmetrically (B) cleaved chloro dimers [100]**

Figure 1.11 shows both the substitution of the remaining thf ligand after the addition of the respective bidentate ligands and the breaking of a bridging chloro bond by the secondary amine ligands.

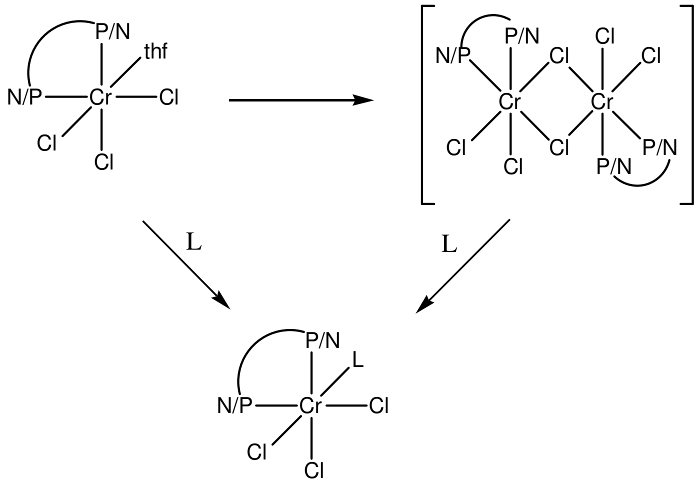


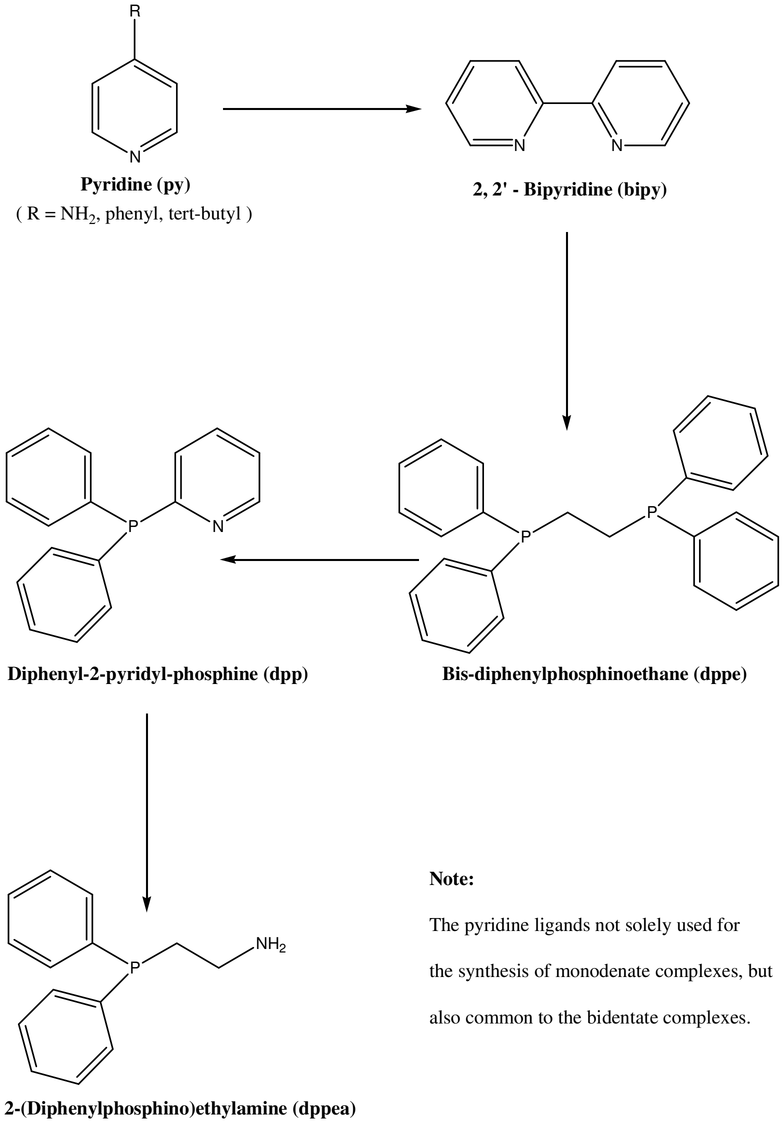
Figure 1.11 **Direct ligand substitution and symmetrical dimeric cleavage pathways [100]**

It is of interest to note that McGuinness et al. recently published work on chromium(III) complexes of bis(carbene)pyridine ligands with their focus on insights into the extended metallocycle mechanism of chain growth [42]. With respect to the bidentate pyridyl–carbene addition to [CrCl$_3$(thf)$_3$], they also discuss the formation of monomeric and dimeric species.

1.7.2 LIGANDS

The choice of classes of compounds investigated in this study has stemmed from the fact that ligands containing phosphorus and nitrogen donor atoms are for the most part the cornerstone of the successful catalytic precursors of ethylene tri– and tetramerisation. Thus, in an attempt to gain further insight into structural and reactivity properties, various monodentate and bidentate P and N ligands were coordinated to Cr(III) to produce largely novel compounds. Although some of these compounds have been synthesised previously, novel synthetic routes were used, and new structural and new spectroscopic insights (through extensive use of, inter alia, IR and Raman spectroscopy) were gained.

The choice of ligands can be divided into distinct ligand categories, the addition of pyridine and sterically and electronically differing para–substituted derivatives thereof being the common thread throughout. At the start of each chapter the reasoning behind the particular ligand choices is presented. There was a logical progression from N-monodentate ligands to mixed P–N bidentate ligands. Figure 1.12 outlines all the ligands investigated, with arrows indicating the progression to the next ligand.



Note:

The pyridine ligands not solely used for the synthesis of monodenate complexes, but also common to the bidentate complexes.

Figure 1.12 Ligands incorporated in this study

1.7.3 CHARACTERISATION AND ANALYSIS

The characterisation and study of these compounds involved a number of analytical techniques, each of which when studied independently is a source of valuable information. However, the full potential of these techniques is only realised when one combines and integrates all the various results as in fact all the techniques utilised in this study complement each other.

1.7.3.1 X–ray Crystallography

X–ray crystallography is the most favoured technique for characterising and studying novel compounds and thus a great deal of emphasis was placed on the pursuit of crystals of a sufficient size for the single–crystal diffractometer. However, as is widely recognised in the scientific community, this can be a difficult and, at times, frustrating practice which requires a combination of patience, perseverance and luck.

A number of crystal–growing techniques were employed and a total of eight structures were solved. The biggest problem encountered was that most of the compounds in this study were generally insoluble and only dissolved in a small number of solvents. These included and were limited to DMSO, DMF, CH_3CN and $ClCH_2CN$. The problem was confounded by the fact that both DMSO and DMF have high vapour pressures and are thus not conducive to evaporation. Nevertheless, all compounds underwent solubility tests in a large number of solvents, both polar and non–polar. Also varied was the type of vessel, which ranged from glass polytops and NMR tubes to Schlenk tubes, all with varying degrees of success.

It should be noted that the solutions for which these techniques were used came not only from dissolving the synthesised precipitates in appropriate solvents, but also directly from the reaction medium, as well as from the supernatant produced when the solution was washed with ether as part of the work–up.

The actual process of growing the crystals took the form of slow evaporation, slow cooling, vapour diffusion and the Hanging Drop Method.

The slow evaporation was carried out at room temperature, as well as at 4 and -30 °C. The second method of slow cooling was based on sound theory as the slower crystals grow, the lower the levels of entropy induced defects to its perfection [43]. The compounds were dissolved in solvents and heated. They were then placed in beakers of water which had been heated to temperatures of 40, 60 and 80 °C.

Vapour diffusion, otherwise known as "isothermal distillation" was the third method used and is based on the concept of polarity. The compounds were dissolved in suitable solvents and placed in test tubes. A less polar solvent than that used for dissolving the samples is placed in beakers. The test tubes are then placed in the beakers and sealed. The theory is that the less polar solvent diffuses through the vapour phase into a solution of a compound in the more polar solvent and hence reduces the solubility. This slow diffusion should stimulate crystals to form.

A variation of vapour diffusion is the Hanging Drop Method which is a technique normally reserved for the crystallisation of macromolecules such as proteins. A drop of compound dissolved in solvent is placed in vapour equilibrium with a liquid reservoir of solvents. For equilibrium to be achieved, vapour must begin to leave the drop and reach the reservoir. The sample increases in supersaturation. The concentration of both the compound and the solvent increases as solvent leaves the drop for the reservoir. Therefore when both the drop and the reservoir have equal concentrations, equilibrium is reached [44].

1.7.3.2 Infrared and Raman Spectroscopy

With respect to these specific types of compound, IR and Raman spectroscopy have to an extent been under–utilised. MIR spectra are able to confirm the presence or indeed absence of the respective ligands while, perhaps more importantly, FIR spectra can indicate metal–ligand vibrations that will give a real indication of complexation (note that the Raman spectra incorporate both regions). In addition such metal-ligand vibrations may assist in the differentiation of monomeric and dimeric species with the presence of bridging and terminal chlorine atoms. The shifting of bands can also indicate that the complexes have been formed through comparison of the respective ligand spectra with those of the complexes.

IR and Raman are spectroscopic techniques that go hand in hand when analysing the vibrational modes of compounds.

The fundamental difference between these techniques is that vibrations that are IR active cause a change in the dipole moment of the molecule, whereas Raman active vibrations change the molecular polarisability [45].

Interestingly, the particular vibrational values (measured in wavenumbers) of both IR and Raman spectra are dependent on both the masses of the atoms (whereby heavier atoms vibrate at lower frequencies than lighter ones) and the relative strength of the bonds. A further influential factor is the environment of the molecule, i.e. the molecular substituents and molecular geometry which affect the vibrational force constant and in turn affect the vibrational energy (band position) [46].

The study of the Raman and IR activities of the fundamental vibrations of these compounds can be summarised by the Rule of Mutual Exclusion. This states that if a molecule has a centre of symmetry, then Raman active vibrations are IR inactive, and vice versa. If there is no centre of symmetry, then some (but not necessarily all) vibrations may be both Raman and IR active. However, one must be cautious in comparing the presence and absence of bands in these two spectroscopic techniques as a vibration may be Raman or IR active but either too weak to be observed [47] or involved in band overlapping.

Unfortunately, not all the compounds in this study gave good Raman spectra. The problem was that of fluorescence and this can be correlated to the electronic nature of the samples. Fluorescence occurs when an electronically excited molecule decays back to the ground state spontaneously, emitting radiation at a frequency characteristic of the transition between the excited and ground states. As a result such radiation engulfs the weak Raman signal [47].

No such problems were encountered in the IR spectra of the compounds. Although it is discussed in detail in Chapter 2, special mention must be made here of the favourable characteristics of pyridine–IR, stemming from their simplicity, as this played a large role in the decision to incorporate pyridine ligands into all the complexes in this study.

1.7.3.3 NMR Spectroscopy

Unfortunately, the identification and characterisation of these types of species by NMR spectroscopy is complicated by the paramagnetic nature of the chromium in solution, with the problem stemming from the presence of unpaired electrons. This causes the relaxation times of the nuclei to shorten and gives rise to severe line broadening, which makes interpretation of the spectra rather difficult [48].

However, paramagnetic effects are not always undesirable as in certain instances they are required or are advantageous in helping to shorten interpulse times or increase pulse angles. This is achieved via the addition of trace amounts of compounds such as $Cr(acac)_3$. $Cr(acac)_3$ is a preferred choice as it is coordinatively saturated and kinetically inert, yet no more than 0.03 M conc. can be added as any more results in unwanted line broadening [48]. Paramagnetic substances can also cause the shifting of signals that can aid in spectral analysis. This has, however, proved to be a successful technique only with the lanthanides as most other ions suffer from severe line broadening which outweighs the benefits of the shift effects [49]. Paramagnetic usefulness also stems to ^{13}C NMR spectroscopy as interactions with paramagnetic chelate complexes sometimes serves a useful purpose by suppressing the NOE [50].

This particular study incorporated a novel approach with respect to paramagnetic species of this type and NMR spectroscopy, whereby insights into ligand coordination and reaction progress were identified. What is indicated by the findings is that upon coordination to the Cr(III) metal centre, the free ligand resonances disappear as a direct result of their proximity to the paramagnetic centre. This phenomenon is observed only where the donor atoms themselves are either conjugated or aromatic as ligands such as thf and dppe are all visible in their respective spectra.

For the aromatic ligands, the appearance of new ligand signals was expected upon coordination but in the range $\delta = -4$ to 16 ppm, no such resonances were identified. It follows that the signals are NMR silent in this range due to paramagnetic effects. The range was broadened from -30 to 30 ppm, but still no new resonances were observed.

These intriguing observations led to the development of a series of novel ^{1}H NMR experiments, whereby the substitution of thf in $[CrCl_3(thf)_3]$ with the respective nitrogen and phosphorus donor ligands was followed by proton NMR spectroscopy. This took place via the slow addition of stoichiometric amounts of the ligands in acetone-d_6 to $[CrCl_3(thf)_3]$ in an NMR tube. By obtaining a series of spectra in rapid succession (approximately every four minutes), the substitution reactions that took place could be closely followed and, in addition, the time required for reaction completion was indicated by the complete disappearance of the ligand resonances.

Where applicable, ^{13}C NMR and ^{31}P NMR were also utilised in this study and the resulting spectra were largely unaffected by paramagnetic effects.

It must be noted that no kinetic studies were undertaken from the resulting spectra. This was due largely to the problems with integration described above, as well as to the fact that the ratio of signals (integrals) does not depend on the concentration of the sample alone. For instance, the dilution of an NMR sample by 50% would give the same ratio of signals (integrals) irrespective of the initial concentration and in order to study kinetics, exact concentrations are important.

1.7.3.4 Computational Studies

In today's scientific era computational chemistry continues to gain momentum as an important source of information. At the forefront of quantum mechanical methodology is the now well–established DFT; this prominence is understandable considering its accuracy and computational speed [51]. One of the many capabilities involves the calculating of vibrational frequencies which can then be compared with those obtained experimentally and thus assist in molecular identification. With regard to the compounds in this study, in which IR and Raman spectroscopy were utilised extensively, such a comparative study is of benefit. One must, however, note that the calculated vibrational frequencies usually overestimate the experimental fundamentals for a variety of reasons. These include neglect of anharmonicity and the inaccurate description of the electron–electron interaction. The need for a scaling factor that will correct the calculated values to match the experimental observables is thus evident. This factor was computed by dividing the experimental values by those that were calculated.

DFT was also used to generate the frontier orbitals of a number of the complexes as such investigations reveal information pertaining to reaction behaviour. These HOMO and LUMO shed light on the regions of the complexes that are susceptible to electrophilic and nucleophilic attack respectively.

1.7.3.5 Mass Spectrometry

The need to confirm that any single crystal determinations did indeed reflect the composition of the bulk precipitated samples is of importance for this study. Precipitates were studied by physical (microscope, etc.) and spectroscopic methods (IR and Raman). In addition, the use of FAB-MS allowed for such information to be attained and provided additional structural information through the identification of fragmentation patterns which could not be gained by techniques such as elemental analysis. The presence of chlorine atoms in all the compounds was also a factor in the decision to use mass spectrometry. The isotopic distribution patterns could be studied and compared to theoretically generated patterns via the use of an isotopic distribution calculator. All FAB-MS spectral data are included in the supportive material section.

1.8 EXPERIMENTAL

1.8.1 SAFETY REMARKS

As in any scientific study involving the use of chemicals, awareness of the safety precautions that must be taken is of paramount importance. All the chemicals used in synthesising the compounds carried safety symbols indicating their harmful and toxic nature.

To eliminate or at least minimise the risks involved in handling these chemicals, a number of standard safety precautions must be adhered to. These include the wearing of safety glasses, lab coats and latex gloves, as well as carrying out all operations within a functional fume cupboard.

As well as the chemical precautions, there are also the apparatus–based precautions which include the proper management of the distillations used to dry the solvents. Both the daily running and the disposal of the solvent distillations need careful attention. In terms of daily running, the stills must be carefully monitored. Equally important is the disposal of the still residues. As all solvents differ in terms of the appropriate method of disposal, it is important to adhere to the respective solvent’s method.

All solvents in this study were dried via the addition of metal sodium, with benzophenone utilised as an indicator. The disposal of such a still involved the removal of remnant thf, followed by the slow addition of isopropanol over a period of three days as a means of ensuring that all sodium was inactive and thus safe.

1.8.2 GENERAL REMARKS

All reactions and manipulations were performed under an inert atmosphere using standard Schlenk tube techniques. Ligands were purchased from Sigma Aldrich and used without further purification.

The synthetic pathway for these reactions was modelled on the similar tridentate ligand substitution reactions, whereby the thf molecules of $[CrCl_3(thf)_3]$ were displaced by the respective ligands [32, 34]. The ease with which the thf molecules are substituted allows for mild reaction conditions.

Arriving at these conditions was achieved via a process of essentially trial and error, whereby various solvents, temperatures and time scales were tested. In the end the solvents of choice were thf (reaction medium) and diethyl ether (work–up). As a direct consequence of the high solubility of the chromium precursor and ligands in thf, elevated temperatures were unnecessary and thus most reactions were carried out at room temperature. Although some of the reactions appeared to be immediate due to colour changes and in some cases the formation of precipitates, others, such as the bipyridine experiments, took substantially longer. Furthermore, the addition of the secondary ligands did not always yield an obvious recognisable change. As a result all reactions were allowed to stir overnight to ensure completion.

A positive attribute of the majority of the formed precipitates was their stability in air, heat and light. These characteristics are certainly attractive to a practising catalytic chemist as any further manipulations are straightforward.

1.8.3 STANDARD COLOUR CHANGES

The addition of the pure amine ligands resulted in dark green solutions with precipitates of a slightly lighter green. In contrast, the phosphorus ligand, dppe, yielded a dark and light blue solution and precipitate respectively. It was therefore not unexpected to find that the addition of the ‘green’ pyridine ligands to the ‘blue’ dppe compound resulted in blue/green solutions and precipitates. The same was true for the mixed P–N ligands.

Although the colour changes that were indicative of ligand substitution were immediate in most cases, the slower coordination speed of the bipyridine ligand was of benefit as it allowed the observation of an intermediate light blue colour which is, according to our interpretation, associated with dimer formation.

1.8.4 SYNTHESIS OF THE STARTING MATERIAL [$CrCl_3(thf)_3$]

According to literature, there are various ways of preparing [$CrCl_3(thf)_3$]. For comparison, two of these methods were carried out [77, 78]. The resulting products of both methods were identical in colour and gave identical IR spectra with the characteristic thf bands present. However, while some initial test reactions were being carried out, the addition of bipyridine yielded the crystal structure [$CrCl_3(bipy)(H_2O)$]. This result cast a certain amount of doubt on the purity of the synthesised [$CrCl_3(thf)_3$] as it was plausible that unreacted water from the chromium hexahydrate starting material was still present. Therefore, to alleviate all doubts concerning purity, all reactions were carried out using the [$CrCl_3(thf)_3$] that was purchased from Sigma Aldrich.

1.8.5 GENERAL PROCEDURE AND INSTRUMENT DATA: INFRARED AND RAMAN SPECTROSCOPY

The instrumentation used to collect the required MIR vibrational data was a Perkin Elmer Spectrum RX-1, FT–IR System. The analysis of all the compounds was carried out in the solid state. A quantity of 2 mg of each complex and ~100 mg of KBr powder were ground together using a pestle and mortar until a fine homogeneous powder remained. The KBr is used as a diluting agent as it does not absorb above 250 cm^{-1} [52], which means that all bands seen in the spectra relate to the complexes. The fine powder was then pressed using a hydraulic press until a clear pellet was produced for analysis. In each interferogram 32 scans were signal averaged, with a spectral resolution of 2 cm^{-1}.

As some of the ligands were in the liquid state, sample preparation was not as straightforward as with the standard KBr pellets used in the solid state MIR. A number of sample preparation methods were tried in order to obtain spectra of a high quality.

The first method was the dissolution of the ligands in thf. Unfortunately, the spectra obtained were of poor quality because concentration problems led to background subtraction abnormalities, which in turn did not allow clear band resolution as was seen from solvent–sample superposition. As thf by its very nature has many vibrations, it was thought that this superposition could be minimised by using a vibrationally simpler solvent such as CCl_4. This attempt was, however, unsuccessful as both ligands were found to be insoluble in CCl_4.

The expense of these ligands, coupled within the small amounts available, did not allow further solubility tests and so another method was tried. This proved to be very successful indeed as it avoided the use of solvents and required minimal amounts of the ligands. A drop of ligand was placed between two KBr pellets. The resulting spectrum was well defined with no background interference.

The FIR data was collected using a Bruker IFS113V spectrometer. The sample preparation was slightly different from that above as polyethylene was used in place of KBr. A quantity of 2 mg of sample was shaken vigorously in ~200 mg of polyethylene. The resulting mixture was pressed into a clear pellet for analysis using a hydraulic press. In each interferogram 32 scans were signal–averaged, with a spectral resolution of 2 cm^{-1}.

In order to reduce the extreme fluorescence experienced with the initially tested 514.5 nm laser excitation, an FT–Raman Spectrometer was used which contained an Nd:YAG laser to excite the Raman effect. The Nd:YAG laser has a wavelength of 1 064 nm and at this wavelength there are fewer electronic transitions, which in many instances are responsible for a high fluorescence background. The laser power was 250 mW and 256 scans were accumulated with a resolution of 4 cm^{-1}. As with the majority of the IR experiments, the analysis was carried out in the solid state but, unlike the IR studies, very little sample preparation was required. A small amount of each complex was placed in an aluminium holder and loaded into the sample compartment. The only necessary and important factor to be considered is that the sample must be in the foci of the laser beam and collection lens [53].

1.8.6 GENERAL PROCEDURE AND INSTRUMENT DATA: X-RAY CRYSTALLOGRAPHY

All data sets were collected at 20 ºC on a Siemens P4 diffractometer fitted with a Bruker 1K CCD detector and SMART control software [54] using graphite–monochromated, Mo Ka radiation by means of a combination of phi and omega scans. Data reduction was performed using SAINT+ [54] and the intensities were corrected for absorption using SADABS [54].

The structures were solved by direct methods using SHELXTS [54] and refined by full–matrix least squares using SHELXTL [54] and SHELXL–97 [55]. Drawings of the structure were produced using Ortep–3 for Windows [56], Mercury [57] and POV–Ray for Windows [58].

1.8.7 GENERAL PROCEDURE AND INSTRUMENT DATA: ^{1}H NMR SCALE EXPERIMENTS

A dry degassed NMR tube was charged with small amounts of $[CrCl_3(thf)_3]$ (*ca* 4 mg) and placed under vacuum on the Schlenk line, after which it was purged with argon by three purge cycles. Stoichiometric amounts of the respective ligands were weighed out into sample vials. Acetone-d_6 was added to the ligands and injected into the NMR tube via a rubber septum (after ensuring complete dissolution). The tube was immediately placed in the NMR spectrometer, where a lock signal had already been obtained using an acetone-d_6 reference standard. A ^{1}H spectrum was obtained every few minutes to track the progress of the reaction.

Acetone-d_6 was the solvent of choice where the readily soluble ligands were added together, while for spectra of the insoluble final products, DMSO-d_6 was used. Comparisons between the different solvent spectra revealed that the chemical shifts were identical and not affected by the change in solvent. This was advantageous as the spectra were therefore comparable. The instrument was a Bruker Avance 500 with the spectra measured at 500.13 MHz.

1.8.8 GENERAL PROCEDURE AND INSTRUMENT DATA: COMPUTATIONAL STUDIES

A *quantum-chemical ab-initio calculation* of the total molecular energy E at the ground state of the potential-minimum configuration of a molecule, called the "fully optimised geometrical structure", yields the sum total of the two effects: those caused by *short-range forces* and *long-range forces*. These are calculated for the isolated molecules in the gas phase, and exclude specific intermolecular interactions such as packing forces The molecular structure of each molecule was optimised using the molecular symmetry point group C_1, and no further enforcement of higher symmetry was attempted due to the lack of any obvious additional point group symmetry operators in the molecules for which solid–state structures were available.

Ab-initio quantum-chemical computations were carried out on an IBM–cluster with a pre–compiled set of Gaussian-03 molecular orbital programs [59] configured for parallel computing under LINUX [60]. Default computational settings for Gaussian-03 *ab-initio* DFT/B3LYP calculations were implemented, while a 6-311G (p, d) basis set was used as described in the Gaussian manual [61]. This basis set was chosen instead of the more elaborate 6-311++G(3df,3pd) basis set to represent a balance between computational level and computational economy. More details about the background of the computational methodology can be found in the books by Hirst [62], Kohanoff [63], and Foresman and Frisch [64], as well as in the original references cited in the Gaussian Manual [59].

In order to determine whether the optimised geometry, where the slope approaches ($\partial E/\partial X$) → 0, where X is the structural parameter being subjected to refinement, occurs at a potential minimum and not at a saddle point, the harmonic molecular vibrational modes and their associated frequencies were calculated at the optimised geometric configuration [65]. It was established that all the optimised geometries of the molecules studied yielded only positive vibrational frequencies, i.e. all the optimised geometries were thus determined at *potential energy minimum positions*. The energies and other computed physical properties may, therefore, be compared and contrasted with confidence. Due to the nature of the calculations, the absolute energy values are not of significance and thus are not reported.

All calculations were carried out using the spin quartet ground state. In addition to previous Cr(III) computational literature [66, 67, 68], this selection was confirmed by the excellent agreement between the calculated and experimental vibrational spectra of this study.

1.8.9 GENERAL PROCEDURE AND INSTRUMENT DATA: MASS SPECTROMETRY

Mass spectroscopy data was collected by means of Fast Atom Bombardment using a VG70SE with xenon atom gun. This was operated at 8Kv using a 3-nba matrix.