

The Synthesis and Characterisation of Novel Fluorinated Compounds Suitable for Evaluation as Oil Additives

**Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester**

by

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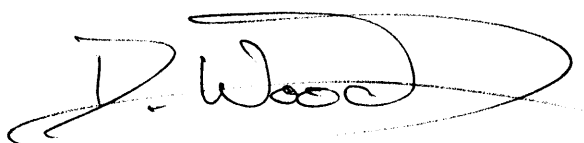


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Statement

The experimental work in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between October 1998 and April 2002. The work has not been submitted, and is not presently being submitted, for any other degree at this or any other university.

Signed:

A handwritten signature in black ink, appearing to read 'D. Wood', with a large, sweeping loop at the end.

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Other Voices

“Real knowledge is to know the extent of ones ignorance.”

– Confucius

“A man may die, nations may rise and fall, but an idea lives on.”

– John F. Kennedy

“Know your enemy, and in one hundred battles you will never be defeated”

– Sun Tsu

“The harder you work the harder it is to surrender”

– Vince Lombardi

“In the middle of difficulty lies opportunity”

– Albert Einstein

“When in a room only lit by a candle and the wind blows, you can either enjoy the breeze or loath the darkness”

– Rizwan Haroon

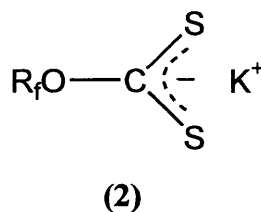
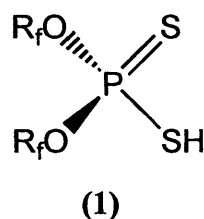
“Experience is a hard teacher because she gives the test first, the lesson afterward.”

– Vernon Law

Abstract

A review of the history, development and application of lubricant additives in mineral oils is presented, along with recent developments in base fluids leading to need for fluoruous phase soluble compounds in this area.

The experimental work illustrated in this thesis describes the synthesis of a series of perfluoroalkyl-derivatised dithiophosphate ($R_f = (CH_2)_2C_6F_{13}$, $(CH_2)_2C_4F_9$, $(CH_2)_3CF_3$) (1) and xanthate ($R_f = (CH_2)_2C_6F_{13}$, $(CH_2)_2C_4F_9$, $(CH_2)_3C_8F_{17}$, $(CH_2)_3C_6F_{13}$, $(CH_2)_3CF_3$) (2) ligands and closely related perprotio analogues ($R_H = C_8H_{17}$), which have been analysed by 1H , ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry and elemental analysis. The influence of the electronic properties of the perfluoroalkyl groups have been investigated in a study of the coordination chemistry of these ligands to a range of transition metal centres including $[(PPh_3)_2CuL]$, $[Cp^*RhCIL]$, $[NiL_2]$ and $[ZnL_2]$.



The complexes have been analysed using a variety of techniques including multi-nuclear NMR spectroscopy, mass spectrometry, X-ray crystallography and elemental analysis.

The anti-wear and extreme pressure properties of a selected number of compounds formed have been evaluated using industry standard SRV testing procedures, allowing a direct comparison of the perfluoroalkyl-derivatised complexes with their perprotio congeners.

Preliminary work is also described on the formation of perfluoroalkyl-derivatised dithiocarbamate and phenate compounds, which could also potentially find applications within the lubricant industry as anti-wear and detergent additives respectively.

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Glossary and Abbreviations

Some of the terms which are used widely within the oil and lubricant industries are not as readily recognised within the field of chemistry. The following list outlines definitions of those expressions and a list of abbreviations which have been used within this thesis.

Additive Package – The pre-formulated mixture containing all of the required additives which can then be blended with the base fluid.

Ash – Inorganic, oil-insoluble decomposition products of additives compounds. Usually formed by a side reaction, such as inevitable combustion of metal-containing additives.

Ashless – Used to describe an additive compound which does not contain a metal and, therefore, on combustion does not form an ash.

Base Fluid – The basic mineral, or synthetic, oil that the additive package is blended with to form the finished lubricant.

Boundary Lubrication – Lubrication at high loads where there is only a very thin film between the components.

Break-in – An initial transition process occurring in newly established wearing contacts. This period is often accompanied by uncharacteristic properties of friction and wear rate, compared to the long term behaviour of the system.

Brightstock – A high viscosity base oil produced by de-asphalting.

Cloud Point – The temperature at which wax begins to crystallise from the oil.

Combustion – Used in terms of oil additives as the unfavourable, yet inevitable, thermal decomposition products of the additive molecules due to the lubricants being used at high temperatures.

Electric Oils – Used in industrial transformers for electrical insulation and heat transfer.

Flash Point – The lowest temperature at which auto-ignition of vapour may occur.

Fluid-Film Lubrication – Lubrication where the load allows a coherent fluid film between the components.

Grease – A semi-fluid to solid product of a dispersion of a solid thickener in a liquid lubricant.

Lubricant – Any material between two surfaces which reduces the friction and wear between them.

Mineral Oil – Oil from natural sources which consists of a mixture of organic components with similar boiling points.

Mixed Friction – Intermittent contact due to the lubricant film not being thick enough to totally separate the two components.

Overbased – These are detergents which contain a higher than 1:1 ratio of metal base:polar substrate. This provides a large amount of base to neutralise acidic components produced by unwanted side reactions, such as oxidation of the oil.

Pour Point – The lowest temperature at which the oil can be made to flow by gravity alone.

Process Oils – Used in various industrial applications such as plasticisers.

Raffinate – Alkane phase left after solvent extraction has removed the unwanted aromatic components.

Seizure – Localised fusion of metal surfaces of the disk and plate in SRV test machinery.

Sludge – An aggregation of ash particles which form large insoluble particles within the system.

Solvent Neutral – Oils which have been solvent-refined with a neutral pH.

Wax – The organic materials which crystallise out of solution from mineral oil base fluids. This increases as the temperature is reduced. Therefore, for low temperature applications, 'de-waxing' is first carried out.

Wear – The physical damaged caused to a solid surface by two components being in contact with each other within a system.

Wetability – The ability of an oil to form a thin film on a surface rather than collect into beads.

White Oil – Highly refined, colourless oils, often used in medical applications.

δ	Chemical Shift
Δ	Heat
ν	Stretching frequency
Ar	Aryl fragment
atm	Atmosphere

bipy	2,2'-Bipyridine
COD	1,5-Cyclooctadiene
COSY	Correlation spectroscopy
Cp*	Pentamethylcyclopentadienyl
cSt	Centistokes
d	Doublet
dd	Doublet of doublets
DMP	Dess-Martin Periodinane
DMSO	Dimethylsulphoxide
dt	Doublet of triplets
DTC	Dithiocarbamate
DTP	Dithiophosphate
EA	Elemental analysis
EI	Electron impact
EP	Extreme pressure
ES	Electrospray
ESCA	Electron Spectroscopy for Chemical Analysis
Et	Ethyl fragment
FAB	Fast atom bombardment
HSAB	Hard/Soft Acid/Base
Hz	Hertz
IR	Infra Red
<i>J</i>	Coupling constant
m	Multiplet
Me	Methyl fragment
MHz	Megahertz
Mp	Melting point
N	Newton (1 N = 1 kgms ⁻²)
NMR	Nuclear magnetic resonance
OCP	Olefin copolymer
PAO	Poly(alpha-olefin)
PCC	Pyridinium chlorochromate
PFPE	Perfluoropolyether
Ph	Phenyl

PIB	Polyisobutene
PP3	1,3-perfluorodimethylcyclohexane
ppm	Parts per million
q	Quartet
R	Undefined molecular fragment
R _f	Undefined fluorinated molecular fragment
RT	Room temperature
s	Singlet
SRV	Schwingung, Reibung, Verschleiss (oscillating, friction, wear)
t	Triplet
tt	Triplet of triplets
TMS	Tetramethylsilane
um	Unresolved multiplet
ZDDP	Zinc dialkyldithiophosphate
ZDTP	Zinc dithiophosphate

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My sincerest thanks go to all of you.

A handwritten signature in black ink, appearing to read 'Dan', with a long horizontal stroke underneath.

CHAPTER ONE

Introduction



**University of
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1.1 Introduction to Friction and Wear

1.1.1 Friction

Although the work in this thesis focuses primarily on synthetic and analytical chemistry, it is essential to appreciate the basic engineering principles behind friction and wear since these will help to provide a working knowledge of the processes for which the potential additives, reported here, are intended. On all surfaces which are not anatomically smooth there will be asperities protruding from the surface. It is these asperities which interlock when two surfaces are moving in opposing directions, resulting in a retardation of motion. This retardation of motion is known as friction,¹ with the energy lost being dissipated as heat. The amount of friction produced depends upon the roughness of the surface. The smoother the surface is, the less friction is produced on movement. If the same two moving surfaces which are in contact with each other are now separated by a viscous fluid (a lubricant), asperity contact is reduced thus reducing the overall friction of the system. This reduction of friction coefficient is one of the primary principles of lubrication. In the vast majority of engineering systems there is some asperity breakthrough, where the film of lubricant is not thick enough to totally separate the two components. This continual intermittent contact is known as “mixed friction” and can have an asperity breakthrough range of anywhere between 1 % and 90 %.²

1.1.2 Wear

Wear in this context can be defined as the mechanical damage caused by two metal surfaces being in contact and rubbing against each other. Work has been carried out to establish exactly how metal components wear, and it has been found that there are a number of different mechanisms³ categorised as adhesive, abrasive, fatigue and corrosive wear.

1.1.2.1 Adhesive Wear

Adhesive wear is caused by asperities on the metal surfaces interlocking, deforming and welding together. This work hardens the junction of the asperities making it stronger than the base metal. When the components move, the junction stays intact causing large lumps to be pulled from the base metal. Wear by this mechanism can be limited in a number of ways. Firstly, different metals do not weld as well to each other. So, if each component has a different composition adhesive wear will be reduced. Also, alloys do not weld as efficiently as pure materials so their use is widespread. Finally, it is possible to use pure metals with minimal adhesive wear if they are already at maximum hardness. This means that they cannot work harden further at the asperity junction.

The Archard Theory⁴ states that harder materials give rise to lower wear. It is possible to use this concept to reduce the amount of wear in a system by depositing a very hard coating onto the components by either plasma spraying or sputtering.⁵ Although this has been found to be successful in a number of systems there are two main problems. Firstly, this technique is extremely expensive so its use is limited to applications where performance is vital. Secondly, if the adhesion of the coating to the base metal is weak, under a high loading the coating is likely to peel away.

At low temperatures, fatty materials can be used to minimise adhesive wear, whereas at higher temperatures, oxygen, phosphorus and sulfur compounds have been found to be effective.

1.1.2.2 Abrasive Wear

Unlike adhesive wear, which under no circumstances is desirable, abrasive wear can be useful. For example, it is abrasive wear which makes grinding and cutting wheels both efficient and effective tools. This mechanism of wear occurs when hard particles or a rough surface run against a relatively smooth surface causing damage to the smooth surface. The hard particles are usually work hardened wear particles from adhesive wear. These can be removed with adequate oil filtration and, therefore, abrasive wear can be reduced to a minimum.

For pure elements, the abrasive wear rate is inversely proportional to hardness.⁶ This means that the wear rate can be reduced by surface hardening. Care must be

taken to make sure that the hardened surface does not flake to give very hard abrasive particles which would merely exacerbate the problem. If the hard surface does crack and flake away, this exposes pure active metal which is likely to undergo adhesive wear.

1.1.2.3 Fatigue Wear⁷

As surfaces run in contact with each other, opposing asperities deform and ultimately fatigue causes them to break off. It is possible that these asperities suffer fatigue due to temperature flashes which lead to large thermal stresses at the asperity junction. It has been found that the harder the material is, the greater resistance it has to fatigue. If fatigue does occur, wear debris can give rise to abrasive wear. This may, in turn, clean the surface and give rise to adhesive wear.

1.1.2.4 Corrosive Wear

Oxygen, moisture or other active chemicals which are present in the lubricant form a layer on the surface of the components preventing them from adhering. This layer is rubbed off during contact and has to be reformed before the next contact. As this layer is rubbed off, a certain amount of material is worn away. This mechanism is known as corrosive wear.

Observations show that wear debris usually consists of flakes. This would be consistent with the surface delaminating. The actual mechanism of the wear seems to change as the process goes on. Firstly abrasive wear cleans the surface which promotes asperity welding and adhesive wear. This adhesive wear generates work hardened particles which cause abrasion. Furthermore, since the surface is cleaner it can also corrode faster.

A detailed theory of wear and its mechanism is currently unavailable. However, research has shown that wear can be minimised by using hard materials, a suitable lubricant and ensuring that the lubricant is filtered as efficiently as possible to remove any wear debris formed.

1.2 The History and Principles of Lubrication

Lubricants have been used since ancient times and have been developed from what were crude materials to the very sophisticated packages commercially available today. Throughout history the development of lubricants has always been driven by the needs of other industries, such as transport and engineering, which as they have become more advanced, have demanded greater performance from the machinery being used. The middle ages saw the first real widespread use of lubricants, but it was the industrial revolution which sparked the first major period of development in this area.⁸ It was also at this time that preliminary analysis into the mechanisms by which these substances are effective took place.

The first lubricants to be used were oils obtained from animal fats and vegetables. These were used until mineral oil reserves were discovered in the 18th and 19th centuries and major lubricant production began. During the majority of the 20th century, mineral oils have almost exclusively been used as base fluids with the introduction of additives to make the lubricant more efficient and more durable. More recently, synthetic base fluids have been manufactured,⁹ based upon mineral oil formulations, primarily due to the possibility of tuning the properties of the synthetic oil to meet the needs of the application. This step forward in lubricant technology did not take place until the mid 1930's, but today synthetic base fluids are used for a variety of applications,¹⁰ especially ones involving high loads and temperatures such as those in the aviation industry.

Originally, it was thought that the lubricant filled the hollows in the surface of a material and, therefore, reduced its roughness. This view was considered to be correct for some time until studies in 1883 by Tower¹¹ showed that there was a coherent film of lubricant between two moving parts. This was to become known as "fluid-film lubrication". In 1922, Hardy proposed another form of protection given by oils working at high loads known as "boundary lubrication".¹² Here, as a result of the very high loads being applied, it is impossible for there to be a coherent fluid film between the moving parts. There is, however, a surface coating of lubricant on the components, of molecular thickness, which leads to a lowering of the friction coefficient.

Lowering of friction between two components is perhaps the main, but not the only, attribute required from a commercial lubricant. This is a very important property as it reduces wear between metal components due to lower asperity contact while also preventing loss of useful energy due to excessive friction. However, the total lubricant package must also:

- Act as a coolant to remove heat from hot components or that due to friction and thus stop the system from overheating.
- Give corrosion protection to components by inhibiting chemical attack from a wide variety of contaminants such as water, combustion products and particulate matter.
- Give seal protection to avoid oil leakage and contamination.
- Suspend contaminants such as wear debris and combustion by-products so as to leave the component surfaces clean.
- Operate over the range of temperatures required for the specific application without a dramatic drop in the efficiency of the lubrication.

It is inconceivable that a base fluid, be it mineral or synthetic, could achieve these aims alone. Therefore, lubricant manufacturers use additive packages to tune the properties of the base fluid to those required for the proposed application.

1.3 Natural Base Fluids

The majority of natural lubricant base fluids are produced from large scale refining of crude oil. This can be done to provide oils which give good performance at relatively inexpensive economic cost. Since crude oil is a very complex mixture of components, the refining process consists of a number of steps.¹³ Also, since crude oil has been formed as a result of chemical reactions taking place over millions of years, the contents of each oilfield have slightly different chemical compositions. This difference is not usually in the types of substance in the mixture but the relative amounts of each.

1.3.1 Composition of Crude Oil

The composition of crude oil can be divided into hydrocarbon and non-hydrocarbon classes of compounds. The hydrocarbon compounds have desired properties for lubricant applications and consist of a full range of alkanes, alkenes, alicyclics and aromatics. The relative ratios of each of these groups gives the overall crude oil a specific viscosity and pour point.

The second, non-hydrocarbon, group of compounds consists of organic molecules incorporating heteroatoms such as sulfur, nitrogen and oxygen. Organosulfur compounds are found to be far more prevalent than nitrogen and oxygen containing compounds. The majority of these compounds have a negative effect on lubricant performance since they can be prone to oxidative degradation. However, certain organosulfur compounds are known to act as naturally-occurring antioxidants. Therefore, it is frequently desirable to retain some of these during the refining process.

1.3.2 Base Oil Manufacturing Methods¹⁴

Very early lubricants were produced by simple distillation of crude oil where removal of low boiling fractions leaves a residue which could be used as a lubricant. Over many years it was found that this residue could be refined further to produce a higher quality end product and simple processing techniques such as separating lube distillates by vacuum distillation, and removing wax by chilling and filtering were developed. However, these were very labour intense batch processes which left little room for expansion in production capacity. Today, although some of the principles remain the same, modern technology has been used to make the refining process more energy and cost efficient, and most lubricant production plants are now integrated with mainstream oil refineries. The majority of the processes undertaken to produce the final base fluid are physical separation techniques. These lead to large quantities of unwanted by-products, thus making atom efficiency very low, and it is not unusual for the actual output of the base fluid to be less than 10 % of the crude oil initially used.¹⁵ It is, however, possible to use many of the by-products for other applications such as fuel oils, waxes and bitumen.

The basic techniques which are employed in turning crude oil into an effective lubricant base fluid are:

- Distillation
- De-asphalting
- Solvent Extraction
- Solvent De-waxing
- Finishing

Brief outlines of all of these methods of refinery are given below.

1.3.2.1 Distillation

This is the primary process for separating different fractions of crude oil. Initially, the crude oil feedstock is distilled at atmospheric pressure to remove fractions which boil below 350 °C. At temperatures above this, thermal decomposition is likely to take place so further distillation of the atmospheric residue is carried out under reduced pressure to remove the lube distillates. The vacuum column is usually packed with mesh or rings to increase the efficiency of fractionation, with pressures as low as 60 mm/Hg being reached using either steam injectors or mechanical pumps to provide the vacuum. The required lube distillates can be removed from the column *via* side streams, with the very high boiling residue being drawn from the bottom of the column. Distillation of this nature usually provides three usable lube distillates and a residue, each with physical properties which are defined within narrow ranges. To achieve high quality and consistency of fractionation it is necessary to minimise the overlap of the distillate fractions taken. Also, by ensuring that the vacuum is as high as possible, it is feasible to separate very heavy distillate fractions, rather than losing the material in the distillation residue. The separated fractions and the residue are then allowed to cool before moving on to the later refinement processes.

1.3.2.2 De-asphalting

The vacuum distillation residue is a black, viscous material because it contains a large amount of asphaltic and resinous materials. When these are removed, a high viscosity base fluid known as “brightstock” remains. Low molecular weight

hydrocarbons such as liquefied propane, are used to dissolve the desirable components while leaving the asphaltic material in a separate phase. Separation of this phase and removal of the solvent leads to brightstock of high purity. This treatment is carried out in an extraction tower where good mixing of feedstock and propane is essential. To achieve this, in a similar way to a fractionating column, the tower can be packed with a number of materials such as ceramic rings. In addition to the extraction tower, a large amount of equipment is required for recovery of de-asphalted oil and solvent recycling. Other hydrocarbons, usually higher alkanes, can be used in place of propane but these tend to give a lower grade of de-asphalted oil. The asphalt which is recovered from the process can be used as feedstock for making bitumen or blended into fuel oil.

1.3.2.3 Solvent Extraction

This process is used as a method of improving the viscosity/temperature characteristics of the base fluid and also its oxidative stability. The solvent selectively dissolves the undesirable aromatic components, known as the “extract”, while leaving the desirable saturated components, known as the “raffinate”, as a separate phase. These can then easily be separated to give a base fluid with advantageous properties over those of the feedstock. The solvents used for the extraction are carefully chosen for selectivity, ease of recovery, cost and a number of other factors. The most widely used solvent is furfural, but others such as sulfur dioxide and phenol in decalin are also commercially used.

Each lube distillate fraction is processed separately due to the different processing conditions needed to obtain the optimum results for each base fluid. The extraction solvent to oil ratio is important as too little solvent will not totally remove the undesired aromatics, whereas over extraction will lead to the loss of useful components. Efficient mixing is also crucial to minimise the amount of solvent required. This is usually achieved by using an extraction tower which is packed with ceramic disks or vertically mounted rotating disc contactors. As with de-asphalting, equipment is necessary to remove the solvent from both the raffinate phase where a small amount will be dissolved, and the extract phase. After the solvent has been removed from the two phases independently, it is recombined and recycled.

1.3.2.4 Solvent De-waxing¹⁶

The material which crystallises out of raffinate or lube distillates at low temperatures is known as wax, and prevents the oil from flowing as it should. The de-waxing process must remove a sufficient amount to allow the base oil to give the required low temperature properties. This is usually only necessary for paraffinic feedstocks as naphthenic oils are relatively free from wax. Linear alkanes crystallise easily to form the main constituent of wax in lighter distillates, while *iso*-alkane waxes form in the heavier fractions. Originally the waxy oil was cooled down and filtered in large plate and frame presses, but this has given way to less labour intensive solvent de-waxing treatments. These processes rely on good solubility of the oil and low solubility of wax in the chosen solvent, which should have a low boiling point to allow easy recovery. Solvents commercially used include single solvents such as propane and mixed systems such as dichloromethane/dichloroethane. Using pairs of solvents has been found to give greater control over oil solubility and wax crystallisation. Usually, the process of de-waxing is carried out by mixing the solvent and the oil together, then slowly chilling to the temperature required for filtration. This temperature should be several degrees below that of the required pour point to leave a base fluid with sufficient low temperature properties. Filtration is then carried out in large rotary drum filters which remove any solidified wax particulates. The solvent can then be recovered and recycled. If very low pour points are required, the process becomes extremely costly as more components are removed from the oil and yields become very low. To produce base fluids of this nature, a variation on solvent de-waxing, called urea de-waxing, is used. Here, at low temperatures the urea co-crystallises with the wax to give larger crystals, thus making filtration easier and giving an oil of very low pour point.

1.3.2.5 Finishing

After all of the previous refining steps, trace impurities may still be present in the oil. These trace impurities lead to problems such as poor oxidative and thermal stability, and tend to be non-hydrocarbon compounds. Previously, impurities were selectively adsorbed onto materials such as clay and bauxite, but these created problems with waste disposal. Now a technique known as “hydrofinishing” is used.

This differs from the previous processing methods as it is not a physical separation. Instead, it involves a chemical process in which the impurities are selectively catalytically hydrogenated to form harmless products. The catalyst used is either nickel- or molybdenum-based¹⁷ and supported on alumina, which allows the reaction to proceed both cheaply and under relatively mild conditions. Hydrofinishing of this nature selectively removes organonitrogen compounds, which are mainly responsible for poor colour and stability of the base oil, while leaving the organosulfur compounds, which impart natural anti-oxidation stability, unaffected.

1.3.3 Base Oil Categories

There are a number of different classes of base oils. The most important are the paraffinic and naphthenic oils which are widely produced and used in many applications across the world. There are other, more specialised categories which are made by a limited number of refineries which are either by-products from the conventional processes or speciality products made by additional refining steps. All of the main base oil categories are outlined below.

- Paraffinics - Most of the base fluids currently used are paraffinic, and they are available in a full range of viscosities from very light oils to viscous brightstock. These base oils are typically made from crude oils with a relatively high alkane content, such as those found in the Middle East and the North Sea. They have a high viscosity index, reasonable low temperature properties and good stability. They are frequently referred to as “solvent neutrals” (SN) where “solvent” means the base oil has been solvent refined and “neutral” means that the oil is of neutral pH.
- Naphthenics - The use of these oils is less widespread than that of the paraffinics, so they are produced in smaller quantities by a limited number of refineries usually in North and South America. They have naturally low pour points, are wax-free and have excellent solvency. Their viscosity index is inferior to that of the paraffinic oils, but they are used in a wide variety of applications where this is not a problem. One of the main advantages of these oils is that a de-waxing step is not

necessary, leading to a reduction in cost and time taken during refinement.

White Oils - These are very highly refined oils which consist only of saturated compounds. Here, all aromatics have been removed by either selective hydrogenation or treatment with fuming sulfuric acids. These oils are so highly refined they can be used in the medical and food industries, and are called “white oils” due to their colourless appearance.

Electric Oils - As the name suggests, these oils are used for electronic applications such as electrical insulation and heat transfer for industrial transformers. Due to the need for low viscosity and excellent low temperature properties, they are made from either naphthenic or catalytically de-waxed paraffinic crude oils

Process Oils - These are used in a number of industrial applications such as mould release oils and plasticisers in tyres. They usually consist of the highly aromatic extracts which are a by-product of the conventional base fluid manufacturing process.

1.3.4 Physical Properties

Before a base fluid can be chosen for a specific application, or, perhaps more accurately, an application can be chosen for a specific base fluid, a series of tests must be carried out to ascertain a number of physical properties of the oil. The main properties are outlined below, but this is by no means a comprehensive list. In addition to these, the measurement of a number of thermal, electrical and surface properties¹⁸ can give excellent information when trying to tailor a base fluid to a proposed application.

1.3.4.1 Viscosity

Viscosity is a vital property because it influences the ability of a lubricant to form a lubricating film or reduce friction and wear. The absolute viscosity of an oil can be measured using a rotary viscometer in which a rotor spins in a container of the fluid and the torque is measured. Another method of defining viscosity is to measure the

rate of flow of the liquid through a capillary under the influence of gravity.¹⁹ This gives the kinematic viscosity and is defined as follows:

$$\text{Kinematic viscosity} = \frac{\text{Absolute viscosity}}{\text{Liquid density}}$$

The unit of kinematic viscosity is m^2s^{-1} but is more commonly referred to as centistokes (cSt) where $1 \text{ cSt} = 10^{-6} \text{ m}^2\text{s}^{-1}$. There are other empirical scales of viscosity in use but the cSt scale is widely used throughout the lubricant industry. The kinematic viscosity of an oil is often quoted rather than the absolute viscosity due to the simplicity and precision with which it can be measured.

1.3.4.2 Viscosity Index

This gives the relationship between the viscosity and the temperature of an oil as a dimensionless number. The kinematic viscosity is measured at 40 °C and 100 °C, and the viscosity change, or index, is compared with an empirical reference scale.²⁰ The higher the viscosity index, the less effect temperature has on the viscosity of the oil. A high viscosity index would be crucial for an oil which is to be used over a large temperature range, as comparable viscosity properties would be present at all times. The viscosity index is extensively used throughout the lubricant industry and is a useful tool in comparing base fluids, although it does have limitations. Care must be taken when extrapolating values for viscosity beyond the measured temperature range of 40 °C to 100 °C. This may result in inaccurate information, especially at low temperatures where the formation of wax may affect the kinematic viscosity considerably.

1.3.4.3 Low Temperature Properties

When a sample of oil is cooled, its viscosity increases in a predictable manner until a temperature is reached where wax crystals start to form. This is known as the “cloud point” and is a value which is often measured and quoted for oils. As the temperature is decreased further, a matrix of wax crystals begins to form and eventually causes an apparent solidification of the oil.

1.3.4.4 High Temperature Properties

The high temperature properties of an oil are governed by the boiling range characteristics of the oil. The volatility of an oil is important because it gives an indication of how much is likely to be lost in service due to vaporisation. The flash point of an oil is also of importance from a safety perspective. This is the lowest temperature at which auto-ignition of vapour occurs above the heated oil sample.

1.4 Synthetic Base Fluids

The development of synthetic base fluids has been driven over time by two forces. The first is a consequence of there being a finite amount of natural mineral oil available, therefore, at some time in the future, an alternative fuel/lubricant source will be necessary. The second driving force is more economical than chemical. For very specialised applications very complicated, costly and inefficient refinement processes are necessary before the oil meets essential requirements. If synthetic fluids could be produced and blended to give similar properties to the highly refined oils, a limitless base fluid of high purity with no refining costs would be available. Since these initial goals have been met, research has continued to give a number of synthetic fluids which give better performance under certain circumstances than any highly refined mineral oils.²¹ This research is driven by other industries placing increasing demands on the lubricant systems that are in use.

In the early 1930's synthetic hydrocarbon and ester technologies were being developed in both the U.S.A.²² and Germany²³ simultaneously. These efforts were not commercialised at the time due to the costs of manufacture and the widespread introduction of additives which could be used to tailor the properties of mineral oils to give similar performance. After World War II, increasing requirements from the aviation industry stimulated further research into synthetic fluids which could be used over a very wide temperature range.

Synthetic base fluids are now found in all areas of lubrication technology. Many different compounds have been tested and found to work efficiently, but the six classes outlined below are the ones which are currently in widespread use.

1.4.1 Poly(alpha-olefins)

Poly(alpha-olefin), often abbreviated to PAO, refers to hydrogenated oligomers of an α -olefin, usually α -decene. Base fluids of this type operate over a very high temperature range and also have good low temperature properties. They can be produced in high purity and have excellent thermal and oxidative stability, leading to their usage in a wide range of applications. Several methods of oligomerisation have been used to produce these fluids, with three being of importance.

The first method is free radical oligomerisation,²⁴ which can be considered as thermal oligomerisation using a peroxide initiator. In general, controlling the degree of polymerisation is difficult using this method. This gives rise to a product of low quality and is, therefore, of limited use to the lubricant industry.

The second method is a Ziegler-catalysed polymerisation.²⁵ Here, a triethyl aluminium/titanium tetrachloride catalyst is often used, with the ratio of the two metals making a significant difference to the composition of the products. This method is, therefore, preferred over the free radical route due to the control that the chemist has over the properties of the final compounds. The disadvantages of this method include the tendency to give a broad distribution of oligomers, and the need for the presence of a solvent leading to difficulties with handling and separation.

The final, and now most widely used, method of production is by way of Friedel-Crafts catalysed oligomerisation. Initially, AlCl_3 was used as the catalyst when the process was first developed in 1931,²⁶ but as a result of the reactivity of this catalyst, problems were encountered with cracking and isomerisation leading to a complex mixture of products. More recently BF_3 -based catalysts have been used²⁷ which remove some of the problems associated with earlier catalytic systems, but side reactions and rearrangements can affect the overall properties of the materials produced.

1.4.2 Alkylated Aromatics

Base fluids of this type are typically alkyl benzenes which are either purpose made, or by-products from other processes such as the manufacture of dialkyl benzenes. The majority of alkyl benzenes have suitable lubricant properties such as low pour point, high thermal stability and good solvency since the aromatic ring gives

reasonably high polarities. This is of particular importance if the subsequent addition of an oil additive package is necessary.

Alkyl benzenes can be synthesised in a number of ways which all involve a catalysed reaction of benzene with either an olefin or an alkyl chloride.²⁸ The catalysts and conditions chosen can give control over molecular weight and structure which in turn gives control over the properties of the product. A typical structure of an alkylated aromatic likely to be used as a lubricant is shown in Figure 1.1.

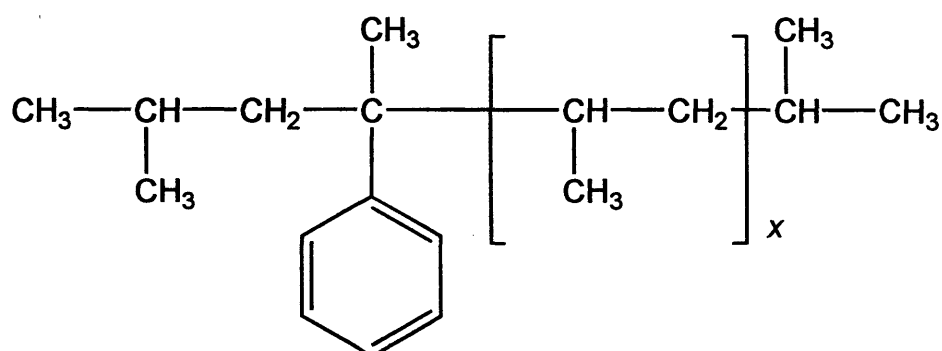


Figure 1.1 Synthetic alkyl benzene

Typically, when $x = 3$, the base fluid has a very high viscosity index and a pour point which can be as low as -40°C . Pour points as low as this can be achieved due to the base fluid being synthetic and so essentially wax free. For this reason, lubricants of this nature have been used extensively for extremely low temperature usage, such as refrigerator oils and Arctic applications. They also have widespread use in other industries, such as rolling and drawing oils, due to their low production costs and sulfur-free composition.

1.4.3 Polybutenes

These materials are usually polymers of *iso*-butene, but the whole series of polybutenes are known by the chemically incorrect abbreviation PIB (polyisobutene). These have uses in a number of applications as synthetic base fluids, but they are also used as viscosity index improvers when blended with mineral oils. They do have limitations as base fluids and are usually only used where volatility and oxidative stability are less important, and low deposit formation is more critical.

Polybutenes (Figure 1.2) are produced by catalysed polymerisation of a hydrocarbon stream containing *iso*-butene. If mixed butenes are present in the stream, an *iso*-butene/butene co-polymer is formed.²⁹ The amount of *n*-butene present in the co-polymer greatly affects the molecular weight and consequently the physical properties of the product.

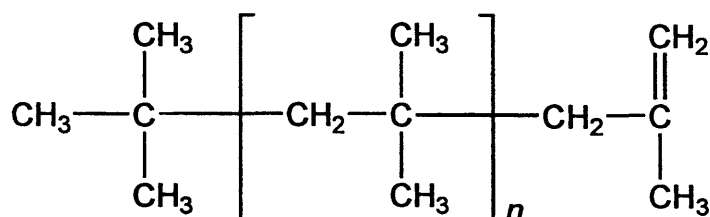


Figure 1.2 General polybutene structure

In general, polybutenes have a high solubility in hydrocarbon solvents, so they are often used in conjunction with other natural or synthetic base fluids. Currently, one of the largest markets for polybutenes is in two-stroke engine oils where they are used as a 30 % combination with mineral oil. They are also widely used as metal working lubricants, industrial gear oils and as wire rope protectives.

1.4.4 Synthetic Esters

Many early lubricants were natural esters which were contained in animal fats or vegetable oils such as rapeseed or castor oil. During and after World War II, a number of synthetic esters were developed from long chain acids and alcohols and were found to be excellent low temperature lubricants.³⁰ During the 1960's, they were used as gas turbine lubricants in the aviation industry as a result of their low volatility, due to intermolecular forces, and their high thermal stability. Today, they are used for a wide variety of applications especially where good low temperature characteristics are required and in the aviation industry. They are manufactured by a catalysed reaction of acid and alcohol to give ester and water.³¹ The reaction can be drawn to completion by azeotropic removal of the water. A number of different alcohols and acids can be used to produce a desired ester with properties which have been tailored to meet the needs of the intended application. The length of the

hydrocarbon chains, and the degree of substitution, on both the alcohol and the acid can have marked effects on a number of properties such as viscosity index, solvency and hydrolytic stability. Also, since the fluid consists of a single compound of uniform structure, the chemist can easily make very small adjustments to one or more properties of the base fluid by “fine tuning” the exact alcohol and acid used. Esters of this type have high biodegradability, low toxicity and provide clean engine emissions. For these environmental reasons, the use of synthetic esters could become far more prevalent over the coming years.

1.4.5 Polyalkylene Glycols

The term polyalkylene glycol covers a range of polymeric compounds with a number of differing properties. In general, they have a wide viscosity range with low pour points and excellent viscosity indices. They also offer good thermal stability, lubricity and low toxicity, making them a desirable class of lubricant base fluids for a number of different applications.

Polyalkylene glycols are usually produced by a base-catalysed polymerisation of an epoxide in the presence of an alcohol initiator,³² typically butanol. The reaction is highly exothermic and gives rise to products of a relatively narrow weight distribution. The molecular weights and, therefore, the viscosities of the products can be controlled by the quantity of epoxide added, making them a very versatile class of lubricants. They have found numerous applications as brake fluids and fire-resistant fluids along with more conventional uses as compressor lubricants and gear oils.

1.4.6 Phosphate Esters

Phosphate esters have been produced since the 1920's and have been used as plasticisers, lubricant additives and base fluids for hydraulic and compressor oils. They can be produced by the reaction of phosphoryl chloride with alcohols or phenols³³ (Figure 1.3), with the substituent groups making a significant difference to the properties of the product. Early manufacture utilised feedstocks derived from the distillation of coal tar to give a complex mixture of cresols and xylenols. The

presence of *ortho*-cresol results in a ester with significant neurotoxic effects, leading to the reduced use of these natural phosphate esters.

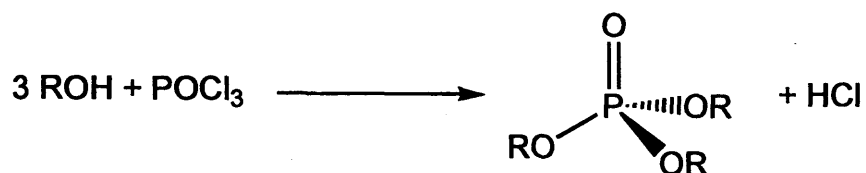


Figure 1.3 Formation of phosphate esters

The vast majority of phosphate esters currently in use are “synthetic”, using very pure alcohols and phenols as the feedstock. The physical properties of these compounds vary considerably according to the organic substituents, which can give a wide range of viscosities.

When used as base fluids, the phosphate esters exhibit exceptional load carrying and anti-wear properties. Their most important properties, however, are their fire resistance and excellent lubricity. Pyrolysis generates phosphoric acid which is a powerful flame retardant,³⁴ making these compounds the perfect lubricants for a wide range of applications close to potential sources of ignition.

1.4.7 Fluorinated Base Fluids

Fluorinated synthetic base fluids have recently been introduced for certain applications due to their high stability to both elevated temperatures and loads, along with low volatility and wide liquid range. Lubricants of this type, due to their high cost of production, are usually used where performance is vital and economic cost is unimportant. The most commonly used examples of these are perfluoropolyalkylethers,³⁵ such as the commercially available Fomblin® range. As research in this area develops, it has been found that the traditional additives used in organic oils were less effective due to their low solubility in these solutions. This is only to be expected due to the very low miscibility of many organic and perfluorocarbon solvents. The most effective way of increasing the solubility of species in perfluorocarbon solvents is to incorporate highly fluorinated aliphatic chains. These act to solublise the compound in the same way as alkyl chains afford solubility in organic solvents. Work has been carried out in this area by Fultz *et al.*³⁶ who, by

adding fluorous moieties, looked at the synthesis of a range of compounds, such as phosphines and alcohols, which were soluble in perfluoro-polyalkylether lubricants. The area of perfluorocarbon solubility of metal complexes is an ongoing area of research, and is especially important in the area of fluorous biphasic catalysis.^{37,38} Here, a metal catalyst is anchored in the fluorous phase using ligands prepared with highly fluorinated side chains known as fluorous “ponytails”. Examples of ligands which have been used are phosphines³⁹ and phosphites,⁴⁰ and the conditions under which molecules can be classed as preferentially fluorous phase soluble have also been reported.⁴¹

1.5 Additives in Lubricants

Until the 1930's, the lubricants in use were made up of the base fluids only. As machinery became progressively more sophisticated, the oils available were becoming less effective. This led to machinery having longer down-times and having to be replaced more often as excessive wear dramatically reduced the lifetime of the components. It was at this time that oil companies started to introduce additives into the base fluids to try to alleviate some of these problems. Today, manufacturers can use up to twenty components blended together in appropriate ratios, forming a total additive package used at concentrations of 0.05 to 10 % of the finished lubricant. Brief summaries of the most important classes of additives are given in this section with the exception of anti-wear and detergent additives which will be considered in sections 1.6 and 1.7 respectively, since these bear special relevance to the work discussed in this thesis.

Ongoing research in all of these areas is still currently being undertaken, with developments being made by lubricant manufacturers all over the world. At present, a typical additive package formulation⁴² is represented by Table 1.1. The percentages of each class of component shown can be adjusted by the additive manufacturers. This leads to the possibility of tailoring the properties for individual clients, depending upon the intended application.

Component	Percentage
Dispersants	55
Detergents	20
Anti-wear	11
Inhibitors	8
Other	6

Table 1.1 Typical formulation of an oil additive package

It is common for the additive manufacturers to pre-blend the components to form an overall additive package. This can then be passed to the lubricant manufacturer, where it is blended with the base fluid to form the finished lubricant.

1.5.1 Pour Point Depressants

In 1932, the first of the commercially-used additives, pour point depressants, were introduced.⁴³ These act to reduce the lowest temperature at which the lubricant will flow. At low temperatures, wax in the base fluid will crystallise to form a gel-like structure which may impede the flow of the lubricant to critical parts of the system. The pour point depressant is effective by adsorbing on to the surface of wax crystals as they form, thus preventing further crystal growth and stopping the crystals absorbing oil molecules to form a gel. With only small wax particles present, it is possible for the oil to flow freely even at reduced temperatures.

Currently, additives such as polyacrylates (Figure 1.4) and polymethacrylates (Figure 1.5) are the most commonly used pour point depressants and are used in typical concentrations of 0.1 to 1 %.⁴⁴

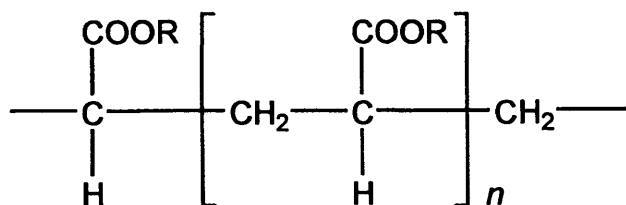


Figure 1.4 General structure of polyacrylates

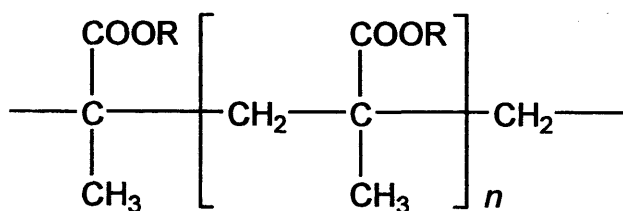


Figure 1.5 General structure of polymethacrylates

1.5.2 Viscosity Modifiers

Viscosity modifiers were the next additives to be introduced in the 1950's.⁴⁵ These have the purpose of making the viscosity of the oil less sensitive to temperature changes leading to the lubricant giving acceptable performance over a range of temperatures. Compounds commonly used for this are high molecular weight polymers (relative molecular mass from 50,000 to 500,000) such as olefin copolymers (OCP's).⁴⁶ One such example is the ethylene propylene copolymer (Figure 1.6).

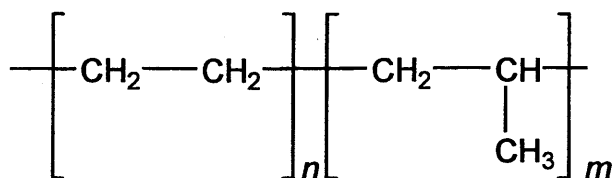


Figure 1.6 Ethylene propylene copolymer

Other classes of chemicals which are used are polymethacrylates, which are multi-functional additives discussed earlier, and styrene diene copolymers⁴⁷ such as hydrogenated styrene isoprene copolymer (Figure 1.7).

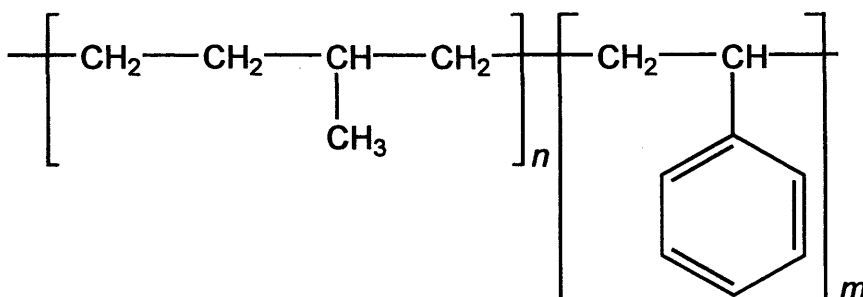


Figure 1.7 Hydrogenated styrene isoprene copolymer

All of the above compounds act as thickeners due to their intrinsic viscosity in solution affecting the overall physical properties of the lubricant. For ease of application, viscosity modifiers are usually diluted in a low viscosity base oil in concentrations of 5 to 50 % depending on the solubility and viscosity of the polymer.

1.5.3 Dispersants

In the 1960's, ashless dispersants were introduced. These act in a similar way to detergents (see section 1.7, p 26-30) but contain no metal. These have a polar head, but here it is derived from an organic functionality, usually from oxygen or nitrogen moieties, and a long oleophilic tail. There are two advantages of these additives over the earlier detergents; firstly there is no metal, therefore no ash is formed on combustion. Secondly, they are able to solublise larger particulates up to ~ 50 nm diameter (*c.f.* ~ 20 nm for detergents) by forming a micelle around the insoluble particle and anchoring it in solution. Compounds which are commonly used as the polar head group are succinate esters⁴⁸ (Figure 1.8) and Mannich bases⁴⁹ (Figure 1.9). In both cases, polyisobutene (PIB) is usually used as the oleophilic tail.

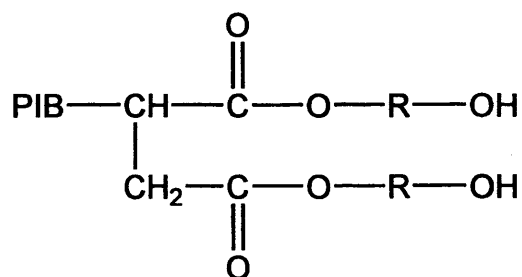


Figure 1.8 Succinate ester dispersant

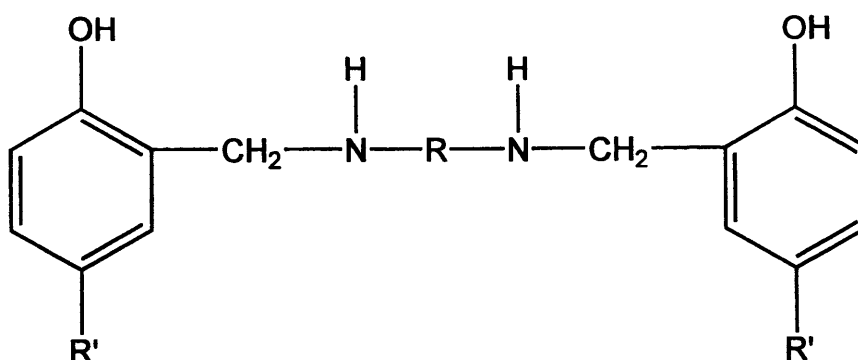


Figure 1.9 Mannich base dispersant

There have also been reports of phosphorus-containing dispersants being used such as hydroxypropyl esters of phosphorus acids⁵⁰ (Figure 1.10).

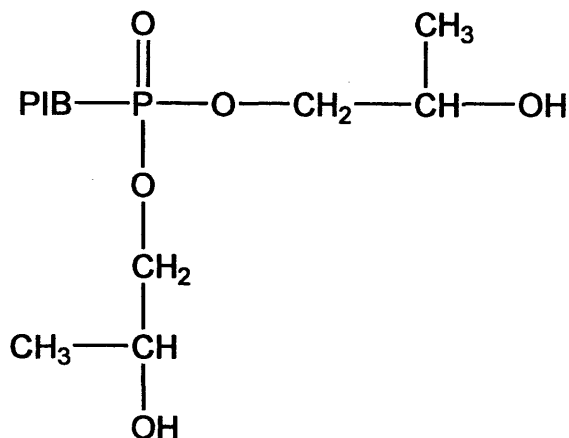


Figure 1.10 Hydroxypropyl ester of phosphorous acid

It is not unusual for lubricant formulations to contain more than one dispersant, especially when the application requires high performance over a large temperature range.

1.5.4 Inhibitors

Inhibitors, sometimes referred to as the “anti” additives, have the purpose of preventing or minimising detrimental processes such as foam formation, corrosion and rusting. These were first introduced to commercial oils in the 1970’s. Antifoam agents are effective by slowing the release of the gases churned into the oil. Since these additives are sparingly soluble, they separate from the oil on the surface of the air bubbles and cause them to burst by reducing their surface tension. Silicon-containing compounds are commonly used as antifoams⁵¹ (Figure 1.11) with typical treatment doses being as low as 10 ppm

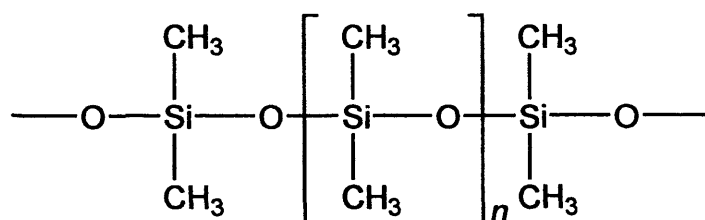


Figure 1.11 Polymethyl siloxane antifoam

1.5.5 Friction Modifiers

The final class of additives to be introduced were friction modifiers, also in the 1970's. By definition, the base fluid itself is the primary friction modifier but, due to increasing requirements placed on the oils, additional synthetic ones had to be added. These are surface active agents which improve boundary lubrication, and are often sulfurised fatty acids⁵² (Figure 1.12).

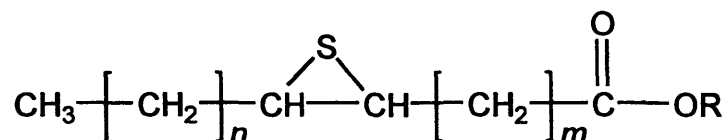


Figure 1.12 Sulfurised fatty acid friction modifier

1.6 Multifunctional Anti-Wear Additives

Since the 1940's, anti wear and extreme pressure additives have been blended into lubricants. The first class of compound to be used were zinc dithiophosphates,⁵³ commonly abbreviated to ZDTP's. These are still widely in use today as they are both relatively cheap to produce and are proven as effective multi-functional additives,⁵⁴ giving anti-oxidation properties in addition to wear inhibition.

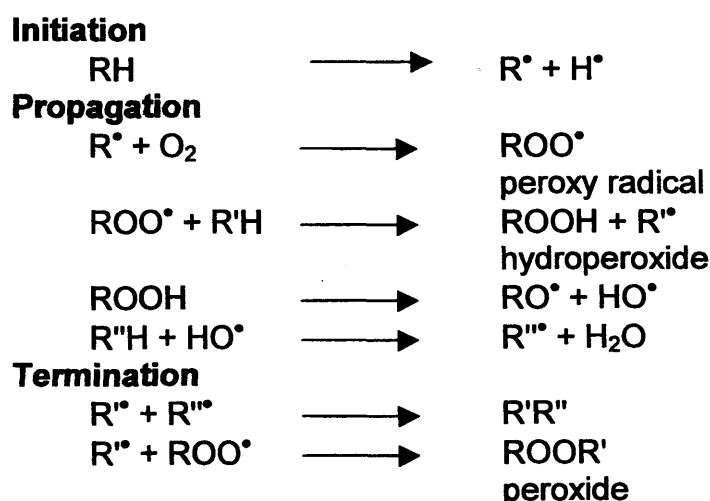


Figure 1.14 Oxidation chain reaction

Many studies have been carried out into the mode of action of ZDTP's as anti-oxidants, and a number of mechanisms have been proposed.⁵⁵ Although the exact mechanism is still unclear, it is believed that decomposition products act to disrupt the chain propagation steps of oxidation radical chain reactions (Figure 1.14). This occurs *via* a complex pattern involving hydroperoxides and peroxy radicals which act as either free radical traps or peroxide decomposers.

There have also been reports of how these zinc compounds act as anti-wear agents by aiding boundary lubrication.^{56, 57} Zinc is not the only metal centre to be effective in compounds of this nature. Synthesis and evaluation of other metal complexes such as those containing titanium,⁵⁸ cadmium⁵⁹ and nickel,⁶⁰ have all been reported in the literature. Molybdenum dithiophosphates have also previously been tested⁶¹ and have been found to be effective multifunctional additives. These are very efficient as anti-wear additives as one of the decomposition products is MoS₂ which is deposited as a surface coating thereby increasing boundary lubrication. Different ligands such as dithiocarbamates have also been studied⁶² and these have been reported as also being efficient additives when attached to the metal centres listed above.

Ashless anti-oxidant and anti-wear additives have been developed⁶³ more recently than the metal-containing ones, but do offer some distinct advantages. As they contain no metal, there is no ash formed on combustion. This leads to less sludge being deposited and, therefore, less need for detergent and dispersant additives to keep the system clean. They differ chemically from the metal containing compounds by the metal centre being replaced by an alkyl bridge (Figure 1.15), with the size of the alkyl bridge varying with the application.

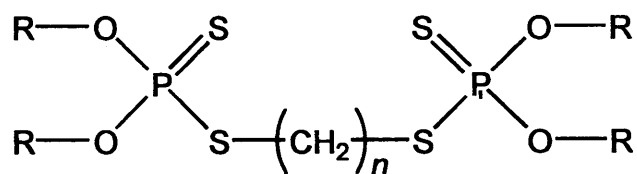


Figure 1.15 General structure of ashless dithiophosphates

This area of chemistry is of significant interest for research, as these ashless compounds begin to replace the metal-containing ones in mainstream applications. This is primarily due to the environmental concerns associated with the disposal of organic oils containing metal complex residues.

1.7 Detergents

The two basic roles of a lubricating oil are to reduce friction and wear and to act as a coolant to remove energy from the system. To achieve, and then maintain, these functions, it is imperative that the oil flows properly throughout the system. Detergents and dispersants help to preserve this property by minimising oil thickening and thereby maintaining a steady viscosity. They also act to solublise carbon sludge deposits which may block fuel lines and physically prevent the oil flow.

These additives work in a similar way to household detergents, and are active by forming an “inverse” micelle. Common household detergents, used in aqueous systems, have a hydrophilic head and a hydrophobic tail,⁶⁴ whereas these, used in hydrocarbon solvents, have a oleophilic tail and a oleophobic head (Figure 1.16).

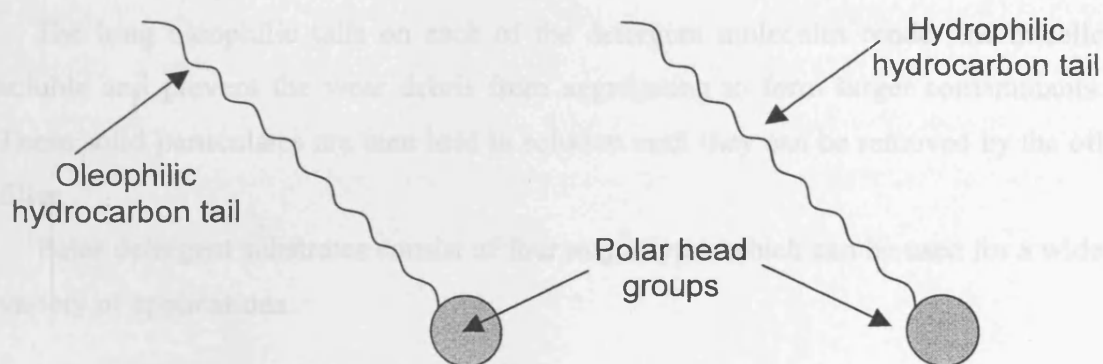


Figure 1.16 Comparison of oil (left) and water (right) soluble detergents

The polar head contains a metal cation which is usually either calcium, magnesium⁶⁵ or sodium. These have replaced barium⁶⁶ over a period of time because, although barium-based detergents have been found to be both efficient and reasonably cost effective, the environmental issues associated with the use of heavy metals have made their continued application prohibitive.

Detergents of this nature operate by surrounding small particles of sludge or wear debris to form a micelle⁶⁷ (Figure 1.17) due to interactions between the polar head and the metal particulate.

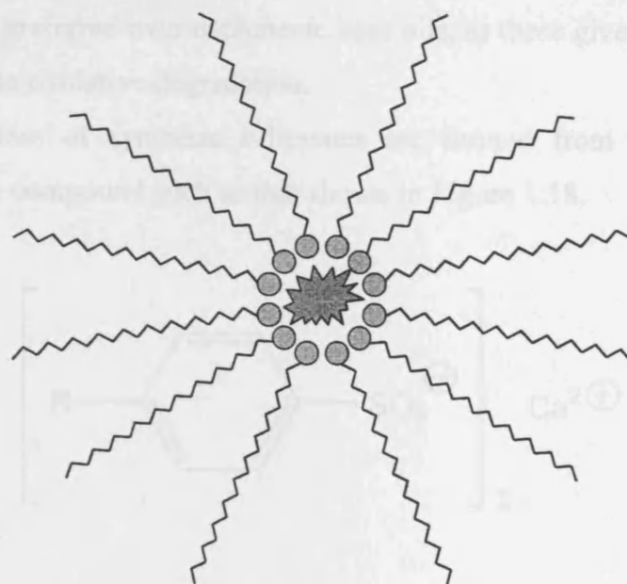


Figure 1.17 Aggregation of detergent molecules around wear debris

The long oleophilic tails on each of the detergent molecules render the micelle soluble and prevent the wear debris from aggregating to form larger contaminants. These solid particulates are then held in solution until they can be removed by the oil filter.

Polar detergent substrates consist of four major types which can be used for a wide variety of applications.

1.7.2 Phenates

1.7.1 Sulfonates

There are two types of sulfonate detergent in use. The first are “natural” or petroleum sulfonates. These are formed as a by-product in the synthesis of white oil from mineral oil. This is done by mixing mineral oil with sulfuric acid to form white oil plus a sulfonic acid mixture which can be treated with sodium hydroxide to yield two different types of soaps. After extraction with an alcoholic solvent, the sodium sulfonates can be recovered and converted to other metal salts by means of metathesis reactions. The chemical structure of these materials are not known with any certainty, and the metal sulfonate recovered is believed to be a mixture of a number of different compounds. Changing the base oil used at the start of the white oil process is the only way of modifying the sulfonates recovered, with paraffinic base

oils being greatly preferred over naphthenic base oils, as these give sulfonates with far higher resistance to oxidative degradation.

The second class of synthetic sulfonates are formed from an alkyl aromatic substrate to give a compound such as that shown in Figure 1.18.

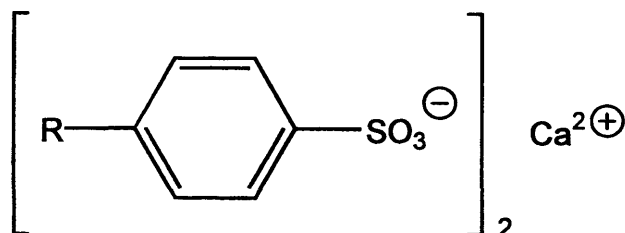


Figure 1.18 General structure of sulfonates

Materials of this nature can be produced by a number of different routes.⁶⁸ These include the reaction of benzene alkylates with gaseous SO_3 , sulfoxidation and bisulfite addition. A sulfochlorination, known as the Reed process, has also been employed in the commercial manufacture of sulfonate detergents. Overbased sulfonates are often used, and give similar performance advantages to the overbased phenates described in the following section.

1.7.2 Phenates

Normal phenates based on metal salts of derivatised phenols and biphenols (Figure 1.19) are widely used detergents especially in commercial engine lubricants. They can be prepared by simple deprotonation of the appropriate phenol, often synthesised *via* a Friedel-Crafts type alkylation, using either a metal oxide or hydroxide.⁶⁹

In addition to normal biphenates, a number of other compounds have been investigated whereby the aromatic rings are coupled together either by a sulfur atom or an alkyl group. This affects the geometry of the molecule and, as a result of this, the way in which it performs as a detergent.

Since a very important function of a phenate is acid neutralisation, excess base is often incorporated into these materials. This gives rise to an “overbased” compound which is a term frequently used within the industry to describe a material containing

greater than a stoichiometric amount of base. Figure 1.20 shows a schematic representation of an overbased phenate sulfide.

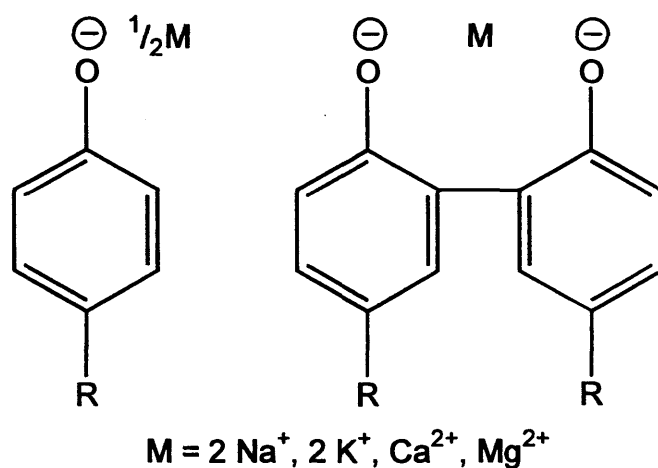


Figure 1.19 Normal phenates prepared from phenols and biphenols

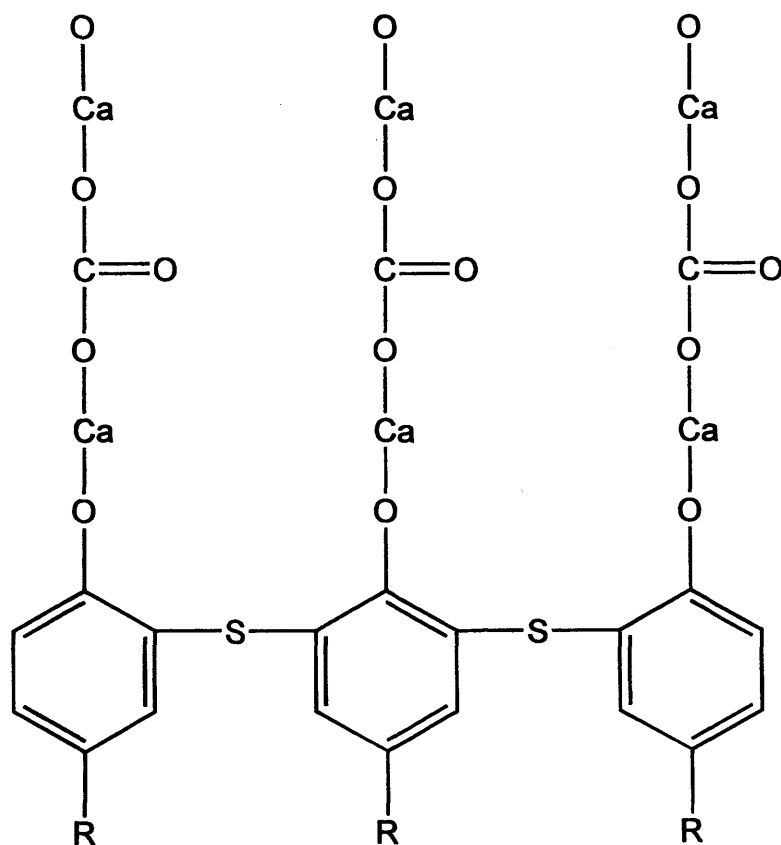


Figure 1.20 General structure of an overbased phenate sulfide

Often phenates containing two or three times the stoichiometric amount of metal are used, and these have been found to give better performance than neutral phenates. Compounds of this nature where the alkyl group typically consists of twelve or more carbon atoms have found widespread use over a variety of applications.

1.7.3 Salicylates

Salicylates are derived from phenate detergent substrates following the Kolbe-Schmitt reaction⁷⁰ shown in Figure 1.21. Usually the potassium salicylate is not isolated, with calcium or magnesium salicylates being prepared *via* metathesis reactions using the appropriate metal chloride.⁷¹

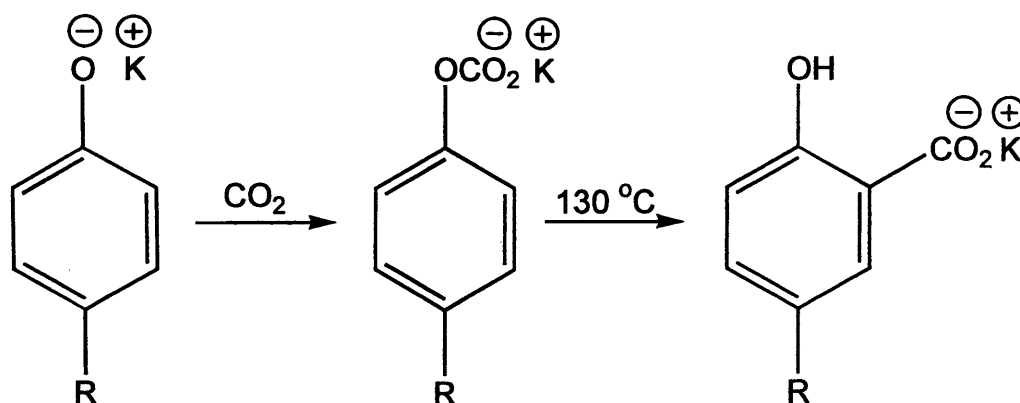


Figure 1.21 Preparation of salicylates *via* the Kolbe-Schmitt reaction

The length of the alkyl chain can differ greatly in these compounds, and is often between twelve and thirty two carbons in length. This has a significant effect on the solubility of these detergents, making them compatible with a number of different base fluids over a range of polarities.

1.8 Outline of Thesis

The work contained in this thesis describes the synthesis of a number of dithiophosphate, xanthate, dithiocarbamate and phenate ligands bearing long perfluoroalkyl chains. The coordination chemistry of these ligands has been

thoroughly investigated by the formation of a number of different metal complexes, with characterisation being carried out by a variety of analytical techniques. The driving force for this work is the potential application of some of these compounds as novel anti-wear and detergent oil additives, which could be used in specialised hydrocarbon and fluorocarbon lubricants. The anti-wear and extreme pressure properties of a selected number of metal complexes formed have been examined using SRV testing apparatus, with results being compared to the base fluid alone.

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2.1 Introduction

2.1.1 Lewis Acid-Base Theory

Lewis acid-base theory, also known as donor-acceptor theory, is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is defined as an electron pair donor and an acid is defined as an electron pair acceptor. The Lewis theory gives the emphasis on the donation and acceptance of electron pairs.

CHAPTER TWO

Dithiophosphate Ligands and Coordination Chemistry

2.1.2 The Hard and Soft Acids and Bases (HSAB) Principle

The Hard and Soft Acids and Bases Principle is an extremely useful qualitative theory that enables predictions of what acids will form in a particular reaction of interest. Lewis acids and bases. Although there have been numerous attempts to make this theory quantitative by assigning numbers representing "hardness" and "softness" of acids and bases, these attempts have particularly unsuccessful.

The basic premise of the Hard Soft Acid-Base Theory is simply that hard acids prefer hard bases and soft acids prefer soft bases. Hard acids and bases can be defined as follows:

Hard acids are:

- Small, high positive charge of the central atom
- High electronegativity
- High ionization potential
- Reluctant to form covalent bonds

High charge often results in small size, because the bonding electrons are concentrated toward the nucleus by the substantial charge positive charge. Examples of hard acids



**University of
Leicester**

2.1 Introduction

2.1.1 Lewis Acid-Base Theory¹

Lewis acid/base theory, also known as donor-acceptor theory, is a broad, widely applicable approach to the classification of chemical substances and the analysis of chemical reactions. According to this theory, a base is defined as an electron pair donor, and an acid as an electron pair acceptor. Donation of an electron pair from base to acid results in the joining of the acid and base *via* a covalent bond. The bonded acid-base species can be termed an *adduct*, a *coordination compound*, or a *complex*. The Lewis theory puts the emphasis on the donation and acceptance of electrons, and can be applied to all organometallic coordination chemistry. Further refinement to the Lewis theory has led to acids and bases being further classified into “Hard”, “Soft” and “Borderline” groups.

2.1.2 The Hard and Soft Acid and Base (HSAB) Principle^{2,3}

The Hard and Soft Acid and Base Principle is an extremely useful qualitative theory that enables predictions of what adducts will form in a complex mixture of potential Lewis acids and bases. Although there have been numerous attempts to make the theory quantitative by assigning numbers representing "hardness" and "softness" to acids and bases, these have not been particularly successful.⁴

The basic premise of Hard/Soft Acid/Base Theory is simply that hard acids prefer hard bases and soft acids prefer soft bases, where these terms can be defined as follows:

Hard acids are often characterized by:

- Low electronegativity of the acidic atom
- Relatively small size
- Relatively high charge

High charge often results in small size, because the remaining electrons are contracted toward the nucleus by the substantial excess positive charge. Examples of hard acids

are the metal cations from the s and f blocks, and the higher-charged ions from the left side of the d block.

Hard bases are often characterized by:

- Very high electronegativity of the donor atom
- Relatively small size of the donor atom

The combination of high electronegativity and small size results in a non-polarizable electron cloud surrounding the donor atom, which is often oxygen.

Soft acids are characterized by an acceptor atom of:

- Intermediate to high electronegativity
- Relatively large size
- Relatively low charge

The combination of low charge and large size of the species results in a polarizable electron cloud. Examples of soft acids are certain metal cations from the right side of the d block.

Soft bases are characterized by donor atom of:

- Intermediate to high electronegativity
- Large size leading to polarizability

In addition to the fundamental "hard" and "soft" categories, two additional categories are useful. *Borderline acids* are intermediate between hard and soft acids, therefore, they tend to have lower charge and somewhat larger size than hard acids, and higher charge and somewhat smaller size than soft acids. *Borderline bases* are intermediate between hard and soft bases, so they tend to be larger and less electronegative than hard bases but smaller and more electronegative than soft bases. Bases in which the donor atom is nitrogen or chlorine often fall into this category. Because hard acids and bases tend to be highly charged and non-polarizable, the interaction between them is largely ionic. In contrast, soft acids and soft bases have covalent interactions as a result of their polarizable nature. Table 2.1 shows examples of all six classes of Lewis acids and bases.

Class	Acid	Base
Hard	H^+, Li^+, Na^+, K^+	H_2O, OH^-, F^-, Cl^-
	$Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+}$	$PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, NO_3^-$
	$Al^{3+}, Sc^{3+}, Ga^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}$	ROH, RO^-, R_2O
	$Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, U^{4+}$	NH_3, RNH_2, N_2H_4
Soft	$Cu^+, Ag^+, Au^+, Tl^+, Hg^+$	R_2S, RSH, RS^-
	$Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}$	I^-, SCN^-, CN^-, CO
	Tl^{3+}	$R_3P, (RO)_3P, H^-, R^-$
Borderline	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}$	N_3^-, Br^-
	Ru^{2+}	NO_2^-, SO_3^{2-}
	Rh^{3+}, Ir^{3+}	N_2

Table 2.1 Examples of hard, soft and borderline Lewis acids and bases

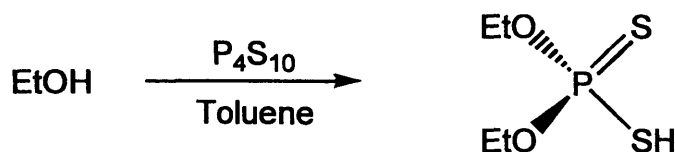
The HSAB theory can be refined to take account of a number of factors which can influence the degree of hardness and softness. In addition to the nature of the acceptor atom, hardness/softness of acids can be affected by several factors. Firstly, hardness increases with increasing charge (e.g. Tl^{3+} is harder than Tl^+), and secondly the nature of other groups attached. Attaching soft bases to an acceptor atom increases its softness, whilst attaching hard bases increases the hardness of the acceptor atom.

The degree of hardness/softness of bases can be affected in a similar way. Firstly, charge affects the hardness/softness of bases, with increased negative charge increasing the polarizability, hence the softness. Finally, other attached groups can affect the hard/soft character of a base. Hard substituents increase hardness whilst soft substituents increase softness (e.g. NF_3 is a harder base than $N(CH_3)_3$). This infers that the HSAB Principle can now be defined as: "harder acids prefer harder bases; softer acids prefer softer bases".

During the course of this work, the ligand classes studied (dithiophosphate, xanthate and dithiocarbamate) all contained sulfur donor atoms and, therefore, fall into the category of soft Lewis bases. Investigation into the coordination chemistry of these ligands has mainly focussed on complexation to either "soft" or "borderline" metal centres, such as Cu^+ , Ni^{2+} , Zn^{2+} and Rh^{3+} , to give a series of stable adducts.

2.1.3 Dithiophosphate Ligands and Coordination Compounds

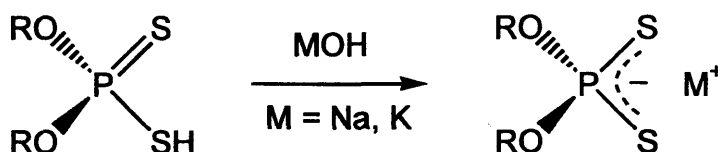
The dithiophosphate class of ligands can be prepared by direct addition of eight equivalents of alcohol to P_4S_{10} , to form a four coordinate, pseudo-tetrahedral compound. Although these compounds were first made many years ago, the vast majority of work presented in the literature centres around the diethyl compound⁵ (Scheme 2.1).



Scheme 2.1 Formation of diethyl dithiophosphoric acid

Despite the lack of reports in the academic literature of dithiophosphates of higher alcohols, potentially any length of chain could be used, and compounds of this nature have often found application in the petrochemical industry.

Dithiophosphoric acids of this nature can easily be deprotonated by a metal hydroxide to form an alkali metal salt (Scheme 2.2) which can then be subsequently used to produce a number of other metal complexes.



Scheme 2.2 Formation of alkali metal dithiophosphate salts

Dithiophosphate ligands have the ability to adopt monodentate, bidentate or bridging coordination modes (Figure 2.1), and here a brief, selective overview of their coordination chemistry is included to illustrate key points of interest. In addition to this, a more comprehensive study has recently been compiled by Haiduc *et al.*⁶

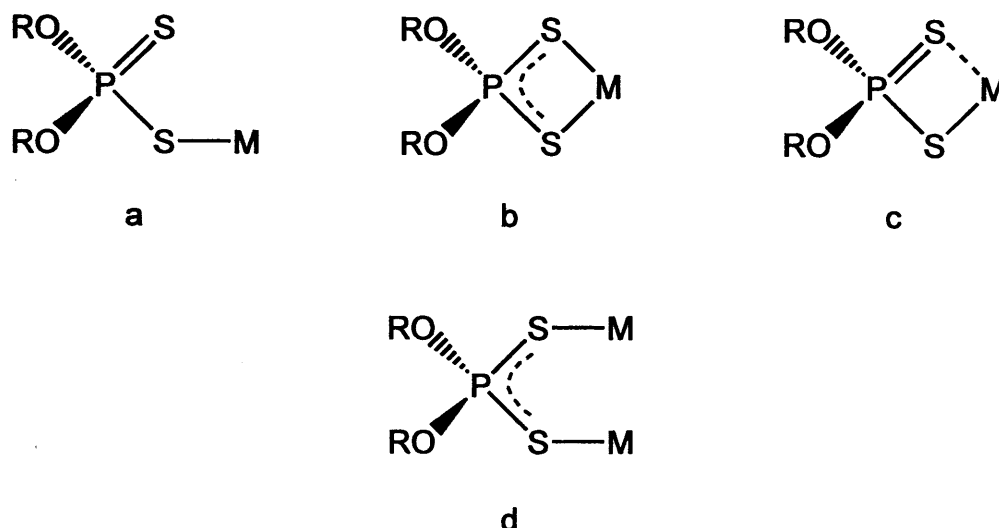


Figure 2.1 Possible bonding modes of dithiophosphate ligands monodentate (a), isobidentate (b), anisobidentate (c) and bridging (d)

Although the monodentate situation is rare it has been observed,⁷ while the isobidentate, anisobidentate and bridging modes are far more common. The most well known of these, and most widely studied, series of coordination compounds are the zinc dialkyldithiophosphates (ZDDP's) (Figure 2.2), which act as multifunctional oil additives and have been used commercially since the 1940's. Here long alkyl tails are necessary to impart solubility of the additive in the base fluid, with octyl or higher groups being commonly used.

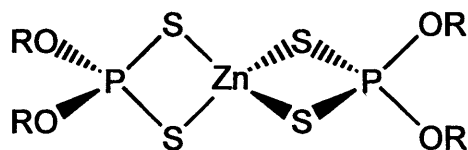


Figure 2.2 General structure of zinc dithiophosphates

The general structure of a ZDDP, shown above, is commonly known as the “normal” or “neutral” form. This exists in equilibrium with an alternative “basic” form when in solution (Figure 2.3).

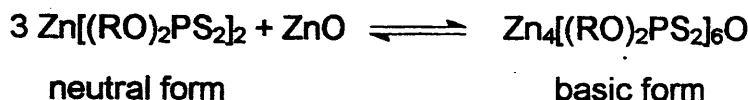


Figure 2.3 Equilibrium of neutral and basic forms

The structure of the basic form has been proven to be four zinc atoms tetrahedrally arranged around an oxygen atom with six ligands bridging the four metals, with the “breakdown” of the basic to the neutral form being reported by Harrison and Kikabhai⁸ (Figure 2.4).

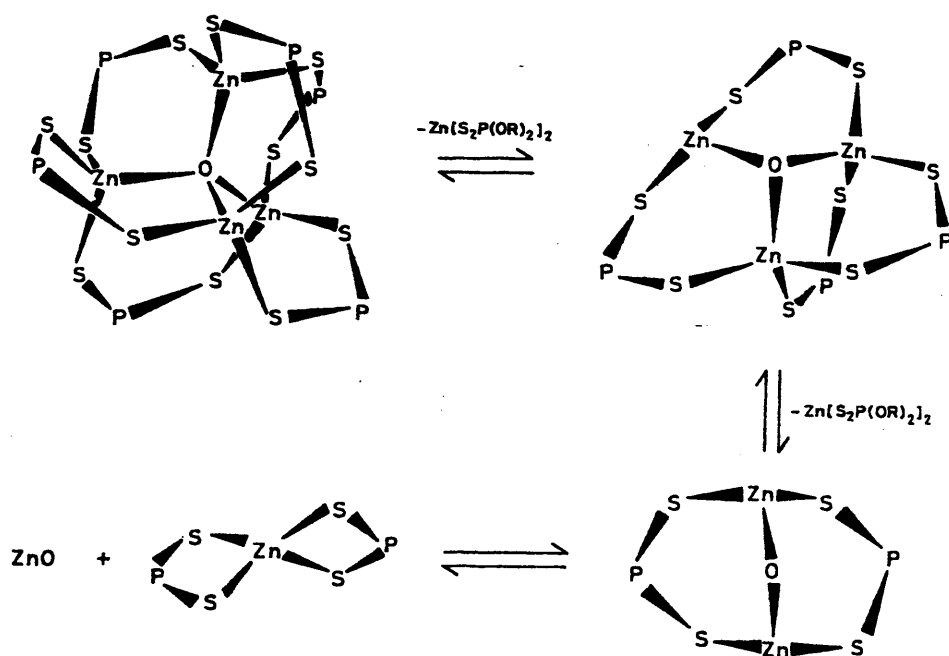


Figure 2.4 Schematic representation of the breakdown of basic ZDDP, where the alkoxy groups have been omitted for clarity⁸

It has been reported that it is possible to exclusively synthesise either the neutral⁹ or the basic¹⁰ forms, but obtaining characterisation of the pure materials proves difficult as an equilibrium between the two forms occurs. Studies have shown, however, that the position of the equilibrium is affected by the polarity of the solvent,¹¹ with more polar solvents pushing the equilibrium towards the neutral form. Although Figure 2.2 acts as a convenient representation of the neutral form, a subsequent report has shown the actual structure to adopt a DTP-bridged dimer configuration.¹²

In addition to zinc, a number of other metal centres have been used in dithiophosphate compounds for oil additive applications. These include bismuth(II),¹³ titanium(IV)¹⁴ and nickel(II)¹⁵ which have all previously been found to be efficient anti-wear and extreme pressure additives, while antimony(III) dithiophosphates¹⁶ are often used as passivating agents in petroleum refining.

Although linear alkyl tails are usually used as the solubilising units, both branched alkyl and aryl groups have also been reported.¹⁷ The performance of the additive is greatly affected by the nature of the alcohol used in its synthesis, with aryl precursors giving high thermal stability while alkyl alcohols give products with far greater hydrolytic stability. It is not, therefore, uncommon to find a mixture of the two in additive packages, giving effective performance under a variety of conditions.

In addition to the compounds used as lubricant additives, other examples of dithiophosphate complexes are prevalent in the chemical literature. A number of compounds bearing ligands which bridge across metal centres have been reported. Byrom *et al.*¹⁸ produced Cd(II) and Zn(II) dimers for use in semiconductor applications which have been characterised by X-ray crystallographic studies (Figure 2.5).

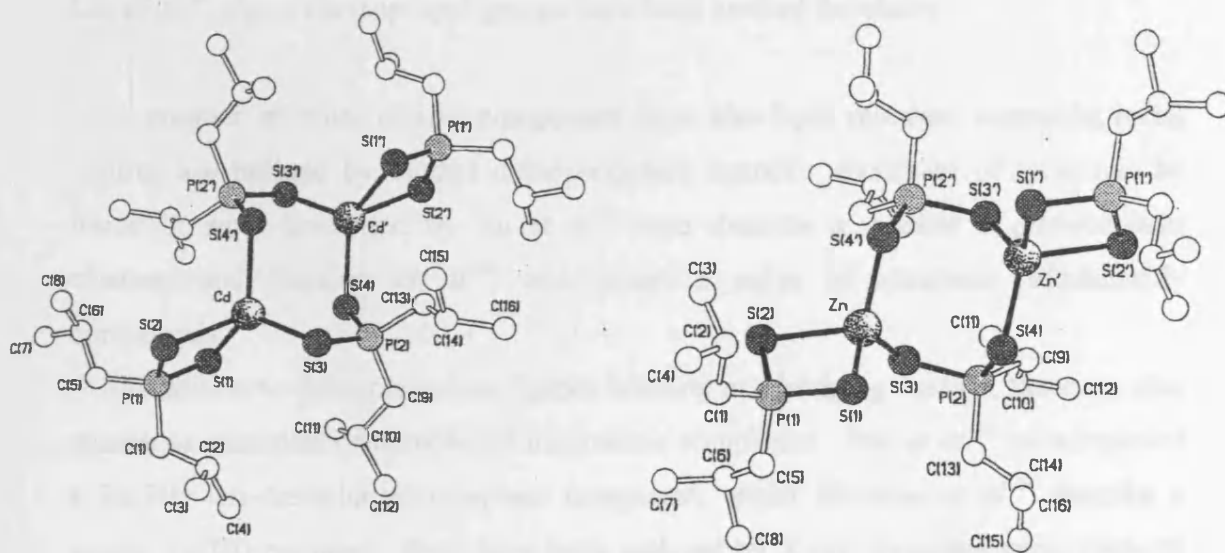


Figure 2.5 Cd(II) and Zn(II) dithiophosphate dimers reported by Byrom *et al.*¹⁸

Nag *et al.*¹⁹ have observed a comparable mode of coordination where dithiophosphate ligands bridge across Ag(I) metal centres bearing triphenyl phosphine

groups to give a similar dimer structure while Liu *et al.*²⁰ have reported the synthesis of hexa-silver(I) clusters containing diisopropyl dithiophosphate ligands (Figure 2.6).

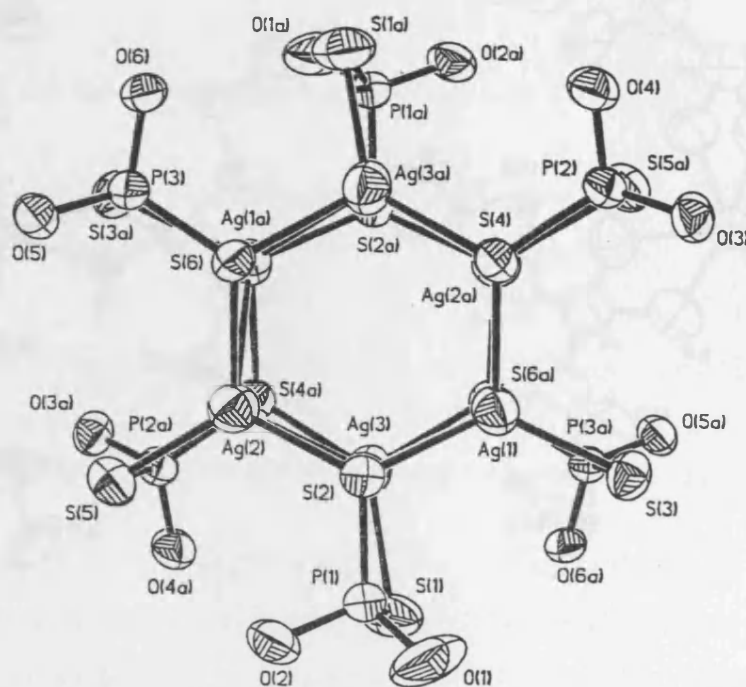


Figure 2.6 Crystal structure of the hexa-silver(I) dithiophosphate cluster reported by Liu *et al.*²⁰ where the isopropyl groups have been omitted for clarity

A number of other cluster compounds have also been reported where the metal centres are bridged by diethyl dithiophosphate ligands. Examples of these can be found in work presented by Hu *et al.*²¹ who describe a number of molybdenum clusters, and Narayan *et al.*²² who report a series of trinuclear palladium(II) compounds.

In addition to dithiophosphate ligands bonding in a bridging manner, there are also numerous examples of homoleptic monomeric complexes. Jain *et al.*²³ have reported a Ru(III) *tris*-diethyldithiophosphate compound, whilst Biscarini *et al.*²⁴ describe a similar Cr(III) complex. Both have been analysed by X-ray crystallographic methods and show that the three dithiophosphate ligands in each case are binding *via* a bidentate mode to give stable octahedral complexes (Figure 2.7) with the ligand retaining its four coordinate, pseudo tetrahedral geometry.

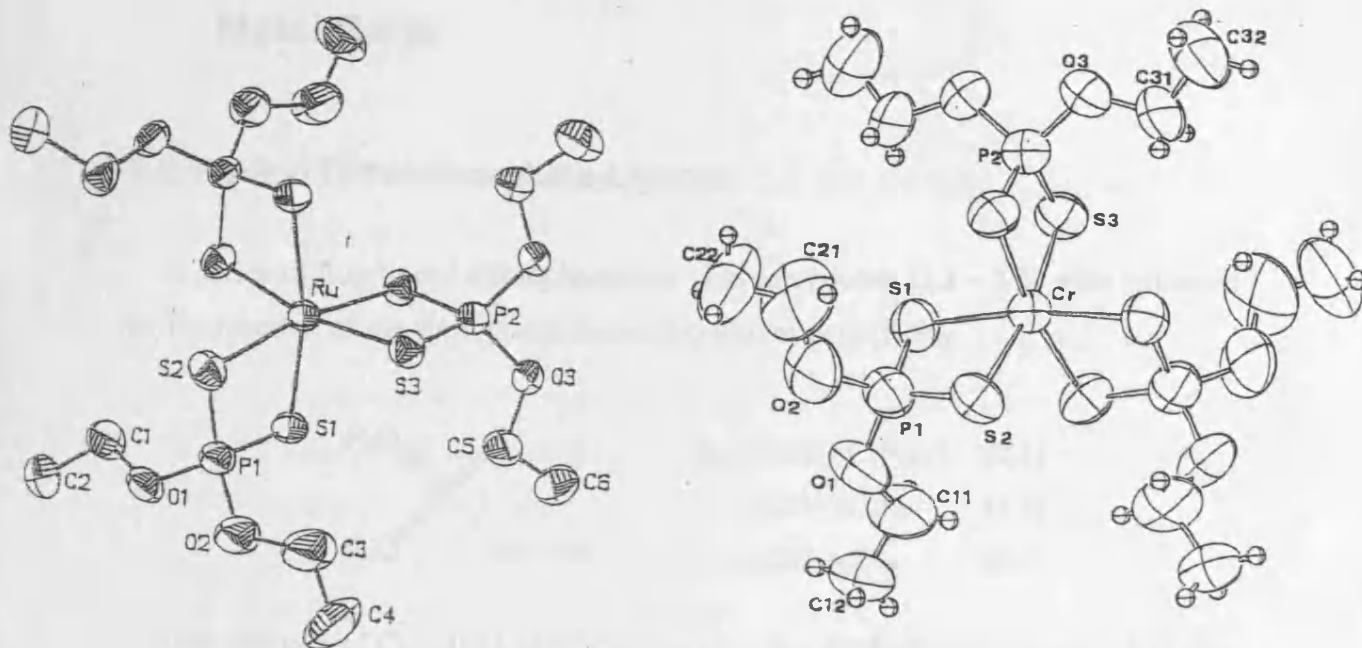


Figure 2.7 Crystal structures of Ru(III)²³ (left) and Cr(III)²⁴ (right) *tris*-dithiophosphate complexes

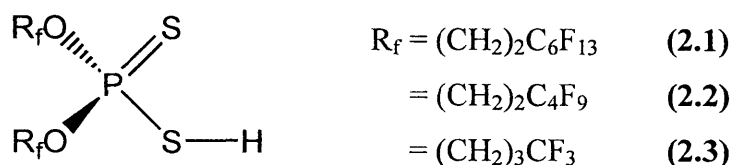
Coordination of dithiophosphate ligands to a number of other transition metal centres has also been studied including lead(II),²⁵ platinum(II)²⁶ and tellurium(IV).²⁷ Recently, Haiduc and Goh²⁸ have presented a report which gives a more comprehensive review of other organometallic dithiophosphate compounds.

The work presented below summarises attempts to form a number of alkyl, perfluoroalkyl, aryl and perfluoroalkyl-aryl dithiophosphate ligands, along with a study of their coordination chemistry to a variety of transition metal centres.

2.2 Synthesis of Dithiophosphate Ligands and Alkali Metal Salts

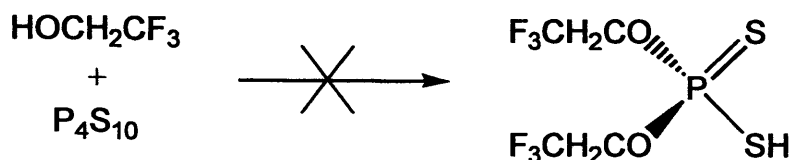
2.2.1 Alkyl Dithiophosphate Ligands

A series of fluorinated dithiophosphoric acid compounds (**2.1** – **2.3**) were produced by the reaction of the appropriate fluorinated alcohol with P_4S_{10} .



The addition of $C_6F_{13}(CH_2)_2OH$ to P_4S_{10} gives the dithiophosphoric acid (**2.1**) after heating at reflux in toluene for up to 12 hours. Reaction progress can be monitored qualitatively by estimating the amount of the insoluble P_4S_{10} left in the reaction mixture, which is clear at completion. Hydrogen sulfide was eliminated as a by-product and was scrubbed by passing the exhaust gas through saturated $NaOH_{(aq)}$ followed by saturated $FeCl_{3(aq)}$. Reactions under these conditions have been reported previously using protio alcohols,⁵ but the work reported here are the first syntheses of highly fluorinated dialkyl dithiophosphoric acids.

Here, the presence of the perfluoroalkyl tails are an attempt to impart fluorous phase solubility on subsequent metal complexes. Due to the electron withdrawing properties of the perfluoroalkyl groups in the alcohol, their electronic properties and, therefore, reactivity differ in comparison to conventional hydrocarbon alcohols. For this reason it is essential to have a spacer group, here a C_2H_4 group, between the perfluoroalkyl tail and the oxygen atom. This acts to shield the oxygen from the high electron withdrawing effects of the perfluoroalkyl group, thus allowing it to be sufficiently nucleophilic to react with P_4S_{10} . The importance of this spacer group can be demonstrated by an attempt to form the corresponding dithiophosphoric acid using 2,2,2-trifluoroethanol (Scheme 2.3). This proved to be unsuccessful, even after heating to reflux in toluene for 1 week, suggesting that a single carbon atom spacer does not give sufficient electronic insulation to allow reaction to take place.

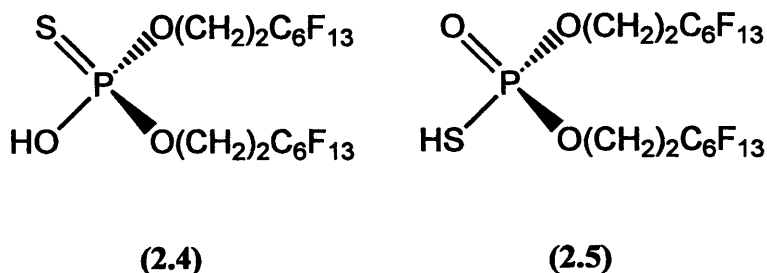


Scheme 2.3 Unsuccessful attempt to form a fluorinated dithiophosphoric acid with a single carbon spacer group

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (2.1) showed a singlet at 87 ppm. while also showing an impurity, also a singlet, at 72 ppm. Although it is recognised that the integration of ^{31}P NMR is not particularly accurate,²⁹ the impurity was estimated to be 3-5 % of the overall composition.

Various methods of purification were undertaken to try to separate the two species. Initially Kugelröhr distillation was carried out. This proved unsuccessful as the two species co-distilled at 125 °C / 0.02 mmHg, suggesting a similar molecular weight. This method removed all other trace impurities except for the predominant one at 72 ppm. Also, it must be noted that there was a significant amount of decomposition product left as a distillation residue, making it possible to recover only ~ 50 % of the starting mass.

A fluorous extraction was also attempted, by dissolving (2.1) in toluene and extracting with PP3. This also removed all traces of impurity except the predominant one at 72 ppm, but afforded the mixture of products in a higher yield than the distillation. The fact that the impurity was taken up into a perfluorinated solvent would suggest that the impurity contains similar fluorous character to the product. Initially, the impurity was thought to possibly have arisen from a small percentage of the P_4S_{10} hydrolysis product being either present in the starting material, or being formed as the reaction takes place. It was hypothesised that the impurity present could be either (2.4) or (2.5).



To try to reduce the number of suspected impurities to one, reaction with chlorotrimethyl silane was attempted. Owing to the hard nature of the silicon reagent this should react with the hard alcohol functionality in preference to the softer thiol functionality. This experiment failed to shift the position of the resonance of the impurity in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, thus suggesting that (2.5) is most likely to be the impurity, although NMR studies carried out by Burn *et al.*³⁰ would suggest that the impurity could be in the correct region to possibly be assigned as (2.4).

Identical results were obtained from several repetitions of the experiment even though stringent measures were taken to ensure that all solvents and glassware were thoroughly dried and all transfers were carried out under nitrogen. The only point at which moisture may have entered the system was through insufficient drying of the alcohol reagent.

Further purification techniques were also employed in an attempt to separate product from impurity. As a result of the polarity difference of the oxygen and the sulfur, separation by chromatographic methods was thought to be possible. Thin layer chromatography on both alumina and silica media proved to be inconclusive, so small scale column chromatography was attempted using both media. After being passed down the column using diethyl ether as the eluant, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed a number of unassignable resonances, suggesting significant decomposition.

Due to the high solubility of (2.1) in all organic solvents tested, it was impossible to attempt a recrystallisation of the free acid. This method of purification was, however, attempted on the sodium and potassium salts, which have a more crystalline nature (Section 2.2.2).

As all methods of purification of (2.1) proved to be unsuccessful, leaving a small impurity, similar problems were expected in the formation of (2.2) and (2.3). This, however, did not prove to be the case with neither reaction giving rise to an impurity in that region of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra, with pure samples being afforded by a simple Kugelröhr distillation.

When (2.2) and (2.3) were synthesised they gave similar resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at chemical shifts very close to that of both (2.1) and its protio analogue²⁹ (Table 2.2). This would suggest that the presence and length of the fluorine tail has little effect on the electronic environment of the phosphorus when the C_2H_4 or C_3H_6 spacer group is in place.

Compound	$^{31}\text{P}\{^1\text{H}\}$ Resonance / ppm
(2.1)	87
$(\text{H}_{13}\text{C}_6\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{S})\text{SH}^{22}$	86
(2.3)	87
(2.3)	86

Table 2.2 Chemical shifts of $^{31}\text{P}\{^1\text{H}\}$ resonances of (2.1) and (2.2)

Proton and fluorine NMR spectra of both (2.1) and (2.2) showed the expected number of resonances, and were similar to the alcohol precursors. The ^1H NMR spectra of both showed the signal for the $\alpha\text{-CH}_2$ next to the oxygen (Figure 2.8) as a doublet of triplets (Figure 2.9), downfield of the $\beta\text{-CH}_2$ triplet of triplets signal (Figure 2.10).

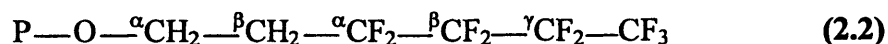
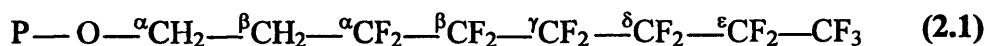


Figure 2.8 Assignments of proton and fluorine resonances for (2.1) and (2.2)

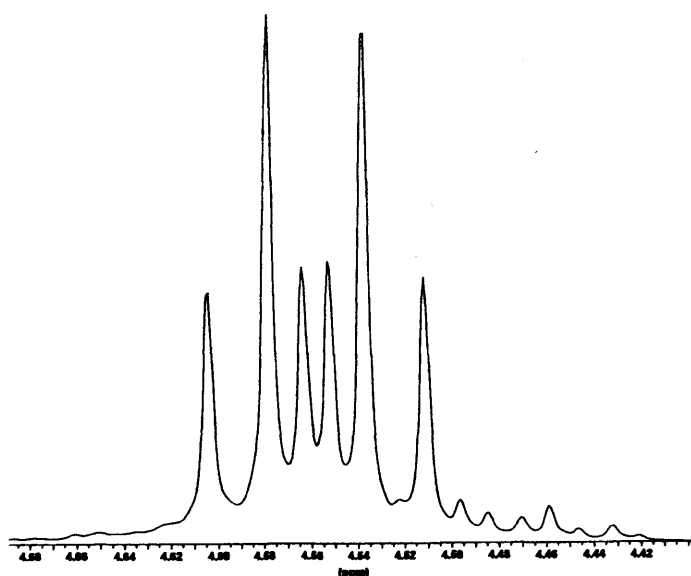


Figure 2.9 Doublet of triplet resonance assigned to $\alpha\text{-CH}_2$ of (2.1)

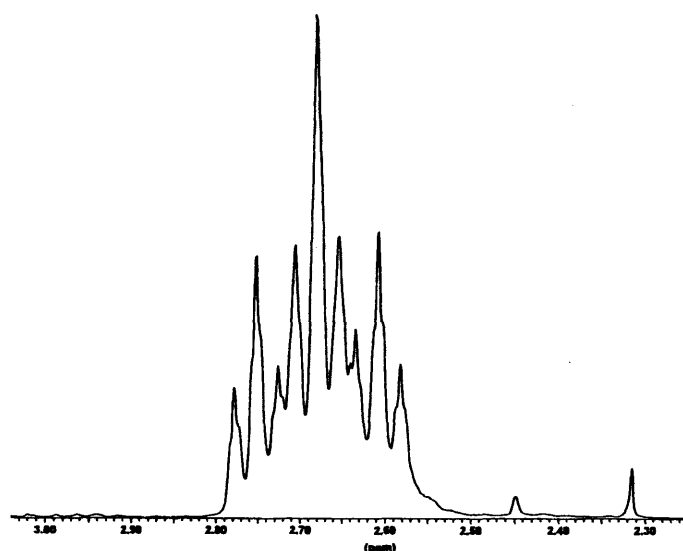


Figure 2.10 Triplet of triplet resonance assigned to $\beta\text{-CH}_2$ of (2.1)

The ^{19}F $\{^1\text{H}\}$ NMR spectra showed six resonances for (2.1) (Figure 2.11) and four resonances for (2.2) (Figure 2.12) due to the number of inequivalent fluorine environments in each case.

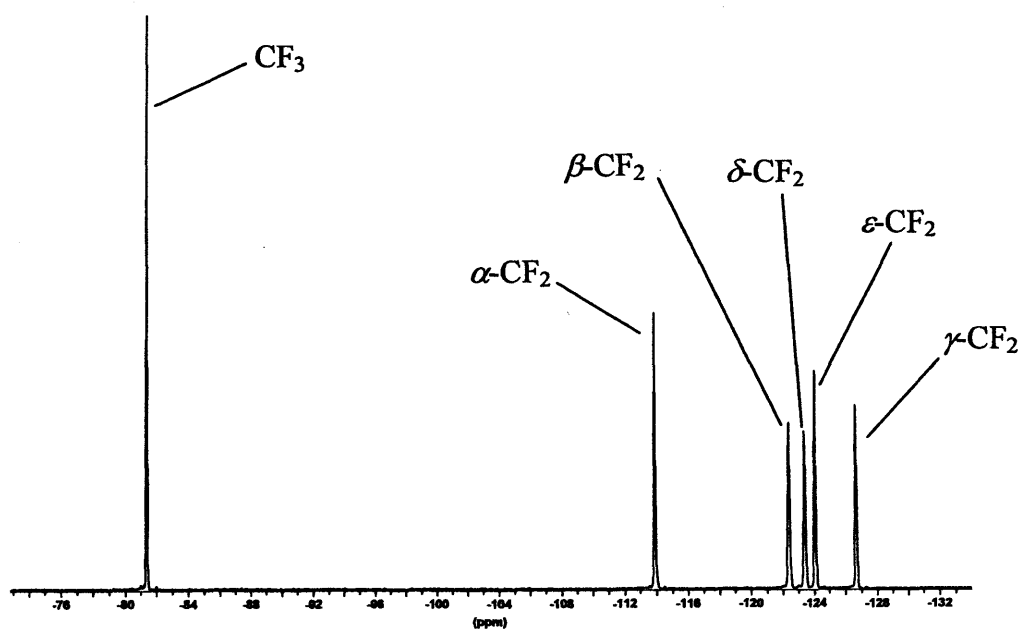


Figure 2.11 ^{19}F $\{^1\text{H}\}$ NMR spectrum of (2.1) showing six resonances

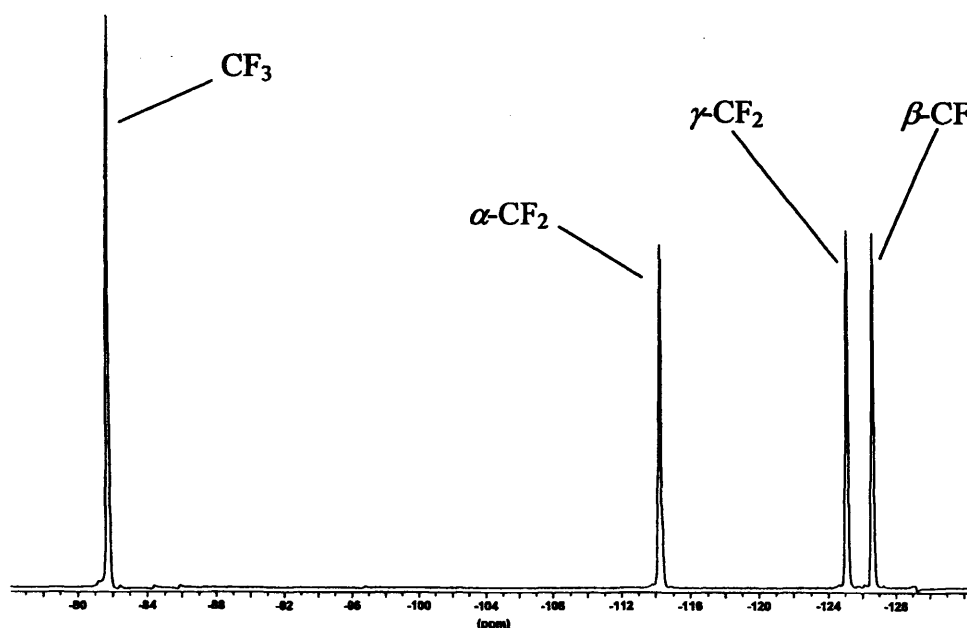


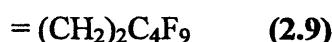
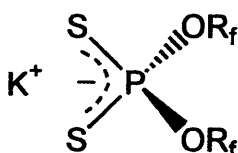
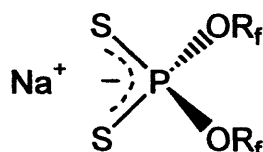
Figure 2.12 ^{19}F { ^1H } NMR spectrum of (2.2) showing four resonances

Assignments of these resonances for the C_6F_{13} perfluoroalkyl tail have been made in previous work,³² with the C_4F_9 tail assignments being confirmed with the aid of a ^{19}F - ^{19}F COSY experiment. The ^{19}F { ^1H } NMR spectrum of (2.3) showed a single resonance at -67 ppm, significantly shifted in comparison to the CF_3 resonance in (2.1) and (2.2), as a result of the neighbouring carbon bearing no fluorine atoms. In addition to NMR spectroscopy, further analysis has been carried using both mass spectrometry and elemental analysis. Although acids (2.1-2.3) were expected to be air- and moisture-stable, they were stored, and subsequently used, under a dry, inert atmosphere.

2.2.2 Sodium and Potassium Dithiophosphate Salts

Initially, both sodium and potassium salts of (2.1) were produced to allow recrystallisation to be attempted so as to remove impurity (2.5). These salts were also used as intermediates, in which the dithiophosphate moiety is more nucleophilic, for further reaction. Classically from the literature,³³ salts of this kind have been made in ethanol, but here 2,2,2-trifluoroethanol was used as the solvent to aid solubility, while also minimising the possibility of alkoxy exchange.

Formation of these salts was achieved by adding a stoichiometric amount of either NaOH or KOH, which had been ground to a powder. After stirring for 2 hours at room temperature the $^{31}\text{P} \{^1\text{H}\}$ NMR singlet resonance corresponding to the salts (2.6-2.9) had been shifted downfield from that of (2.1) and (2.2) due to the formation of the anion.



The $^{31}\text{P} \{^1\text{H}\}$ NMR resonances for both the sodium and potassium salts occur in almost the same place (Table 2.3) as expected, with only a small shift from the protio analogue of (2.8). The potassium salt did, however, seem to be of a more crystalline composition. It is likely that this arises due to the potassium cation being larger in size than the sodium cation, and thereby being closer in size to the anion.

Compound	$^{31}\text{P} \{^1\text{H}\}$ NMR Resonance / ppm
(2.6)	117
(2.7)	117
(2.8)	116
(2.9)	117
$(\text{H}_{13}\text{C}_6\text{CH}_2\text{CH}_2\text{O})_2\text{P}(\text{S})\text{SK}^{+22}$	114

Table 2.3 $^{31}\text{P} \{^1\text{H}\}$ NMR data of sodium and potassium salts

When a stoichiometric amount of metal hydroxide was added to (2.1) the chemical shift of the impurity also shifted thus implying that it had also been deprotonated. Purification was attempted by washing the metal salts (2.6) and (2.8) with a number of organic solvents including toluene. At this point, when impure starting material is

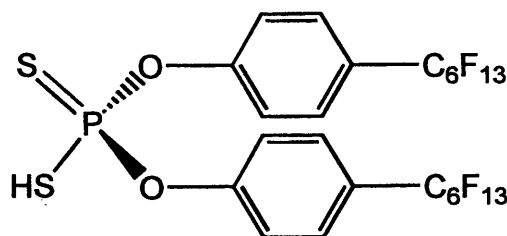
used, all other trace impurities are removed except the predominant one. Removal of this last impurity proved unsuccessful as did various small scale attempts at recrystallisation from a series of solvents. Attempts were made to grow crystals of both (2.6) and (2.8) from methanol for single crystal X-ray analysis which also proved to be unsuccessful.

When a deficit of sodium hydroxide was added, the phosphorus resonance moved downfield from that of (2.1), but not as far as that for (2.6). What was being observed here was an average position of the acid and the salt arising from a rapid proton exchange taking place. It could also be observed that the position of the signal due to the impurity was unchanged. All attempts to isolate the salt formed from the uncomplexed impurity, including precipitation with toluene, and washing of evaporated reaction residues with organic solvents failed to give pure (2.6). Due to the fact that (2.6) and (2.8) are used as intermediate materials for further reaction, as a consequence of the increased nucleophilicity of the anion, it was possible to selectively make the salt as outlined above then, without isolation, react this with the required metal precursor to afford pure products.

Although the formation of alkali metal salts of (2.3) were necessary for subsequent coordination chemistry, they were formed *in situ* and used without being isolated.

2.2.3 Aryl Dithiophosphate Ligands

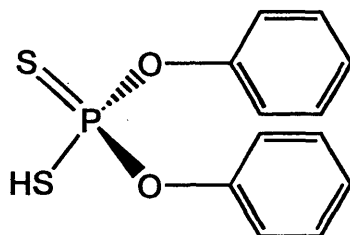
Following on from the fluorinated O,O-dialkyl dithiophosphoric acids (2.1-2.3), attempts were made to synthesise a perfluoroalkyl derivatised O,O-diaryl dithiophosphoric acid (2.10).



(2.10)

This reaction was carried out in similar manner to before, by adding the derivatised phenol, described in Chapter 5, to a slurry of P_4S_{10} in toluene, and heating to reflux for 72 hours until the solution became clear. The reaction time required for this system was far longer than that for any of the dithiophosphoric acids prepared previously (~4-12 hours). This can be attributed to the oxygen of the phenoxy group being less nucleophilic than an alkoxy oxygen due to the charge being stabilised by the delocalised phenyl ring. Furthermore, the electron withdrawing effect of the perfluoroalkyl tail would be expected to exacerbate this problem. The ^{31}P { 1H } NMR spectrum showed a number of unassignable peaks, suggesting a high degree of decomposition, possibly due to the long reaction time, but it also included a peak at around 88 ppm assigned to (2.10). No further purification of this ligand was carried out, but a small amount of coordination chemistry was attempted using it.

The reaction was repeated using underivatised phenol in a similar manner to form O,O-diphenyl dithiophosphoric acid (2.11), with the reaction time being ~ 8 hours.



(2.11)

From this it is possible to conclude that the additional reduction of nucleophilicity of the phenoxy oxygen, when the perfluoroalkyl substituent is present, is preventing formation of the ligand in high purity due to the extended reaction time needed. It is, therefore, necessary to modify the electronic properties of the phenol to make it more like either an alcohol or underivatised phenol. This could potentially be done by using precursors which would either add an additional alkyl spacer before or after the phenyl ring (Figure 2.13).

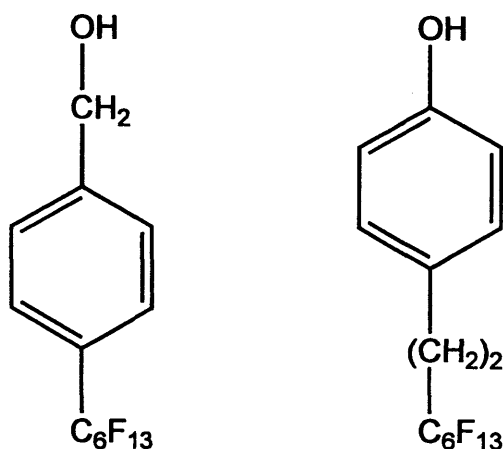


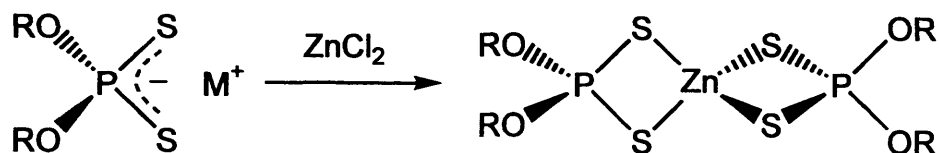
Figure 2.13 Perfluoroalkyl derivatised benzyl alcohol (left) and derivatised phenol with additional spacer

The derivatised benzyl alcohol could potentially be synthesised *via* a copper mediated cross-coupling reaction, using a established methodology previously,³⁴ and reacted with P_4S_{10} in a similar manner as outlined above. The formation of dibenyl dithiophosphoric acids have been reported previously by Begley *et al.*³⁵ although here the benzyl group carried no substituents. The synthesis of the phenol with the additional alkyl spacer is discussed in Chapter 5. The ethyl spacer group has already been shown to act as an efficient electronic insulator, potentially allowing this derivatised phenol to have a similar reactivity to underivatised phenol.

2.3 Zinc and Nickel Dithiophosphate Complexes

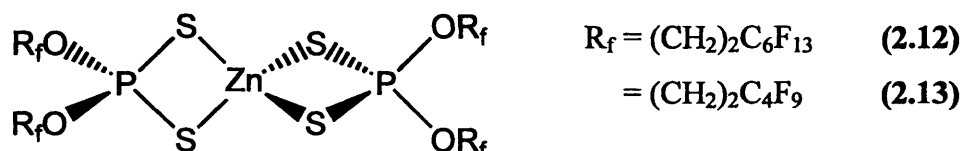
As outlined in Section 2.1, zinc dithiophosphates have found numerous applications in the petrochemical industry. Compounds of this kind can be formed by the reaction of the alkali metal salt of the ligand with either zinc chloride or zinc sulfate (Scheme 2.4), to form a four coordinate, tetrahedral product. Usually the reaction is carried out in the alcohol that the initial dithiophosphoric acid was made from, so as the possibility of alkoxy exchange has no bearing on the final product. In the case of the fluorinated compounds reported below, 2,2,2-trifluoroethanol has been

used as the reaction solvent, as the $[\text{F}_3\text{CH}_2\text{CO}]^-$ group has been found to be insufficiently nucleophilic to exchange with the perfluoroalkoxy groups.



Scheme 2.4 Formation of zinc dithiophosphate complexes

Here two fluorinated zinc dithiophosphate complexes (2.12) and (2.13) have been produced by reaction of (2.8) and (2.9) with zinc sulfate in 2,2,2-trifluoroethanol at 40 °C to afford white, crystalline solids.



Purification of (2.12) and (2.13) was carried out by dissolving the reaction product in 1,3-perfluorodimethylcyclohexane and washing with water to remove any sodium sulfate or unreacted zinc sulfate. Due to solubility problems, initial $^{31}\text{P} \{^1\text{H}\}$ NMR analysis of (2.12) was carried out in 1,3-perfluorodimethylcyclohexane with a D_2O insert to provide the lock. This showed two resonances corresponding to the two forms of the complex. It has been shown for typical alkyl zinc dithiophosphates that the relative quantities of the two species can be varied by altering reaction conditions such as pH or polarity of the solvent used; more polar solvents pushing the equilibrium towards the neutral form.¹¹ In d_6 -DMSO, a single $^{31}\text{P} \{^1\text{H}\}$ NMR resonance was observed for (2.12) (Figure 2.14) which is assigned to the neutral form. The $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of (2.13) was obtained in d_6 -DMSO only and also gave a singlet assigned to the neutral form in a similar region to that of (2.12).

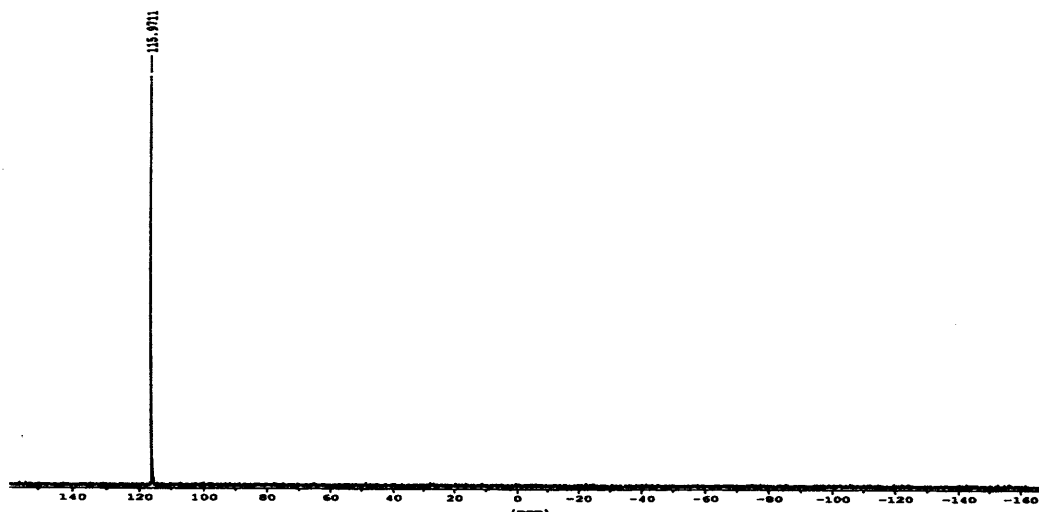
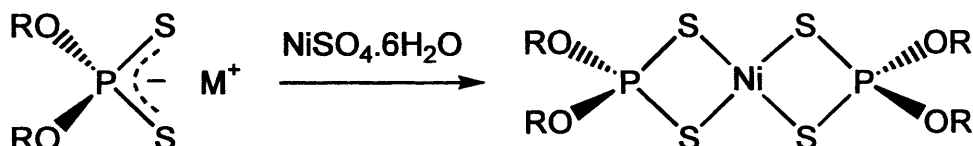


Figure 2.14 The ^{31}P $\{^1\text{H}\}$ NMR spectrum of neutral fluorinated ZDDP (2.12)

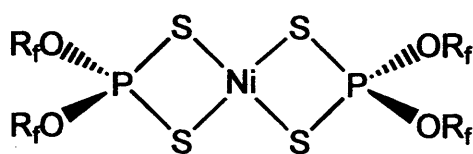
As a consequence of the low solubility in organic solvents and high thermal stability of these compounds, traditional analytical techniques prove to be extremely difficult, with elemental analysis results being particularly poor. Also, the ability of these type of compounds to exist in two forms adds to the difficulty of characterization, with neither parent ion for neutral or basic forms being visible in fast atom bombardment mass spectrometry. All attempts to grow single crystals suitable for X-ray analysis also proved unsuccessful.

As with the zinc dithiophosphates, nickel complexes can be formed simply by the reaction of an alkali metal dithiophosphate with a nickel(II) salt in the appropriate alcohol (Scheme 2.5). The nickel compounds formed are four coordinate, square planar compounds.



Scheme 2.5 Formation of nickel dithiophosphate complexes

Here a series of three fluorinated nickel dithiophosphate complexes are reported (2.14-2.16) along with data for an octyl perprotio analogue (2.17).



$$R_f = (CH_2)_2C_6F_{13} \quad (2.14)$$

$$= (CH_2)_2C_4F_9 \quad (2.15)$$

$$= (CH_2)_3CF_3 \quad (2.16)$$

$$= C_8H_{17} \quad (2.17)$$

Similar characterisation problems to the zinc complexes are also encountered with this system. Presence of sharp peaks in both the ^{19}F and $^{31}P \{^1H\}$ NMR spectra prove that complexes of this kind adopt the diamagnetic square planar configuration, although further analysis attempted by mass spectrometry and elemental analysis gave no meaningful results.

As with the ZDDP complexes, a similar type of equilibrium between monomer and oligomer form could be expected as a result of the ligand being able to bridge across metal centres. For this reason, and also due to solubility problems in other organic solvents, $^{31}P \{^1H\}$ NMR spectra were run in d_6 -DMSO so as to push equilibrium towards the monomer form. Table 2.4 shows $^{31}P \{^1H\}$ NMR resonances of the zinc and nickel compounds (2.12-2.17) prepared.

Compound	$^{31}P \{^1H\}$ NMR Resonance / ppm
(2.12)	116
(2.12) ^a	103, 106
(2.13)	117
(2.14)	117
(2.15)	116
(2.16) ^b	94, 95
(2.17)	115

^a Recorded in PP3 with D₂O insert. ^b recorded in CDCl₃.

Table 2.4 $^{31}P \{^1H\}$ NMR resonances of (2.12-2.17) obtained in d_6 -DMSO

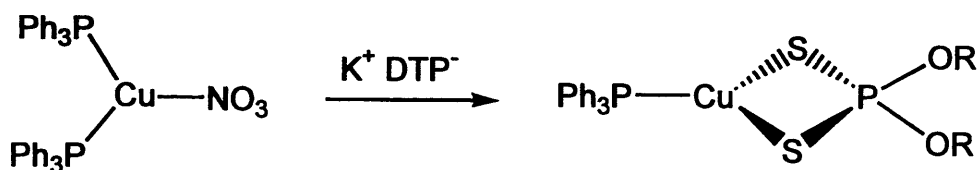
For all or the compounds dissolved in d_6 -DMSO, the neutral form only is present, with chemical shifts for all compounds being very similar at around 116 ppm. Where other solvents have been used two resonances are visible due to the two possible forms, with large solvent shifts of the neutral form being observed.

In addition to zinc dithiophosphates, nickel complexes of this kind have also been used extensively as lubricant additives, with preliminary friction, wear and extreme pressure tests on selected nickel compounds being reported in Chapter 6.

2.4 Copper Dithiophosphate Complexes

Initially attempts were made to prepare Cu(II)L_2 complexes of the same nature as the zinc and nickel compounds discussed previously. This was done by simple addition of a copper(II) halide to a stirred solution of the potassium dithiophosphate. After an initial colour change, a white solid was precipitated from solution over a period of ten minutes. The presence of sharp peaks in the $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of the copper complex formed, would suggest that the metal centre has been reduced from the paramagnetic copper(II) to the diamagnetic copper(I) species. Reductions of this nature have been observed previously when attempting coordination of dithioimidophosphinates with copper(II) metal centres.³⁶ Fackler *et al.*^{37,38} has shown that copper(I) dithiophosphates can form clusters of 6 or 8 metals with the bidentate ligands bridging. Further characterisation of the copper(I) dithiophosphate compounds formed here was attempted with all efforts to prove structures *via* mass spectrometry and single crystal X-ray analysis proving unsuccessful.

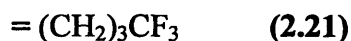
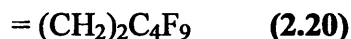
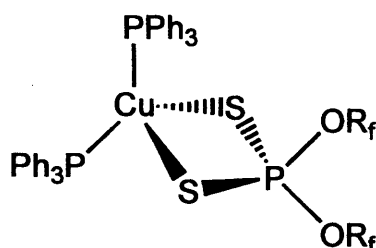
As a result of all of the metal complexes discussed so far being especially difficult to analyse, an attempt to acquire a better understanding of the coordination chemistry of these ligands was necessary. In an attempt to do this a number of heteroleptic complexes of transition metals were synthesised, which could provide far better analytical possibilities. The first system considered contained a copper(I) metal centre. Novosad *et al.*³⁹ have shown that *bis*-triphenylphosphine copper(I) nitrate reacts with the potassium salt of dichalogenoimidophosphinate ligands, affording tri-coordinate copper complexes where one triphenyl phosphine has been eliminated. It was hypothesised that similar elimination may be expected if the reaction was repeated using the potassium salts of dithiophosphoric acids (Scheme 2.6).



Scheme 2.6 Hypothesised formation of heteroleptic copper(I) complex

The copper(I) precursor⁴⁰ was added to a stirred solution of potassium dithiophosphate in methanol, with the product being afforded as a white crystalline precipitate over a period of one hour. From integration of signals in both the ^{31}P $\{^1\text{H}\}$ and the ^1H NMR spectra it seems that in these cases, the second triphenyl phosphine was not displaced but remained coordinated, giving a four coordinate tetrahedral arrangement at the metal centre, which is attributable to the smaller bite angle of the dithiophosphate in comparison to the PNP-type ligands previously studied.

A series of copper *bis*-triphenylphosphine complexes with differing alkyl and perfluoroalkyl groups were subsequently produced (2.18-2.21).



All of these reactions were carried out in similar fashion with the alkali metal salt of the dithiophosphate, either being produced previously and isolated, or made *in situ*. Initially, (2.18) was produced by reaction of the (2.8) with *bis*-triphenylphosphine copper nitrate by stirring in methanol at room temperature for 30 minutes. After this time a white solid was observed in the reaction mixture and, after cooling in ice, was isolated by suction filtration.

The suspected structure was proved by growing a single crystal suitable for X-ray analysis, by slow evaporation from methanol. This showed the four coordinate, tetrahedral copper centre bearing two triphenyl phosphine groups, with the molecule occupying two discrete orientations within the unit cell (Figure 2.15). Crystal data and structure refinement for (2.18) can be found in the Appendix, whilst a complete

set of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

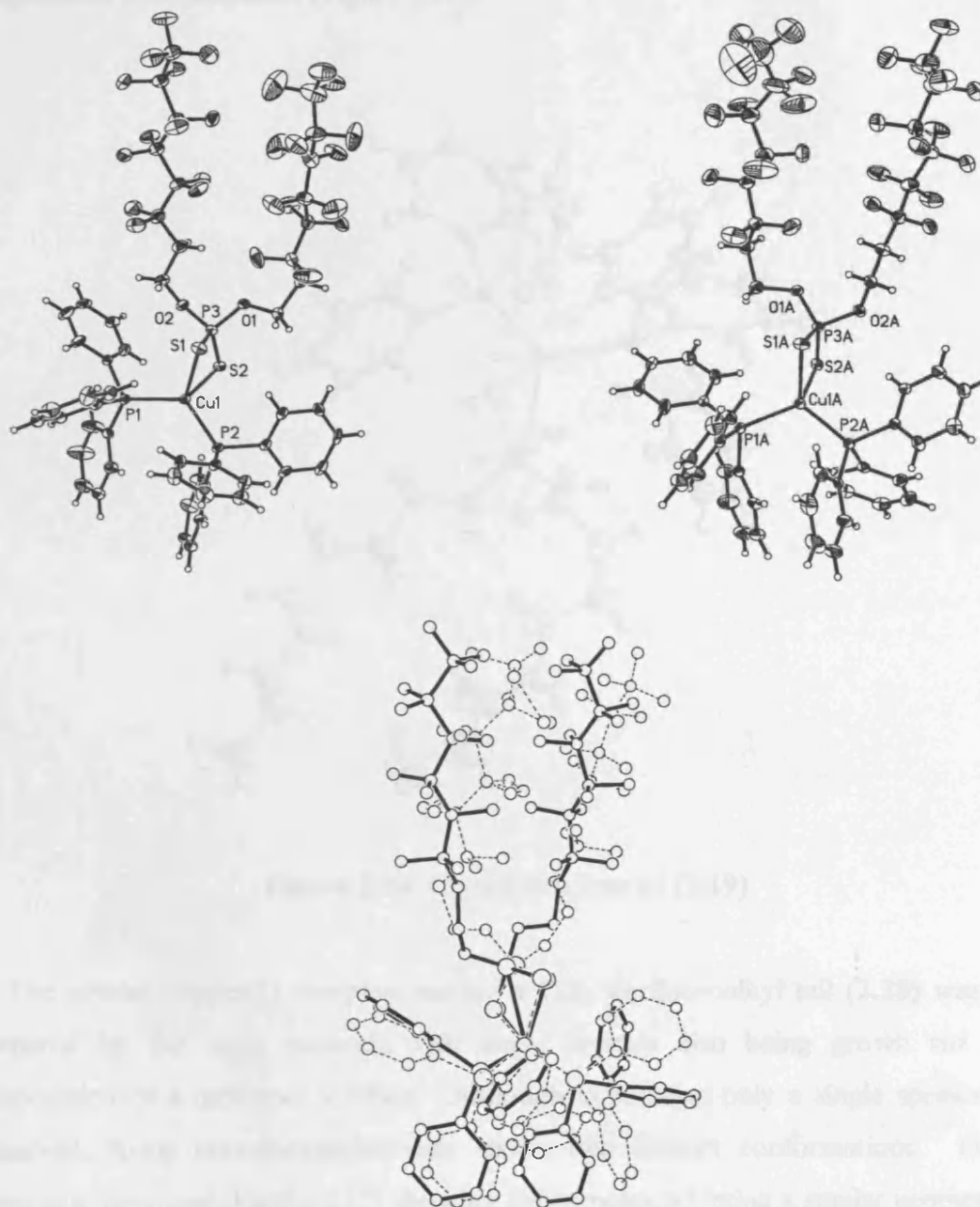


Figure 2.15 Crystal structure of (2.18) showing two discrete molecules within the unit cell (top) and the two orientations overlaid (bottom)

Both orientations show that the ligand is coordinating to the metal centre in a bidentate fashion as expected, and the perfluoroalkyl tails radiate away from the

phosphorus parallel to each other. This mode of coordination is identical to that observed in the protio analogue (**2.19**) which was prepared in a similar manner. Single crystals suitable for X-Ray analysis of this compound were prepared by slow evaporation from methanol (Figure 2.16).

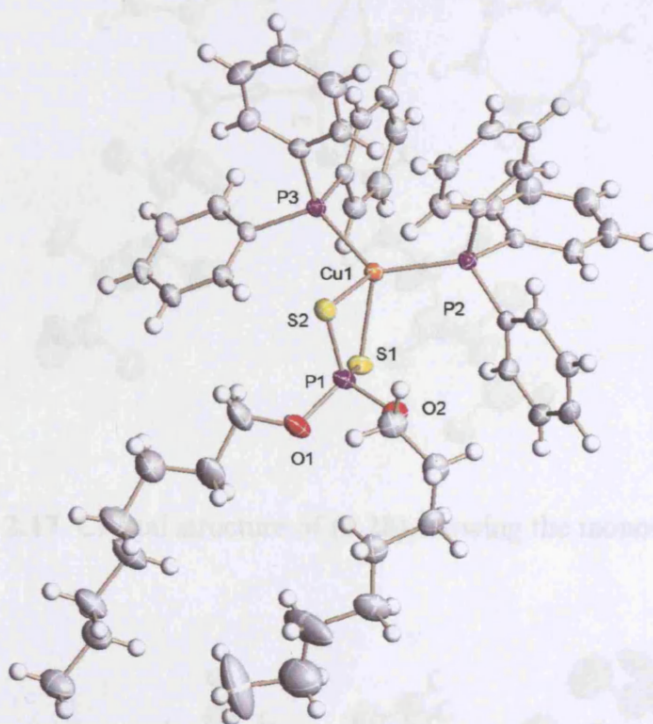


Figure 2.16 Crystal structure of (**2.19**)

The similar copper(I) complex bearing a C_4F_9 perfluoroalkyl tail (**2.20**) was also prepared by the same method, with single crystals also being grown *via* slow evaporation of a methanol solution. Although in solution only a single species was observed, X-ray crystallographic data shows two distinct conformations. Firstly, there is a monomer (Figure 2.17) showing the complex adopting a similar geometry to (**2.18**) and (**2.19**). Secondly, an alternative structure is observed whereby two ligands bridge across two metal centres to form a dimer (Figure 2.18). The result of this is the effective loss of a triphenyl phosphine group from each metal centre, with the fourth coordination site being filled by a bridging sulfur. This type of dimerisation is perhaps not so unlikely when considering that copper complexes of this nature have a propensity to both form clusters and eliminate a triphenyl phosphine under certain circumstances.

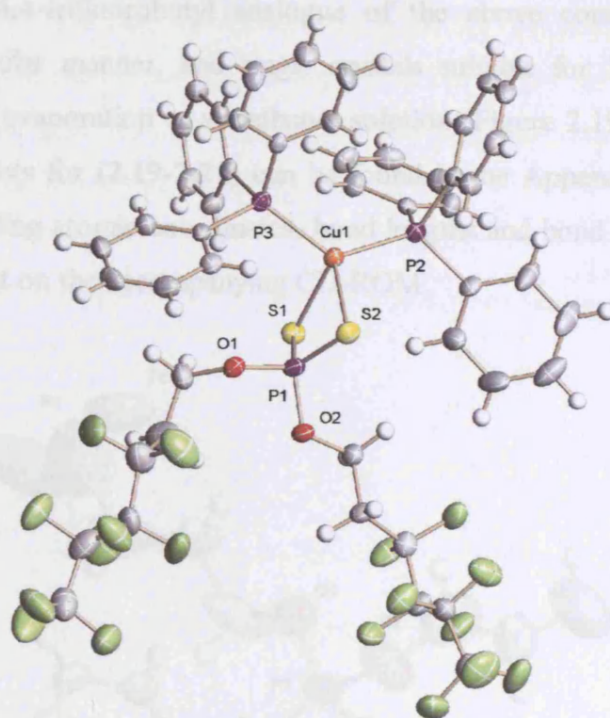


Figure 2.17 Crystal structure of (2.20) showing the monomer form

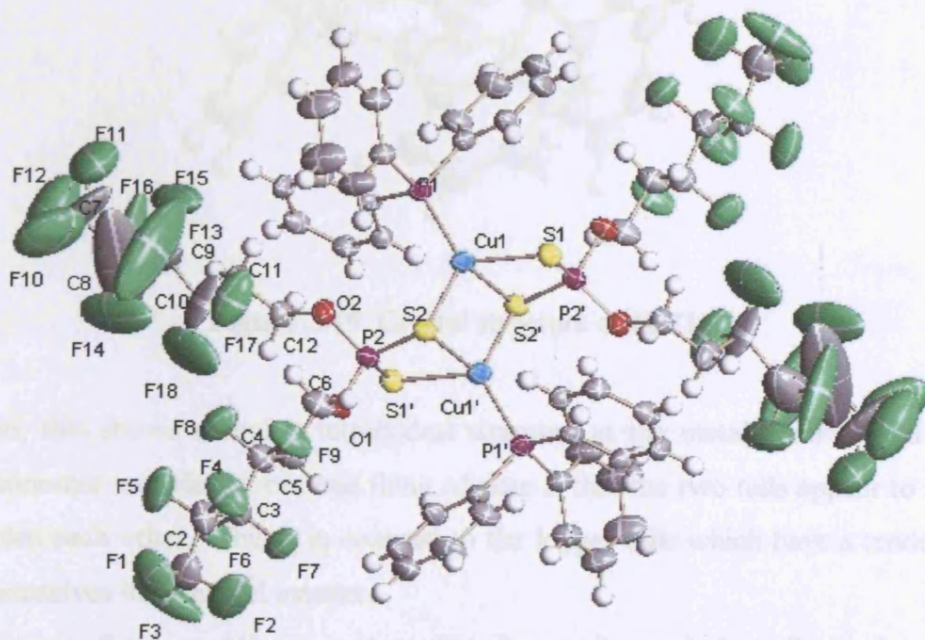


Figure 2.18 Crystal structure of (2.20) showing the dimer form

Finally, the 4,4,4-trifluorobutyl analogue of the above compounds (**2.21**) was synthesised in similar manner, and single crystals suitable for X-ray analysis were produced by slow evaporation of a methanol solution (Figure 2.19). Crystal data and structure refinements for (**2.19-2.21**) can be found in the Appendix, whilst complete sets of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

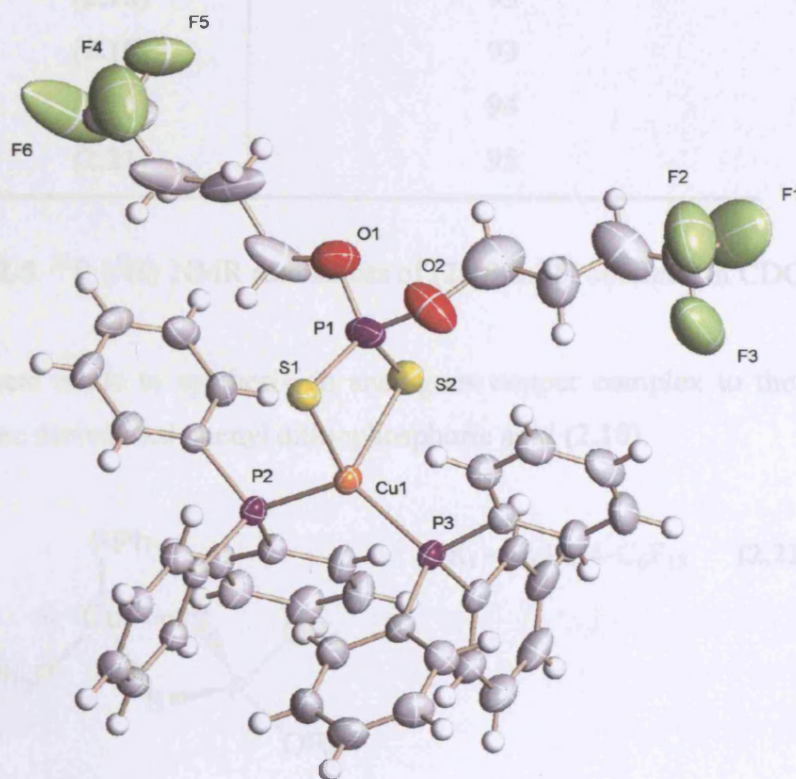


Figure 2.19 Crystal structure of (**2.21**)

Again, this shows a similar tetrahedral structure at the metal centre to all of the other monomer complexes, but one thing of note is that the two tails appear to radiate away from each other. This is in contrast to the longer tails which have a tendency to align themselves in a parallel manner.

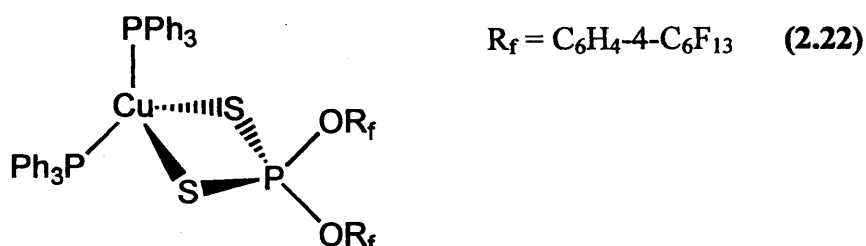
The same four coordinate system has been observed for all of the dialkyl dithiophosphoric acid ligands on reaction with the *bis*-triphenylphosphine copper nitrate precursor, including the hydrocarbon analogues of the fluorinated compounds studied.

If the ^{31}P $\{^1\text{H}\}$ NMR data for compounds (2.18-2.21) (Table 2.5) are considered, both fluorinated and non-fluorinated compounds have very similar chemical shifts, suggesting that the presence of the perfluoroalkyl tails has very little bearing on the electronic environment around the phosphorus atom.

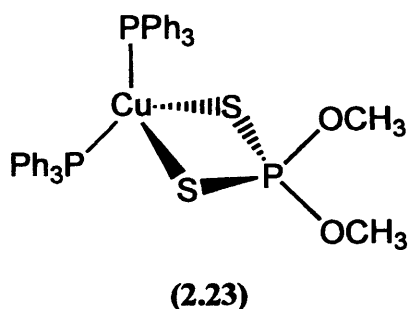
Compound	^{31}P $\{^1\text{H}\}$ NMR Resonance / ppm
(2.18)	95
(2.19)	93
(2.20)	94
(2.21)	95

Table 2.5 ^{31}P $\{^1\text{H}\}$ NMR resonances of (2.18-2.21) obtained in CDCl_3

Attempts were made to synthesis an analogous copper complex to those above, using the impure derivatised phenyl dithiophosphoric acid (2.10).



When coordination of this ligand was carried out in methanol, exchange of the derivatised phenoxy group was observed with a methoxy group from the solvent. This led to the product of the reaction being a non-fluorinated dimethyl dithiophosphate (2.23). This exchange can be attributed to the methoxy group being more nucleophilic, therefore acting as a better electron donor than the derivatised phenoxy group.



This exchange was confirmed by ^{31}P NMR spectroscopy which showed a septet (Figure 2.20) which collapsed to a singlet when proton decoupled. ^{13}C NMR spectroscopy also showed a doublet in the methoxy region due to coupling to phosphorus.

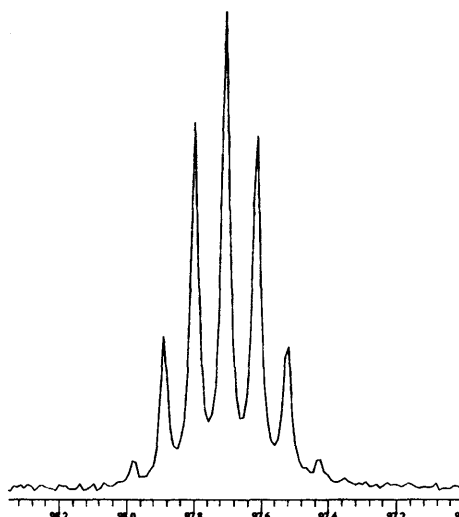
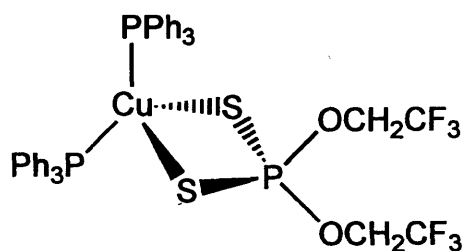


Figure 2.20 ^{31}P NMR spectrum of copper dimethyl dithiophosphate

The reaction was repeated in 2,2,2-trifluoroethanol, as this is considered to be a far poorer donor than methanol. Again, exchange with the reaction solvent was observed, leading to the formation of the 2,2,2-trifluoroethyl derivatised dithiophosphate (2.24).



(2.24)

A single crystal was grown from the reaction mixture suitable for X-ray analysis over a period of time, thus proving that exchange of the phenyl group had taken place. (Figure 2.21). This was an unexpected result, as initial attempts to synthesise O,O-di-

(2,2,2-trifluoroethoxy) dithiophosphoric acid, proved to be unsuccessful (Scheme 2.3) as a result of a one carbon spacer group being insufficient to allow reaction.

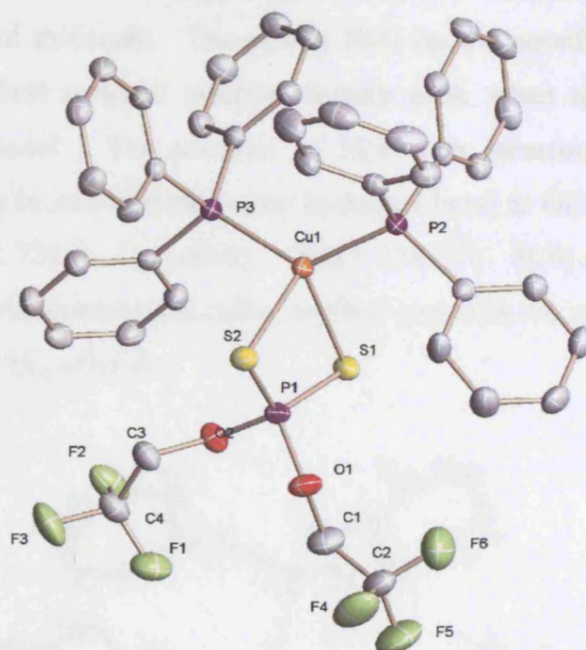
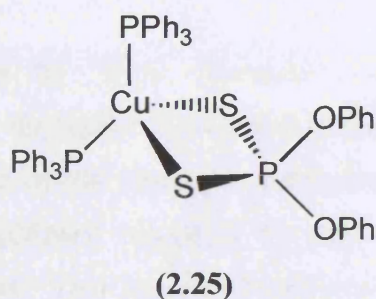


Figure 2.21 Crystal structure of (2.24) showing the possibility of alkoxy exchange with 2,2,2-trifluoroethanol

It was, however possible to synthesise an analogous copper complex using the underivatised O,O-diphenyl dithiophosphoric acid ligand (2.25) from the free ligand (2.11) using a similar method. Again, it was possible to grow a crystal of the product which was suitable for X-ray analysis by slow solvent evaporation from methanol.



The crystal structure (Figure 2.22) shows one sulfur has been exchanged for an oxygen. This hydrolysis is a consequence of the length of time which the compound

was in solution while the crystal was growing, as the ^{31}P $\{^1\text{H}\}$ NMR spectrum of the ligand showed no sign of the hydrolysis product. It is also interesting to note that this oxygen is not coordinated to the copper centre, with the vacant coordination site being filled by a methanol molecule. The proton H(4) on the coordinated methanol was located as the highest residual electron density peak when all other atoms were included in the model. The position of H(4) was structurally and chemically reasonable resulting in an intramolecular hydrogen bond to O(3) $\{\text{O}(4)\text{--H}(4) = 0.98 \text{ \AA}$, $\text{H}(4)\dots\text{O}(3) = 1.724 \text{ \AA}$, $\text{O}(4)\text{--H}(4)\dots\text{O}(3) = 158.2^\circ\}$. H(4) was included in final refinement cycles with coordinates riding on O(4) and with the isotropic displacement parameter set to 1.5 U_{eq} of O(4).

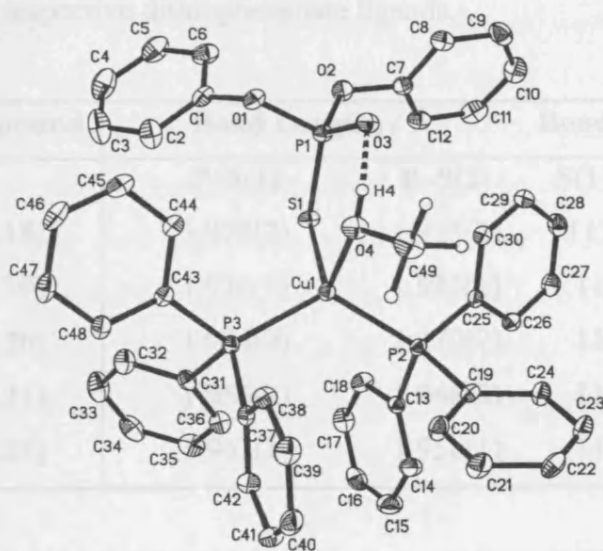


Figure 2.22 Crystal structure of (2.25) showing ligand binding in a monodentate manner

Single crystal analysis by X-ray diffraction can give extremely accurate information regarding how the ligand coordinates, in addition to the geometry around the metal centre. From the crystal structures determined for compounds (2.18-2.21) and (2.24), data can be gathered regarding the bite angle of the ligand and the coordination mode it adopts. Here analysis focuses on Cu-S and P-S bond lengths and angles with the atoms concerned highlighted in Figure 2.19 in bold type.

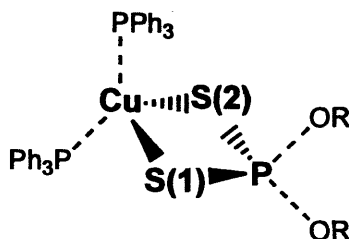


Figure 2.19 Section highlighted in bold type represents atoms of interest in X-ray crystal structure analysis of copper dithiophosphate complexes

Firstly, if the ligand is considered, P–S bond lengths and S(1)–P–S(2) bond angles for compounds (2.18–2.21) and (2.24) (Table 2.6) can allow comparison between the bite angles of the respective dithiophosphate ligands.

Compound	Bond Lengths / Å		Bond Angle / °
	P–S(1)	P–S(2)	S(1)–P–S(2)
(2.18)	1.978(2)	1.973(2)	113.21(10)
(2.19)	1.978(1)	1.981(1)	112.08(5)
(2.20)	1.954(2)	1.970(2)	113.63(7)
(2.21)	1.955(2)	1.968(2)	113.93(9)
(2.24)	1.963(1)	1.958(1)	113.54(3)

Table 2.6 Selected P–S bond lengths and angles from (2.18–2.21) and (2.24)

This data shows that the presence and length of perfluoroalkyl tails has very little effect on the phosphorus–sulfur bond distances, with all compounds having symmetrical P–S bonds of just under 2 Å. The S(1)–P–S(2) bond angles are also virtually unaffected by the perfluoroalkyl groups and are all just over the perfect tetrahedral angle of 107.5 °.

Secondly, Cu–S bond lengths and S(1)–Cu–S(2) bond angles for compounds (2.18–2.21) and (2.24) (Table 2.7) can allow comparison between the geometries around the metal centre of the respective copper dithiophosphate compounds.

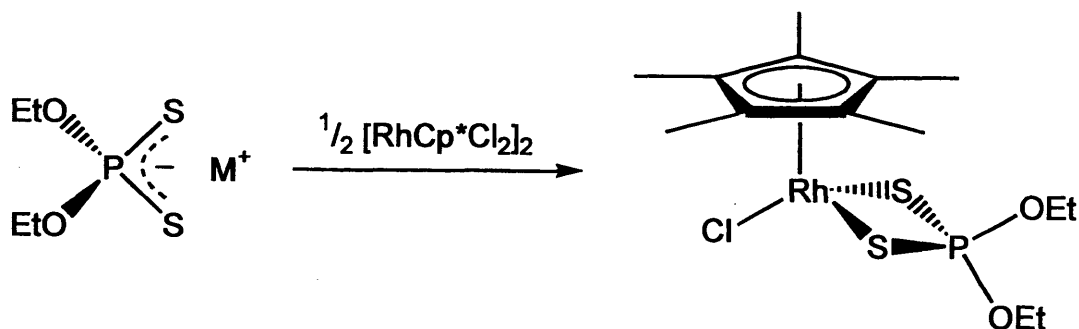
Compound	Bond Lengths / Å		Bond Angle / °
	Cu–S(1)	Cu–S(2)	S(1)–Cu–S(2)
(2.18)	2.470(2)	2.481(2)	83.57(6)
(2.19)	2.408(1)	2.515(1)	83.63(3)
(2.20)	2.530(1)	2.404(1)	83.67(4)
(2.21)	2.451(1)	2.541(1)	84.28(5)
(2.24)	2.444(1)	2.525(1)	84.29(2)

Table 2.7 Selected Cu–S bond lengths and angles from (2.18-2.21) and (2.14)

This data shows that the presence and length of perfluoroalkyl tails has very little effect on the copper–sulfur bond distances, with all compounds giving good agreement. Interestingly, only (2.18) seems to be bonding *via* the isobidentate mode, where both Cu–S bonds are the same length. All of the other compounds studied bond *via* the anisobidentate mode, where one Cu–S bond is longer than the other, in these cases by ~ 0.1 Å. Although the copper centre adopts a four coordinate, pseudo tetrahedral geometry, the S(1)–Cu–S(2) bond angles are far removed from the 107.5° necessary for a perfect tetrahedron. This could be attributed to steric hindrance of the bulky triphenyl phosphine groups, or the small bite angle of the dithiophosphate ligand.

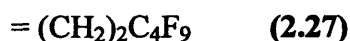
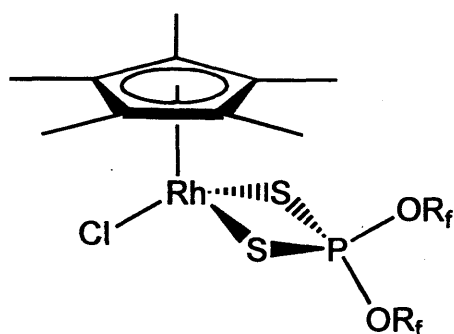
2.5 Rhodium and Iridium Dithiophosphate Complexes

Some work has previously been carried out on the coordination of dithiophosphate ligands to rhodium(III) metal centres. Singh and Mehrotra⁴¹ produced a series of compounds with the general formula (COD)Rh[S₂P(OR)₂], as with other reported coordination chemistry, only short-chain dithiophosphate ligands were used. In addition to this, Jain and Vargese⁴² produced an alternative rhodium(III) dithiophosphate complex (Scheme 2.7).

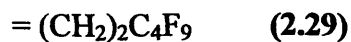
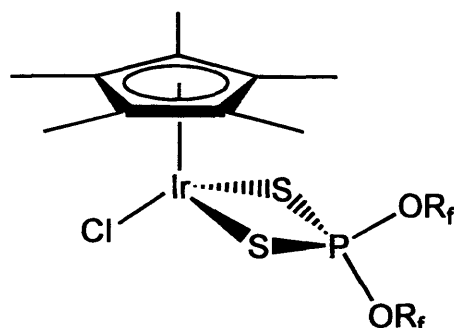


Scheme 2.7 Formation of a rhodium(III) dithiophosphate complex

Using similar methodology, two perfluoroalkyl derivatised analogues (2.26) and (2.27) were synthesised by the reaction of the appropriate alkali metal dithiophosphate salt with $[\text{Cp}^*\text{RhCl}_2]_2$ at room temperature in dichloromethane.



This work was subsequently extended to incorporate the synthesis of analogous iridium(III) compounds (2.28) and (2.29) prepared in a similar manner from $[\text{Cp}^*\text{IrCl}_2]_2$



If the ^{31}P $\{^1\text{H}\}$ NMR data for rhodium(III) compounds (2.26) and (2.27) (Table 2.8) is considered, it can be deduced that the perfluorinated tails have very little effect

on the phosphorus environment as both the chemical shift and the $^2J_{(\text{Rh-P})}$ coupling constants give excellent agreement with the literature values for the ethyl analogue.

Compound	$^{31}\text{P} \{^1\text{H}\}$ NMR Resonance / ppm	$^2J_{(\text{Rh-P})}$ / Hz
(2.26)	99	13.2
(2.27)	99	13.1
(2.28)	102	-
(2.29)	102	-
Ethyl analogue ³³	98	12.9

Table 2.8 $^{31}\text{P} \{^1\text{H}\}$ NMR resonances of (2.26-2.29) obtained in CDCl_3

The iridium(III) compounds (2.26) and (2.27) also show excellent agreement with each other but the resonances are shifted downfield slightly compared to the rhodium(III) analogues.

^1H and ^{19}F NMR spectroscopy showed that in these complexes, the two tails on the ligand are chemically inequivalent. This is due to the geometry around both the metal and phosphorus centres, with the tetrahedral nature of the phosphorus putting one of the tails closer to the Cp^* ring. In the ^1H NMR spectrum two separate resonances are seen in the OCH_2 region (Figure 2.23), whereas in the free ligand, and other metal salts, only one doublet of triplets resonance is present due to equivalence of the tails.

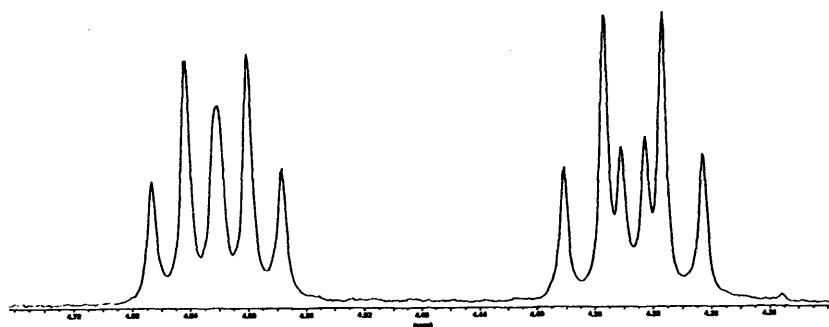


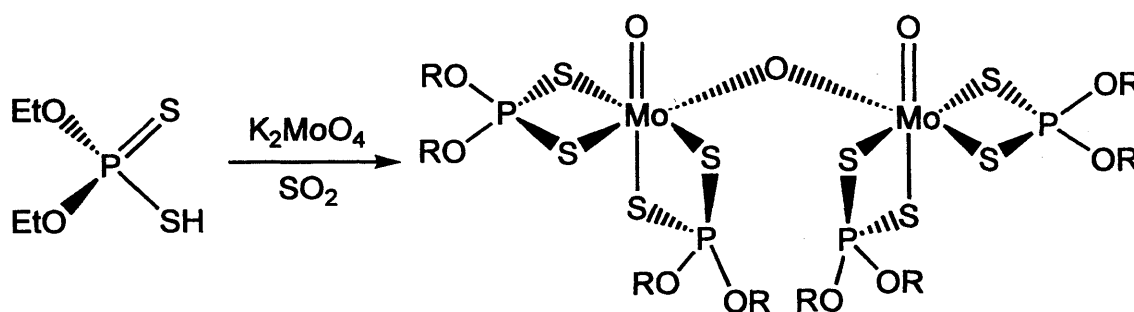
Figure 2.23 Part of ^1H NMR spectrum of (2.28) showing inequivalence of the fluorinated alkyl tails.

The α -CF₂ resonance in the ¹⁹F NMR spectrum showed a similar splitting when compared to the free ligand, but signals corresponding to the other fluorine environments show greater equivalence when moving further down the tail away from the metal centre.

In addition to NMR spectroscopy, mass spectrometry and elemental analysis of these compounds has been carried out showing good agreement with the predicted results. This proves that these compounds can be formed in a similar manner to ethyl analogues, therefore suggesting that in these systems, the presence of the perfluoroalkyl tail has little influence on the coordination chemistry of these ligands.

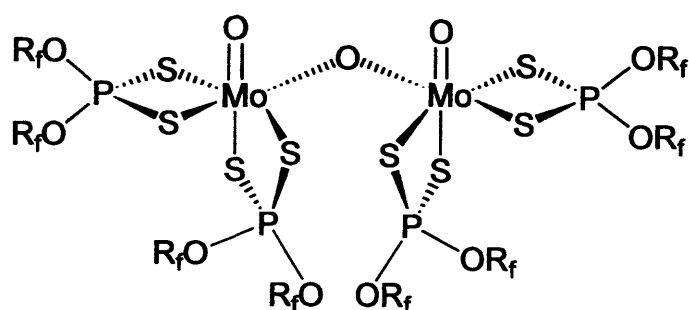
2.6 Molybdenum Dithiophosphate Complexes

It is believed that the molybdenum(V) species is the required molybdate to give anti-oxidation and anti-wear protection when added to an oil package even though, when in solution, they are known to disproportionate. The literature method⁴³ for the formation of molybdate complexes of this type with protio dithiophosphoric acids uses water, at room temperature, which has been saturated with SO₂ to reduce the molybdenum(VI) starting material to molybdenum(V), followed by reaction with the dithiophosphoric acid (Scheme 2.8).



Scheme 2.8 General route to molybdenum(V) dithiophosphates

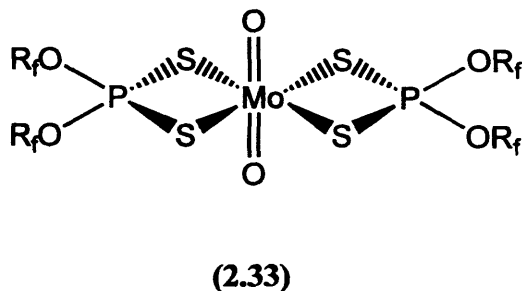
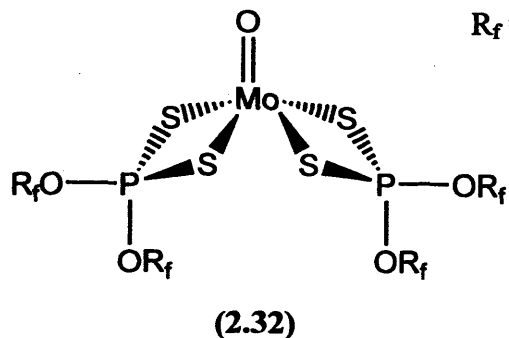
Due to the industrial importance of multifunctional lubricant additives, attempts to synthesise oxo-bridged molybdenum(V) compounds of both (2.1) and (2.2) have been made.



$$R_f = (CH_2)_2C_6F_{13} \quad (2.30)$$

$$= (CH_2)_2C_4F_9 \quad (2.31)$$

Initial attempts using the procedure outlined above were unsuccessful. It is likely that this was due to the lack of solubility of (2.1) in water. This was confirmed by the presence of a dark blue colour in the aqueous reaction mixture corresponding to reduced, but uncomplexed molybdate. It was essential that some water was present in the reaction mixture to solubilise the ionic K_2MoO_4 starting material, thus ruling out the exclusive use of an organic solvent. A rapidly stirred two phase system proved to be an appropriate compromise. After small scale attempts using various solvent systems, conditions were optimised using a water/PP3 biphasic system. The fluorocarbon phase was intended not only to solubilise the free acid, but also to keep the molybdate product (2.30) in solution. This proved to be ineffective as, after stirring at room temperature overnight, a significant amount of purple product had been precipitated. The upper aqueous layer which was a deep blue colour, indicating the presence of uncomplexed molybdenum(VI), was separated from the fluorocarbon layer. After removal of the solvent *in vacuo*, the purple solid product was dissolved in α, α, α -trifluorotoluene and washed with water. After removal of the solvent, the crystalline solid was washed with toluene to remove other impurities such as uncomplexed acid. Although the desired molybdenum(V) species (2.30) is paramagnetic, it was possible to see a broad resonance corresponding to this in the $^{31}P \{^1H\}$ NMR spectrum. It was also possible to see two other sharp resonances corresponding to the diamagnetic molybdenum(IV) and molybdenum(VI) disproportionation products (2.32) and (2.33).



When the spectrum was run using α, α, α -trifluorotoluene as the solvent with a D_2O lock, the amount of disproportionation products were negligible compared to the molybdenum(V) product. However, when the sample was dissolved in acetone, the spectrum showed peaks for the disproportionation products only, showing that the nature of the solvent has a great effect on the rate of disproportionation.

The perfluorohexyl analogue (2.31) could be formed in a similar manner although the product was a purple semi-solid with a gum-like consistency, as opposed to being crystalline as (2.30). This made subsequent handling and analysis more difficult. It was noted, however, that (2.31) seemed to disproportionate more rapidly when in solution than (2.30).

When equivalent spectroscopic analysis was carried out on Molyvan[®] L, the commercially available non-fluorinated analogous compound, there appeared to be a large number of unassignable peaks, but no visible resonance for the molybdenum(V) species. This could be due to the fact that for ease of use the commercial additive is supplied dissolved in mineral oil, therefore complete disproportionation may have already taken place. Furthermore, the presence of a number of other resonances between 20 and 112 ppm, some of which being of far greater intensity than the two peaks assigned, would suggest that further decomposition of the original material has also taken place. Literature values have been taken as a non-fluorinated analogue for comparison⁴⁴ and Table 2.9 shows the $^{31}P \{^1H\}$ NMR data for both the fluorinated and non-fluorinated compounds.

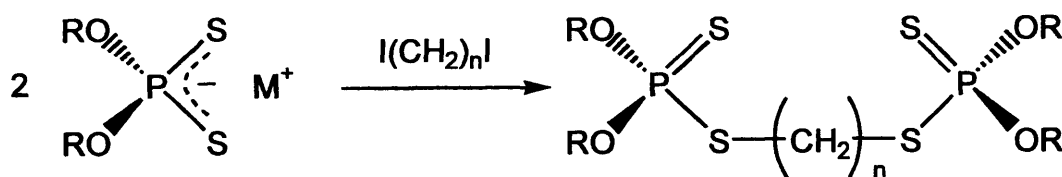
Ligand	³¹ P { ¹ H} NMR Resonance / ppm		
	Mo ^V Species	Mo ^{IV} Species	Mo ^{VI} Species
(2.30)	100	133	89
(2.31)	99	133	88
Molyvan [®] L	-	133	85
Typical chemical shifts ⁴⁴	93	133	85

Table 2.9 ³¹P {¹H} NMR data of molybdate complexes

The table shows good agreement of the chemical shifts of all species. Owing to solubility problems with (2.30) and (2.31), the solvent system used to acquire the spectra was different for that used for the literature values. This could potentially be the cause of the slight inconsistency in molybdenum(V) resonances.

2.7 Ashless Dithiophosphate Compounds

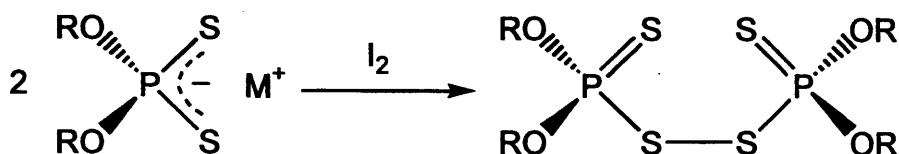
Previous work has shown that ashless compounds, where the metal centre is replaced by an alkyl bridge, can also be used efficiently as multifunctional oil additives, potentially replacing more traditional ZDDP-type additives. These are traditionally produced⁴⁵ by the reaction of alkali metal salts of dithiophosphoric acids with the appropriate α, ω -diiodoalkane (Scheme 2.9).



Scheme 2.9 General formation of ashless dithiophosphates

Usually compounds with bridge lengths of between one and six carbons are used, but potentially any diiodoalkane could be used.

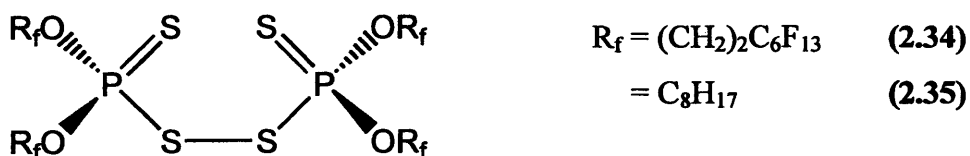
Disulfide compounds, where there is no alkyl group linking the two ligands, have also been proven to be good extreme pressure additives.⁴⁶ These can be synthesised simply by the reaction of alkali metal salts of dithiophosphoric acids with iodine (Scheme 2.10).



Scheme 2.10 General formation of dithiophosphoric disulfides

Here the formation of potassium iodide acts as the driving force of the reaction while the two ligands join together to form the disulfide. As with all of the potential oil additives, their solubility properties can be tailored as necessary by using starting materials with appropriate tail lengths.

During the course of this work examples of both disulfides and alkyl bridged ashless compounds have been synthesised and are discussed below. Work initially centred around forming a perfluoroalkyl derivatised disulfide, and its protio analogue, as these make up the simplest of the ashless compounds.



Here, 2,2,2-trifluoroethanol was used as the reaction solvent to aid the solubility of the potassium salt whilst also ensuring that alkoxy exchange did not take place. The ³¹P {¹H} NMR spectrum of (2.34) showed a single resonance at 87 ppm which is close to that for the original acid (2.1) but a considerable shift from the potassium salt precursor (2.8). The ¹H NMR spectrum, however, showed a complex second order signal for the α-CH₂ with some sort of additional coupling which had not been seen in either the free acid (2.1) or other metal salts. To try to assign this a series of homo- and hetero-nuclear decoupling experiments were undertaken on a high field, 400 MHz NMR spectrometer (Figure 2.24).

The results of these showed that there was no coupling of the α -CH₂ protons to any of the fluorine atoms in the perfluoroalkyl tail. This can be deduced as the fluorine coupled and fluorine decoupled proton NMR spectra are identical in the α -CH₂ region.

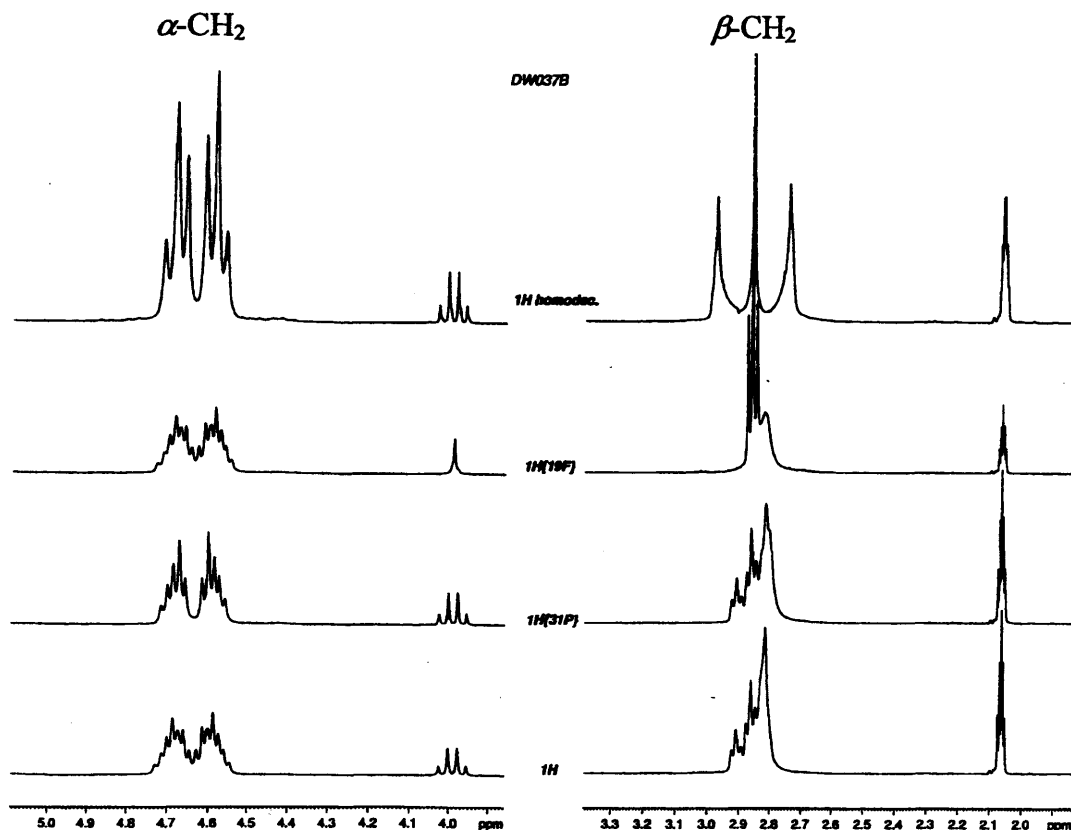


Figure 2.24 ¹H NMR spectra for dithiophosphoric disulfide (2.34)

The analysis shows that, along with the expected $^3J_{\text{H-P}}$ and $^2J_{\text{H-H}}$ couplings, there is some additional interaction taking place. It was hypothesised that this could be due to long range $^6J_{\text{H-H}}$ coupling. To try to resolve this a simulation of the homodecoupled ¹H NMR spectrum was attempted using gNMR v4.0.⁴⁷ To allow the simulation to produce a pattern which matched the experimental spectrum it was necessary to make the two α -CH₂ protons inequivalent, therefore allowing a geminal coupling between the two to be taken into account. The coupling constant for this is of the correct magnitude for protons on an sp³ carbon.⁴⁸ To aid the simulation of the ¹H spectrum the ³¹P NMR spectrum was simultaneously simulated. Graphical representations of these spectra can be seen in Figures 2.25 and 2.26.

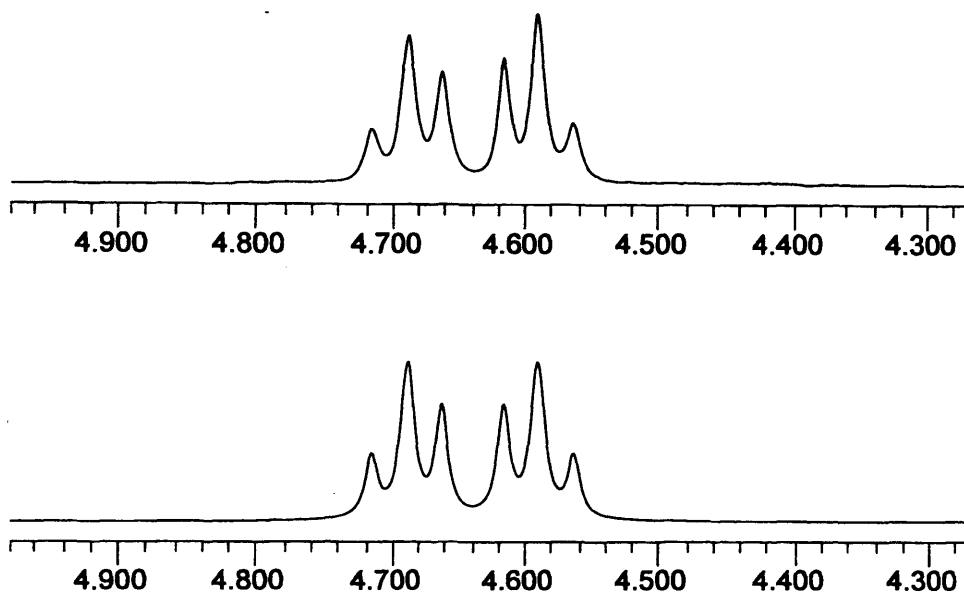


Figure 2.25 Experimental (top) and simulated (bottom) homodecoupled ^1H NMR spectrum of dithiophosphoric disulfide (2.34)

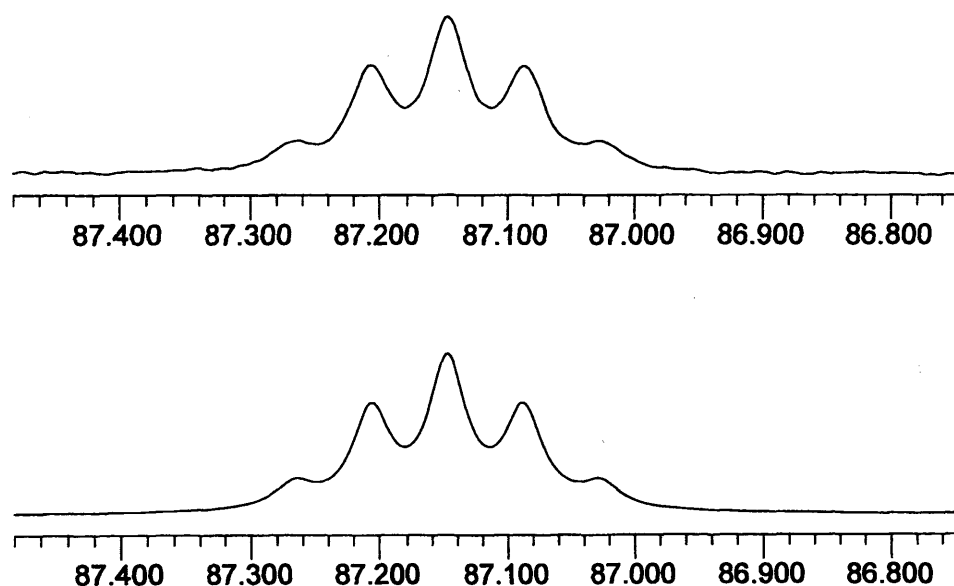


Figure 2.26 Experimental (top) and simulated (bottom) ^{31}P NMR spectrum of dithiophosphoric disulfide (2.34)

The simulation also suggests that there is some long range $^6J_{\text{H-H}}$ coupling to the magnetically inequivalent $\alpha\text{-CH}_2$ proton on the second tail of the dithiophosphate ligand, albeit very small (Figure 2.27).

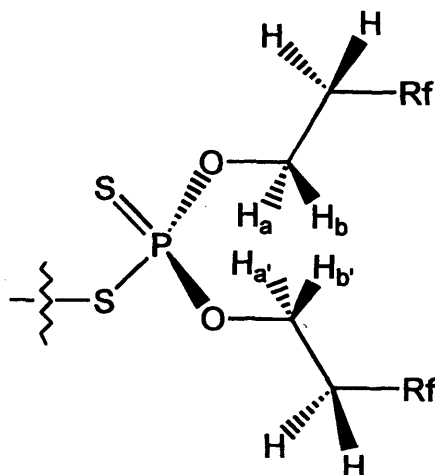


Figure 2.27 Representation of (2.34) showing the possibility of $^6J_{H-H'}$ coupling due to the magnetic inequivalence of the α -CH₂ protons

The table below lists the coupling constants generated by the simulation of the homodecoupled ^1H NMR spectrum of (2.34) (Table 2.10).

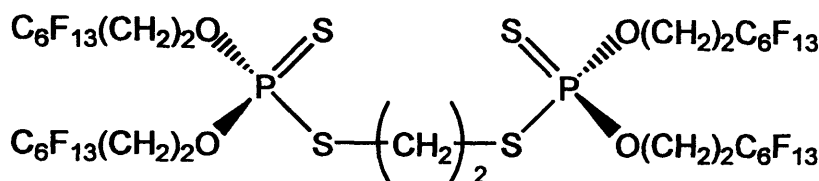
Coupling	Coupling Constant / Hz
$^2J_{H-H}$	-11.31
$^3J_{H-P}$	9.76
$^6J_{H-H'}$	0.53

Table 2.10 Coupling constants generated by the simulation of the homodecoupled ^1H NMR spectrum of (2.34)

In addition to NMR spectroscopy, mass spectrometry and elemental analysis of (2.34) has been carried out showing good agreement with the predicted results.

The protio analogue (2.35) was prepared in similar manner and showed very similar resonances in the ^1H NMR spectrum around the α -CH₂ region. Attempts to grow crystals suitable for single crystal X-ray analysis of both (2.34) and (2.35) from a variety of solvents proved to be unsuccessful.

The second member of the ashless dithiophosphate group of compounds to be synthesised was the one bearing an ethyl bridge (2.36).



(2.36)

Compounds of this type have been formed before using salts of protio dithiophosphoric acids as precursors.⁴⁵ Here, a solution of the sodium salt (2.6), in 2,2,2-trifluoroethanol, was stirred at room temperature for three days in the presence of 1,2-diiodoethane. After allowing the reaction mixture to stand for 1 week, a white crystalline solid was seen to be slowly precipitating out of solution.

³¹P {¹H} NMR spectroscopy showed that the signal for the ethyl ashless compound (2.36), like the disulfide (2.34), was very close to that for the free acid (2.1) (Table 2.11).

Compound	³¹ P { ¹ H} NMR Resonance / ppm
Acid (2.1)	87
(2.34)	87
(2.35)	85
(2.36)	88

Table 2.11 Comparison of ³¹P {¹H} NMR resonances of compounds (2.1) and (2.34-2.36)

The proton NMR spectrum of (2.36), however, did include a singlet at 2.7 ppm. corresponding to the four equivalent protons in the ethyl bridge, in addition to the two signals for the α - and β -CH₂ groups.

2.8 Chapter Conclusions

All of the perfluoroalkyl ligand syntheses were carried out in similar fashion to protio analogues, and short-chain dithiophosphates reported in the literature, providing that a C₂H₄, or greater, spacer group was used to inhibit the electron withdrawing effect of the perfluoroalkyl groups. When an aryl or methyl spacer group was used, however, the perfluoroalkyl tails did seem to either decelerate or totally retard the reaction.

The study of the coordination chemistry of the fluorinated and non-fluorinated, ligands produced, show that reactivity is virtually unaffected by the presence and the length of perfluoroalkyl groups. This can be deduced from the analytical data for the fluorinated copper and rhodium complexes giving excellent agreement with both non-fluorinated compounds produced here and work reported previously. What is affected considerably, however, is the solubility of a number of the highly fluorinated compounds in organic solvents, when compared to their protio analogues. Throughout the course of this work, problems associated with solubility have arisen frequently, and in the majority of cases have been resolved by modifying the solvent system. In certain instances, these problems have either prevented reaction, or more often made analysis of the compounds produced extremely difficult.

2.9 Experimental Procedures

2.9.1 Synthesis of Dithiophosphate Ligands and Alkali Metal Salts

Preparation of O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphoric acid (2.1)

1H,1H,2H,2H-perfluoro-*n*-octanol (43.82 g, 1.20×10^{-1} mol) was added dropwise over a period of 1 hour to a stirred slurry of P₄S₁₀ (6.69 g, 1.50×10^{-3} mol) in dry, degassed toluene (150 cm³) in a three necked round bottom flask fitted with a Rotaflo tubing adaptor and a condenser. The condenser was linked to a scrubber system of saturated solutions of aqueous NaOH followed by FeCl₃.6H₂O to neutralise H₂S being

formed by the reaction. The system was flushed with nitrogen for ~20 minutes *via* the tubing adaptor inlet before the reaction mixture was heated to reflux for 12 hours, with rapid stirring under a dynamic flow of nitrogen, until the solution had become clear. The solvent was then removed *in vacuo* giving an off white, waxy solid (46.76 g, 5.69×10^{-2} mol) in 95% crude yield. Purification was attempted by both fluorous extraction using 1,3-perfluorodimethylcyclohexane, and Kugelröhr distillation both leaving a small impurity.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.4 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.5 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 4H, $^3J_{\text{H-H}}$ 6.6 Hz, $^3J_{\text{H-F}}$ 18 Hz, $\beta\text{-CH}_2$), 2.1 (br s, 1H, SH); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.5 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -114.2 (um, 2F, $\alpha\text{-CF}_2$), -122.5 (um, 2F, $\beta\text{-CF}_2$), -123.5 (um, 2F, $\delta\text{-CF}_2$), -124.2 (um, 2F, $\epsilon\text{-CF}_2$), -126.8 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 87.4 (s, dithiophosphoric acid); m/z (FAB) 821 ($[\text{M} - \text{H}]^+$, 100 %); Found C, 23.62; H, 1.10; P, 7.62; S, 7.64. $\text{C}_{16}\text{H}_9\text{F}_{26}\text{O}_2\text{PS}_2$ requires C, 23.36; H, 1.09; P, 3.77; S, 7.79; IR (nujol) ν 850(s, br), 1018(vs, br), 1042(w), 1187(w), 1215(w) cm^{-1} .

Preparation of O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphoric acid (2.2)

1H,1H,2H,2H-perfluoro-*n*-hexanol (24.69 g, 9.85×10^{-2} mol, 15.53 cm^3) was added in five aliquots over a period of 30 minutes to a stirred slurry of P_4S_{10} (5.19 g, 1.17×10^{-2} mol) in dry, degassed toluene (70 cm^3) in a three necked round bottom flask fitted with a Rotaflo tubing adaptor and a condenser. The condenser was linked to a scrubber system of saturated solutions of aqueous NaOH followed by $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ due to H_2S being formed by the reaction. The system was flushed with nitrogen for ~20 minutes *via* the tubing adaptor inlet before the reaction mixture was heated at reflux for 12 hours, with rapid stirring under a dynamic flow of nitrogen, until the solution had become clear. The solvent was then removed *in vacuo* giving a pale orange, viscous liquid (28.64 g, 4.60×10^{-2} mol, 98 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.5 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.4 Hz, $\alpha\text{-CH}_2$), 2.7 (tt, 4H, $^3J_{\text{H-H}}$ 6.5 Hz, $^3J_{\text{H-F}}$ 18 Hz, $\beta\text{-CH}_2$), 3.7 (br s, 1H, SH); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.7 (um, 3F, CF_3), -114.2 (um, 2F, $\alpha\text{-CF}_2$), -125.1 (um, 2F, $\gamma\text{-CF}_2$), -126.6 (um, 2F, $\beta\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 86.7 (s, dithiophosphoric acid); m/z (FAB) 621 ($[\text{M} - \text{H}]^+$, 100 %); Found C, 24.04; H, 1.55;

P, 5.21; S, 8.69. $C_{12}H_9F_{18}O_2PS_2$ requires C, 24.16; H, 1.46; P, 4.98; S, 10.31; IR (nujol) ν 876(s), 1006(s), 1046(sh), 1135(vs), 1224(s, br) cm^{-1} .

Preparation of O,O-di(4,4,4-trifluoro-n-butyl) dithiophosphoric acid (2.3)

4,4,4-trifluoro-*n*-butanol (2.50 g, 1.95×10^{-2} mol) was added in two aliquots over a period of 30 minutes to a stirred slurry of P_4S_{10} (1.08 g, 2.44×10^{-3} mol) in dry, degassed toluene (100 cm^3) in a three necked round bottom flask fitted with a Rotafl tubing adaptor and a condenser. The condenser was linked to a scrubber system of saturated solutions of aqueous NaOH followed by $FeCl_3 \cdot 6H_2O$ due to H_2S being formed by the reaction. The system was flushed with nitrogen for ~30 minutes *via* the tubing adaptor inlet before the reaction mixture was heated at reflux for 4 hours, with rapid stirring under a dynamic flow of nitrogen, until the solution had become clear. The solvent was then removed *in vacuo* giving a pale yellow, viscous oil (3.19 g, 9.11×10^{-3} mol, 93 %).

$\delta_H(CDCl_3)$ 4.2 (dt, 4H, $^3J_{H-P}$ 10 Hz, $^3J_{H-H}$ 6.4 Hz, α -CH₂), 2.3 (um, 4H, γ -CH₂), 2.1 (um, 4H, β -CH₂), 3.6 (br s, 1H, SH); $\delta_F(CDCl_3)$ -66.7 (um, 3F, CF₃); $\delta_P\{^1H\}$ ($CDCl_3$) 86.4 (s, dithiophosphoric acid); m/z (EI) 349 ($[M - H]^-$, 100 %).

Preparation of Na{O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphate} (2.6)

O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphoric acid (5.20×10^{-1} g, 6.33×10^{-4} mol) was dissolved in 2,2,2-trifluoroethanol (30 cm^3) by rapidly stirring in a three necked round bottom flask, under a static nitrogen atmosphere. NaOH (2.53 g, 6.33×10^{-4} mol) was ground to a powder and dissolved in the minimum amount of 2,2,2-trifluoroethanol (5 cm^3). This was then syringed into the dithiophosphoric acid solution and allowed to stir at room temperature for 2 hours. The solvent was removed *in vacuo*, and the resulting solid was washed with toluene to remove any uncomplexed starting material. After suction filtration the product was afforded as a white crystalline solid in a stoichiometric yield (5.30×10^{-1} g, 6.33×10^{-4} mol).

$\delta_{\text{H}}(d_4\text{-MeOH})$ 4.2 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.5 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 4H, $^3J_{\text{H-H}}$ 6.6 Hz, $^3J_{\text{H-F}}$ 18 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(d_4\text{-MeOH})$ -82.9 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -115.0 (um, 2F, $\alpha\text{-CF}_2$), -123.4 (um, 2F, $\beta\text{-CF}_2$), -124.4 (um, 2F, $\delta\text{-CF}_2$), -125.2 (um, 2F, $\epsilon\text{-CF}_2$), -127.8 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ ($d_4\text{-MeOH}$) 117.5 (s, Na^+ salt); m/z (FAB) 867 ($[\text{M} + \text{Na}]^+$, 100 %), m/z (EI) 821 ($[\text{M} - \text{Na}]^-$, 100 %); Found C, 21.88; H, 1.44; P, 3.89; S, 7.06. $\text{C}_{16}\text{H}_8\text{F}_{26}\text{NaO}_2\text{PS}_2$ requires C, 22.75; H, 0.95; P, 3.67; S, 7.58; IR (nujol) ν 1014(s), 1047(s), 1076(s), 1136(s), 1238(s) cm^{-1} .

Preparation of Na{O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphate} (2.7)

O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphoric acid (8.01×10^{-1} g, 1.28×10^{-3} mol) was dissolved in 2,2,2-trifluoroethanol (30 cm^3) by rapidly stirring in a three necked round bottom flask, under a static nitrogen atmosphere. NaOH (5.00×10^{-2} g, 1.28×10^{-3} mol) was ground to a powder and dissolved in the minimum amount of 2,2,2-trifluoroethanol. This was then syringed into the dithiophosphoric acid solution and allowed to stir at room temperature for 2 hours. The solvent was removed *in vacuo*, and the resulting solid was washed with toluene to remove any uncomplexed starting material. After suction filtration the product was afforded as a white crystalline solid in a stoichiometric yield (8.25×10^{-1} g, 1.28×10^{-3} mol).

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.2 (dt, 4H, $^3J_{\text{H-P}}$ 10.5 Hz, $^3J_{\text{H-H}}$ 6.7 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 4H, $^3J_{\text{H-H}}$ 6.7 Hz, $^3J_{\text{H-F}}$ 19 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -83.2 (tt, 3F, $^3J_{\text{F-F}}$ 11 Hz, $^4J_{\text{F-F}}$ 3 Hz, CF_3), -115.3 (um, 2F, $\alpha\text{-CF}_2$), -126.2 (um, 2F, $\gamma\text{-CF}_2$), -127.8 (um, 2F, $\beta\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 117.5 (s, Na^+ salt); m/z (EI) 621 ($[\text{M} - \text{Na}]^-$, 100 %); Found C, 22.28; H, 1.27; P, 5.10; S, 8.73. $\text{C}_{12}\text{H}_8\text{F}_{18}\text{O}_2\text{PS}_2\text{Na}$ requires C, 22.37; H, 1.26; P, 4.81; S, 9.95. IR (nujol) ν 1014(s), 1046(s), 1080(s), 1136(vs, br), 1236(s) cm^{-1} .

Preparation of K{O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphate} (2.8)

O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphoric acid (1.83 g, 2.22×10^{-3} mol) was dissolved in 2,2,2-trifluoroethanol (35 cm^3) by rapidly stirring in a three necked round bottom flask, under a static nitrogen atmosphere. KOH (1.30×10^{-1} g,

2.22×10^{-3} mol) was ground to a powder then added, *via* a solid delivery tube, to the dithiophosphoric acid solution and allowed to stir at room temperature for 2 hours. The solvent was removed *in vacuo*, and the resulting solid was washed with toluene to remove any uncomplexed starting material. After suction filtration the product was afforded as a white crystalline solid in a stoichiometric yield (1.91 g, 2.22×10^{-3} mol). $\delta_{\text{H}}(d_4\text{-MeOH})$ 4.2 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.5 Hz, $\alpha\text{-CH}_2$), 2.4 (tt, 4H, $^3J_{\text{H-H}}$ 6.6 Hz, $^3J_{\text{H-F}}$ 18 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(d_4\text{-MeOH})$ -81.1 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -113.1 (um, 2F, $\alpha\text{-CF}_2$), -121.6 (um, 2F, $\beta\text{-CF}_2$), -122.6 (um, 2F, $\delta\text{-CF}_2$), -123.4 (um, 2F, $\epsilon\text{-CF}_2$), -126.0 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ ($d_4\text{-MeOH}$) 116.1 (s, K^+ salt); m/z (FAB) 899 ($[\text{M} + \text{K}]^+$, 100 %), m/z (EI) 821 ($[\text{M} - \text{K}]^+$, 100 %); Found C, 21.80; H, 0.95; P, 3.80; S, 6.98. $\text{C}_{16}\text{H}_8\text{F}_{26}\text{KO}_2\text{PS}_2$ requires C, 22.33; H, 0.93; P, 3.60; S, 7.44; IR (nujol) ν 1004(w), 1077(w), 1134(s), 1195(s), 1224(s) cm^{-1} .

Preparation of $\text{K}\{O,O\text{-di}(1\text{H},1\text{H},2\text{H},2\text{H}\text{-perfluoro-}n\text{-hexyl})\text{ dithiophosphate}\}$ (2.9)

O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphoric acid (2.20 g, 3.53×10^{-3} mol) was dissolved in 2,2,2-trifluoroethanol (25 cm^3) by rapidly stirring in a three necked round bottom flask, under a static nitrogen atmosphere. KOH (2.00×10^{-1} g, 3.53×10^{-3} mol) was ground to a powder then added, *via* a solid delivery tube, to the dithiophosphoric acid solution and allowed to stir at room temperature for 2 hours. The solvent was removed *in vacuo*, and the resulting solid was washed with toluene to remove any uncomplexed starting material. After suction filtration the product was afforded as a white crystalline solid in a stoichiometric yield (2.33 g, 3.53×10^{-3} mol). $\delta_{\text{H}}(d_4\text{-MeOH})$ 4.4 (dt, 4H, $^3J_{\text{H-P}}$ 10.5 Hz, $^3J_{\text{H-H}}$ 6.8 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 4H, $^3J_{\text{H-H}}$ 6.7 Hz, $^3J_{\text{H-F}}$ 19 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(d_4\text{-MeOH})$ -83.2 (tt, 3F, $^3J_{\text{F-F}}$ 10 Hz, $^4J_{\text{F-F}}$ 3 Hz, CF_3), -115.3 (um, 2F, $\alpha\text{-CF}_2$), -126.2 (um, 2F, $\gamma\text{-CF}_2$), -127.7 (um, 2F, $\beta\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ ($d_4\text{-MeOH}$) 117 (s, K^+ salt); m/z (EI) 621 ($[\text{M} - \text{K}]^+$, 100 %); Found C, 21.68; H, 1.03; P, 4.89; S, 8.74. $\text{C}_{12}\text{H}_8\text{F}_{18}\text{O}_2\text{PS}_2\text{K}$ requires C, 21.82; H, 1.23; P, 4.69; S, 9.71; IR (nujol) ν 1000(w), 1078(w), 1134(s), 1195(s), 1220(s) cm^{-1} .

Preparation of O,O-di(4-tridecafluoro-n-hexyl phenyl) dithiophosphoric acid (2.10)

To a stirred slurry of P_4S_{10} (5.49×10^{-1} g, 1.23×10^{-3} mol) in dry, degassed toluene (100 cm^3) in a three necked round bottom flask fitted with a Rotaflo tubing adaptor and a condenser, was added (4-tridecafluoro-*n*-hexyl) phenol (4.01 g, 9.87×10^{-3} mol, cm^3) dissolved in toluene (30 cm^3) in five aliquots over a period of 30 minutes. The condenser was linked to a scrubber system of saturated solutions of aqueous NaOH followed by $FeCl_3 \cdot 6H_2O$ due to liberation of H_2S by the reaction. The system was flushed with nitrogen for ~20 minutes *via* the tubing adaptor inlet before the reaction mixture was heated at reflux for 3 days, with rapid stirring under a dynamic flow of nitrogen. The solvent was removed *in vacuo* affording an off-white mixture of products. Purification of the resulting mixture proved to be impossible.

Preparation of O,O-di-phenyl dithiophosphoric acid (2.11)

To a stirred slurry of P_4S_{10} (2.00 g, 4.50×10^{-3} mol) in dry, degassed toluene (80 cm^3) in a three necked round bottom flask fitted with a Rotaflo tubing adaptor and a condenser, was added phenol (3.39 g, 3.60×10^{-3} mol) dissolved in toluene (30 cm^3) over a period of 30 minutes. The condenser was linked to a scrubber system of saturated solutions of aqueous NaOH followed by $FeCl_3 \cdot 6H_2O$ due to liberation of H_2S by the reaction. The system was flushed with nitrogen for ~20 minutes *via* the tubing adaptor inlet before the reaction mixture was heated to reflux with rapid stirring under a dynamic flow of nitrogen, until the solution had become clear. The solvent was removed *in vacuo*, yielding a waxy, off-white, solid (3.89 g, 1.38×10^{-2} mol, 77 %).

$\delta_H(\text{CDCl}_3)$ 7.5 (m, 10H, ArH), 4.5 (s, 1H, SH), $\delta_P\{^1H\}(\text{CDCl}_3)$ 88.0 (s, dithiophosphoric acid); m/z (EI) 281 ($[M - H]^+$, 100 %).

2.9.2 Zinc and Nickel Dithiophosphate Complexes

Preparation of [Zn bis-{O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphate}] (2.12)

The zinc salt was prepared by taking a solution of Na{O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate} (5.30×10^{-1} g, 6.33×10^{-4} mol) in 2,2,2-trifluoroethanol and adding zinc sulfate (1.00×10^{-1} g, 3.51×10^{-4} mol) dissolved in a minimum amount of water. After warming to 40 °C with rapid stirring for 2 hours, the solvent was removed leaving a white crystalline solid. This was dissolved in 1,3-perfluorodimethylcyclohexane and washed with water to remove any sodium sulfate or unreacted zinc sulfate. The white solid product was isolated by suction filtration.

δ_P (PP3 / D₂O lock) 103.1 (s, neutral form), 106.0 (um, basic form); δ_P (DMSO / D₂O lock) 116.0 (s, neutral form); IR (nujol) ν 1085(w), 1124(w), 1145(s), 1193(s, br), 1236(s) cm⁻¹.

Preparation of [Zn bis-{O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphate}] (2.13)

Zinc sulfate (1.38×10^{-1} g, 4.82×10^{-4} mol) dissolved in a minimum amount of water was added to a solution of Na{O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphate} (6.18×10^{-1} g, 9.60×10^{-4} mol) in 2,2,2-trifluoroethanol. After warming to 40 °C with rapid stirring for 2 hours, the solvent was removed leaving a white crystalline solid. This was dissolved in 1,3-perfluorodimethylcyclohexane and washed with water to remove any sodium sulfate or unreacted zinc sulfate. The white solid product (3.04×10^{-1} g, 2.33×10^{-4} mol, 49 %) was isolated by suction filtration.

δ_H (*d*₆-DMSO) 4.1 (dt, 4H, ³J_{H-P} 10.5 Hz, ³J_{H-H} 6.4 Hz, α -CH₂), 2.6 (tt, 4H, ³J_{H-H} 6.1 Hz, ³J_{H-F} 19.9 Hz, β -CH₂); δ_F (*d*₆-DMSO) -81.2 (t, 3F, ³J_{F-F} 9.3 Hz, CF₃), -113.5 (t, 2F, ³J_{F-F} 11.7 Hz, α -CF₂), -124.8 (um, 2F, γ -CF₂), and -126.4 (um, 2F, β -CF₂); δ_P {¹H} (*d*₆-DMSO) 116.8 (s, neutral form); IR (nujol) ν 1012(vw), 1048(w), 1136(s), 1226(s) cm⁻¹.

Preparation of [Ni bis-{O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate}] (2.14)

Sodium hydroxide (3.60×10^{-2} g, 9.10×10^{-4} mol) was added to a stirred solution of O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate (8.63×10^{-1} g, 1.05×10^{-3} mol) in 2,2,2-trifluoroethanol (25 cm³). After 30 minutes NiSO₄·6H₂O (1.20×10^{-1} g, 4.50×10^{-4} mol), dissolved in a minimum amount of water, was added and the mixture was stirred for 1 hour. After this time the solid purple product (5.58×10^{-1} g, 3.28×10^{-4} mol, 73 %) was filtered under vacuum and allowed to dry in air.

$\delta_{\text{H}}(d_6\text{-DMSO})$ 4.2 (dt, 4H, $^3J_{\text{H-P}}$ 10.5 Hz, $^3J_{\text{H-H}}$ 6.8 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 4H, $^3J_{\text{H-H}}$ 6.2 Hz, $^3J_{\text{H-F}}$ 18.5 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(d_6\text{-DMSO})$ -82.0 (um, 3F, CF₃), -113.7 (um, 2F, $\alpha\text{-CF}_2$), -122.9 (um, 2F, $\beta\text{-CF}_2$), -123.9 (um, 2F, $\delta\text{-CF}_2$), -124.3 (um, 2F, $\epsilon\text{-CF}_2$), -127.2 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ ($d_6\text{-DMSO}$) 116.8 (s, neutral form); IR (nujol) ν 1083(w), 1123(s), 1144(s), 1202(s, br), 1237(s) cm⁻¹.

Preparation of [Ni bis-{O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphate}] (2.15)

Sodium hydroxide (5.70×10^{-1} g, 1.43×10^{-3} mol) was added to a stirred solution of O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphate (8.91×10^{-1} g, 1.43×10^{-3} mol) in 2,2,2-trifluoroethanol (25 cm³). After 30 minutes NiSO₄·6H₂O (1.88×10^{-1} g, 7.16×10^{-4} mol), dissolved in a minimum amount of water, was added and the mixture was stirred for 1 hour. After this time the solid purple product (8.14×10^{-1} g, 6.26×10^{-4} mol, 87 %) was filtered under vacuum, washed with cold 2,2,2-trifluoroethanol and allowed to dry in air.

$\delta_{\text{P}}\{^1\text{H}\}$ ($d_6\text{-DMSO}$) 116.3 (s, neutral form); IR (nujol) ν 876(w), 1006(s), 1144(s), 1135(vs), 1224(vs, br) cm⁻¹.

Preparation of [Ni bis-{O,O-di(4,4,4-trifluoro-*n*-butyl) dithiophosphate}] (2.16)

Powdered potassium hydroxide (3.60×10^{-2} g, 6.44×10^{-4} mol) was added to a rapidly stirred solution of O,O-di(4,4,4-trifluoro-*n*-butyl) dithiophosphoric acid (2.25

$\times 10^{-1}$ g, 6.44×10^{-4} mol) in 2,2,2-trifluoroethanol (30 cm^3). After stirring for 30 minutes, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (7.60×10^{-2} g, 3.22×10^{-4} mol) was added *via* a solid delivery tube, and the resulting reaction mixture was stirred for a further 2 hours. After this time the product was isolated as a purple solid by suction filtration, and purified by washing with cold 2,2,2-trifluoroethanol (1.66×10^{-1} g, 2.19×10^{-4} mol, 68 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.2 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.4 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 4H, $\gamma\text{-CH}_2$), 2.0 (um, 4H, $\beta\text{-CH}_2$; $\delta_{\text{F}}(\text{CDCl}_3)$ -66.6 (um, 3F, CF_3); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 93.7 (s, neutral form), 95.3 (um, basic form).

Preparation of [Ni bis-{O,O-diethyl dithiophosphate}] (2.17)

Powdered sodium hydroxide (2.25×10^{-1} g, 5.64×10^{-3} mol) was added to a rapidly stirred solution of O,O-diethyl dithiophosphoric acid (2.00 g, 5.64×10^{-3} mol) in 2,2,2-trifluoroethanol (30 cm^3). After stirring for 30 minutes, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (7.41×10^{-1} g, 2.82×10^{-3} mol) was added *via* a solid delivery tube, and the resulting reaction mixture was stirred for a further 2 hours. After this time the product was isolated as a purple solid by suction filtration, and purified by washing with cold 2,2,2-trifluoroethanol (8.74×10^{-1} g, 1.14×10^{-3} mol, 41 %).

$\delta_{\text{P}}\{^1\text{H}\}$ ($d_6\text{-DMSO}$) 114.6 (s, neutral form).

2.9.3 Copper Dithiophosphate Complexes

*Preparation of [Cu(PPh₃)₂{O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate}] (2.18)*

$[(\text{PPh}_3)_2\text{CuNO}_3]$ (2.37×10^{-1} g, 3.65×10^{-4} mol) was added as a solid to a solution of $\text{K}\{\text{O,O-di(1H,1H,2H,2H-perfluoro-}n\text{-octyl) dithiophosphate}\}$ (3.14×10^{-1} g, 3.65×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 30 minutes. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After allowing the reaction mixture to

stand for a further 30 minutes at room temperature, the white solid (0.382 g, 2.71×10^{-4} mol, 74 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (m, 30H, PPh_3), 3.8 (dt, 4H, $^3\text{J}_{\text{H-P}}$ 10 Hz, $^3\text{J}_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.2 (tt, 4H, $^3\text{J}_{\text{H-F}}$ 19 Hz, $^3\text{J}_{\text{H-H}}$ 7.0 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.3 (tt, 3F, $^3\text{J}_{\text{F-F}}$ 10 Hz, $^4\text{J}_{\text{F-F}}$ 3 Hz, CF_3), -113.9 (t, $^3\text{J}_{\text{F-F}}$ 11 Hz, 2F, $\alpha\text{-CF}_2$), -122.5 (um, 2F, $\beta\text{-CF}_2$), -123.2 (um, 2F, $\delta\text{-CF}_2$), -124.2 (um, 2F, $\varepsilon\text{-CF}_2$), -126.7 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 94.7 (s, ligand), 2.0 (s, PPh_3); m/z (FAB) 587 ($[\text{M} + \text{L}]^+$, 100 %), 1146 ($[\text{M} - \text{PPh}_3]$, 30 %); Found C, 43.93; H, 2.35; P, 6.53; S, 4.59. $\text{C}_{52}\text{H}_{38}\text{F}_{26}\text{O}_2\text{P}_3\text{S}_2\text{Cu}$ requires C, 44.32; H, 2.72; P, 6.59; S, 4.55; IR (nujol) ν 1000(s), 1078(w), 1134(s), 1195(w), 1220(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O}, \text{O-dioctyl dithiophosphate}\}]$ (2.19)

$[(\text{PPh}_3)_2\text{CuNO}_3]$ (4.58×10^{-1} g, 7.05×10^{-4} mol) was added as a solid to a solution of $\text{K}\{\text{O}, \text{O-dioctyl dithiophosphate}\}$ (2.77×10^{-1} g, 7.05×10^{-4} mol) in methanol (30 cm^3). The mixture was then rapidly stirred at room temperature overnight. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white solid (6.44×10^{-1} g, 6.84×10^{-4} mol, 97 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (m, 30H, PPh_3), 3.7 (dt, 2H, $^3\text{J}_{\text{H-P}}$ 10.2 Hz, $^3\text{J}_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.4 (um, 2H, $\beta\text{-CH}_2$) 1.2 (um, 10H, 5 mid-chain CH_2), 0.8 (t, 3H, $^3\text{J}_{\text{H-H}}$ 7.0 Hz); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 92.9 (s, ligand), 2.8 (s, PPh_3); IR (nujol) ν 965(s), 1028(w), 1095(s), 1120(w), 1434(vs) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O}, \text{O-di}(1\text{H}, 1\text{H}, 2\text{H}, 2\text{H-perfluoro-}n\text{-hexyl) dithiophosphate}\}]$ (2.20)

$[(\text{PPh}_3)_2\text{CuNO}_3]$ (4.01×10^{-1} g, 6.17×10^{-4} mol) was added as a solid to a solution of $\text{K}\{\text{O}, \text{O-di}(1\text{H}, 1\text{H}, 2\text{H}, 2\text{H-perfluoro-}n\text{-hexyl) dithiophosphate}\}$ (4.07×10^{-1} g, 6.17×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature overnight. The volume of solvent was reduced to half the initial amount

and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the solid (4.69×10^{-1} g, 3.88×10^{-4} mol, 63 %) was isolated by suction filtration. $\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (m, 30H, PPh_3), 3.8 (dt, 4H, $^3J_{\text{H-P}}$ 9.9 Hz, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.2 (tt, 4H, $^3J_{\text{H-F}}$ 19 Hz, $^3J_{\text{H-H}}$ 7.0 Hz, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.5 (tt, 3F, $^3J_{\text{F-F}}$ 10 Hz, $^4J_{\text{F-F}}$ 3.1 Hz, CF_3), -114.2 (um, 2F, $\alpha\text{-CF}_2$), -125.1 (um, 2F, $\gamma\text{-CF}_2$), -126.5 (um, 2F, $\beta\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 94.3 (s, ligand), 1.9 (s, PPh_3); m/z (FAB) 587 ($[\text{M} + \text{L}]^+$, 100 %), 946 ($[\text{M} - \text{PPh}_3]$, 20 %); Found C, 46.52; H, 2.96; P, 7.72; S, 5.14. $\text{C}_{48}\text{H}_{38}\text{F}_{18}\text{O}_2\text{P}_3\text{S}_2\text{Cu}$ requires C, 47.67; H, 3.17; P, 7.68; S, 5.30; IR (nujol) ν 1068(w), 1135(s), 1183(w), 1235(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O},\text{O-di}(4,4,4\text{-trifluoro-}n\text{-butyl})\text{ dithiophosphate}\}]$ (2.21)

Powdered potassium hydroxide (3.61×10^{-2} g, 6.44×10^{-4} mol) was added to a rapidly stirred solution of O,O-di(4,4,4-trifluoro-*n*-butyl) dithiophosphoric acid (2.25×10^{-1} g, 6.44×10^{-4} mol) in methanol (30 cm^3). $[(\text{PPh}_3)_2\text{CuNO}_3]$ (4.18×10^{-1} g, 6.44×10^{-4} mol) was added as a solid to the solution and the mixture was then rapidly stirred at room temperature for 30 minutes. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white solid (3.32×10^{-1} g, 3.54×10^{-4} mol, 55 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (m, 30H, PPh_3), 3.9 (dt, 4H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.4 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 4H, $\gamma\text{-CH}_2$), 1.9 (um, 4H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -66.8 (um, 3F, CF_3); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 94.5 (s, ligand), 1.7 (s, PPh_3); Found C, 56.06; H, 4.48; P, 6.93; S, 6.05. $\text{C}_{44}\text{H}_{42}\text{F}_6\text{O}_2\text{P}_3\text{S}_2\text{Cu}$ requires C, 56.38; H, 4.52; P, 9.91; S, 6.84. IR (nujol) ν 1008(s), 1096(w), 1150(s), 1233(w), 1254(s), 1434(vs) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O},\text{O-diphenyl dithiophosphate}\}]$ (2.25)

$[(\text{PPh}_3)_2\text{CuNO}_3]$ (2.42×10^{-1} g, 3.72×10^{-4} mol) was added as a solid to a solution of K{O,O-diphenyl dithiophosphate} (1.19×10^{-1} g, 3.72×10^{-4} mol) in methanol (20 cm^3). The mixture was then rapidly stirred at room temperature overnight. The

volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white solid (2.42×10^{-1} g, 2.78×10^{-4} mol, 75 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (m, 40H, Ar and PPh_3); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 86.0 (s, ligand), 3.4 (s, PPh_3); IR (nujol) ν 1094(w), 1161(w), 1190(s), 1210(s), 1489(s) cm^{-1} .

2.9.4 Rhodium and Iridium Dithiophosphate Complexes

Preparation of [$\text{Cp}^\text{RhCl}\{\text{O},\text{O}-\text{di}(1\text{H},1\text{H},2\text{H},2\text{H}-\text{perfluoro-}n\text{-octyl})\text{ dithiophosphate}\}$]* (2.26)

To a slurry of $\text{Na}\{\text{O},\text{O}-\text{di}(1\text{H},1\text{H},2\text{H},2\text{H}-\text{perfluoro-}n\text{-octyl})\text{ dithiophosphate}\}$ (1.54×10^{-1} g, 1.82×10^{-4} mol) in dichloromethane (30 cm^3), $[\text{RhCl}_2\text{Cp}^*]_2$ (5.60×10^{-2} g, 9.12×10^{-5} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over MgSO_4 and CaCl_2 . The solvent was removed *in vacuo*, affording the product as a dark red oil (1.90×10^{-1} g, 1.74×10^{-4} mol, 95 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.4 (dt, 2H, $^3\text{J}_{\text{H-P}}$ 10.6 Hz, $^3\text{J}_{\text{H-H}}$ 5.5 Hz, $\alpha\text{-CH}_2$), 4.3 (dt, 2H, $^3\text{J}_{\text{H-P}}$ 10.1 Hz, $^3\text{J}_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 2H, $^3\text{J}_{\text{H-H}}$ 6.9 Hz, $^3\text{J}_{\text{H-F}}$ 18.1 Hz, $\beta\text{-CH}_2$), 2.4 (tt, 2H, $^3\text{J}_{\text{H-H}}$ 5.7 Hz, $^3\text{J}_{\text{H-F}}$ 18.6 Hz, $\beta\text{-CH}_2$), 1.7 (s, 30H, Cp^*); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.3 (t, 6F, $^3\text{J}_{\text{F-F}}$ 9.3 Hz, CF_3), -113.6 (t, $^3\text{J}_{\text{F-F}}$ 12.6 Hz, 2F, $\alpha\text{-CF}_2$), -113.8 (t, $^3\text{J}_{\text{F-F}}$ 11.9 Hz, 2F, $\alpha\text{-CF}_2$), -122.4 (um, 4F, $\beta\text{-CF}_2$), -123.4 (um, 4F, $\delta\text{-CF}_2$), -124.1 (um, 4F, $\epsilon\text{-CF}_2$), -126.7 (um, 4F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 99.3 (d, $^2\text{J}_{\text{P-Rh}}$ 13.2 Hz); m/z (FAB) 1058 ($[\text{M} + \text{Cl}]^+$, 100 %); Found C, 28.23; H, 2.01; P, 2.47; S, 5.77. $\text{C}_{26}\text{H}_{23}\text{ClF}_{26}\text{O}_2\text{PS}_2\text{Rh}$ requires C, 28.52; H, 2.12; P, 2.83; S, 5.86. IR (nujol) ν 1081(w), 1124(s), 1146(vs), 1204(vs), 1238(vs) cm^{-1} .

Preparation of $[Cp^*RhCl\{O,O\text{-di}(1H,1H,2H,2H\text{-perfluoro-}n\text{-hexyl)}\text{ dithiophosphate}\}]$ (2.27)

To a slurry of Na{O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphate} (1.03×10^{-1} g, 1.60×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (4.90×10^{-2} g, 8.00×10^{-5} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over $MgSO_4$. The solvent was removed *in vacuo*, affording the product as a dark red oil (1.20×10^{-1} g, 1.34×10^{-4} mol, 84 %).

$\delta_H(CDCl_3)$ 4.4 (dt, 2H, $^3J_{H-P}$ 10.8 Hz, $^3J_{H-H}$ 5.4 Hz, $\alpha\text{-CH}_2$), 4.3 (dt, 2H, $^3J_{H-P}$ 9.7 Hz, $^3J_{H-H}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.5 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.4 Hz, $\beta\text{-CH}_2$), 2.4 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.2 Hz, $\beta\text{-CH}_2$), 1.7 (s, 30H, Cp^*); $\delta_F(CDCl_3)$ -81.5 (um, 6F, CF_3), -114.0 (um, 2F, $\alpha\text{-CF}_2$), 114.1 (um, 2F, $\alpha\text{-CF}_2$), -125.0 (um, 2F, $\gamma\text{-CF}_2$), -126.5 (um, 2F, $\beta\text{-CF}_2$); $\delta_P\{^1H\}$ ($CDCl_3$) 99.3 (d, $^2J_{P-Rh}$ 13.1 Hz); m/z (FAB) 859 ($[M + Cl]^+$, 100 %); IR (nujol) ν 1004(w), 1075(s), 1185(vs), 1202(vs), 1235(vs, br) cm^{-1} .

Preparation of $[Cp^*IrCl\{O,O\text{-di}(1H,1H,2H,2H\text{-perfluoro-}n\text{-octyl)}\text{ dithiophosphate}\}]$ (2.28)

To a slurry of Na{O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate} (1.54×10^{-1} g, 1.82×10^{-4} mol) in dichloromethane (25 cm^3), $[IrCl_2Cp^*]_2$ (7.30×10^{-2} g, 9.12×10^{-5} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over $MgSO_4$ and $CaCl_2$. The solvent was removed *in vacuo*, affording the product as an orange oil (1.42×10^{-1} g, 1.20×10^{-4} mol, 66 %).

$\delta_H(CDCl_3)$ 4.6 (dt, 2H, $^3J_{H-P}$ 10.6 Hz, $^3J_{H-H}$ 5.8 Hz, $\alpha\text{-CH}_2$), 4.3 (dt, 2H, $^3J_{H-P}$ 9.7 Hz, $^3J_{H-H}$ 7.1 Hz, $\alpha\text{-CH}_2$), 2.6 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.8 Hz, $\beta\text{-CH}_2$), 2.5 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.5 Hz, $\beta\text{-CH}_2$), 1.7 (s, 30H, Cp^*); $\delta_F(CDCl_3)$ -81.3 (t, 6F, $^3J_{F-F}$ 10 Hz, CF_3), -113.5 (t, $^3J_{F-F}$ 11 Hz, 2F, $\alpha\text{-CF}_2$), -113.7 (t, $^3J_{F-F}$ 11 Hz, 2F, $\alpha\text{-CF}_2$), -122.3 (um, 4F, $\beta\text{-CF}_2$), -123.3 (um, 4F, $\delta\text{-CF}_2$), -124.0 (um, 4F, $\epsilon\text{-CF}_2$), -126.6 (um, 4F, $\gamma\text{-CF}_2$); $\delta_P\{^1H\}$ ($CDCl_3$) 101.7 (s); m/z (FAB) 1149 ($[M + Cl]^+$, 100 %); Found C, 26.33; H,

2.05; P, 2.93; S, 5.15. $C_{26}H_{23}ClF_{26}O_2PS_2Ir$ requires C, 26.37; H, 1.96; P, 2.62; S, 5.42. IR (nujol) ν 1082(w), 1124(s), 1146(vs), 1205(vs), 1238(vs, br) cm^{-1} .

*Preparation of [Cp*IrCl{O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphate}]*
(2.29)

To a slurry of Na{O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphate} (1.04×10^{-1} g, 1.61×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (6.40×10^{-2} g, 8.04×10^{-5} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20\text{ cm}^3$) and dried over $CaSO_4$. The solvent was removed in vacuo, affording the product as a dark red oil (1.14×10^{-1} g, 1.16×10^{-4} mol, 72 %).

$\delta_H(CDCl_3)$ 4.5 (dt, 2H, $^3J_{H-P}$ 10.8 Hz, $^3J_{H-H}$ 5.4 Hz, $\alpha-CH_2$), 4.3 (dt, 2H, $^3J_{H-P}$ 9.7 Hz, $^3J_{H-H}$ 7.0 Hz, $\alpha-CH_2$), 2.5 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.4 Hz, $\beta-CH_2$), 2.4 (tt, 2H, $^3J_{H-H}$ 7.2 Hz, $^3J_{H-F}$ 18.2 Hz, $\beta-CH_2$), 1.7 (s, 30H, Cp*); $\delta_F(CDCl_3)$ -81.5 (um, 6F, CF_3), -113.8 (um, 2F, $\alpha-CF_2$), 114.1 (um, 2F, $\alpha-CF_2$), -125.0 (um, 2F, $\gamma-CF_2$), -126.5 (um, 2F, $\beta-CF_2$); $\delta_P\{^1H\}$ ($CDCl_3$) 101.9 (s); m/z (FAB) 949 ($[M + Cl]^+$, 100 %); IR (nujol) ν 1026(s), 1074(s), 1134(vs), 1200(s), 1229(vs, br) cm^{-1} .

2.9.5 Molybdenum Dithiophosphate Complexes

Preparation of [Oxo-Mo(^{VI}) {O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphate}] (2.30)

O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphoric acid (18.96 g, 2.30×10^{-2} mol) was dissolved in 1,3-perfluorodimethylcyclohexane (100 cm^3) and poured into a 500 cm^3 three necked round bottomed flask containing distilled water (150 cm^3), fitted with a solid delivery tube, a syringe connected to an SO_2 cylinder and a tubing adaptor outlet connected to a saturated aqueous $Ca(OH)_2$ scrubber. Sulfur dioxide was passed through the rapidly stirred biphasic system for ~30 minutes to ensure that the

solution was saturated. $[\text{K}_2\text{MoO}_4]$ (3.02 g, 1.27×10^{-2} mol) was then slowly added *via* the solid delivery tube. After 2 hours, colour change had been observed in both layers. The fluoruous layer had become purple, while the aqueous layer was dark blue, suggesting the presence of reduced but uncomplexed molybdate. More K_2MoO_6 was added, and SO_2 was passed through the rapidly stirred solution for a further 2 hours. The reaction mixture was then allowed to stand overnight. Nitrogen was passed through the solution to remove any dissolved SO_2 before the solvent was decanted from the solid purple product. This was extracted from any residual 1,3-perfluorodimethylcyclohexane by dissolving in α, α, α -trifluorotoluene followed by separating the two layers. The product was isolated by removing the α, α, α -trifluorotoluene *in vacuo* to give a purple solid (18.37 g, 5.21×10^{-3} mol) in 91 % crude yield. Purification was carried out by washing with toluene followed by suction filtration of the product.

$\delta_{\text{P}}\{^1\text{H}\}$ (α, α, α -trifluorotoluene/ D_2O lock) 100 (br s, Mo^{V} species), 133 (s, Mo^{IV} species), 89 (s, Mo^{VI} species); Found C, 21.77; H, 0.76; P, 3.96; S, 6.37. $\text{C}_{64}\text{H}_{36}\text{F}_{104}\text{Mo}_2\text{O}_{11}\text{P}_4\text{S}_8$ requires C, 21.79; H, 0.91; P, 3.52; S, 7.26. IR (nujol) ν 959(w, $\text{M}=\text{O}$), 1083(w), 1125(w), 1145(s), 1206(br), 1239(s) cm^{-1} .

Preparation of [Oxo-Mo⁽ⁿ⁾{O,O-di(1H,1H,2H,2H-perfluoro-n-hexyl) dithiophosphate}] (2.31)

O,O-di(1H,1H,2H,2H-perfluoro-*n*-hexyl) dithiophosphoric acid (3.82 g, 6.14×10^{-3} mol) was dissolved in 1,3-perfluorodimethylcyclohexane (100 cm^3) and poured into a 500 cm^3 three necked round bottomed flask containing distilled water (150 cm^3), fitted with a solid delivery tube, a syringe connected to an SO_2 cylinder and a tubing adaptor outlet connected to a saturated aqueous $\text{Ca}(\text{OH})_2$ scrubber. Sulfur dioxide was passed through the rapidly stirred biphasic for ~30 minutes to ensure that the solution was saturated. $[\text{K}_2\text{MoO}_4]$ (1.10 g, 4.60×10^{-3} mol) was then slowly added *via* the solid delivery tube. After 2 hours, colour change had been observed in both layers. The fluoruous layer had become purple, while the aqueous layer was dark blue, suggesting the presence of reduced but uncomplexed molybdate. More K_2MoO_6 was added, and SO_2 was passed through the rapidly stirred solution for a further 2 hours.

The reaction mixture was then allowed to stand overnight. Nitrogen was passed through the solution to remove any dissolved SO₂ before the solvent was decanted from the solid purple product. This was extracted from any residual 1,3-perfluorodimethylcyclohexane by dissolving in α, α, α -trifluorotoluene followed by separating the two layers. The product was isolated by removing the α, α, α -trifluorotoluene *in vacuo* to give a purple semi-solid (1.94 g, 7.14×10^{-4} mol) in 47 % crude yield. Purification was attempted by washing with toluene followed by decantation and drying of the product *in vacuo*.

$\delta_P\{^1H\}$ (α, α, α -trifluorotoluene/D₂O lock) 99 (br s, Mo^V species), 133 (s, Mo^{IV} species), 88 (s, Mo^{VI} species); IR (nujol) ν 957(w, M=O), 1082(w), 1125(w), 1142(s), 1207(br), 1235(s) cm⁻¹.

2.9.6 Ashless Dithiophosphate Compounds

Preparation of [O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphoric disulfide] (2.34)

A three necked round bottomed flask was fitted with a solid delivery tube, a stopper and a Rotaflo tubing adaptor. K[O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithio-phosphate] (4.50×10^{-1} g, 5.79×10^{-4} mol) was dissolved in 2,2,2-trifluoroethanol (35 cm³) by rapid stirring and resublimed iodine (7.00×10^{-2} g, 2.89×10^{-4} mol) was loaded into the solid delivery tube. The apparatus was flushed with nitrogen for ~20 minutes before the iodine was added in two aliquots to the solution of the potassium salt. After rapid stirring for 12 hours at room temperature all of the iodine had dissolved and an orange colour in the solution could be observed. The solvent was removed *in vacuo* to give an off white solid which was then washed by stirring for 30 minutes in H₂O to remove any KI formed. The white solid (3.80×10^{-1} g, 2.32×10^{-4} mol, 80 %) was isolated by suction filtration and dried *in vacuo*.

$\delta_H(d_6\text{-Acetone})$ 4.6 (dt, 4H, $^3J_{H-P}$ 10 Hz, $^3J_{H-H}$ 6.5 Hz, $\alpha\text{-CH}_2$), 2.8 (tt, 4H, $^3J_{H-H}$ 6.6 Hz, $^3J_{H-F}$ 18 Hz, $\beta\text{-CH}_2$); $\delta_F(d_6\text{-Acetone})$ -82.2 (t, 3F, $^3J_{F-F}$ 9 Hz, CF₃), -114 (um, 2F, $\alpha\text{-CF}_2$), -123.3 (um, 2F, $\beta\text{-CF}_2$), -124.5 (um, 2F, $\delta\text{-CF}_2$), -125.2 (um, 2F, $\varepsilon\text{-CF}_2$), -

127.4 (um, 2F, γ -CF₂); $\delta_P\{^1H\}$ (*d*₆-Acetone) 87 (s, disulfide); *m/z* (FAB) 821 (100 %), 1643 ([M + H]⁺, 10 %); Found C, 23.10; H, 1.07; P, 4.11; S, 7.31. C₃₂H₁₆F₅₂O₄P₂S₄ requires C, 23.39; H, 0.97; P, 3.78; S, 7.79. IR (nujol) ν 1081(w), 1125(w), 1144(s), 1207(br), 1235(s) cm⁻¹.

Preparation of [O,O-dioctyl dithiophosphoric disulfide] (2.35)

Powdered potassium hydroxide (1.18 x 10⁻¹ g, 2.12 x 10⁻³ mol) was added to a rapidly stirred solution of O,O-dioctyl dithiophosphoric acid (7.50 x 10⁻¹ g, 2.12 x 10⁻³ mol) in 2,2,2-trifluoroethanol (30 cm³). After stirring for 30 minutes, resublimed iodine (0.54 x 10⁻¹ g, 2.12 x 10⁻³ mol) was added *via* a solid delivery tube. After rapid stirring for 12 hours at room temperature all of the iodine had dissolved and an orange colour in the solution could be observed. The solvent was removed *in vacuo* and the required product was taken up into hexane (30 cm³) and filtered. The product was isolated by removing the solvent *in vacuo* to give an off white solid (4.55 x 10⁻¹ g, 6.44 x 10⁻⁴ mol, 61 %).

δ_H (CDCl₃) 4.0 (um, 2H, α -CH₂), 1.6 (um, 2H, β -CH₂) 1.3 (um, 10H, 5 mid-chain CH₂), 0.8 (t, 3H, ³J_{H-H} 7.0 Hz); $\delta_P\{^1H\}$ (CDCl₃) 85.3 (s, disulfide); IR (nujol) ν 855(s, br), 928(w), 990(vs, br), 1125(w) cm⁻¹.

Preparation of [1,2-Ethanedithiol S,S-bis-(O,O-di(1H,1H,2H,2H-perfluoro-n-octyl) dithiophosphate] (2.36)

Na[O,O-di(1H,1H,2H,2H-perfluoro-*n*-octyl) dithiophosphate] (7.70 x 10⁻¹ g, 9.15 x 10⁻⁴ mol) was dissolved in 2,2,2-trifluoroethanol (30 cm³) and placed in a round bottomed flask. Diiodoethane (1.30 x 10⁻¹ g, 4.57 x 10⁻⁴) was added to the solution which was then stirred rapidly under a static nitrogen atmosphere at room temperature for 3 days. The reaction was monitored as it progressed by ³¹P NMR spectroscopy. As the solution was allowed to stand over a long period of time (*ca* 1 week) white crystals began to form and were isolated by suction filtration (4.40 x 10⁻¹ g, 2.65 x

10^{-4} mol, 58 %). Purification was carried out by recrystallising from 2,2,2-trifluoroethanol affording a white crystalline product.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 4.5 (dt, 8H, $^3J_{\text{H-P}}$ 10 Hz, $^3J_{\text{H-H}}$ 6.5 Hz, $\alpha\text{-CH}_2$), 2.7 (tt, 8H, $^3J_{\text{H-H}}$ 6.6 Hz, $^3J_{\text{H-F}}$ 18 Hz, $\beta\text{-CH}_2$), 2.6 (s, 4H, ethyl bridge); $\delta_{\text{F}}(d_6\text{-Acetone})$ -82.3 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -114 (um, 2F, $\alpha\text{-CF}_2$), -113.9 (t, $^3J_{\text{F-F}}$ 11 Hz, 2F, $\alpha\text{-CF}_2$), -122.5 (um, 2F, $\beta\text{-CF}_2$), -123.4 (um, 2F, $\delta\text{-CF}_2$), -124.2 (um, 2F, $\varepsilon\text{-CF}_2$), -126.9 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}\{^1\text{H}\}$ ($d_6\text{-Acetone}$) 88 (s); IR (nujol) ν 1005(w), 1044(w), 1136(w), 1206(br), 1226(s) cm^{-1} .

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3.1 Introduction

Dithiocarbamate acids were first synthesised in the 19th century,¹ along with their potassium, sodium, barium, lead and copper salts. The trivial name 'xanthate' is derived from the Greek word *xanthos*, meaning "yellow", in reference to the characteristic yellow colour of these acids and some of their metal complexes. In general, xanthates are formed by reacting an alcohol with carbon disulfide in the

CHAPTER THREE

Xanthate Ligands and Coordination Chemistry



This reaction proceeds by deprotonation of the alcohol, to form the alkoxide anion, followed by nucleophilic attack of this on carbon disulfide. A variety of alcohols have been used to form xanthates in this manner, but most research appears to involve only simple hydrocarbon alcohols, with particular emphasis on ethylxanthates. Primary alcohols have been found to react almost completely, especially those bearing a branched alkyl tail. It has been reported that secondary alcohols react less readily, with by-products formed, and tertiary alcohols react only at high temperatures.²

Xanthates have two possible donor donor atoms joined to a single carbon atom, and as a result are considered as "soft" Lewis bases. On complexation with a metal ion, they can act in the same coordination mode as dithiophosphates.

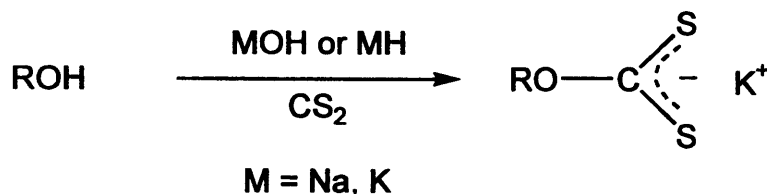
A brief overview of the coordination chemistry of xanthate ligands is included to illustrate key points of interest.



University of
Leicester

3.1 Introduction

Dithiocarbonic acids were first synthesised in the 19th century,¹ along with their potassium, sodium, barium, lead and copper salts. The trivial name “xanthate” is derived from the Greek word *xanthos*, meaning “blond”, in reference to the characteristic yellow colour of these acids and some of their metal complexes. In general, xanthates are formed by reacting an alcohol with carbon disulfide in the presence of an alkali metal hydroxide or hydride² (Scheme 3.1).



Scheme 3.1 General reaction scheme for alkali metal xanthate salts

This reaction proceeds by deprotonation of the alcohol, to form the alkoxide anion, followed by nucleophilic attack of this on carbon disulfide. A variety of alcohols have been used to form xanthates in this manner, but most research appears to involve only simple hydrocarbon alcohols, with particular emphasis on ethylxanthates. Primary alcohols have been found to react almost completely, especially those bearing a branched alkyl tail. It has been reported that secondary alcohols react less readily, with by-products formed, and tertiary alcohols react only at high temperatures.³

Xanthates have two potential sulfur donor atoms joined to a single carbon atom, and as a result of this, are usually classified as class b ligands or “soft” Lewis bases. On complexation to metal centres, xanthate ligands can adopt the same coordination modes as dithiophosphate ligands (Figure 3.1), and here a brief, selective overview of the coordination chemistry of xanthate ligands is included to illustrate key points of interest.

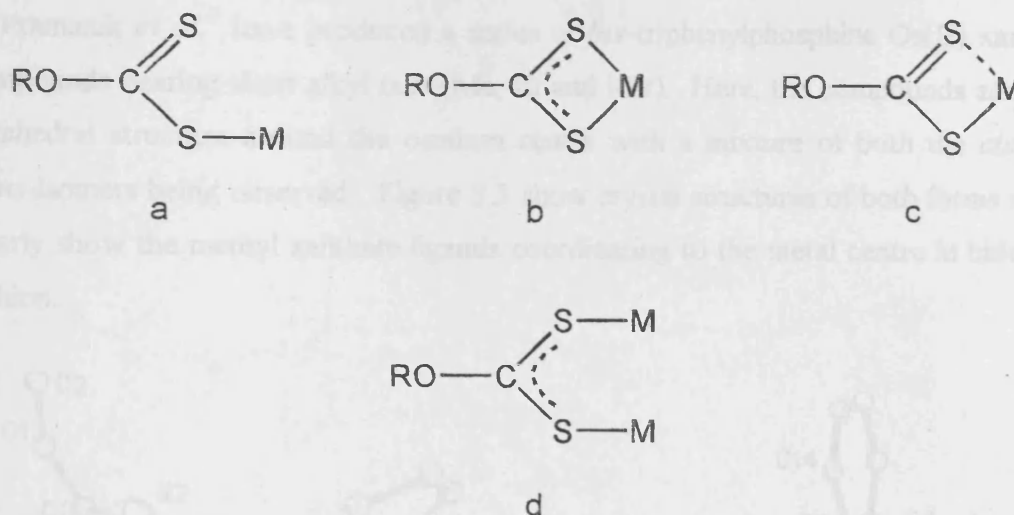


Figure 3.1 Possible bonding modes of xanthate ligands monodentate (a), isobidentate (b), anisobidentate (c) and bridging (d)

In metal complexes reported in the literature, xanthates usually act as bidentate ligands, stabilised by chelation. Trávníček *et al.*^{4,5} have reported the crystal structures of a number of Ni(II) compounds bearing isopropyl or isopentyl xanthate ligands which bind in a bidentate manner. One such example is the triphenylphosphine nickel(II) bromide compound⁶ (Figure 3.2), which exhibits the expected square planar geometry around the nickel centre.

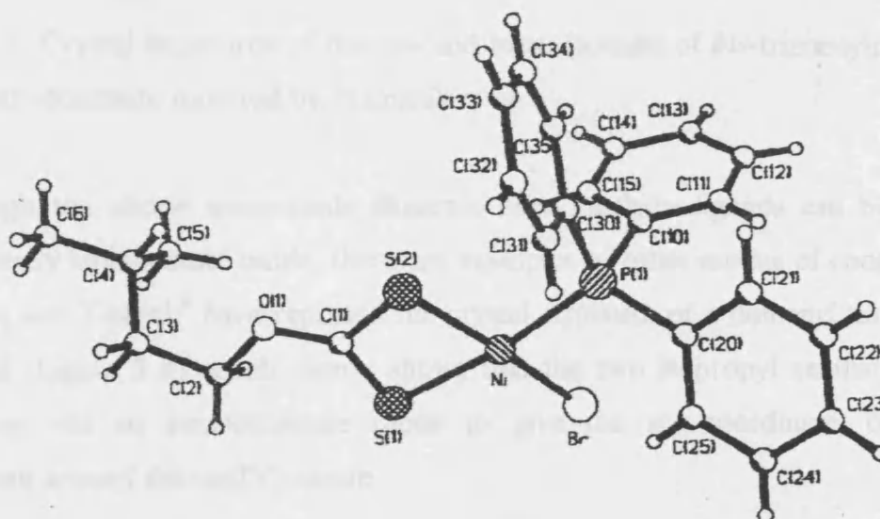


Figure 3.2 Crystal structure of $[\text{NiBr}(\text{S}_2\text{CO}-i\text{-Am})(\text{PPh}_3)]$ compound reported by Trávníček *et al.*⁶

Pramanik *et al.*⁷ have produced a series of *bis*-triphenylphosphine Os(II) xanthate compounds bearing short alkyl tails (Me, Et and *i*-Pr). Here, the compounds adopt an octahedral structure around the osmium centre with a mixture of both the *cis*- and *trans*-isomers being observed. Figure 3.3 show crystal structures of both forms which clearly show the methyl xanthate ligands coordinating to the metal centre in bidentate fashion.

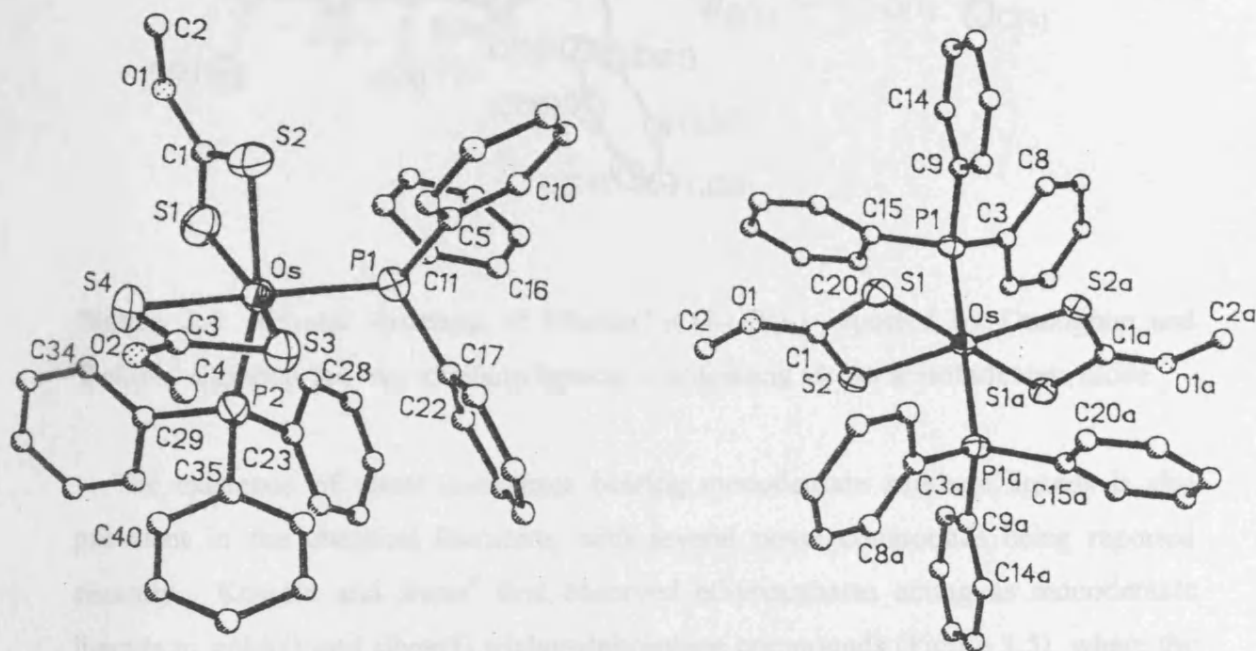


Figure 3.3 Crystal structures of the *cis*- and *trans*-isomers of *bis*-triphenylphosphine Os(II) methylxanthate reported by Pramanik *et al.*⁷

Although the above compounds illustrate how xanthate ligands can bind *via* a predominantly isobidentate mode, there are examples of other modes of coordination. Donoghue and Tiekink⁸ have reported the crystal structure of a diphenyl tin xanthate compound (Figure 3.4) which clearly shows that the two isopropyl xanthate ligands are binding *via* an anisobidentate mode to give the six coordinate, octahedral arrangement around the tin(IV) centre.

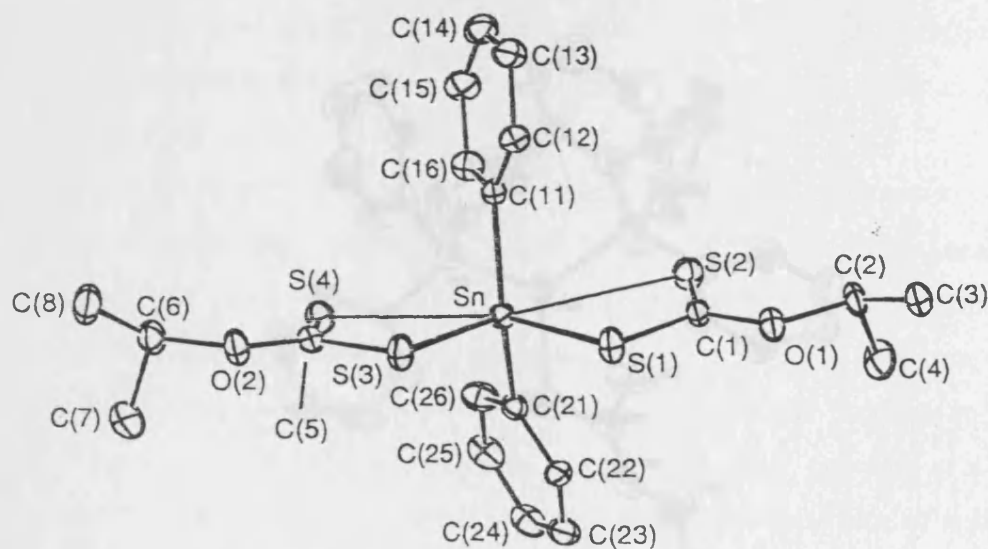


Figure 3.4 Crystal structure of $[\text{Ph}_2\text{Sn}(\text{S}_2\text{CO}-i\text{-Pr})_2]$ reported by Donoghue and Tiekink⁸ showing the two xanthate ligands coordinating *via* an anisobidentate mode

The existence of metal complexes bearing monodentate xanthate ligands is also prevalent in the chemical literature, with several novel compounds being reported recently. Kowala and Swan⁹ first observed ethylxanthates acting as monodentate ligands to gold(I) and silver(I) triphenylphosphine compounds (Figure 3.5), where the two coordinated groups bond in a linear arrangement with the thiocarbonyl sulfur atom not involved in coordination.

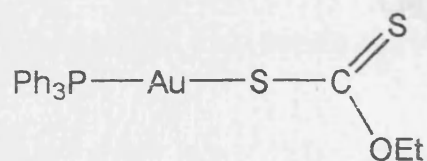


Figure 3.5 Gold(I) xanthate complex, with the thiocarbonyl sulfur atom not involved in coordination reported by Kowala and Swan⁹

This work has since been extended by Assefa *et al.*¹⁰ who have produced a series of gold(I) *bis*-phosphine xanthate complexes exhibiting a trigonal arrangement around the metal centre with the xanthate ligand binding in a monodentate manner (Figure 3.6).

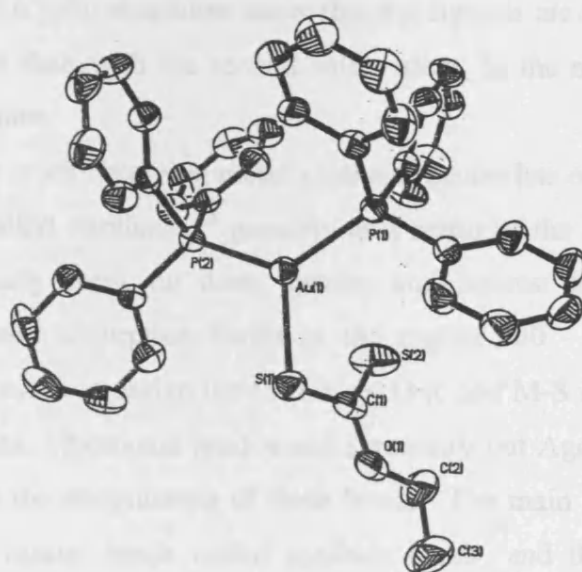


Figure 3.6 Crystal structure of trigonal gold(I) *bis*-phosphine xanthate compound reported by Assefa *et al.*¹⁰

Further examples of xanthate ligands bonding through a single sulfur donor have been reported by Drake *et al.*^{11,12} Here, a number of germanium(IV) compounds with either three or four monodentate xanthate ligands were studied (Figure 3.7).

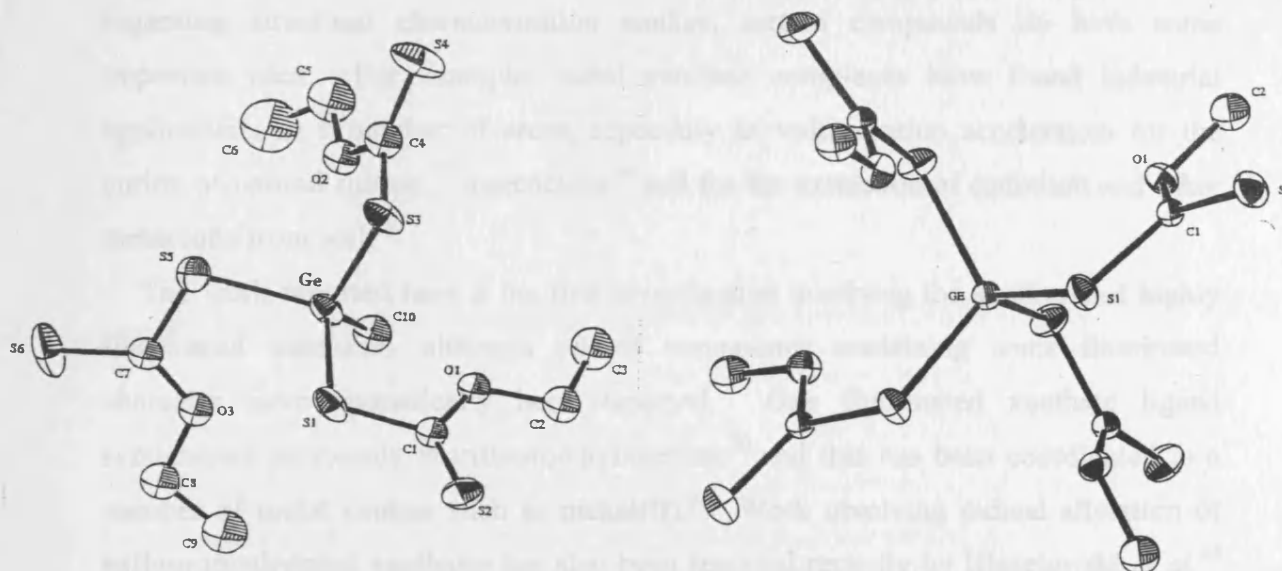


Figure 3.7 Crystal structures of $[\text{MeGe}(\text{S}_2\text{COEt})_3]^{11}$ (left) and $[\text{Ge}(\text{S}_2\text{COMe})_4]^{12}$ (right) reported by Drake *et al.*

Interestingly, the crystal structures show that the ligands are all oriented with the oxygen atom, rather than with the second sulfur atom, in the non-bonding position nearest the metal centre.

Some of the later work involving metal xanthate species has centred on vibrational analysis of simple alkyl xanthates,¹³ possibly as a result of the limited analysis that accompanies the early work on these species and interest has focussed on the characteristic infra-red absorption bands in the region 900 – 1300 cm⁻¹. Many attempts have been made to assign the C-O, C-S, O-R and M-S frequencies¹⁴ as well as S-C-S bond angles, vibrational modes and symmetry but Agarwala *et al.*¹⁵ report “controversy” about the assignments of these bands. The main area of agreement is that there are four mixed bands called xanthate bands, and that these are highly coupled, leading to very complex spectra.

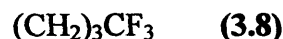
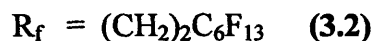
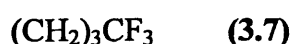
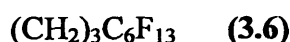
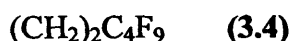
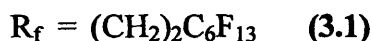
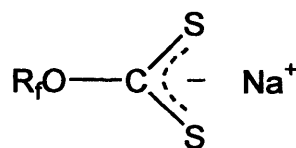
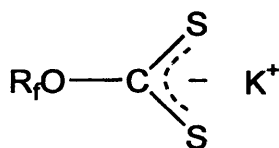
Attempts have also been made to synthesise a series of aryl xanthates and a number of metal complexes containing xanthates of this nature have been reported.¹⁶ For these to form successfully, alkyl substituents are necessary in the *ortho* positions on the phenyl ring, as underivatised phenol does not react under these conditions. The electron-donating substituents are required to render the phenoxide anion sufficiently nucleophilic to react with CS₂.

Although the majority of work on xanthate compounds reported in the literature is regarding structural characterisation studies, certain compounds do have some important uses. For example, metal xanthate complexes have found industrial applications in a number of areas, especially as vulcanisation accelerators for the curing of natural rubber,¹⁷ insecticides¹⁸ and for the extraction of cadmium and other metal ions from soil.¹⁹

The work reported here is the first investigation involving the synthesis of highly fluorinated xanthates, although related compounds containing some fluorinated character have sporadically been reported. One fluorinated xanthate ligand synthesised previously is trifluoroethylxanthate²⁰ and this has been coordinated to a number of metal centres such as nickel(II).²¹ Work involving radical allylation of trifluoromethylated xanthates has also been reported recently by Blazejewski *et al.*²² Here, attempts to form a number of novel alkyl- and perfluoroalkyl-derivatised xanthate ligands, along with a study of their coordination chemistry to a variety of transition metal centres, is described for a direct comparison with the synthesis and coordination chemistry of the dithiophosphate ligands outlined in Chapter 2.

3.2 Synthesis of Xanthate Ligands

Classically, compounds of this nature are synthesised either in the absence of a solvent,²³ or by using an excess of the alcohol as the solvent,²⁴ followed by the addition of metal hydroxide and CS₂. Here, due to the cost of the fluorinated alcohols, using an excess was far from desirable. Also, since some of the fluorinated alcohols are semi-solid at room temperature, mixing would potentially be problematic if reactions were attempted in the absence of solvent. To overcome this, diethyl ether was used as all of the alcohols were soluble but no competitive reaction is possible, which could be the case if an alcoholic solvent was used. A series of alkyl- and perfluoroalkyl-derivatised alkali metal xanthates (3.1-3.8) were produced by the reaction of the appropriate alcohol with CS₂ in the presence of alkali metal hydride.

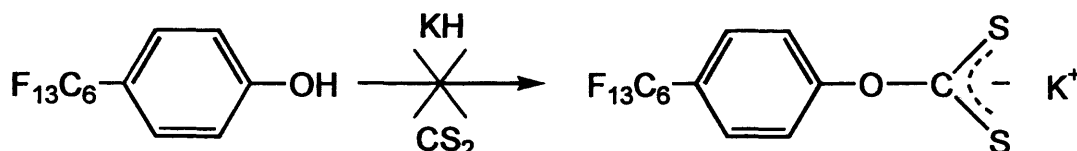


The required products were collected as flocculent, pale yellow solids and purified by washing with cold hexane. The potassium salts appeared to be more stable in comparison to their sodium analogues, and could be stored in air indefinitely without any decomposition being observed. It is likely that this added stability arises due to the potassium cation being larger in size than the sodium cation, and thereby being closer in size to the anion.

Since the alcohol starting materials are the same as those used to produce the dithiophosphate ligands, discussed in Chapter 1, the proton and fluorine NMR spectra of these xanthates are very similar to those for the corresponding dithiophosphate

ligands, and also to those for the parent alcohol themselves. In the case of (3.5) the fluorine NMR spectra still exhibits only six distinct resonances, with those associated with additional ζ - and η -CF₂ groups overlapping the δ -CF₂ signal.

As expected, the attempted syntheses of both aryl- and perfluoroaryl-derivatised xanthate ligands proved to be unsuccessful (Scheme 3.2).

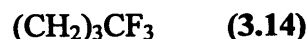
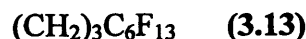
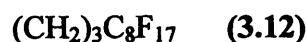
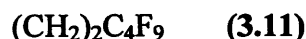
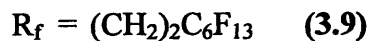
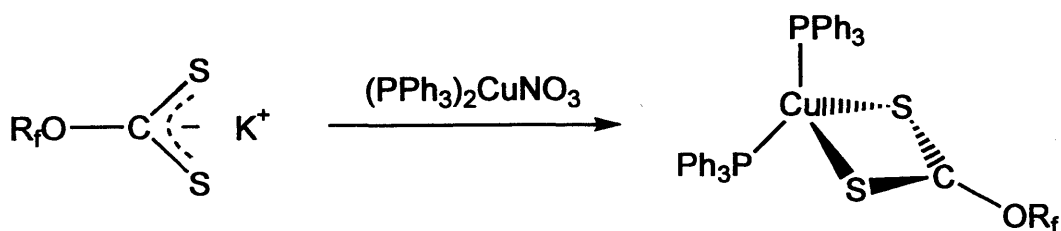


Scheme 3.2 Attempted synthesis of perfluoroaryl xanthate ligand

This is attributed to the reduction in nucleophilicity of the perfluoroalkyl-derivatised phenol when compared to that of phenol, as a result of the high electron withdrawing influence of the perfluoroalkyl tail.

3.3 Copper Xanthate Complexes

A series of copper *bis*-triphenylphosphine xanthate complexes with differing alkyl and perfluoroalkyl groups were produced (3.9-3.14) (Scheme 3.3).



Scheme 3.3 Synthesis of *bis*-triphenylphosphine copper xanthate complexes

All of these reactions were carried out in a similar fashion to those for the dithiophosphate analogues, by the addition of the alkali metal salt of the xanthate to the *bis*-triphenylphosphine copper nitrate precursor.²⁵ Complex (3.9) was produced by reaction of (3.2) with *bis*-triphenylphosphine copper nitrate by stirring in methanol at room temperature for 30 minutes. After this time a white solid was observed in the reaction mixture which, after cooling in ice, was isolated by suction filtration. The protio analogue (3.10) was synthesised using a similar procedure and the structure proved by single crystal X-ray structural analysis on a single crystal grown from methanol. This showed the four coordinate, tetrahedral copper centre bearing two triphenylphosphine groups, with the molecule occupying a single orientation within the unit cell (Figure 3.8).

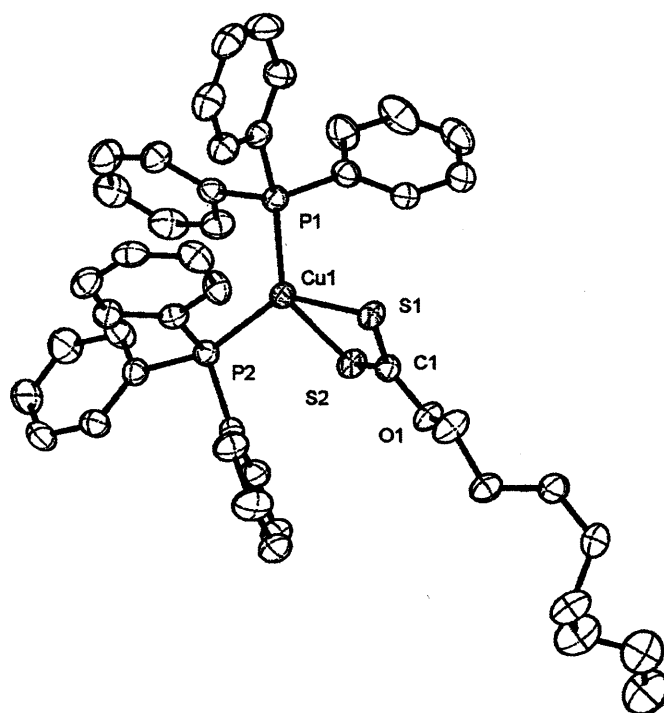


Figure 3.8 Crystal structure of (3.10)

The 4,4,4-trifluoro-*n*-butyl analogue (3.14) was synthesised in a similar manner, and single crystals suitable for X-ray structural analysis were produced by slow evaporation of a methanol solution. Crystal data and structure refinements for (3.10) and (3.14) can be found in the Appendix, whilst complete sets of data regarding

atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

Again, (3.14) shows a similar tetrahedral structure to (3.10), with increased disorder being observed at the terminal CF₃ group (Figure 3.9).

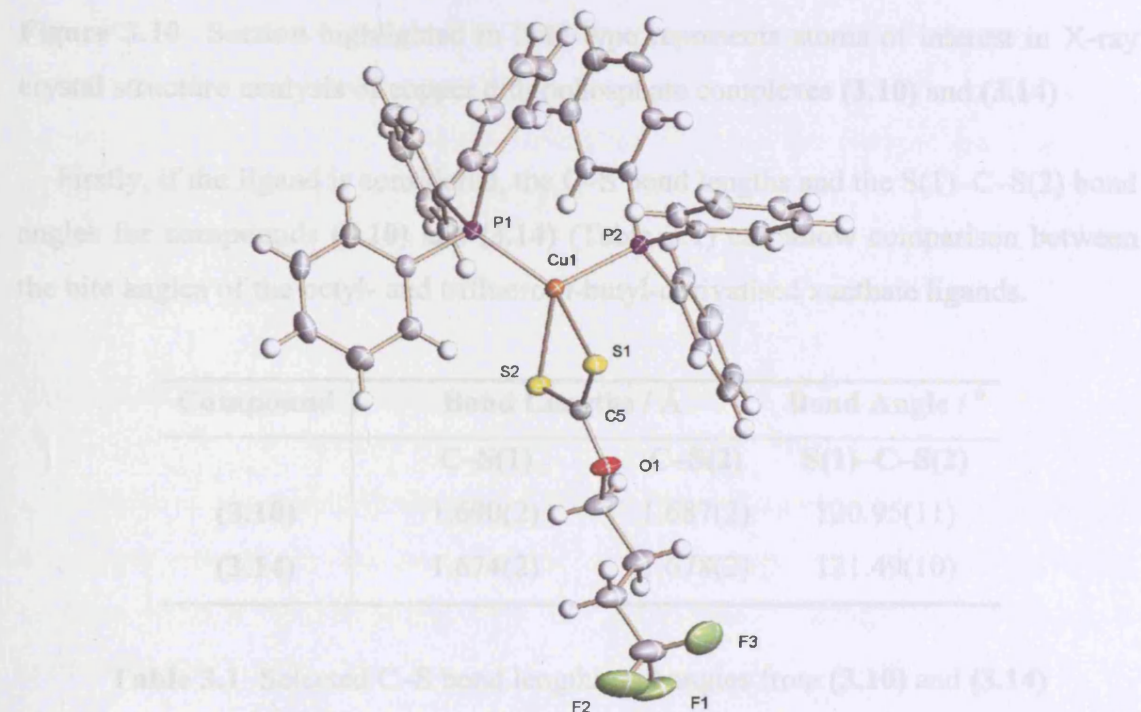


Figure 3.9 Crystal structure of (3.14)

Attempts were made to grow crystals of other copper xanthate complexes suitable for X-ray analysis, but despite using a number of techniques and solvent systems, these proved to be unsuccessful. (Table 3.2) can allow a comparison between the

As with the copper dithiophosphate complexes, discussed in Chapter 2, data can be obtained from single crystal X-ray diffraction regarding both the geometry around the copper centre and how the ligand coordinates. From the crystal structures determined for compounds (3.10) and (3.14), the bite angle of the ligand and the coordination mode it adopts has been studied. Here, analysis focuses on the Cu-S and C-S bond lengths and angles with the atoms concerned highlighted in Figure 3.10 in bold type.

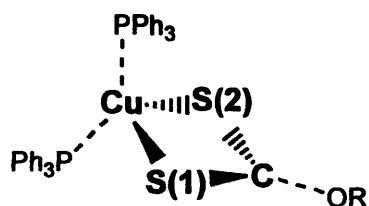


Figure 3.10 Section highlighted in bold type represents atoms of interest in X-ray crystal structure analysis of copper dithiophosphate complexes (3.10) and (3.14)

Firstly, if the ligand is considered, the C–S bond lengths and the S(1)–C–S(2) bond angles for compounds (3.10) and (3.14) (Table 3.1) can allow comparison between the bite angles of the octyl- and trifluoro-*n*-butyl-derivatised xanthate ligands.

Compound	Bond Lengths / Å		Bond Angle / °
	C–S(1)	C–S(2)	S(1)–C–S(2)
(3.10)	1.690(2)	1.687(2)	120.95(11)
(3.14)	1.674(2)	1.678(2)	121.49(10)

Table 3.1 Selected C–S bond lengths and angles from (3.10) and (3.14)

Both compounds have symmetrical C–S bonds of just below 1.7 Å. The S(1)–C–S(2) bond angles are also virtually unaffected by the fluorinated moiety and are both just greater than the perfect trigonal angle of 120 °.

Secondly, the Cu–S bond lengths and the S(1)–Cu–S(2) bond angles for compounds (3.10) and (3.14) (Table 3.2) can allow a comparison between the geometries around the copper centre of the two compounds.

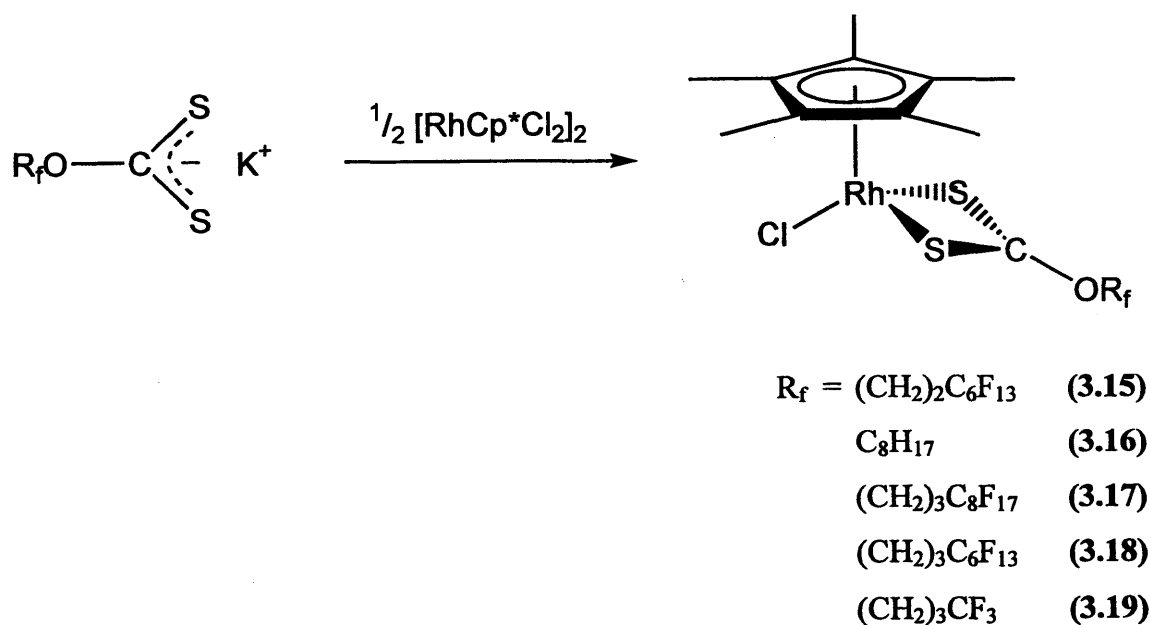
Compound	Bond Lengths / Å		Bond Angle / °
	Cu–S(1)	Cu–S(2)	S(1)–Cu–S(2)
(3.10)	2.422(1)	2.399(1)	75.11(2)
(3.14)	2.407(1)	2.408(1)	74.79(2)

Table 3.2 Selected Cu–S bond lengths and angles from (3.10) and (3.14)

This shows that the trifluoro-*n*-butyl-derivatised ligand seems to be bonding *via* the isobidentate mode, where both Cu–S bonds are the same length. The octyl-derivatised ligand appears to bond *via* the anisobidentate mode, where one Cu–S bond is longer than the other. Although the copper centre adopts a four coordinate, pseudo-tetrahedral geometry, the S(1)–Cu–S(2) bond angles are far removed from the 107.5 ° necessary for a perfect tetrahedron. Similarly small angles were observed in the analogous dithiophosphate complexes, with the steric effect of the bulky triphenylphosphine groups possibly having an effect on the reduced bond angle in addition to the small bite angle of the ligand.

3.4 Rhodium Xanthate Complexes

A series of rhodium(III) complexes (3.15-3.19), analogous to the dithiophosphate complexes reported by Jain and Vargese²⁶ and those reported in Chapter 2, bearing xanthate ligands with differing alkyl and perfluoroalkyl groups were synthesised (Scheme 3.4).



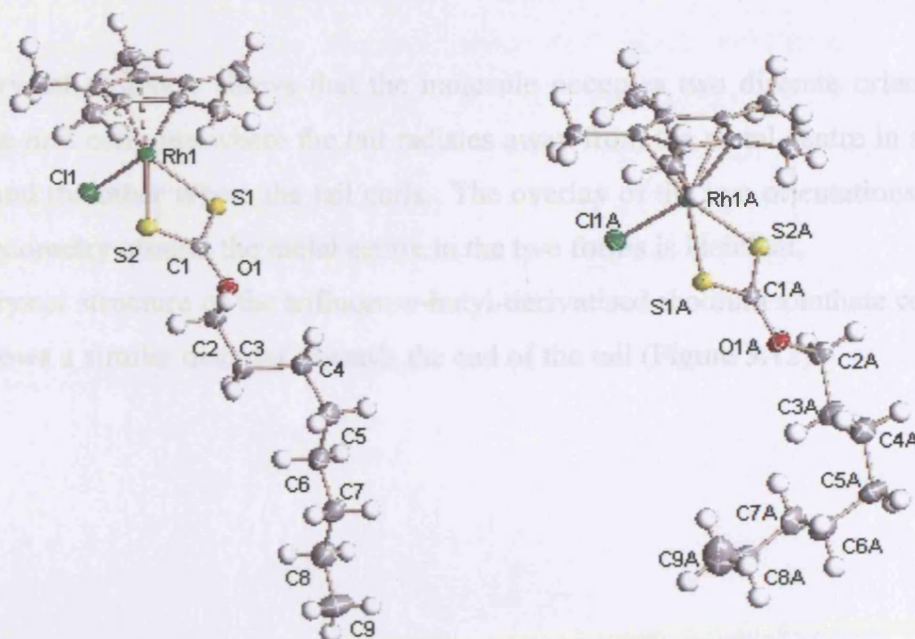
Scheme 3.4 Formation of a rhodium(III) xanthate complexes

These were prepared by the reaction of the appropriate alkali metal xanthate salt with $[\text{Cp}^*\text{RhCl}_2]_2$ at room temperature in dichloromethane. Proton and ^{19}F NMR spectroscopy showed all of the expected resonances with very similar spectra to those of the corresponding alkali metal salt being observed. The ^1H spectra did, however, contain an additional singlet at around 1.7 ppm corresponding to the pentamethyl cyclopentadienyl protons.

Mass spectrometry of the rhodium xanthate compounds all gave good agreement with theoretical values, with the presence a peak corresponding to the $[\text{M} - \text{Cl}]^+$ fragment being prevalent in all spectra.

Crystals suitable for X-ray analysis were grown by slow evaporation from an acetone solution for two of the rhodium complexes (**3.16**) and (**3.19**). Crystal data and structure refinements for (**3.16**) and (**3.19**) can be found in the Appendix, whilst complete sets of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

The octyl-derivatised complex (Figure 3.11) shows the ligand bonding to the metal in a bidentate fashion to give a pseudo-octahedral geometry with the pentamethyl cyclopentadienyl group occupying three coordination sites to give the characteristic piano stool structure.



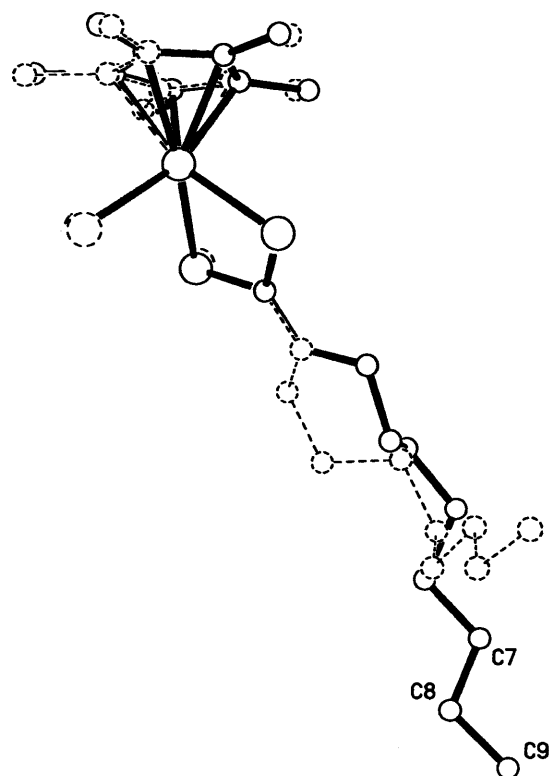


Figure 3.11 Crystal structure of (3.16) showing two discrete molecules within the unit cell (previous page) and the two orientations overlaid (above)

The crystal structure shows that the molecule occupies two discrete orientations within the unit cell, one where the tail radiates away from the metal centre in a linear manner and the other where the tail curls. The overlay of the two orientations shows that the geometry around the metal centre in the two forms is identical.

The crystal structure of the trifluoro-*n*-butyl-derivatised rhodium xanthate complex (3.19) shows a similar disorder towards the end of the tail (Figure 3.12).

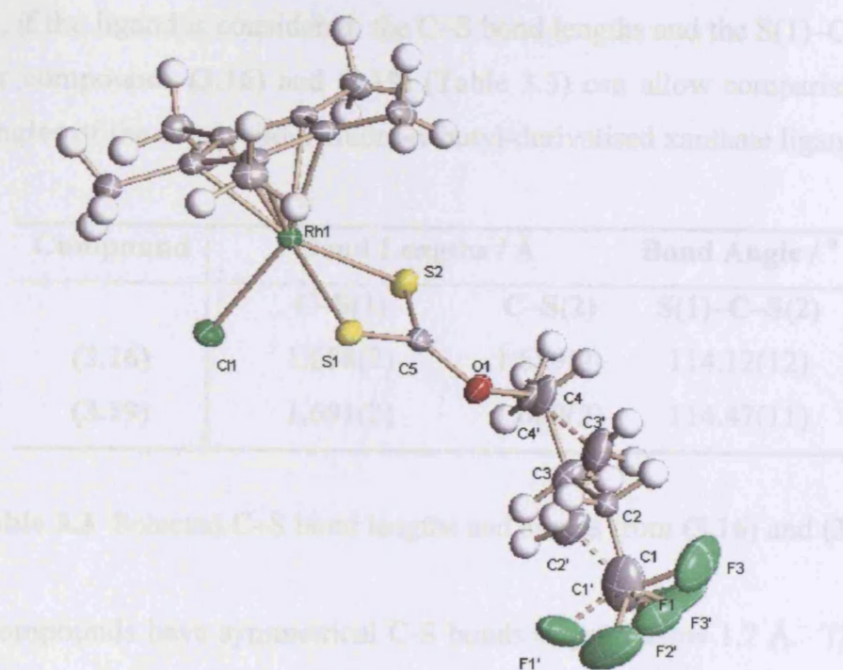


Figure 3.12 Crystal structure of (3.19)

Attempts were made to grow crystals of other rhodium xanthate complexes suitable for X-ray analysis, but despite using a number of techniques and solvent systems, these proved to be unsuccessful.

Both geometry around the rhodium centre and ligand coordination can be investigated using X-ray crystallography. From the crystal structures determined for compounds (3.16) and (3.19), data can be gathered regarding the bite angle of the ligand and the coordination mode it adopts. Here analysis focuses on Rh-S and C-S bond lengths and angles with the atoms concerned highlighted in Figure 3.13 in bold type.

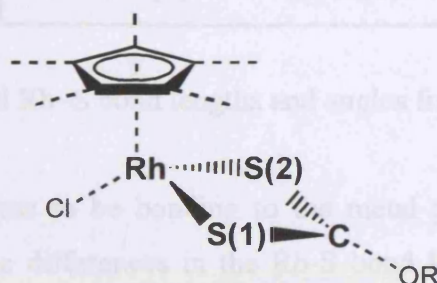


Figure 3.13 Section highlighted in bold type represents atoms of interest in X-ray crystal structure analysis of rhodium xanthate complexes (3.16) and (3.19)

Firstly, if the ligand is considered, the C–S bond lengths and the S(1)–C–S(2) bond angles for compounds (3.16) and (3.19) (Table 3.3) can allow comparison between the bite angles of the octyl- and trifluoro-*n*-butyl-derivatised xanthate ligands.

Compound	Bond Lengths / Å		Bond Angle / °
	C–S(1)	C–S(2)	S(1)–C–S(2)
(3.16)	1.688(2)	1.689(2)	114.12(12)
(3.19)	1.691(2)	1.689(2)	114.47(11)

Table 3.3 Selected C–S bond lengths and angles from (3.16) and (3.19)

Both compounds have symmetrical C–S bonds of just below 1.7 Å. The S(1)–C–S(2) bond angles are also virtually unaffected by the fluorinated moiety and are both smaller than the perfect trigonal angle of 120 ° and that observed for the copper(I) xanthate complexes. The tightening of the S(1)–C–S(2) angle is probably related to the contraction in the S(1)–Rh–S(2) bond angle (see below) which, in turn, is likely to be related to the greater steric bulk of the Cp* unit in these rhodium complexes.

Secondly, the Rh–S bond lengths and the S(1)–Rh–S(2) bond angles for compounds (3.16) and (3.19) (Table 3.4) can allow a comparison between the geometries around the rhodium centre of the two compounds.

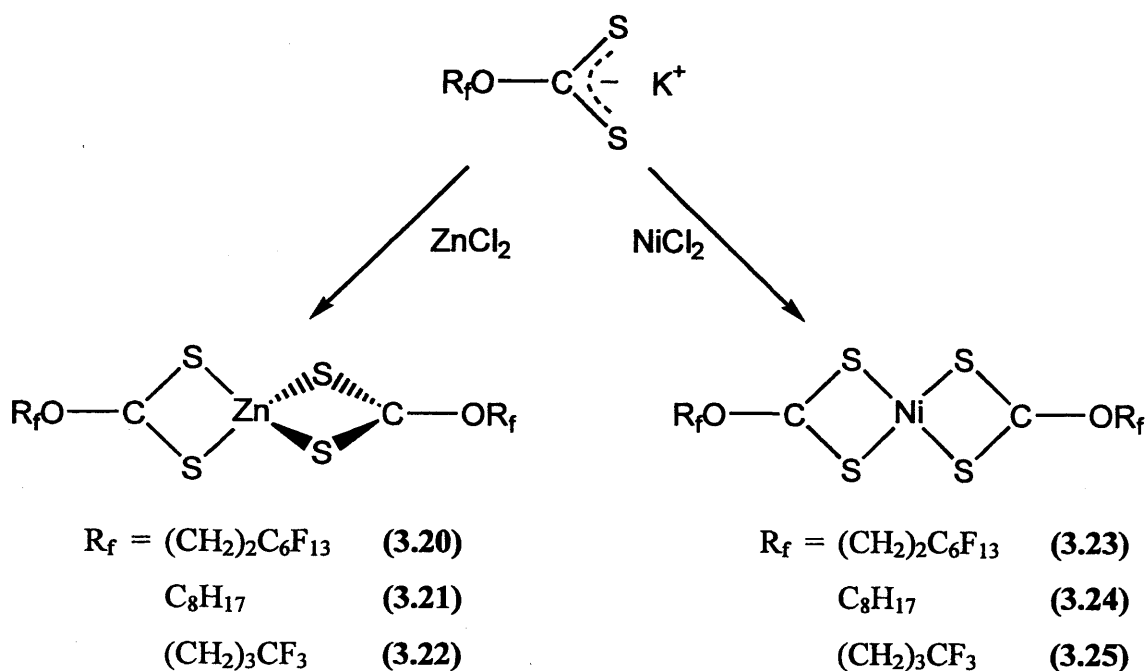
Compound	Bond Lengths / Å		Bond Angle / °
	Rh–S(1)	Rh–S(2)	S(1)–Rh–S(2)
(3.16)	2.381(1)	2.391(1)	72.86(2)
(3.19)	2.394(1)	2.401(1)	72.71(2)

Table 3.4 Selected Rh–S bond lengths and angles from (3.16) and (3.19)

Both compounds appear to be bonding to the metal predominantly through the isobidentate mode, as the differences in the Rh–S bond lengths are very small, but they are not completely symmetrical. The S(1)–Rh–S(2) bond angles give good agreement with each other but are far smaller than the perfect octahedral angle of 90 °.

3.5 Zinc and Nickel Xanthate Complexes

A series of zinc and nickel xanthate complexes have been formed bearing both alkyl and perfluoroalkyl tails (Scheme 3.5).



Scheme 3.5 Synthesis of zinc and nickel xanthate complexes

The appropriate alkali metal salt was stirred in ethanol with either zinc chloride or nickel chloride. The resulting precipitates were collected and purified by washing with cold ethanol. These compounds are analogous to the dithiophosphate compounds, discussed in Chapter 2, with similar difficulties occurring during both the synthesis and characterisation. As xanthate ligands are also capable of bridging across metal centres, it is not inconceivable that these compounds could exist in more than one form, with a similar “neutral-basic” equilibrium to that documented for the dithiophosphate derivatives. Here, however, detecting such oligomerisation for the homoleptic metal xanthates is more difficult as ^{31}P NMR spectroscopy is not available. X-ray crystallography can give clear information on the bonding mode of the ligands, and suitable crystals of (3.25) were grown by slow evaporation of an acetone solution. Crystal data and structure refinement for (3.25) can be found in the Appendix, whilst a complete set of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

In figure 3.14 it can be seen that **(3.25)** adopts a monomeric form, akin to that of the “neutral” dithiophosphate complex. The nickel(II) metal centre clearly exhibits the regular four-coordinate square planar geometry expected for a d^8 metal with soft donor ligands as opposed to the tetrahedral geometries of the zinc complexes.

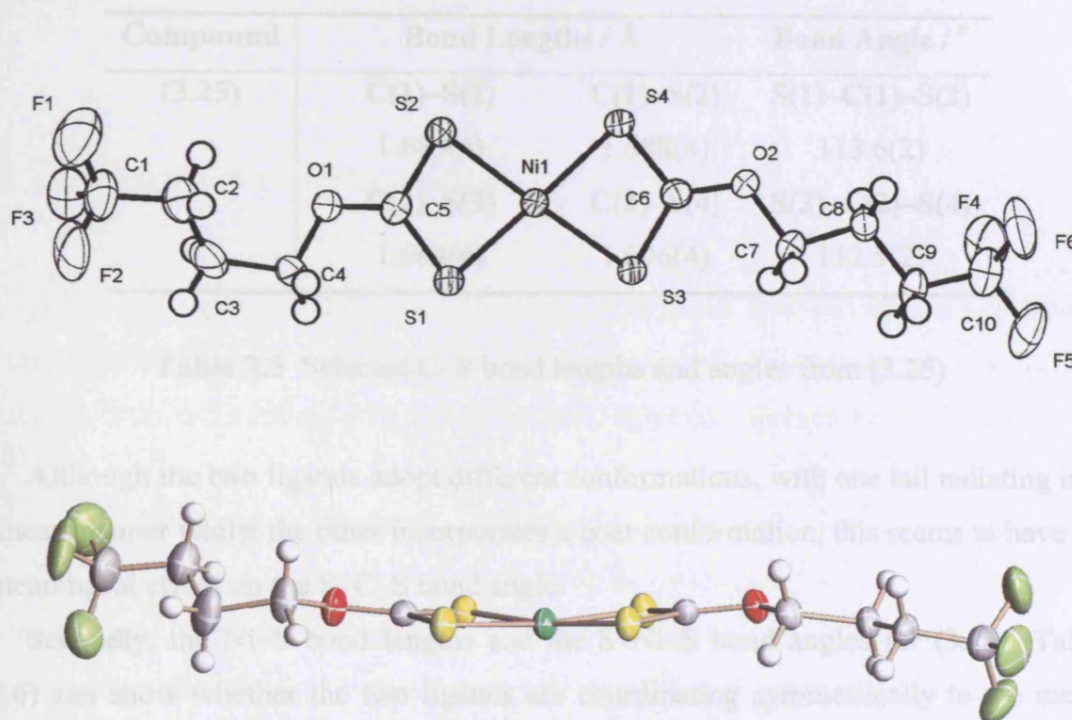


Figure 3.14 Crystal structure of **(3.25)** showing monomer form (top) and square planar configuration (bottom)

From the crystal structure determined for **(3.25)**, information can be gathered regarding the bite angle of the ligand and the coordination mode that it adopts. Here, analysis focuses on Ni–S and C–S bond lengths and angles with the atoms concerned highlighted in Figure 3.15 in bold type.

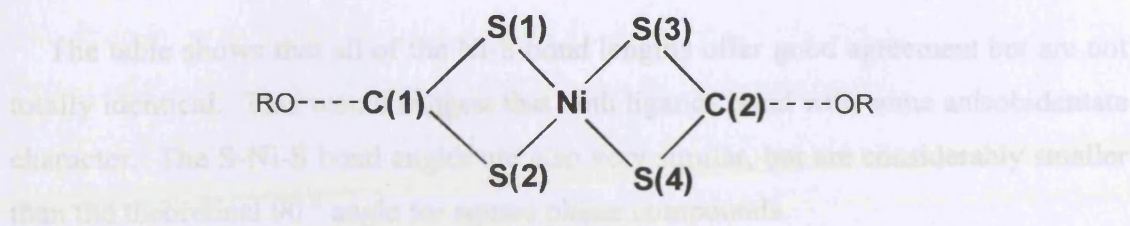


Figure 3.15 Section highlighted in bold type represents atoms of interest in X-ray crystal structure analysis of the nickel xanthate complex **(3.25)**

Firstly, if the ligand is considered, the C–S bond lengths and the S–C–S bond angles for (3.25) (Table 3.5) can allow comparison between the bite angles of the two coordinated trifluoro-*n*-butyl-derivatised xanthate ligands.

Compound	Bond Lengths / Å		Bond Angle / °
(3.25)	C(1)–S(1)	C(1)–S(2)	S(1)–C(1)–S(2)
	1.689(4)	1.688(4)	113.6(2)
	C(2)–S(3)	C(2)–S(4)	S(3)–C(2)–S(4)
	1.684(4)	1.696(4)	112.5(2)

Table 3.5 Selected C–S bond lengths and angles from (3.25)

Although the two ligands adopt different conformations, with one tail radiating in a linear manner whilst the other incorporates a boat conformation, this seems to have no meaningful effect on the S–C–S bond angle.

Secondly, the Ni–S bond lengths and the S–Ni–S bond angles for (3.25) (Table 3.6) can show whether the two ligands are coordinating symmetrically to the metal centre.

Compound	Bond Lengths / Å		Bond Angle / °
(3.25)	Ni–S(1)	Ni–S(2)	S(1)–Ni–S(2)
	2.220(1)	2.214(1)	79.21(4)
	Ni–S(3)	Ni–S(4)	S(3)–Ni–S(4)
	2.216(1)	2.203(1)	79.02(4)

Table 3.6 Selected Ni–S bond lengths and angles from (3.25)

The table shows that all of the Ni–S bond lengths offer good agreement but are not totally identical. This would suggest that both ligands bond with some anisobidentate character. The S–Ni–S bond angles are also very similar, but are considerably smaller than the theoretical 90 ° angle for square planar compounds.

As a consequence of the low solubility in organic solvents and high thermal stability of these compounds, traditional analytical techniques prove to be extremely

difficult, with elemental analysis results being particularly poor. Also, the predicted ability of these type of compounds to exist in more than one form adds to the difficulty of characterization, with neither the parent ion for monomer nor the oligomer being seen by fast atom bombardment mass spectrometry.

3.6 Chapter Conclusions

All of the perfluoroalkyl-derivatised ligand syntheses were carried out in a similar manner to their protio analogues, with the size of the alkyl spacer group seemingly to making little difference. Aryl spacer groups, however, seemed to totally retard the reaction.

The study of the coordination chemistry of the fluorinated and non-fluorinated, ligands produced show that reactivity is virtually unaffected by the presence and the length of the perfluoroalkyl groups. This can be deduced from the analytical data for the fluorinated copper and rhodium complexes giving excellent agreement with the non-fluorinated compounds produced here, in a similar manner to that seen for the perfluoroalkyl-derivatised dithiophosphate ligands discussed previously. Again, what is affected considerably is the solubility of a number of the highly fluorinated compounds in certain organic solvents, when compared to their short-chain protio analogues. Problems were mainly encountered with the characterisation of the homoleptic zinc and nickel compounds, as their NMR spectra were almost identical to those for the parent alkali metal xanthates. Also, due to their exceptionally high thermal stabilities, and the failure to observe parent ion signals in mass spectrometry traces, analysis of some of these compounds proved troublesome. Infra red spectra exhibited the predicted highly complex pattern in the in the 900 – 1300 cm⁻¹ region. No attempt was made here to assign the individual vibrational modes, but the frequencies of the strongest bands have been reported as a fingerprint.

Throughout this work, no instances of alkoxy exchange were observed, with all of the alkali metal xanthates, and subsequent metal complexes, being stable in alcoholic solvents. This is in stark contrast to the dithiophosphate ligands and complexes, where solvent systems had to be chosen carefully to ensure that scrambling of this nature

did not occur. Furthermore, the perfluoroalkyl-derivatised xanthates discussed here seemed to be far more stable to atmospheric conditions, and could be stored under air for long periods of time with no noticeable signs of hydrolysis or decomposition.

3.7 Experimental Procedures

3.7.1 Synthesis of Alkali Metal Salts of Xanthate Ligands

Preparation of K{O-(1H,1H,2H,2H-perfluoro-n-octyl) xanthate} (3.1)

Potassium hydride (2.20×10^{-1} g, 5.49×10^{-3} mol) was carefully added to a stirred solution of 1H,1H,2H,2H-perfluoro-n-octanol (2.00 g, 5.49×10^{-3} mol) and CS₂ (4.18×10^{-1} g, 5.49×10^{-3} mol, 3.30×10^{-1} cm³) in diethyl ether (30 cm³), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. Over time the solution turned a pale yellow colour, followed by the precipitation of a yellow solid. The product was afforded by suction filtration as a flocculent, pale yellow solid (1.30 g, 2.72×10^{-3} mol, 50 %) and purified by washing with hexane.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 4.8 (t, 2H, $^3J_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.8 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}(d_6\text{-Acetone})$ -80.8 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF₃), -112.8 (um, 2F, $\alpha\text{-CF}_2$), -121.5 (um, 2F, $\beta\text{-CF}_2$), -122.5 (um, 2F, $\delta\text{-CF}_2$), -123.2 (um, 2F, $\varepsilon\text{-CF}_2$), -125.8 (um, 2F, $\gamma\text{-CF}_2$); m/z (ES) 439 ([M-K]⁻, 100 %); Found C, 22.41; H, 0.85; S, 13.39. C₉H₄F₁₃OS₂K requires C, 22.60; H, 0.84; S, 13.41; IR (nujol) ν 1043(w), 1060(w), 1080(w), 1113(s), 1142(vs), 1205(vs, br), 1241(vs) cm⁻¹.

Preparation of Na{O-(1H,1H,2H,2H-perfluoro-n-octyl) xanthate} (3.2)

1H,1H,2H,2H-Perfluoro-n-octanol (1.58 g, 4.33×10^{-3} mol) was stirred with dry ether (30 cm³) under a static atmosphere of nitrogen. Sodium hydride (1.04×10^{-1} g, 4.33×10^{-3} mol) was then carefully added to the sodium salt, at which point hydrogen

gas was vigorously evolved. The reaction was stirred for approximately two hours until hydrogen evolution had stopped. Carbon disulfide (30 cm³) was then added in several portions and the reaction vessel heated to reflux overnight. A yellow/orange precipitate was recovered by removing the remaining carbon disulfide *in vacuo* using a pre-trap.

$\delta_{\text{H}}(\text{D}_2\text{O})$ 4.7 (t, 2H, $^3J_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.6 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{C}}\{^1\text{H}\}(\text{D}_2\text{O})$ 232.3 (s, CS₂), 192.9 (um, CF₃), 118.1, 115.6, 113.3, 111.2, 108.5 (all um, $\alpha\text{-}\varepsilon\text{-CF}_2$'s), 65.4 (s, $\alpha\text{-CH}_2$), 30.2 (um, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}(\text{D}_2\text{O})$ -82.6 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF₃), -114.0 (um, 2F, $\alpha\text{-CF}_2$), -123.4 (um, 2F, $\beta\text{-CF}_2$), -124.9 (um, 2F, $\delta\text{-CF}_2$), -125.3 (um, 2F, $\varepsilon\text{-CF}_2$), -128.4 (um, 2F, $\gamma\text{-CF}_2$); *m/z* (ES) 439 ([M-Na]⁺, 100 %); IR (nujol) ν 1025(w), 1052(w), 1113(s), 1142(vs), 1205(vs), 1241(vs) cm⁻¹.

Preparation of K(*O*-octyl xanthate) (3.3)

Potassium hydroxide (2.15 g, 3.84 x 10⁻² mol) was added to octanol (50 cm³) and stirred until dissolved. Carbon disulfide (2.92 g, 3.84 x 10⁻² mol, 2.30 cm³) was added and the resulting mixture was rapidly stirred at room temperature for 2 hours. Over time the solution turned a pale yellow colour, followed by the precipitation of a yellow solid. The product was afforded by suction filtration as a flocculent, pale yellow solid (7.53 g, 3.08 x 10⁻² mol, 80 %).

$\delta_{\text{H}}(d_6\text{-Acetone})$ 4.4 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.9 (um, 2H, $\beta\text{-CH}_2$) 1.5 (um, 10H, 5 mid-chain CH₂), 1.1 (t, 3H, $^3J_{\text{H-H}}$ 7.0 Hz); *m/z* (ES) 177 ([M-K]⁺, 100 %); IR (nujol) ν 1040(w), 1057(s), 1103(sh), 1115(s), 1138(s), 1161(sh) cm⁻¹.

Preparation of K{*O*-(1*H*,1*H*,2*H*,2*H*-perfluoro-*n*-hexyl) xanthate} (3.4)

Potassium hydride (4.55 x 10⁻¹ g, 1.36 x 10⁻² mol) was carefully added to a stirred solution of 1*H*,1*H*,2*H*,2*H*-perfluoro-*n*-hexanol (3.00 g, 1.36 x 10⁻² mol) and CS₂ (8.65 x 10⁻¹ g, 1.36 x 10⁻² mol, 6.83 x 10⁻¹ cm³) in diethyl ether (30 cm³), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. Over time the solution turned a pale yellow colour, followed by the

precipitation of a yellow solid. The product was afforded in two recoveries from the mother liquor by suction filtration as a flocculent, pale yellow solid (2.01 g, 5.31×10^{-3} mol, 39 %) and purified by washing with hexane.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 4.5 (t, 2H, $^3J_{\text{H-H}}$ 7.1 Hz, $\alpha\text{-CH}_2$), 2.4 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{\text{H}\}(d_6\text{-Acetone})$ -82.4 (t, 3F, $^3J_{\text{F-F}}$ 9.29 Hz, CF_3), -114.1 (t, 2F, $^3J_{\text{F-F}}$ 11 Hz, $\alpha\text{-CF}_2$), -124.8 (um, 2F, $\gamma\text{-CF}_2$), -126.4 (um, 2F, $\beta\text{-CF}_2$); m/z (ES) 339 ($[\text{M-K}]^+$, 100 %); Found C, 21.95; H, 1.26; S, 16.69. $\text{C}_7\text{H}_4\text{F}_9\text{OS}_2\text{K}$ requires C, 22.22; H, 1.07; S, 16.95; IR (nujol) ν 1058(w), 1081(w), 1110(s), 1138(vs), 1194(w), 1219(s), 1240(s) cm^{-1} .

Preparation of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-undecyl})\text{xanthate}\}$ (3.5)

Potassium hydride (2.10×10^{-1} g, 5.23×10^{-3} mol) was carefully added to a stirred solution of 1H,1H,2H,2H-perfluoro-*n*-undecanol (2.50 g, 5.23×10^{-3} mol) and CS_2 (3.98×10^{-1} g, 5.23×10^{-3} mol, 3.14×10^{-1} cm^3) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 30 minutes with the evolution of hydrogen. Over time the solution turned a pale yellow colour, followed by the precipitation of a yellow solid. The product was afforded by suction filtration as a flocculent, pale yellow solid (2.20 g, 3.80×10^{-3} mol, 73 %) and purified by washing with hexane.

$\delta_{\text{H}}(d_4\text{-MeOH})$ 4.5 (t, 2H, $^3J_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.3 (um, 2H, $\gamma\text{-CH}_2$), 2.0 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}(d_4\text{-MeOH})$ -81.0 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -114.1 (um, 2F, $\alpha\text{-CF}_2$), -121.5 (um, 2F, $\beta\text{-CF}_2$), -122.4 (um, 6F, $\delta\text{-CF}_2$, $\zeta\text{-CF}_2$, $\eta\text{-CF}_2$), -123.1 (um, 2F, $\varepsilon\text{-CF}_2$), -125.9 (um, 2F, $\gamma\text{-CF}_2$); m/z (ES) 553 ($[\text{M-K}]^+$, 100 %); IR (nujol) ν 1075(w), 1093(s), 1111(w), 1149(s), 1203(s), 1221(s, br) cm^{-1} .

Preparation of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-nonyl})\text{xanthate}\}$ (3.6)

Potassium hydride (2.12×10^{-1} g, 5.29×10^{-3} mol) was carefully added to a stirred solution of 1H,1H,2H,2H-perfluoro-*n*-nonanol (2.00 g, 5.29×10^{-3} mol) and CS_2 (4.03×10^{-1} g, 5.49×10^{-3} mol, 3.18×10^{-1} cm^3) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 30 minutes with the evolution of

hydrogen. Over time the solution turned a pale yellow colour, followed by the precipitation of a yellow solid. The product was afforded by suction filtration as a flocculent, pale yellow solid (2.36 g, 4.79×10^{-3} mol, 91 %) and purified by washing with hexane.

$\delta_{\text{H}}(d_4\text{-MeOH})$ 4.4 (t, 2H, $^3J_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.3 (um, 2H, $\gamma\text{-CH}_2$), 1.9 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}(d_4\text{-MeOH})$ -81.1 (t, 3F, $^3J_{\text{F-F}}$ 9 Hz, CF_3), -114.1 (um, 2F, $\alpha\text{-CF}_2$), -121.6 (um, 2F, $\beta\text{-CF}_2$), -122.5 (um, 2F, $\delta\text{-CF}_2$), -123.1 (um, 2F, $\varepsilon\text{-CF}_2$), -125.9 (um, 2F, $\gamma\text{-CF}_2$); m/z (ES) 453 ($[\text{M-K}]^+$, 100 %); IR (nujol) ν 1079(w), 1093(w), 1114(s), 1145(s), 1207(vs), 1251(vs) cm^{-1} .

Preparation of $K\{O\text{-(4,4,4-trifluoro-}n\text{-butyl)}\text{ xanthate}\}$ (3.7)

Potassium hydride (6.26×10^{-1} g, 1.56×10^{-2} mol) was carefully added to a stirred solution of 4,4,4-trifluoro-*n*-butanol (2.00 g, 1.56×10^{-2} mol) and CS_2 (1.19 g, 1.56×10^{-2} mol, 9.40×10^{-2} cm^3) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. Over time the solution turned a pale yellow colour, followed by the precipitation of a yellow solid. The product was afforded by suction filtration as a flocculent, pale yellow solid (2.61 g, 1.01×10^{-2} mol, 69 %) and purified by washing with hexane.

$\delta_{\text{H}}(\text{D}_2\text{O})$ 4.6 (t, 2H, $^3J_{\text{H-H}}$ 6.7 Hz, $\alpha\text{-CH}_2$), 2.5 (um, 2H, $\gamma\text{-CH}_2$), 2.15 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{D}_2\text{O})$ -66.4 (um, CF_3); m/z (ES) 203 ($[\text{M-K}]^+$, 100 %); IR (nujol) ν 1028(w), 1058(w), 1093(w), 1105(s), 1152(s) cm^{-1} .

Preparation of $\text{Na}\{O\text{-(4,4,4-trifluoro-}n\text{-butyl)}\text{ xanthate}\}$ (3.8)

4,4,4-Trifluoro-*n*-butanol (2.00 g, 1.56×10^{-2} mol) was stirred with dry diethyl ether (30 cm^3) under a static atmosphere of nitrogen. Sodium hydride (6.00×10^{-1} g, 2.5×10^{-2} mol) was then carefully added to the sodium salt, at which point hydrogen gas was vigorously evolved. The reaction was stirred for approximately two hours until hydrogen evolution had stopped. Carbon disulfide (30 cm^3) was then added in several portions and the reaction vessel heated gently over a further two hours,

without the need to reflux. A yellow precipitate (2.99 g, 1.32×10^{-2} mol, 85 %) was isolated by removing the excess carbon disulfide *in vacuo* using a pre-trap.

$\delta_{\text{H}}(\text{D}_2\text{O})$ 4.6 (t, 2H, $^3J_{\text{H-H}}$ 6.7 Hz, $\alpha\text{-CH}_2$), 2.5 (um, 2H, $\gamma\text{-CH}_2$), 2.1 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{C}}\{^1\text{H}\}(\text{D}_2\text{O})$ 233.2 (s, CS_2), 127.9 (q, CF_3 , $^1J_{\text{C-F}}$ 275 Hz), 60.6 (s, $\alpha\text{-CH}_2$), 30.2 (q, $^2J_{\text{C-F}}$ 28 Hz, $\gamma\text{-CH}_2$), 21.5 (um, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{D}_2\text{O})$ -66.4 (um, CF_3); m/z (ES) 203 ($[\text{M-Na}]^+$, 100 %); Found C, 26.07; H, 2.74; S, 26.97. $\text{C}_5\text{H}_6\text{F}_3\text{OS}_2\text{Na}$ requires C, 26.55; H, 2.67; S, 28.35; IR (nujol) ν 1028(w), 1058(w), 1093(w), 1105(s), 1152(s) cm^{-1} .

3.7.2 Copper Xanthate Complexes

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-octyl})\text{xanthate}\}]$ (3.9)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (3.17×10^{-1} g, 4.87×10^{-4} mol) in methanol (25 cm^3) was added to a solution of $\text{Na}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-octyl})\text{xanthate}\}$ (2.25×10^{-1} g, 4.87×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred and slightly warmed overnight. The clean, yellow precipitate (4.32×10^{-1} g, 4.20×10^{-4} mol, 86 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.4 (um, 30H, PPh_3), 4.8 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.7 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{\text{H}\}(\text{CDCl}_3)$ -81.0 (t, 3F, $^3J_{\text{F-F}}$ 9.3 Hz, CF_3), -113.7 (t, 2F, $^3J_{\text{F-F}}$ 12 Hz, $\alpha\text{-CF}_2$), -122.3 (um, 2F, $\beta\text{-CF}_2$), -123.2 (um, 2F, $\delta\text{-CF}_2$), -123.8 (um, 2F, $\epsilon\text{-CF}_2$), -126.5 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}(\text{CDCl}_3)$ 1.0 (s); Found C, 52.59; H, 3.42; P, 6.03; S, 6.28. $\text{C}_{45}\text{H}_{34}\text{F}_{13}\text{OP}_2\text{S}_2\text{Cu}$ requires C, 52.61; H, 3.34; P, 6.03; S, 6.24; IR (nujol) ν 1094(w), 1144(s), 1167(w), 1185(s), 1211(s), 1232(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O-octyl}\text{xanthate}\}]$ (3.10)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (1.06 g, 1.64×10^{-3} mol) in methanol (25 cm^3) was added to a solution of $\text{K}(\text{O-octyl}\text{xanthate})$ (4.00×10^{-1} g, 1.64×10^{-3} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 30 minutes. The volume of solvent was reduced to half the initial amount and a pale yellow

precipitate was observed. After allowing the reaction mixture to stand overnight at room temperature, the yellow precipitate (1.02 g, 1.29×10^{-3} mol, 79 %) was isolated by suction filtration and washed with cold methanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.4 (m, 30H, PPh_3), 4.5 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.9 (um, 2H, $\beta\text{-CH}_2$) 1.4 (um, 10H, 5 mid-chain CH_2), 1.0 (t, 3H, $^3J_{\text{H-H}}$ 7.0 Hz); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) 0.1 (s, PPh_3); IR (nujol) ν 1056(w), 1093(w), 1121(sh), 1141(s), 1162(s), 1178(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-hexyl})\text{xanthate}\}]$ (3.11)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (3.44×10^{-1} g, 5.29×10^{-4} mol) in methanol (25 cm^3) was added to a solution of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-hexyl})\text{xanthate}\}$ (2.00×10^{-1} g, 5.29×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 30 minutes. The volume of solvent was reduced to half the initial amount and a pale yellow precipitate was observed. After allowing the reaction mixture to stand overnight at room temperature, the yellow precipitate (2.80×10^{-1} g, 3.02×10^{-4} mol, 57 %) was isolated in two recoveries from the mother liquor by suction filtration and washed with cold methanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.1 (um, 30H, PPh_3), 4.5 (t, 2H, $^3J_{\text{H-H}}$ 7.1 Hz, $\alpha\text{-CH}_2$), 2.4 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}$ (CDCl_3) -81.4 (t, 3F, $^3J_{\text{F-F}}$ 9.3 Hz, CF_3), -114.0 (t, 2F, $^3J_{\text{F-F}}$ 11 Hz, $\alpha\text{-CF}_2$), -124.8 (um, 2F, $\gamma\text{-CF}_2$), -126.4 (um, 2F, $\beta\text{-CF}_2$); $\delta_{\text{P}}(\text{CDCl}_3)$ 1.0 (s); Found C, 55.72; H, 3.80; P, 6.34; S, 6.92. $\text{C}_{43}\text{H}_{34}\text{F}_{19}\text{OP}_2\text{S}_2\text{Cu}$ requires C, 55.69; H, 3.70; P, 6.68; S, 6.92; IR (nujol) ν 1095(w), 1135(s), 1160(w), 1226(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-undecyl})\text{xanthate}\}]$ (3.12)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (2.19×10^{-1} g, 3.38×10^{-4} mol) in methanol (25 cm^3) was added to a solution of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-undecyl})\text{xanthate}\}$ (2.00×10^{-1} g, 3.38×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 1 hour. The volume of solvent was reduced to half the initial amount and a pale yellow precipitate was observed. After

allowing the reaction mixture to stand overnight at room temperature, the yellow precipitate (2.56×10^{-1} g, 2.24×10^{-4} mol, 66 %) was isolated in two recoveries from the mother liquor by suction filtration and washed with cold methanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (um, 30H, PPh_3), 4.3 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 2H, $\gamma\text{-CH}_2$), 2.0 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{\text{H}\}(\text{CDCl}_3)$ -81.2 (t, 3F, $^3J_{\text{F-F}}$ 9.3 Hz, CF_3), -114.7 (t, 2F, $^3J_{\text{F-F}}$ 12 Hz, $\alpha\text{-CF}_2$), -122.1 (um, 2F, $\beta\text{-CF}_2$), -123.1 (um, 6F, $\delta\text{-CF}_2$, $\zeta\text{-CF}_2$, $\eta\text{-CF}_2$), -123.7 (um, 2F, $\varepsilon\text{-CF}_2$), -126.5 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}(\text{CDCl}_3)$ 0.3 (s);

Found C, 50.26; H, 3.43; P, 5.55; S, 5.54. $\text{C}_{48}\text{H}_{36}\text{F}_{17}\text{OP}_2\text{S}_2\text{Cu}$ requires C, 50.51; H, 3.18; P, 5.43; S, 5.62; IR (nujol) ν 1061(w), 1095(w), 1148(s), 1203(s), 1241(w) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2 \{ \text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-nonyl) xanthate} \}]$ (3.13)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (3.30×10^{-1} g, 5.08×10^{-4} mol) in methanol (25 cm^3) was added to a solution of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H},3\text{H},3\text{H-perfluoro-}n\text{-nonyl) xanthate}\}$ (2.50×10^{-1} g, 5.08×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 45 minutes. The volume of solvent was reduced to half the initial amount and a pale yellow precipitate was observed. After allowing the reaction mixture to stand overnight at room temperature, the yellow precipitate (2.49×10^{-1} g, 2.39×10^{-4} mol, 47 %) was isolated in two recoveries from the mother liquor by suction filtration and washed with cold methanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (um, 30H, PPh_3), 4.3 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 2H, $\gamma\text{-CH}_2$), 1.9 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{\text{H}\}(\text{CDCl}_3)$ -81.2 (t, 3F, $^3J_{\text{F-F}}$ 9.3 Hz, CF_3), -114.7 (t, 2F, $^3J_{\text{F-F}}$ 12 Hz, $\alpha\text{-CF}_2$), -122.3 (um, 2F, $\beta\text{-CF}_2$), -123.3 (um, 2F, $\delta\text{-CF}_2$), -123.7 (um, 2F, $\varepsilon\text{-CF}_2$), -126.5 (um, 2F, $\gamma\text{-CF}_2$); $\delta_{\text{P}}(\text{CDCl}_3)$ 0.7 (s); IR (nujol) ν 1061(w), 1094(w), 1165(s), 1211(s), 1250(s) cm^{-1} .

Preparation of $[\text{Cu}(\text{PPh}_3)_2 \{ \text{O}-(4,4,4\text{-trifluoro-}n\text{-butyl) xanthate} \}]$ (3.14)

A solution of $[(\text{PPh}_3)_2\text{CuNO}_3]$ (5.75×10^{-1} g, 8.84×10^{-4} mol) in methanol (25 cm^3) was added to a solution of $\text{Na}\{\text{O}-(4,4,4\text{-trifluoro-}n\text{-butyl) xanthate}\}$ (2.00×10^{-1} g,

8.84×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature for 45 minutes. The volume of solvent was reduced to half the initial amount and a pale yellow precipitate was observed. After allowing the reaction mixture to stand overnight at room temperature, the yellow precipitate (6.88×10^{-1} g, 8.70×10^{-4} mol, 98 %) was isolated by suction filtration and washed with cold methanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (um, 30H, PPh_3), 4.3 (t, 2H, $^3J_{\text{H-H}}$ 6.6 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 2H, $\gamma\text{-CH}_2$), 1.95 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -66.6 (um, CF_3); $\delta_{\text{P}}(\text{CDCl}_3)$ 0.8 (s); Found C, 61.80; H, 4.31; P, 7.16; S, 7.30. $\text{C}_{41}\text{H}_{36}\text{F}_3\text{OP}_2\text{S}_2\text{Cu}$ requires C, 62.23; H, 4.59; P, 7.83; S, 8.21; IR (nujol) ν 1027(w), 1058(w), 1094(w), 1169(s) cm^{-1} .

3.7.3 Rhodium Xanthate Complexes

Preparation of $[\text{Cp}^\text{RhCl}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-octyl) xanthate}\}]$ (3.15)*

To a slurry of $\text{K}\{\text{O}-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-octyl) xanthate}\}$ (1.50×10^{-1} g, 3.14×10^{-4} mol) in dichloromethane (30 cm^3), $[\{\text{RhCl}_2\text{Cp}^*\}_2]$ (9.70×10^{-2} g, 1.57×10^{-4} mol) was added as a solid, and the resulting mixture rapidly stirred at room temperature for 2 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over MgSO_4 and CaCl_2 . The solvent was removed *in vacuo*, giving a dark red precipitate (1.56×10^{-1} g, 2.19×10^{-4} mol, 70 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.7 (t, 2H, $^3J_{\text{H-H}}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.6 (um, 2H, $\beta\text{-CH}_2$), 1.7 (s, 15H, cp^*); $\delta_{\text{F}}\{^1\text{H}\}(\text{CDCl}_3)$ -81.3 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF_3), -113.7 (um, 2F, $\alpha\text{-CF}_2$), -122.3 (um, 2F, $\beta\text{-CF}_2$), -123.3 (um, 2F, $\delta\text{-CF}_2$), -123.9 (um, 2F, $\varepsilon\text{-CF}_2$), -126.6 (um, 2F, $\gamma\text{-CF}_2$); m/z (FAB) 677 ($[\text{M-Cl}]^+$, 100 %); Found C, 32.23; H, 2.59; S, 9.00. $\text{C}_{19}\text{H}_{19}\text{ClF}_{13}\text{OS}_2\text{Rh}$ requires C, 32.01; H, 2.69; S, 9.00; IR (nujol) ν 1025(w), 1094(w), 1145(s), 1237(vs, br) cm^{-1} .

Preparation of $[Cp^*RhCl(O\text{-}octyl\ xanthate)]$ (3.16)

To a slurry of K(O-octyl xanthate) (7.90×10^{-2} g, 3.24×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (1.00×10^{-1} g, 1.62×10^{-4} mol) was added as a solid, and the resulting mixture rapidly stirred at room temperature for 2 hours. The mixture was filtered, washed with water ($3 \times 20\text{ cm}^3$) and dried over $MgSO_4$ and $CaCl_2$. The solvent was removed *in vacuo*, giving a dark red precipitate (9.10×10^{-2} g, 1.90×10^{-4} mol, 59 %).

$\delta_H(CDCl_3)$ 4.4 (t, 2H, $^3J_{H-H}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (s, 15H, cp^*), 1.5 (um, 2H, $\beta\text{-CH}_2$), 1.2 (um, 10H, 5 mid-chain CH_2), 0.8 (t, 3H, $^3J_{H-H}$ 7.0 Hz); m/z (FAB) 443 ($[M-Cl]^+$, 100 %); Found C, 47.76; H, 6.40; S, 13.09. $C_{19}H_{32}ClOS_2Rh$ requires C, 47.65; H, 6.73; S, 13.39; IR (nujol) ν 1024(w), 1046(vw), 1218(w), 1260(s) cm^{-1} .

Preparation of $[Cp^*RhCl\{O\text{-}(1H,1H,2H,2H,3H,3H\text{-}perfluoro\text{-}n\text{-}undecyl)\ xanthate\}]$ (3.17)

To a slurry of K{O-(1H,1H,2H,2H,3H,3H-perfluoro-*n*-undecyl) xanthate} (1.44×10^{-1} g, 2.43×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (7.50×10^{-2} g, 1.21×10^{-4} mol) was added as a solid, and the resultant mixture rapidly stirred at room temperature for 2 hours. The mixture was filtered, washed with water ($3 \times 20\text{ cm}^3$) and dried over $MgSO_4$ and $CaCl_2$. The solvent was removed *in vacuo*, giving a dark red precipitate (1.54×10^{-1} g, 1.86×10^{-4} mol, 77 %).

$\delta_H(CDCl_3)$ 4.2 (t, 2H, $^3J_{H-H}$ 6.9 Hz, $\alpha\text{-CH}_2$), 2.1 (um, 2H, $\gamma\text{-CH}_2$), 1.8 (um, 2H, $\beta\text{-CH}_2$), 1.6 (s, 15H, cp^*); $\delta_F\{^1H\}(CDCl_3)$ -81.2 (t, 3F, $^3J_{F-F}$ 10 Hz, CF_3), -114.7 (um, 2F, $\alpha\text{-CF}_2$), -122.3 (um, 2F, $\beta\text{-CF}_2$), -123.4 (um, 6F, $\delta\text{-CF}_2$, $\zeta\text{-CF}_2$, $\eta\text{-CF}_2$), -123.8 (um, 2F, $\epsilon\text{-CF}_2$), -126.5 (um, 2F, $\gamma\text{-CF}_2$); m/z (FAB) 791 ($[M-Cl]^+$, 100 %); IR (nujol) ν 1025(w), 1093(w), 1145(s), 1238(s) cm^{-1} .

Preparation of $[Cp^*RhCl\{O-(1H,1H,2H,2H,3H,3H-perfluoro-n-nonyl)\} xanthate]$ (3.18)

To a slurry of $K\{O-(1H,1H,2H,2H,3H,3H-perfluoro-n-nonyl)\} xanthate$ (1.19×10^{-1} g, 2.43×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (7.50×10^{-2} g, 1.21×10^{-4} mol) was added as a solid, and the resultant mixture rapidly stirred at room temperature for 2 hours. The mixture was filtered, washed with water ($3 \times 20\text{ cm}^3$) and dried over $MgSO_4$ and $CaCl_2$. The solvent was removed *in vacuo*, giving a dark red precipitate (1.56×10^{-1} g, 2.15×10^{-4} mol, 88 %).

$\delta_H(CDCl_3)$ 4.2 (t, 2H, $^3J_{H-H}$ 6.9 Hz, $\alpha-CH_2$), 2.2 (um, 2H, $\gamma-CH_2$), 1.8 (um, 2H, $\beta-CH_2$), 1.6 (s, 15H, cp^*); $\delta_F\{^1H\}(CDCl_3)$ -81.2 (t, 3F, $^3J_{F-F}$ 10 Hz, CF_3), -114.8 (um, 2F, $\alpha-CF_2$), -122.3 (um, 2F, $\beta-CF_2$), -123.3 (um, 2F, $\delta-CF_2$), -123.8 (um, 2F, $\epsilon-CF_2$), -126.5 (um, 2F, $\gamma-CF_2$); m/z (FAB) 691 ($[M-Cl]^+$, 100 %); IR (nujol) ν 1024(w), 1094(w), 1145(s), 1237(s) cm^{-1} .

Preparation of $[Cp^*RhCl\{O-(4,4,4-trifluoro-n-butyl)\} xanthate]$ (3.19)

To a slurry of $Na\{O-(4,4,4-trifluoro-n-butyl)\} xanthate$ (7.30×10^{-2} g, 3.23×10^{-4} mol) in dichloromethane (30 cm^3), $[RhCl_2Cp^*]_2$ (1.00×10^{-1} g, 1.62×10^{-4} mol) was added as a solid, and the resultant mixture rapidly stirred at room temperature for 2 hours. The mixture was filtered, washed with water ($3 \times 20\text{ cm}^3$) and dried over $MgSO_4$ and $CaCl_2$. The solvent was removed *in vacuo*, giving a dark red precipitate (1.40×10^{-1} g, 2.94×10^{-4} mol, 91 %).

$\delta_H(CDCl_3)$ 4.45 (t, 2H, $^3J_{H-H}$ 6.8 Hz, $\alpha-CH_2$), 2.2 (um, 2H, $\gamma-CH_2$), 2.0 (um, 2H, $\beta-CH_2$), 1.7 (s, 15H, Cp^*); $\delta_F(CDCl_3)$ -66.7 (um, CF_3); m/z (FAB) 411 ($[M-Cl]^+$, 100 %); Found C, 38.14; H, 4.31; S, 12.03. $C_{15}H_{21}ClF_3OS_2Rh$ requires C, 37.79; H, 4.44; S, 13.45; IR (nujol) ν 1024(w), 1057(vw), 1093(w), 1133(s), 1151(s) cm^{-1} .

3.7.4 Zinc and Nickel Xanthate Complexes

Preparation of [Zn bis-{O-(1H,1H,2H,2H-perfluoro-n-octyl) xanthate}] (3.20)

Zinc (II) chloride (2.90×10^{-2} g, 2.16×10^{-4} mol) was slowly added to a stirred slurry of sodium Na{O-(4,4,4-trifluoro-*n*-butyl) xanthate} (2.00×10^{-1} g, 4.33×10^{-4} mol) over a period of 30 minutes. The white precipitate (1.67×10^{-1} g, 1.77×10^{-4} mol, 82 %) was isolated as a white solid by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.7 (t, 2H, $^3J_{\text{H-H}}$ 6.8 Hz, $\alpha\text{-CH}_2$), 2.6 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}\{^1\text{H}\}(\text{CDCl}_3)$ – 81.3 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF_3), -113.7 (um, 2F, $\alpha\text{-CF}_2$), -122.3 (um, 2F, $\beta\text{-CF}_2$), -123.2 (um, 2F, $\delta\text{-CF}_2$), -123.9 (um, 2F, $\varepsilon\text{-CF}_2$), -126.6 (um, 2F, $\gamma\text{-CF}_2$).

Preparation of [Zn bis-(O-octyl xanthate)] (3.21)

Zinc (II) chloride (1.11×10^{-1} g, 8.18×10^{-4} mol) was slowly added to a stirred slurry of K(O-octyl xanthate) (4.00×10^{-1} g, 1.64×10^{-3} mol) in ethanol (30 cm^3) over a period of 30 minutes. The white precipitate (1.98×10^{-1} g, 4.16×10^{-4} mol, 51 %) was isolated as a white solid by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.6 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.9 (um, 2H, $\beta\text{-CH}_2$) 1.4 (um, 10H, 5 mid-chain CH_2), 1.0 (t, 3H, $^3J_{\text{H-H}}$ 7.0 Hz); IR (nujol) ν 1034(vs), 1048(s), 1089(s), 1130(w), 1198(sh), 1212(vs) cm^{-1} .

Preparation of [Zn bis-{O-(4,4,4-trifluoro-n-butyl) xanthate}] (3.22)

Zinc (II) chloride (1.44×10^{-1} g, 1.06×10^{-3} mol) was slowly added to a stirred slurry of sodium Na{O-(4,4,4-trifluoro-*n*-butyl) xanthate} (2.40×10^{-1} g, 1.06×10^{-3} mol) over a period of 15 minutes. The white precipitate (2.65×10^{-1} g, 5.62×10^{-4} mol, 53 %) was isolated as a white solid by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{D}_2\text{O})$ 4.5 (t, 2H, $^3J_{\text{H-H}}$ 6 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 2H, $\gamma\text{-CH}_2$), 2.1 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{D}_2\text{O})$ -66.7 (um, CF_3); IR (nujol) ν 1028(w), 1058(w), 1093(w), 1105(s), 1152(s) cm^{-1} .

Preparation of [Ni bis-{O-(1H,1H,2H,2H-perfluoro-n-octyl) xanthate}] (3.23)

To a slurry Na{O-(1H,1H,2H,2H-perfluoro-n-octyl) xanthate} (2.47×10^{-1} g, 5.35×10^{-4} mol) in ethanol (30 cm^3), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.27×10^{-1} g, 5.34×10^{-4} mol) dissolved in water was slowly added, and the mixture rapidly stirred at room temperature for 3 hours. The resultant product (3.17×10^{-1} g, 3.38×10^{-4} mol, 63 %) was isolated as a brown solid by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.7 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.6 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.1 (um, 3F, CF_3), -113.7 (um, 2F, $\alpha\text{-CF}_2$), -122.2 (um, 2F, $\beta\text{-CF}_2$), -123.2 (um, 2F, $\delta\text{-CF}_2$), -123.8 (um, 2F, $\epsilon\text{-CF}_2$), -126.5 (um, 2F, $\gamma\text{-CF}_2$); IR (nujol) ν 1021, 1047, 1143 cm^{-1} .

Preparation of [Ni bis-(O-octyl xanthate)] (3.24)

To a slurry of K(O-octyl xanthate) (4.00×10^{-1} g, 1.64×10^{-3} mol) in ethanol (30 cm^3), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.94×10^{-1} g, 8.18×10^{-4} mol) dissolved in water was slowly added, and the mixture rapidly stirred at room temperature for 3 hours. The resultant product (3.22×10^{-1} g, 6.86×10^{-4} mol, 84 %) was isolated as a green solid by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.4 (t, 2H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.8 (um, 2H, $\beta\text{-CH}_2$) 1.2 (um, 10H, 5 mid-chain CH_2), 0.8 (t, 3H, $^3J_{\text{H-H}}$ 7.0 Hz); IR (nujol) ν 1032(s), 1092(w), 1134(w), 1260(s) cm^{-1} .

Preparation of [Ni bis-{O-(4,4,4-trifluoro-*n*-butyl) xanthate}] (3.25)

To a slurry of Na{O-(4,4,4-trifluoro-*n*-butyl) xanthate} (2.43×10^{-1} g, 1.07×10^{-3} mol) in ethanol (30 cm^3), nickel (II) chloride (2.56×10^{-1} g, 1.08×10^{-3} mol) dissolved in water was slowly added, and the mixture rapidly stirred at room temperature for 3 hours. The resultant product (3.22×10^{-1} g, 6.92×10^{-4} mol, 65 %) was isolated by suction filtration and washed with cold ethanol.

$\delta_{\text{H}}(\text{CDCl}_3)$ 4.5 (t, 2H, $^3J_{\text{H-H}}$ 6.7 Hz, $\alpha\text{-CH}_2$), 2.2 (um, 2H, $\gamma\text{-CH}_2$), 2.00 (um, 2H, $\beta\text{-CH}_2$); $\delta_{\text{F}}(\text{CDCl}_3)$ -66.7 (um, CF_3); m/z (FAB) 464 ($[\text{M}^+]$, 20 %); Found C, 26.05; H, 2.45; S, 26.92. $\text{C}_{10}\text{H}_{12}\text{F}_6\text{O}_2\text{S}_4\text{Ni}$ requires C, 25.82; H, 2.60; S, 27.57; IR (nujol) ν 1025(w), 1042(w), 1086(s), 1133(s) cm^{-1} .

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CHAPTER FOUR

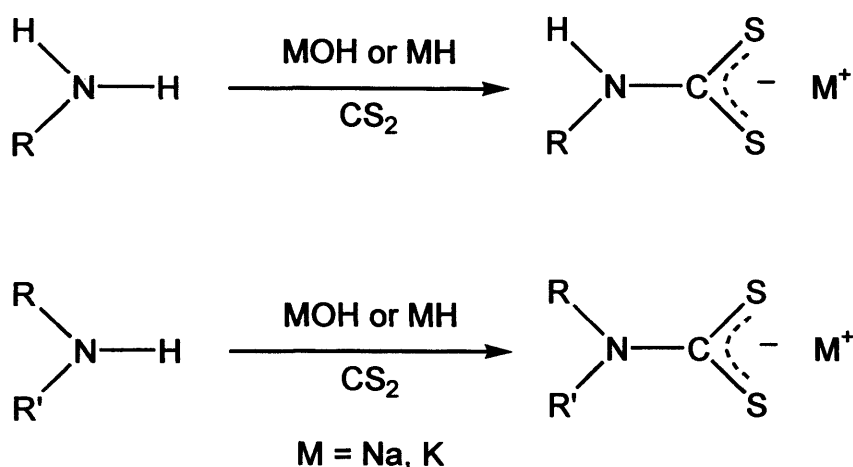
Dithiocarbamate Ligands and Coordination Chemistry



**University of
Leicester**

4.1 Introduction

Dithiocarbamates are the half amides of dithiocarbamic acid, and were first prepared by Debus in 1850¹ as the ammonium salts. Since the first reported preparation, dithiocarbamates have normally been synthesised as alkali metal salts by the nucleophilic reactions between CS₂ and primary or secondary amines in the presence of an alkali metal hydroxide or hydride base (Scheme 4.1).²



Scheme 4.1 General reaction scheme for alkali metal dithiocarbamate salts

Dithiocarbamic acids, the parent compounds, can be obtained as colourless needles from their ammonium salts by treatment with cold acid, but due to their instability, decomposing to thiocyanic acid and hydrogen sulfide, are rarely isolated. The alkali metal salts which are usually hydrated, however, are stable compounds and are dissociated in aqueous solution, whilst remaining associated in organic solvents.

Dithiocarbamates can be oxidised by mild oxidants, such as H₂O₂ or iodine, in aqueous solutions to yield the thiuram disulfides, in a similar manner to the dithiophosphate disulfides, discussed in Chapter 2.

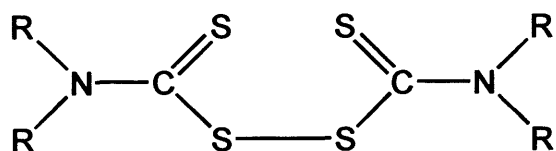


Figure 4.1 General structure of thiuram disulfides

Dithiocarbamates have two potential sulfur donor atoms joined to a single carbon atom, leading to their complexes often being termed 1,1-dithiolato complexes, and are usually classified as class b ligands or "soft" Lewis bases. The strong metal binding properties of the dithiocarbamates was recognised very early in the history of organo-sulfur chemistry along with their ability to adopt monodentate or bidentate coordination modes similar to those for the dithiophosphates and xanthates discussed previously (Figure 4.2),³ and here a brief, selective overview of the coordination chemistry of dithiocarbamate ligands is included to illustrate key points of interest.

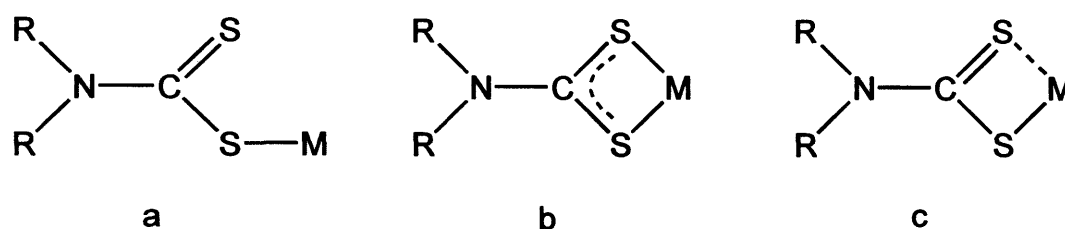


Figure 4.2 Possible bonding modes of dithiocarbamate ligands monodentate (a), isobidentate (b), anisobidentate (c)

When bonded *via* the chelating modes, ligands of this type frequently stabilise the metal centre in an unusually high apparent formal oxidation state such as in $[\text{Fe}^{\text{IV}}(\text{S}_2\text{CNET}_2)_3]^+$ or $[\text{Ni}^{\text{IV}}(\text{S}_2\text{CNET}_2)_3]^+$. They also have a propensity for stabilising novel stereochemical configurations, unusual mixed oxidation states and intermediate spin states. In addition to stabilising monomeric complexes such as these, dithiocarbamate ligands have also been observed to bridge across metal centres *via* a variety of different bonding modes (Figure 4.3).

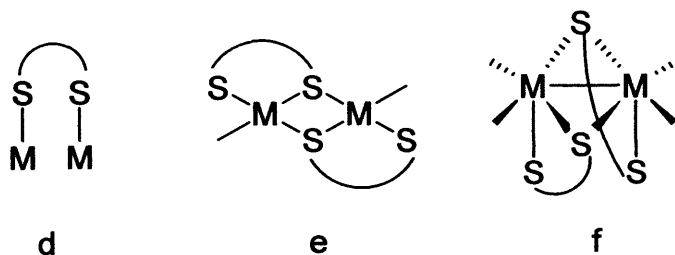


Figure 4.3 Examples of possible bonding modes of dithiocarbamate ligands bridging across metal centres

In certain circumstances different bridging modes can be observed within a single compound. The ruthenium(III) compound $[\text{Ru}_2(\text{S}_2\text{CNEt}_2)_5]^+$, for example, has two isomers both with chelating and different types of bridging dithiocarbamate ligands (Figure 4.4).⁴

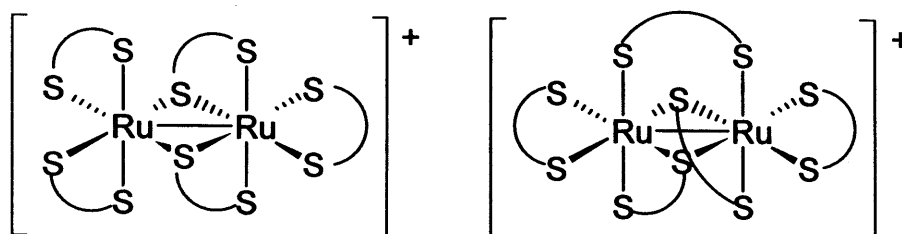


Figure 4.4 Ruthenium dithiocarbamate complex showing multiple ligand-metal bridging modes

Transition metal dithiocarbamates are some of the most widely studied compounds in inorganic chemistry. Many of the heavy metal salts of the dithiocarbamates are coloured and are prepared simply by addition of the metal chloride or sulfate salt, to a solution of an ammonium or alkali metal salt of the dithiocarbamic acid, preferably with exclusion of oxygen. Thorn and Ludwig⁵ give a review of the earlier work summarising the preparations and the properties of both ligands and simple metal complexes. More recently work in this area has focussed on more complicated coordination chemistry to a variety of metal centres. Copper(II) dithiocarbamates are particularly well studied compounds due to their unique structural, magnetic and spectroscopic properties. The chemistry of copper(I) dithiocarbamates, on the other hand, has remained largely unexplored. Synthetic procedures leading to these materials in the past, usually involved reaction of an alkali metal salt of the ligand, with a cuprous compound, generally an oxide or halide. This method, however, yields products which are subject to contamination or oxidation to the cupric derivatives. A more suitable approach was used in studies by Victoriano *et al.*⁶ This involved the reaction of the thiuram disulfides with copper metal in organic solvents to afford copper(I) dithiocarbamates with methyl, ethyl and *iso*-propyl tails. The copper(I) complexes prepared were found to be diamagnetic, soluble solids and their solutions displayed conductivities typical of non-electrolytes.

Further work carried out by Victoriano *et al.*⁷ involved the reaction of tetra-alkylthiuram disulfides with Cu(I) halides to give materials of composition $[\text{Cu}_2(\text{dtc})_3\text{X}_2]$. These species are understood to be a mixture of the ionic species $[\text{Cu}(\text{dtc})_2]^+$ and $[\text{Cu}(\text{dtc})\text{X}_2]^-$ containing both Cu(II) and Cu(III), on the basis of magnetic susceptibilities, IR and ESCA spectroscopies.

Gold(I) dithiocarbamate complexes have been studied by Kowala and Swan,⁸ whilst di- and tetranuclear gold(II) dithiocarbamate complexes were investigated by Laguna *et al.*⁹ Here, although dithiocarbamate ligands usually act in a bidentate manner, a number of gold(II) dimers were reported with the ligand binding *via* a monodentate mode. This was ultimately proven by obtaining single crystal X-ray structural analysis of $[\text{Au}_2(\mu\text{-CH}_2\text{PPh}_2\text{CH}_2)_2\{\text{S}_2\text{CMe}_2\}_2]$ (Figure 4.5) showing two independent molecules, in which the dithiocarbamate ligands exhibit monodentate behaviour.

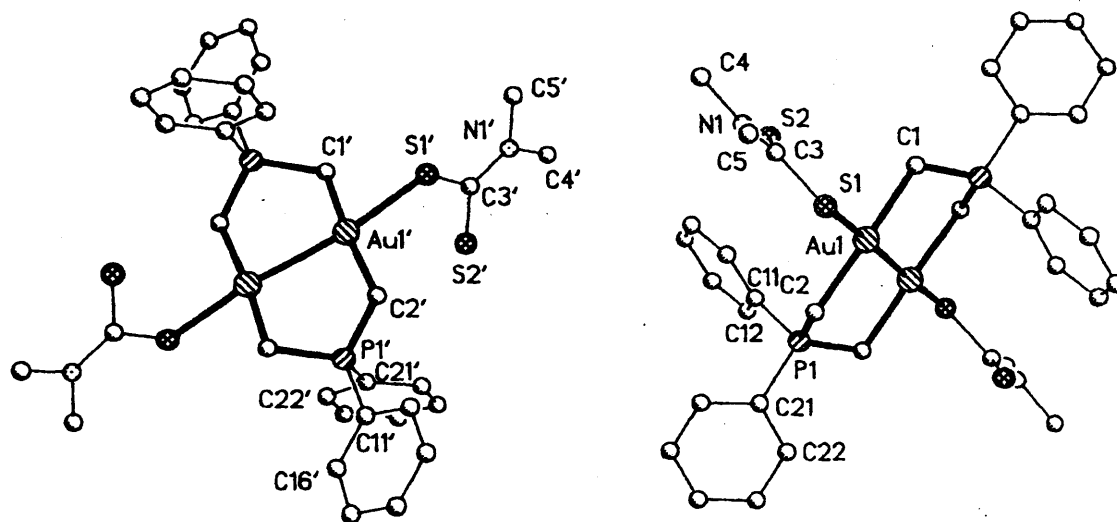


Figure 4.5 Crystal structure of gold(II) dimer reported by Laguna *et al.*⁹ showing monodentate dithiocarbamate ligands

There is interest in cadmium(II) dithiocarbamates $[\text{Cd}(\text{dtc})_2]$ ¹⁰ due to the potential use of dithiocarbamate ligands as antidotes for chronic cadmium poisoning and to the possible use of $[\text{Cd}(\text{dtc})_2]$ as single molecule precursors for the deposition of thin CdS films for use in semi-conductors.¹¹ Garcia-Fontan *et al.*¹² reported the synthesis and structural characterisation of some piperidine-, morpholine-, and piperazine-based

cadmium(II) dithiocarbamates where the ligands having the general formula shown in Figure 4.6.

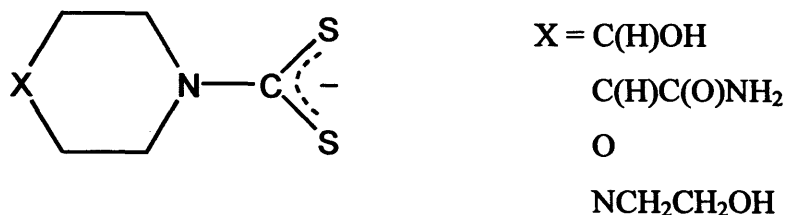


Figure 4.6 Dithiocarbamate ligands used to produce cadmium complexes reported by Garcia-Fontan *et al.*¹²

Although much work has been carried out on mono- and dialkyl-substituted dithiocarbamates, very few heterocyclic dithiocarbamates have been studied. Garg *et al.*¹³ reported the synthesis and characterisation of a number of compounds including complexes of chromium(III), manganese(III), iron(III), cobalt(II), and copper(II) with the tetrahydroquinoline and tetrahydroisoquinoline dithiocarbamate ligands (Figure 4.7).

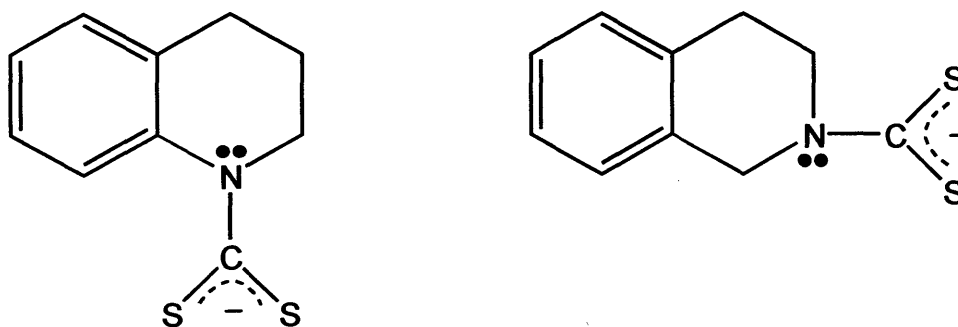


Figure 4.7 Tetrahydroquinoline (left) and tetrahydroisoquinoline (right) dithiocarbamate ligands reported by Garg *et al.*¹³

It was found that complexes of Cr(III), Mn(III) and Fe(III) had the formula [M(dtc)₃] whereas Co(II) and Cu(II) conformed to the [M(dtc)₂] type, where both ligands behave in an isobidentate manner.

More recently, Blake *et al.*¹⁴ reported the single crystal X-ray structure of *bis*-(diethyl-dithiocarbamato) dibromopalladium(IV) and a novel trinuclear palladium(II)

complex, $[(\text{Et}_2\text{NCS}_2)\text{BrPd}]_2\text{Pd}(\text{Et}_2\text{NCS}_2)_2$ (Figure 4.8). The latter of the two species was obtained as a decomposition product in the crystallisation of the former, and has three palladium centres with both bridging and terminal dithiocarbamate ligands attached.

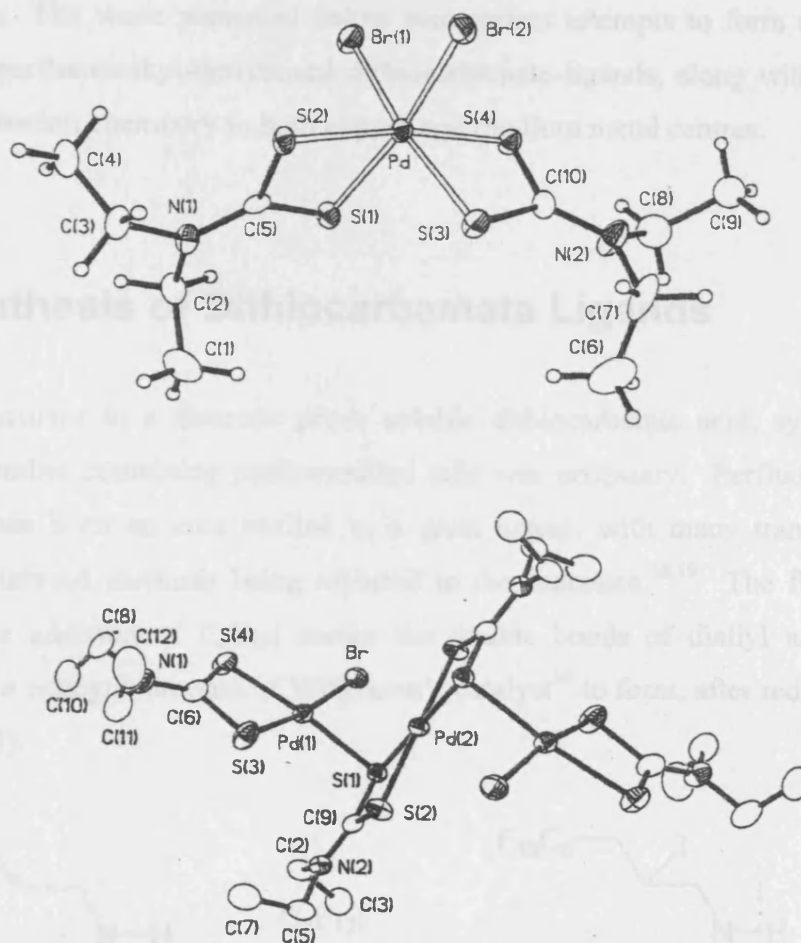


Figure 4.8 Crystal structure of *bis*-(diethyldithiocarbamato) dibromopalladium(IV) (top) and $[(\text{Et}_2\text{NCS}_2)\text{BrPd}]_2\text{Pd}(\text{Et}_2\text{NCS}_2)_2$ (bottom) as reported by Blake *et al.*¹⁴

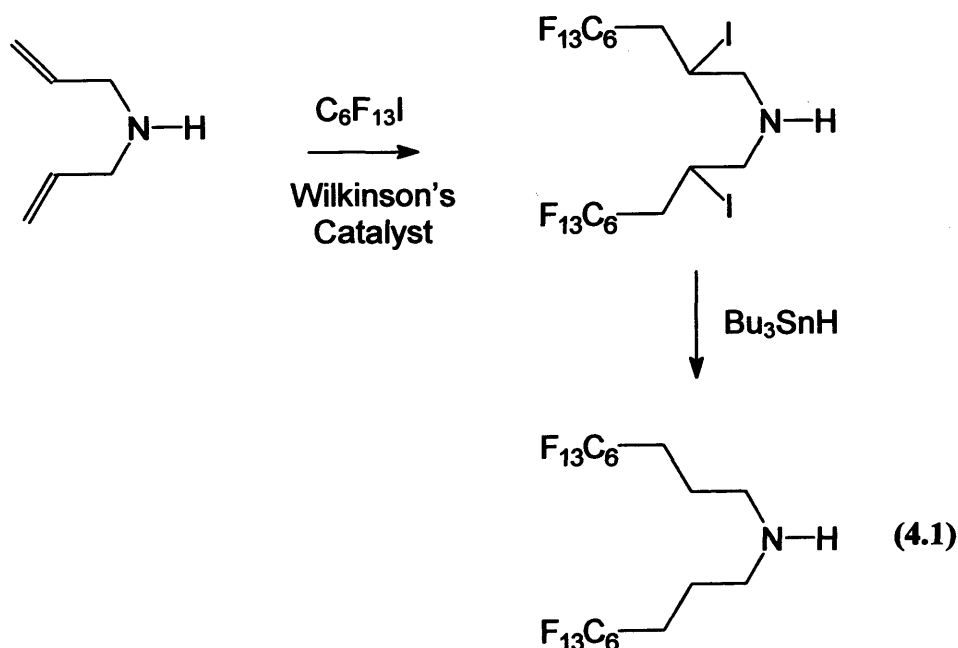
The structure of this palladium complex is unusual given that the palladium(IV) has been reduced to Pd(II), presumably with oxidation of the ligand, and it is surprising that the very stable, well known monomeric Pd(II) complex, was not formed exclusively as the decomposition product in solution.

Complexes containing dithiocarbamate ligands have been extensively studied over the last fifty years, not only because of their intrinsically interesting structural and bonding properties but also because of their varied industrial applications.¹⁵ The

many uses of dithiocarbamate compounds include applications as highly specific analytical reagents, vulcanisation accelerators, semiconductors, fungicides, pesticides and high temperature wear inhibiting additives in lubricants.^{16,17} As with the dithiophosphate and xanthate compounds discussed in Chapters 2 and 3, it is the potential application as oil additives which drives this study of dithiocarbamate compounds. The work presented below summarises attempts to form a number of alkyl- and perfluoroalkyl-derivatised dithiocarbamate ligands, along with a study of their coordination chemistry to both copper and rhodium metal centres.

4.2 Synthesis of Dithiocarbamate Ligands

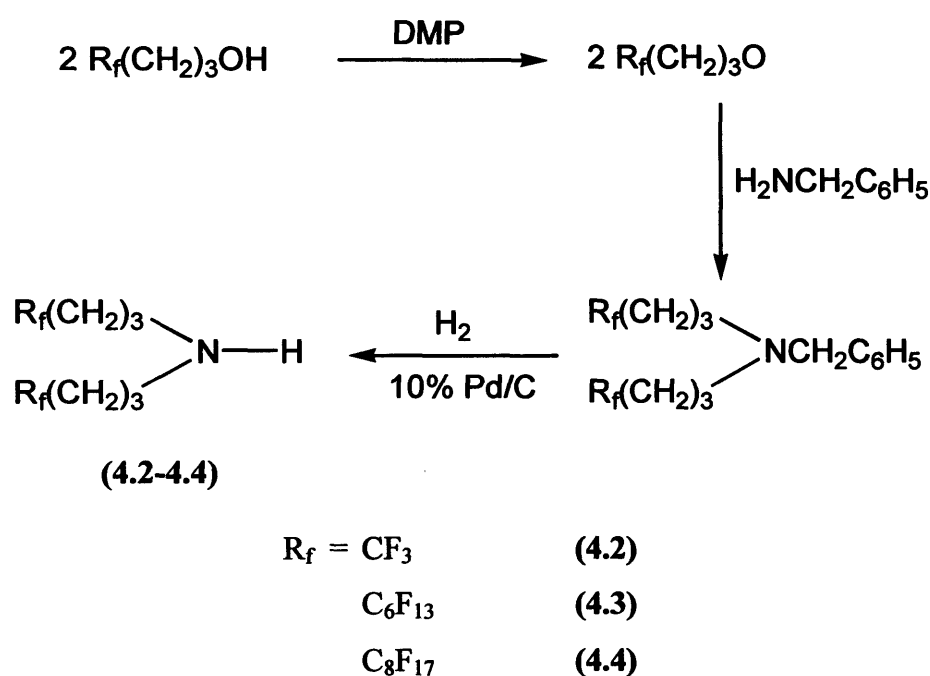
As a precursor to a fluorous phase soluble dithiocarbamic acid, synthesis of a secondary amine containing perfluoroalkyl tails was necessary. Perfluoroalkylation of olefins has been an area studied to a great extent, with many transition metal complex catalysed methods being reported in the literature.^{18,19} The first attempts involved the addition of $C_6F_{13}I$ across the double bonds of diallyl amine in the presence of a catalytic amount of Wilkinson's catalyst²⁰ to form, after reduction, (4.1) (Scheme 4.2).



Scheme 4.2 Attempted formation of a secondary amine bearing perfluoroalkyl tails

The proton NMR spectrum of the product showed that the signals corresponding to the unsaturated protons had disappeared but none of the desired product (4.1) could be isolated. Due to the nature of the radical reaction, it was believed that the diallyl amine had undergone either ring closure or oligomerisation to yield a complex mixture of products.

Focus then shifted towards a three step synthesis of perfluoroalkyl-derivatised secondary amines following the report by Bauer *et al.* published during this study (Scheme 4.3).²¹



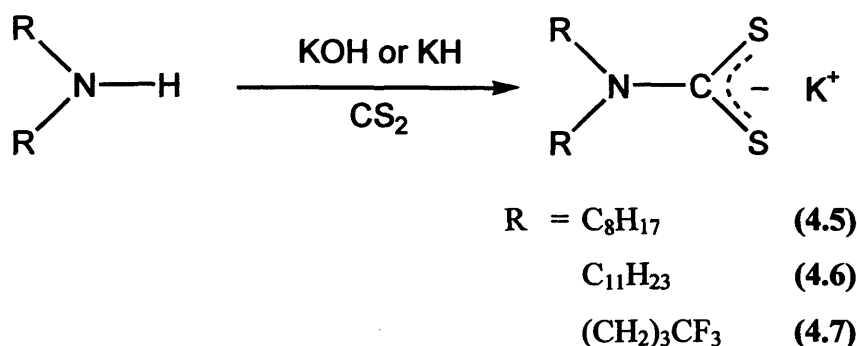
Scheme 4.3 Formation of fluorinated secondary amines²¹

Here, the commercially available perfluoroalkyl-derivatised alcohol was oxidised to the aldehyde, followed by reaction with benzyl amine to give the tertiary amine, then finally hydrogenated to give the required perfluoroalkyl derivatised secondary amine.

Initially, Dess-Martin Periodinane (DMP)^{22,23} was used to selectively oxidise the alcohols to aldehydes but, since DMP is highly unstable,²⁴ synthesis, storage and disposal proved to be problematic. To overcome this, the oxidations were subsequently successfully carried out using pyridinium chlorochromate (PCC).^{25,26} Following the subsequent procedures outlined by Bauer, it was possible to form the 4,4,4-trifluoro-*n*-butyl derivatised secondary amine (4.2) in relatively high yield.

Attempts to form both (4.3) and (4.4) did, however, prove to be more problematic, with complex mixtures of products, observed by a varying number of signals in the α -CF₂ region of the ¹⁹F NMR spectrum, being formed after each step. It was, therefore, impossible to isolate the desired products in sufficient purity or yield to make further reactions, including the synthesis of dithiocarbamates with these long perfluoroalkyl substituents tenable.

However, two commercially available perprotio secondary amines, along with the 4,4,4-trifluoro-*n*-butyl derivatised secondary amine (4.2), were subsequently used to produce a series of new potassium dithiocarbamate compounds of varying tail length, by the facile reaction with CS₂ in the presence of base (Scheme 4.4).

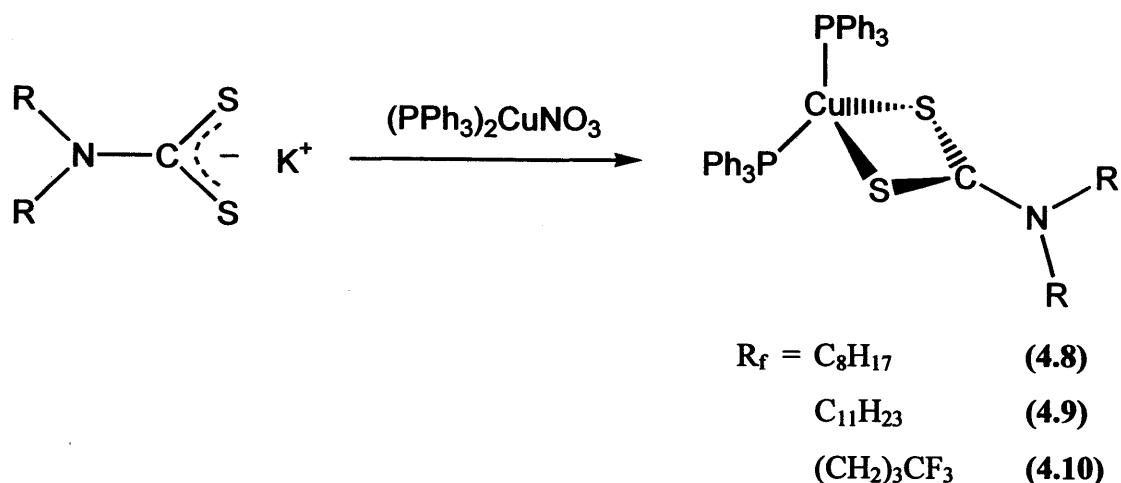


Scheme 4.4 Formation of potassium dithiocarbamate salts

The required products were collected as white solids and purified by washing with cold hexane, and characterised by proton NMR and mass spectrometry. The proton NMR spectra of (4.5-4.7) showed similar resonances to those for the free amines, with the absence of the signal corresponding to the amine proton, while electrospray mass spectrometry traces exhibited signals corresponding to the [M – K]⁺ anion.

4.3 Copper Dithiocarbamate Complexes

A series of copper *bis*-triphenylphosphine complexes with differing alkyl and fluoroalkyl groups were produced (4.8-4.10) (Scheme 4.5).



Scheme 4.5 Synthesis of *bis*-triphenylphosphine copper dithiocarbamate complexes

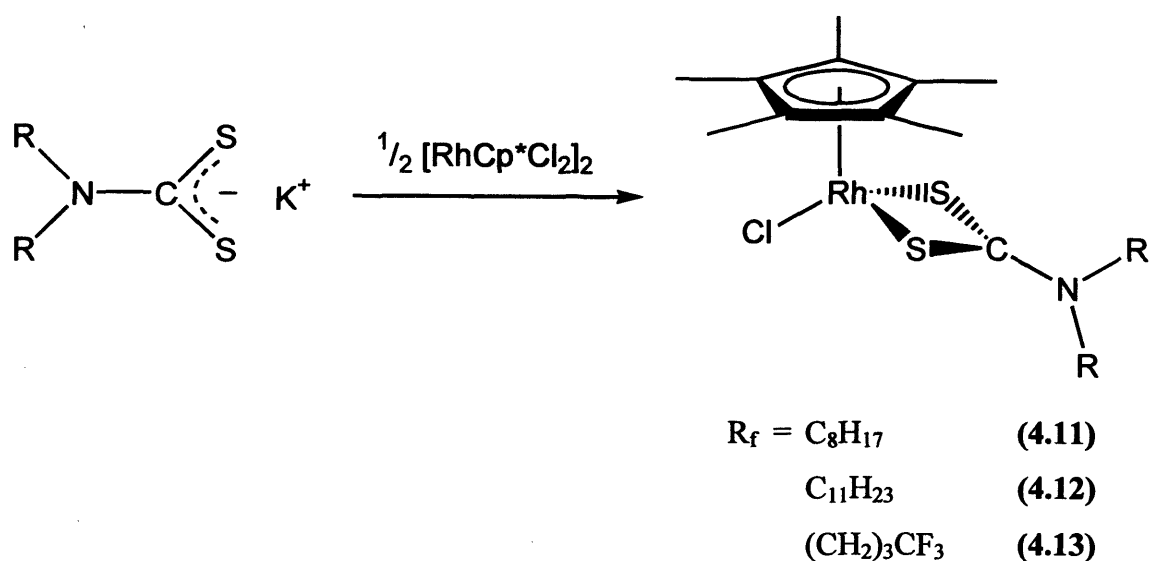
All of these reactions were carried out in a similar fashion to those used to prepare the dithiophosphate and xanthate analogues, by the addition of the alkali metal salt of the dithiocarbamate to the *bis*-triphenylphosphine copper nitrate precursor²⁷ in methanol. After stirring at room temperature for 30 minutes, a white solid was observed in the reaction mixture, which after cooling in ice, was isolated by suction filtration.

Proton NMR spectroscopic studies of the products revealed resonances at similar shifts to those of both the free amines and the alkali metal dithiocarbamate precursors, with an additional signal in the aromatic region corresponding to the triphenyl phosphine protons. Relative integrations of these peaks would suggest that, as with the dithiophosphate and xanthate ligands, both triphenyl phosphine groups remain coordinated, implying a four coordinate, pseudo-tetrahedral structure.

Attempts were made to grow crystals of copper dithiocarbamate complexes (4.8-4.10) suitable for X-ray analysis to ultimately prove the structures, but despite using a number of techniques and solvent systems, these proved to be unsuccessful.

4.4 Rhodium Dithiocarbamate Complexes

A series of rhodium(III) complexes (4.11–4.13), analogous to the dithiophosphate complexes reported by Jain and Vargese²⁸ and those reported in Chapters 2 and 3, bearing dithiocarbamate ligands with differing alkyl and fluoroalkyl groups were synthesised (Scheme 4.6).



Scheme 4.6 Formation of a rhodium(III) dithiocarbamate complexes

These were prepared by the reaction of the appropriate alkali metal dithiocarbamate salt with $[Cp^*RhCl_2]_2$ at room temperature in dichloromethane. Proton and ^{19}F NMR spectroscopy showed all of the expected resonances with very similar spectra to those of the corresponding alkali metal salt being observed. The 1H spectra did, however, contain an additional singlet at around 1.7 ppm corresponding to the pentamethyl cyclopentadienyl protons.

Mass spectrometry of the rhodium dithiocarbamate compounds all gave good agreement with theoretical values, with the presence a peak corresponding to the $[M - Cl]^+$ fragment being prevalent in all FAB spectra.

Crystals suitable for X-ray analysis were grown by slow evaporation from an acetone solution for the rhodium dioctyl dithiocarbamate complex (4.11) (Figure 4.9). Crystal data and structure refinement for (4.11) can be found in the Appendix, whilst

a complete set of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

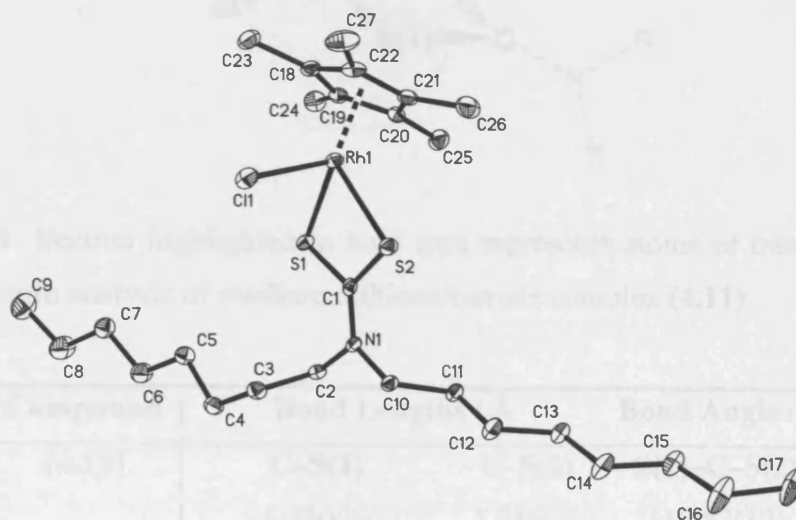


Figure 4.9 Crystal structure of (4.11)

The octyl-derivatised complex shows the ligand bonding to the metal in a bidentate fashion to give a pseudo-octahedral geometry with the pentamethyl cyclopentadienyl group occupying three coordination sites in the well-recognised piano stool arrangement. The two alkyl tails appear to be radiating away from each other as a consequence of near perfect trigonal geometry around the nitrogen atom {C(1)-N-C(2) = 120.36°, C(2)-N-C(10) = 117.99°, C(1)-N-C(10) = 121.13°}, with increased thermal motion being observed towards the terminal CH₃ groups.

Attempts were made to grow crystals of other rhodium dithiocarbamate complexes suitable for X-ray analysis, but despite using a number of techniques and solvent systems, these proved to be unsuccessful.

Both the geometry around the rhodium centre and the ligand coordination can be investigated using X-ray crystallography, although it would be imprudent to draw too many firm conclusions from one structural analysis. From the crystal structure determined for compound (4.11) data can be gathered regarding the bite angle of the ligand and the coordination mode it adopts. Here, analysis focuses on the Rh-S and the C-S bond lengths and angles with the atoms concerned highlighted in Figure 4.10 in bold type.

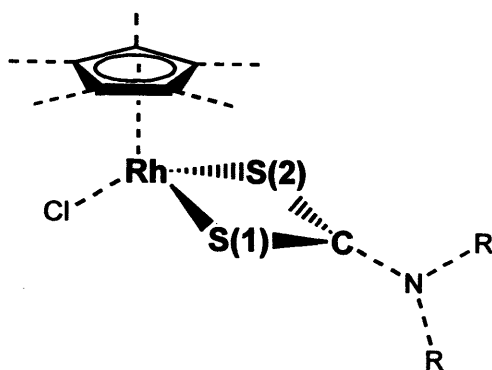


Figure 4.10 Section highlighted in bold type represents atoms of interest in X-ray crystal structure analysis of rhodium dithiocarbamate complex (4.11)

Compound	Bond Lengths / Å		Bond Angle / °
(4.11)	C–S(1)	C–S(2)	S(1)–C–S(2)
	1.720(2)	1.716(2)	110.82(12)
	Rh–S(1)	Rh–S(2)	S(1)–Rh–S(2)
	2.372(1)	2.376(1)	73.15(2)

Table 4.1 Selected C–S and Rh–S bond lengths and angles from (4.11)

This compound has symmetrical C–S bonds of just above 1.7 Å in length, which is slightly longer than those observed in similar rhodium xanthate complexes, while the S(1)–C–S(2) bond angle is both smaller than the perfect trigonal angle of 120 °, and 4 ° smaller than the bite angle of xanthate ligands observed in the analogous rhodium complexes discussed in Chapter 3. The dithiocarbamate ligand appears to be bonding to the metal predominantly through the isobidentate mode, as the differences in Rh–S bond lengths are very small, but they are not completely symmetrical. The S(1)–Rh–S(2) bond angle is very close to that observed in the related xanthate complexes, but is far smaller than the perfect octahedral angle of 90 °.

4.5 Chapter Conclusions

The presence of the CF_3 group on (4.7) appeared to make very little difference to either the stability or reactivity of the dithiocarbamate ligand when compared to the perprotio compounds (4.5) and (4.6) and the extensive coordination chemistry of dithiocarbamate ligands in the literature. The main problems encountered were during the attempted syntheses of the secondary amine precursors with long perfluoroalkyl groups. Here attempts were made to repeat published work, but neither the purities nor the yields reported could be achieved, generating complex mixtures of products after each stage of the multi-step synthesis. Owing to the cost or the perfluoroalkyl-derivatised alcohol starting materials, producing subsequent dithiocarbamate ligands in low purity and yield was considered to be untenable.

The coordination chemistry of the dithiocarbamate ligands studied was relatively straightforward, however, potential problems associated with solubility of perfluoroalkyl-derivatised ligands can be predicted from observed trends in compounds discussed in Chapters 2 and 3. The alkali metal dithiocarbamates, and subsequent coordination compounds, discussed here all appeared to be stable to atmospheric conditions, and could be stored under air for long periods of time with no noticeable hydrolysis or decomposition.

4.6 Experimental Procedures

4.6.1 Synthesis of Alkali Metal Dithiocarbamate Salts

Preparation of di-(4,4,4-trifluoro-n-butyl) amine (4.2)

Solid $[\text{Na}(\text{AcO})_3\text{BH}]$ (3.60 g, 1.70×10^{-2} mol) was added to a solution of $\text{CF}_3(\text{CH}_2)_2\text{CHO}$ (2.00 g, 1.59×10^{-2} mol) and benzylamine (8.50×10^{-1} g, 7.93×10^{-3} mol, $8.7 \times 10^{-1} \text{ cm}^3$) in THF (50 cm^3) and was stirred overnight. 1 M NaOH (50 cm^3) was added to the reaction mixture which was subsequently extracted with diethyl

ether ($3 \times 50 \text{ cm}^3$). The organic layer was dried with MgSO_4 and the solvent was removed *in vacuo* to give a colourless oil which was purified by column chromatography on silica using ether/hexane (1:3 v/v) as the eluent. The tertiary amine was then reduced by dissolving in EtOH/hexane (1:1 v/v) (50 cm^3) followed by the addition of 10% Pd/C ($8.20 \times 10^{-1} \text{ g}$), and being stirred under a static atmosphere of hydrogen overnight. The mixture was then filtered through celite and the solvent was removed *in vacuo* to afford the product as a yellow oil ($6.83 \times 10^{-1} \text{ g}$, $2.88 \times 10^{-3} \text{ mol}$, 36 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 2.6 (t, 2H, $^3J_{\text{H-H}}$ 6.6 Hz, $\alpha\text{-CH}_2$), 2.1 (um, 2H, $\gamma\text{-CH}_2$), 1.7 (um, 2H, $\beta\text{-CH}_2$), 1.4 (br s, 1H, NH); $\delta_{\text{F}}(\text{CDCl}_3)$ -66.8 (um, CF_3); m/z (ES) 236 ($[\text{M-H}]^-$, 100 %).

Preparation of $\text{K}\{N,N\text{-dioctyl dithiocarbamate}\}$ (4.5)

Potassium hydride ($6.64 \times 10^{-1} \text{ g}$, $1.66 \times 10^{-2} \text{ mol}$) was carefully added to a stirred solution of dioctyl amine (4.00 g, $1.66 \times 10^{-2} \text{ mol}$) and CS_2 (1.26 g, $1.66 \times 10^{-2} \text{ mol}$, 1.00 cm^3) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. The solvent was removed *in vacuo* giving the product as an off-white solid (3.74 g, $1.05 \times 10^{-2} \text{ mol}$, 63 %) which was purified by washing with hexane.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 3.8 (t, 4H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (um, 4H, $\beta\text{-CH}_2$) 1.2 (um, 20H, 5 mid-chain CH_2), 0.8 (t, 6H, $^3J_{\text{H-H}}$ 7.0 Hz, CH_3); m/z (ES) 317 ($[\text{M-K}]^-$, 100 %).

Preparation of $\text{K}\{N,N\text{-diundecyl dithiocarbamate}\}$ (4.6)

Potassium hydride ($4.90 \times 10^{-2} \text{ g}$, $1.23 \times 10^{-3} \text{ mol}$) was carefully added to a stirred solution of diundecyl amine ($4.00 \times 10^{-1} \text{ g}$, $1.23 \times 10^{-3} \text{ mol}$) and CS_2 ($9.40 \times 10^{-2} \text{ g}$, $1.23 \times 10^{-3} \text{ mol}$, $1.00 \times 10^{-1} \text{ cm}^3$) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. The solvent was removed *in vacuo* giving the product as an off-white solid ($4.93 \times 10^{-1} \text{ g}$, $1.12 \times 10^{-3} \text{ mol}$, 91 %) which was purified by washing with hexane.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 3.8 (t, 4H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (um, 4H, $\beta\text{-CH}_2$) 1.2 (um, 32H, 8 mid-chain CH_2), 0.8 (t, 6H, $^3J_{\text{H-H}}$ 7.0 Hz, CH_3); m/z (ES) 401 ($[\text{M-K}]^+$, 100 %).

Preparation of $K\{N,N\text{-di}(4,4,4\text{-trifluoro-}n\text{-butyl})\text{ dithiocarbamate}\}$ (4.7)

Potassium hydride (3.60×10^{-2} g, 9.07×10^{-4} mol) was carefully added to a stirred solution of di-(4,4,4-trifluoro-*n*-butyl) amine (2.15×10^{-1} g, 9.07×10^{-4} mol) and CS_2 (6.90×10^{-2} g, 9.07×10^{-4} mol, $1.0 \times 10^{-1} \text{ cm}^3$) in diethyl ether (30 cm^3), and the resulting mixture was rapidly stirred at room temperature for 2 hours with the evolution of hydrogen. The solvent was removed *in vacuo* giving the product as an off-white solid (2.36×10^{-1} g, 6.72×10^{-3} mol, 74 %) which was purified by washing with hexane.

$\delta_{\text{H}}(d_6\text{-Acetone})$ 3.5 (t, 4H, $^3J_{\text{H-H}}$ 6.6 Hz, $\alpha\text{-CH}_2$), 2.1 (um, 4H, $\gamma\text{-CH}_2$), 1.7 (um, 4H, $\beta\text{-CH}_2$), 1.4 (br s, 1H, NH); $\delta_{\text{F}}(d_6\text{-Acetone})$ -66.8 (um, CF_3); m/z (ES) 312 ($[\text{M-K}]^+$, 100 %).

4.6.2 Copper Complexes

Preparation of $[\text{Cu}(\text{PPh}_3)_2\{N,N\text{-dioctyl dithiocarbamate}\}]$ (4.8)

$[(\text{PPh}_3)_2\text{CuNO}_3]$ (5.48×10^{-1} g, 8.43×10^{-4} mol) was added as a solid to a solution of $K\{N,N\text{-dioctyl dithiocarbamate}\}$ (3.00×10^{-1} g, 8.43×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature overnight. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white precipitate (5.28×10^{-1} g, 5.84×10^{-4} mol, 69 %) was isolated by suction filtration.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.2 (um, 30H, PPh_3), 3.7 (t, 4H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (um, 4H, $\beta\text{-CH}_2$) 1.4 (um, 20H, 5 mid-chain CH_2), 0.8 (t, 6H, $^3J_{\text{H-H}}$ 7.0 Hz, CH_3); $\delta_{\text{P}}\{^1\text{H}\}$ (CDCl_3) -1.9 (s, PPh_3).

Preparation of $[Cu(PPh_3)_2\{N,N\text{-diundecyl dithiocarbamate}\}]$ (4.9)

$[(PPh_3)_2CuNO_3]$ (3.70×10^{-1} g, 5.68×10^{-4} mol) was added as a solid to a solution of $K\{N,N\text{-diundecyl dithiocarbamate}\}$ (2.50×10^{-1} g, 5.68×10^{-4} mol) in methanol (30 cm^3). The mixture was then rapidly stirred at room temperature overnight. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white precipitate (3.19×10^{-1} g, 3.23×10^{-4} mol, 57 %) was isolated by suction filtration.

$\delta_H(CDCl_3)$ 7.2 (um, 30H, PPh_3), 3.8 (t, 4H, $^3J_{H-H}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.5 (um, 4H, $\beta\text{-CH}_2$) 1.2 (um, 32H, 8 mid-chain CH_2), 0.8 (t, 6H, $^3J_{H-H}$ 7.0 Hz, CH_3); $\delta_P\{^1H\}$ ($CDCl_3$) -2.2 (s, PPh_3); Found C, 70.93; H, 7.79; N, 1.42, P, 6.68; S, 5.68. $C_{56}H_{76}NP_2S_2Cu$ requires C, 71.66; H, 7.75; N, 1.42; P, 6.26; S, 6.49.

Preparation of $[Cu(PPh_3)_2\{N,N\text{-di(4,4,4-trifluoro-}n\text{-butyl) dithiocarbamate}\}]$ (4.10)

$[(PPh_3)_2CuNO_3]$ (1.85×10^{-1} g, 2.85×10^{-4} mol) was added as a solid to a solution of $K\{N,N\text{-di(4,4,4-trifluoro-}n\text{-butyl) dithiocarbamate}\}$ (1.00×10^{-1} g, 2.85×10^{-4} mol) in methanol (25 cm^3). The mixture was then rapidly stirred at room temperature overnight. The volume of solvent was reduced to half the initial amount and a white precipitate was observed. After cooling the reaction mixture in ice for 1 hour, the white precipitate (1.63×10^{-1} g, 1.81×10^{-4} mol, 64 %) was isolated by suction filtration.

$\delta_H(CDCl_3)$ 7.2 (um, 30H, PPh_3), 3.9 (t, 4H, $^3J_{H-H}$ 7.0 Hz, $\alpha\text{-CH}_2$), 2.1 (um, 4H, $\gamma\text{-CH}_2$), 1.9 (um, 4H, $\beta\text{-CH}_2$); $\delta_F(CDCl_3)$ -66.5 (um, CF_3); $\delta_P(CDCl_3)$ 1.1 (s).

4.6.3 Rhodium Complexes

*Preparation of [Cp*RhCl{N,N-dioctyl dithiocarbamate}] (4.11)*

To a slurry of K{N,N-dioctyl dithiocarbamate} (8.60×10^{-2} g, 2.43×10^{-4} mol) in dichloromethane (30 cm^3), $[\text{RhCl}_2\text{Cp}^*]_2$ (7.50×10^{-2} g, 1.21×10^{-4} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over MgSO_4 and CaCl_2 . The solvent was removed *in vacuo*, affording the product as a dark red oil (1.03×10^{-1} g, 1.75×10^{-4} mol, 72 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 3.5 (t, 4H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (s, 15H, cp*), 1.6 (um, 4H, $\beta\text{-CH}_2$) 1.2 (um, 20H, 5 mid-chain CH_2), 0.8 (t, 6H, $^3J_{\text{H-H}}$ 7.0 Hz, CH_3); m/z (FAB) 555 ($[\text{M} - \text{Cl}]^+$, 100 %).

*Preparation of [Cp*RhCl{N,N-diundecyl dithiocarbamate}] (4.12)*

To a slurry of K{N,N-diundecyl dithiocarbamate} (1.07×10^{-1} g, 2.43×10^{-4} mol) in dichloromethane (30 cm^3), $[\text{RhCl}_2\text{Cp}^*]_2$ (7.50×10^{-2} g, 1.21×10^{-4} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours. The mixture was filtered, washed with water ($3 \times 20 \text{ cm}^3$) and dried over MgSO_4 and CaCl_2 . The solvent was removed *in vacuo*, affording the product as a dark red oil (1.12×10^{-1} g, 1.66×10^{-4} mol, 68 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 3.6 (t, 4H, $^3J_{\text{H-H}}$ 7.0 Hz, $\alpha\text{-CH}_2$), 1.7 (s, 15H, cp*), 1.5 (um, 4H, $\beta\text{-CH}_2$) 1.2 (um, 32H, 8 mid-chain CH_2), 0.8 (t, 6H, $^3J_{\text{H-H}}$ 7.0 Hz, CH_3); m/z (FAB) 639 ($[\text{M} - \text{Cl}]^+$, 100 %).

*Preparation of [Cp*RhCl{N,N-di(4,4,4-trifluoro-n-butyl) dithiocarbamate}] (4.13)*

To a slurry of K{N,N-di(4,4,4-trifluoro-n-butyl) dithiocarbamate} (1.00×10^{-1} g, 2.85×10^{-4} mol) in dichloromethane (30 cm^3), $[\text{RhCl}_2\text{Cp}^*]_2$ (8.80×10^{-2} g, 1.42×10^{-4} mol) was added and the mixture was rapidly stirred at room temperature for 3 hours.

The mixture was filtered, washed with water (3 x 20 cm³) and dried over MgSO₄ and CaCl₂. The solvent was removed *in vacuo*, affording the product as a dark red oil (1.15 x 10⁻¹ g, 1.96 x 10⁻⁴ mol, 69 %).

$\delta_{\text{H}}(\text{CDCl}_3)$ 3.4 (t, 4H, $^3J_{\text{H-H}}$ 6.8 Hz, $\alpha\text{-CH}_2$), 1.7 (s, 15H, Cp^{*}), 1.5 (um, 2H, $\gamma\text{-CH}_2$), 1.2 (um, 2H, $\beta\text{-CH}_2$), $\delta_{\text{F}}(\text{CDCl}_3)$ -66.7 (um, CF₃); *m/z* (FAB) 550 ([M - Cl]⁺, 100 %).

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5.1 Introduction

Since commercial additive packages actually consist of a number of different components, which give the base fluid to the required properties, it is essential that there is compatibility between the additives. It is important to test the properties of each component individually, but it is also expensive to test the blended package as a whole. Often a component which is added to regulate one property of the lubricant can have a detrimental effect on the activity of others, leading to a loss of efficiency from the product.

CHAPTER FIVE

Perfluoroalkyl- Derivatised Phenates

Normal phenates, as described in Chapter 1, can be prepared by simple deprotonation of the aromatic phenol, often synthesised via a Friedel-Crafts type alkylation, using either a metal oxide or hydroxide (Scheme 5.1).

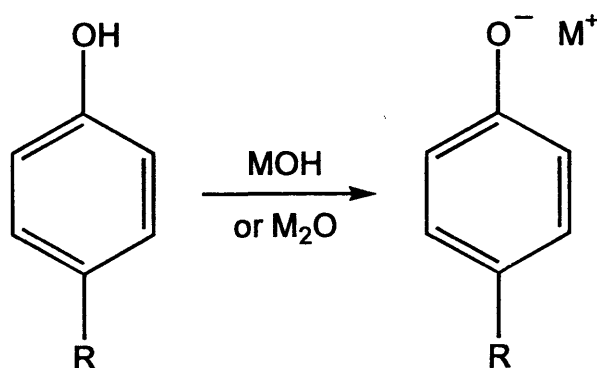


Scheme 5.1 General synthesis of normal phenates

5.1 Introduction

Since commercial additive packages actually consist of a number of different components, which tune the base fluid to the required properties, it is essential that there is compatibility between the additives. It is important to test the properties of each component individually, but it is also imperative to test the blended package as a whole. Often a compound which is added to regulate one property of the lubricant can have a detrimental effect on the activity of others, leading to a loss of efficiency from the theoretical value achieved when the additive was tested alone. Due to the problems associated with the solubilities of conventional hydrocarbon compounds in fluorinated oils, it may not be possible to merely blend the anti-wear compounds reported in Chapters 2, 3 and 4 with other commercially available additives (e.g. detergents, dispersants, friction modifiers, etc.). To blend these anti-wear compounds, discussed previously, with other classes of lubricant additives, such as detergents, it will be necessary to make these soluble in the perfluorocarbon base fluids too. Therefore, here, preliminary work on the synthesis of phenates containing perfluoroalkyl groups as potential detergents is discussed.

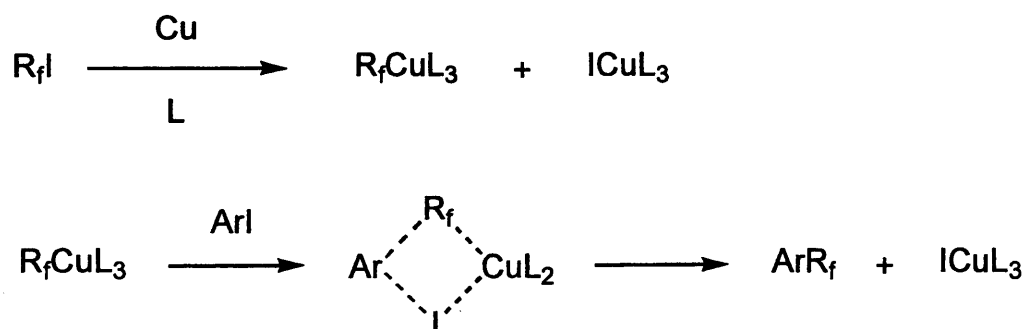
Normal phenates, as described in Chapter 1, can be prepared by simple deprotonation of the appropriate phenol, often synthesised *via* a Friedel-Crafts type alkylation,¹ using either a metal oxide or hydroxide (Scheme 5.1).



Scheme 5.1 General synthesis of normal phenates

Compounds of this type are also important because they can be used as precursors for another class of detergents, salicylates, which can be produced by the addition of CO₂, followed by subsequent rearrangement *via* the Kolbe-Schmitt reaction.²

If detergents of this nature are to be used in fluorous base fluids, a high weight percentage of fluorine is likely to be required to confer solubility. The most obvious way to achieve this is to substitute the hydrocarbon tail for a long perfluoroalkyl group. Previous work carried out by McLoughlin and Thrower,³ which has subsequently been extended by Chen *et al.*,⁴ has provided a convenient method for introducing perfluoroalkyl groups to a range of aromatic substrates. This is achieved *via* a copper mediated cross coupling reaction of a perfluoroalkyl iodide and an iodo-aromatic substrate (Scheme 5.2).



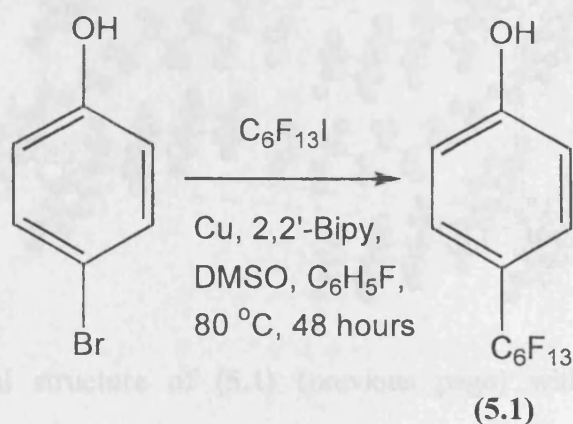
Scheme 5.2 Copper mediated coupling of perfluoroalkyl iodides with aromatic iodides (L = 2,2'-bipyridine)

More recently, Gudmunson⁵ has adapted this methodology to form a series of perfluoroalkyl-derivatised phenols and biphenols, for use in fluorinated phosphorus-based ligand syntheses, which could act as precursors for the fluorinated phenate target molecules.

5.2 Synthesis of Perfluoroalkyl Derivatised Phenols and Biphenols

Perfluoroalkyl derivatised phenol (5.1) was synthesised *via* a copper coupling of 4-bromophenol and C₆F₁₃I, in accordance with the method reported by Gudmunson

(Scheme 5.3). Purification was carried out by distillation using Kugelröhr apparatus, affording a solid white product.



Scheme 5.3 Copper coupling of 4-bromophenol and $C_6F_{13}I$

The proton NMR spectrum exhibits an AA'BB' pattern in the aromatic region typical of a *para*-disubstituted benzene ring. The $^{19}F\{^1H\}$ NMR spectrum exhibits six distinct resonances, due to the six inequivalent fluorine environments, in a similar arrangement to those discussed in Chapter 2. The structure of (5.1) was ultimately proven by undertaking a single crystal X-ray structural analysis (Figure 5.1) after growing suitable crystals by slow evaporation of a diethyl ether solution. Crystal data and structure refinement for (5.1) can be found in the Appendix, whilst a complete set of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.

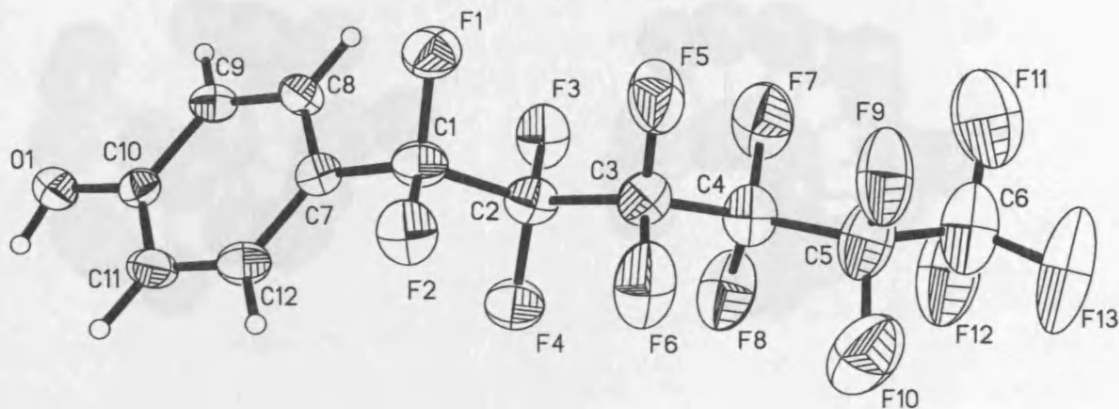


Figure 5.1 Crystal structure of (5.1) showing right-handed (left) and left-handed (right) screw conformations

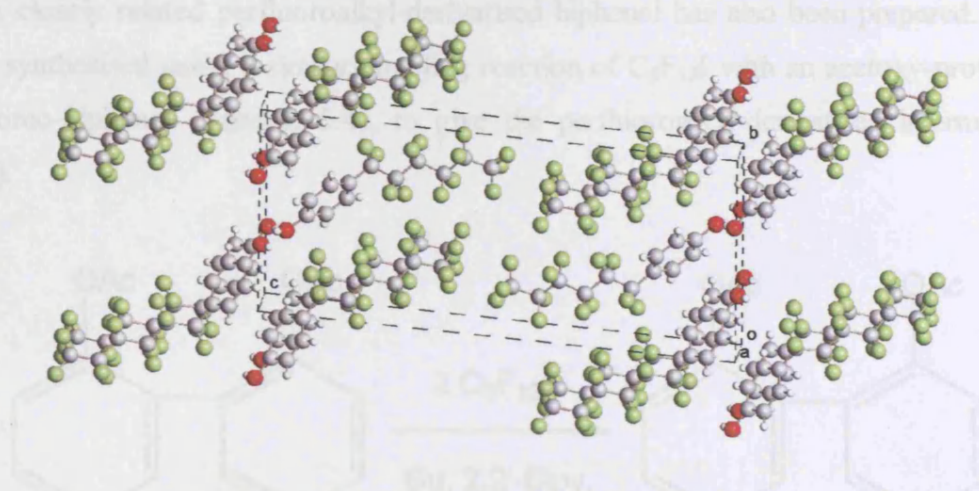


Figure 5.1 Crystal structure of (5.1) (previous page) with unit cell packing arrangement (above)

This shows the expected structure, with the fluoruous chain showing a higher degree of thermal motion towards the terminal CF₃ group. There are two, independent, molecules in the unit cell of 4-tridecafluoro-*n*-hexylphenol (5.1) which align to give similar fluoruous domains. The perfluoroalkyl tails on each independent molecule radiate linearly away from the aryl rings, but one adopts a right-handed screw conformation whilst the other adopts a left-handed screw conformation (Figure 5.2). In the former, there are no significant variations in the C-C and F-C bond lengths and F-C-F and F-C-C bond angles at each carbon atom along the tail. However, in the molecule with the left-handed screw conformation, asymmetries in the F-C bond lengths and the related bond angles reveal distortions which we are unable to account for but these are not associated with any short intermolecular F...F interactions.

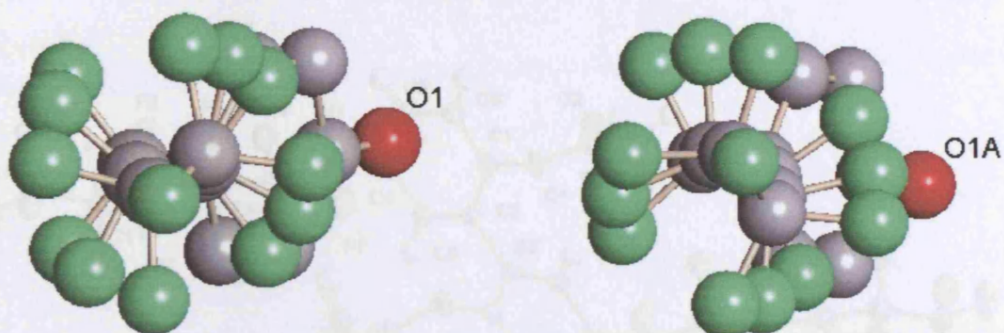
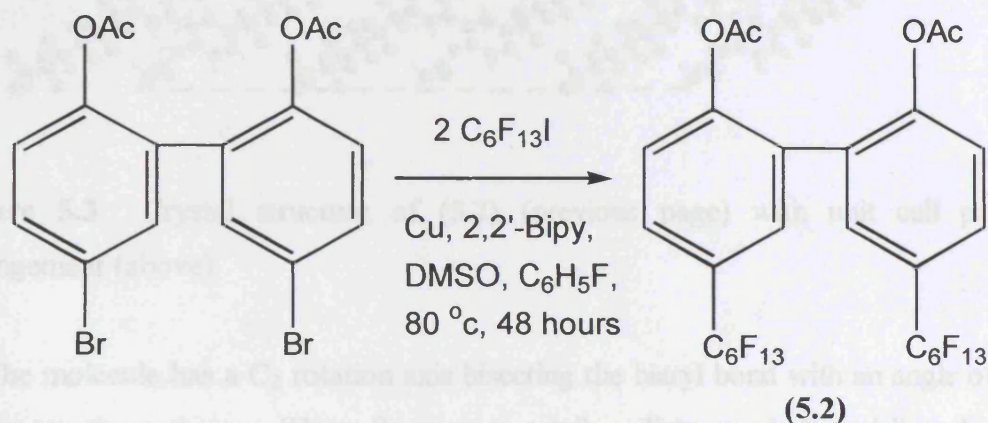


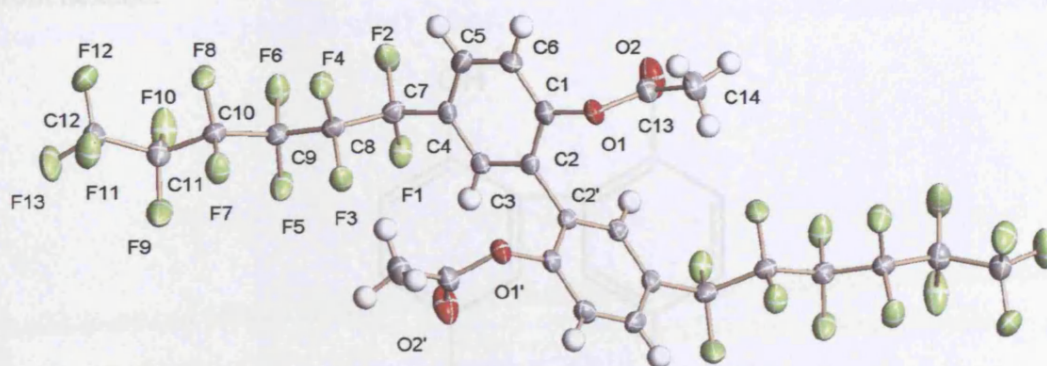
Figure 5.2 Crystal structure of (5.1) showing right-handed (left) and left-handed (right) screw conformations

A closely related perfluoroalkyl-derivatised biphenol has also been prepared. This was synthesised using a similar coupling reaction of $\text{C}_6\text{F}_{13}\text{I}$ with an acetoxy-protected dibromo-biphenol (Scheme 5.4), to give the perfluoroalkyl-derivatised intermediate (5.2).



Scheme 5.4 Copper coupling of 5,5'-dibromo-2,2'-diacetoxybiphenol and $\text{C}_6\text{F}_{13}\text{I}$

Analysis of (5.2) was carried out using proton and $^{19}\text{F}\{^1\text{H}\}$ NMR spectroscopy, with all values showing good agreement with those of the original preparation. The structure of (5.2) was ultimately proven by undertaking a single crystal X-ray structural analysis (Figure 5.3) after growing suitable crystals by slow evaporation of an acetone solution. Crystal data and structure refinement for (5.2) can be found in the Appendix, whilst a complete set of data regarding atomic coordinates, bond lengths and bond angles can be found in electronic format on the accompanying CD-ROM.



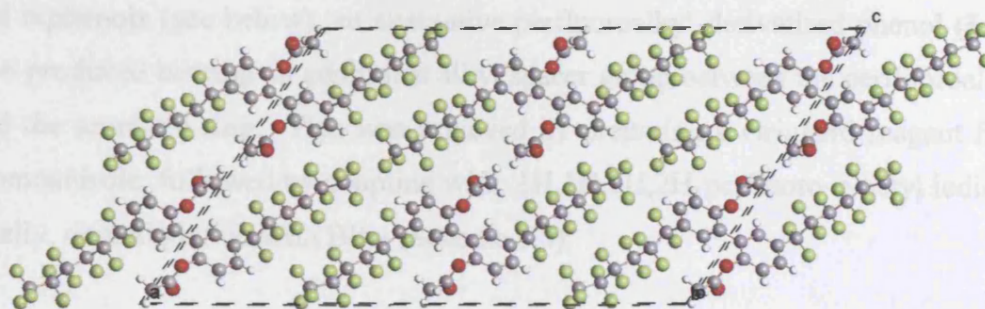
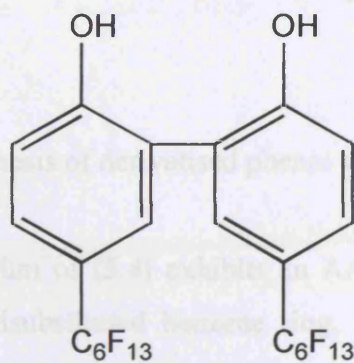


Figure 5.3 Crystal structure of (5.2) (previous page) with unit cell packing arrangement (above)

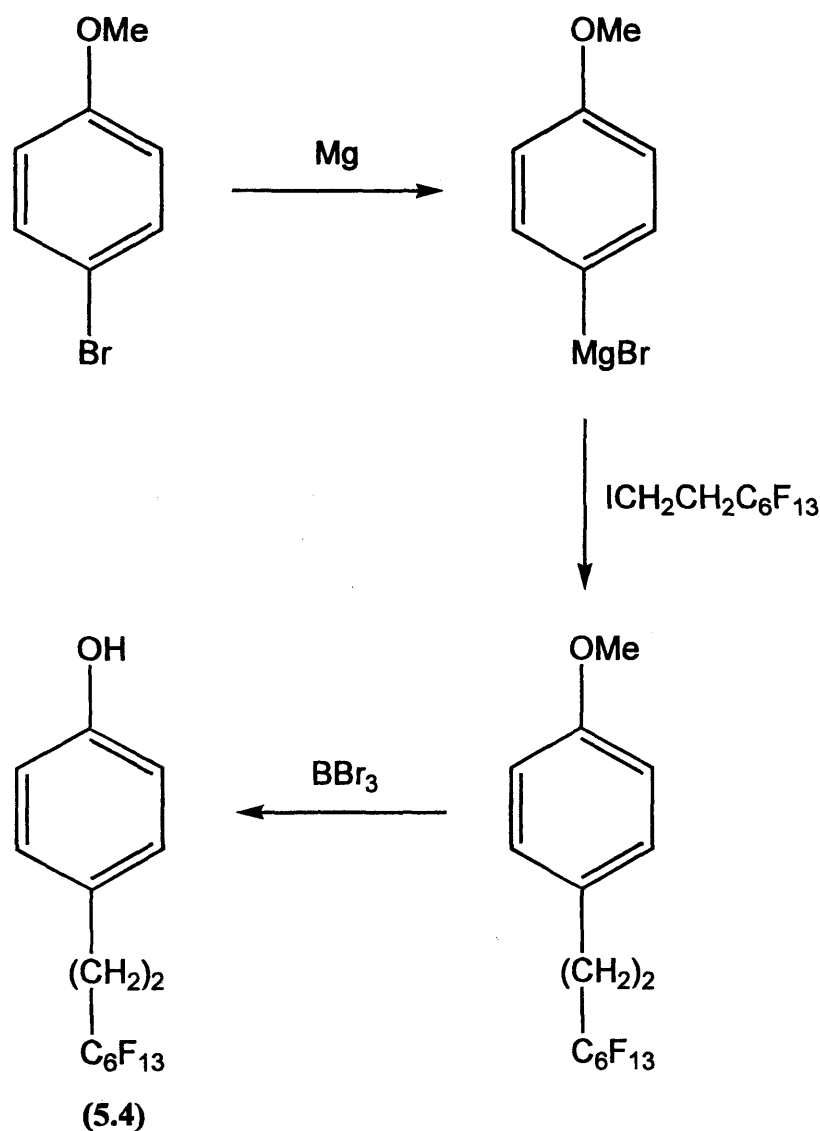
The molecule has a C_2 rotation axis bisecting the biaryl bond with an angle of 87.9° between the aryl rings. These fluorinated ponytails radiate regularly and linearly away from the arene rings wherein the positions of the fluorine atoms are unusually well defined for such a perfluoroalkyl-derivatised molecule and illustrate that the C-F bond lengths become progressively shorter along the tail {av. $1.350 \text{ \AA}$ on C(7) to $1.309 \text{ \AA}$ on C(12)}. The extended view of the structure clearly reveals the fluorine domains in which the perfluoroalkyl groups align and give a number of relatively short, non-bonded, intermolecular F...F contacts. Similar alignment of perfluoroalkyl tails has been observed in previous structural characterisations of perfluoroalkylated metal complexes.^{6,7}

The acetoxypiphenol intermediate was then deprotected using NaH over a period of five minutes, followed by quenching with HCl, to afford the perfluoroalkyl-derivatised biphenol (5.3) as a white solid which was purified by recrystallisation from hexane.



(5.3)

Following unsuccessful attempts to prepare metal salts of these derivatised phenols and biphenols (see below), an alternative perfluoroalkyl-derivatised phenol (**5.4**) was also produced bearing an additional alkyl spacer group between the perfluoroalkyl tail and the aromatic ring. This was achieved by preparing a Grignard reagent from 4-bromoanisole, followed by coupling with 1H,1H,2H,2H-perfluoro-*n*-octyl iodide and, finally, demethylation with BBr₃ (Scheme 5.5).

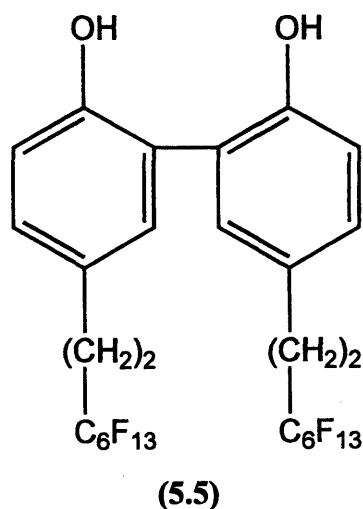


Scheme 5.5 Synthesis of derivatised phenol with additional spacer

The proton NMR spectrum of (**5.4**) exhibits an AA'BB' pattern in the aromatic region typical of a *para*-disubstituted benzene ring, while the ethyl protons gave highly complex resonances from which the individual couplings could not be

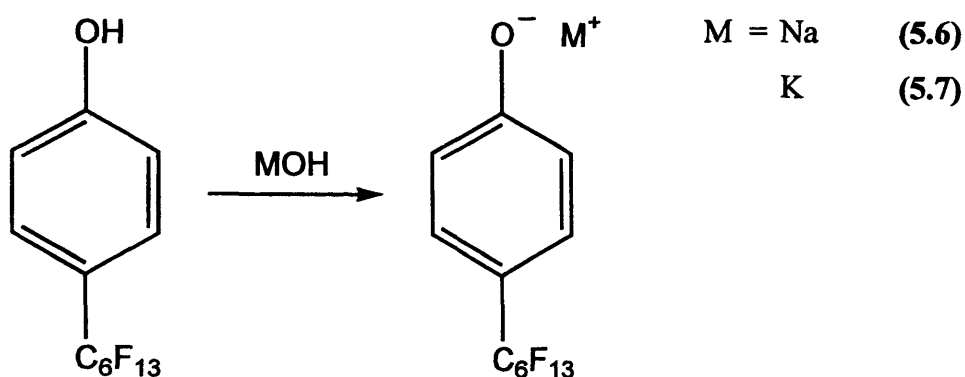
resolved. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum exhibits six distinct resonances, arising from the six inequivalent fluorine environments, at similar chemical shifts to those for (5.1).

Attempts were made to synthesise a fluorinated biphenol containing the additional ethyl spacer group (5.5) using a similar methodology to that used in the synthesis of (5.4). Although a species assigned as (5.5) was observed *via* proton NMR spectroscopy in the reaction mixture, all attempts to isolate the required product proved to be unsuccessful.



5.3 Synthesis of Perfluoroalkyl Derivatised Phenates

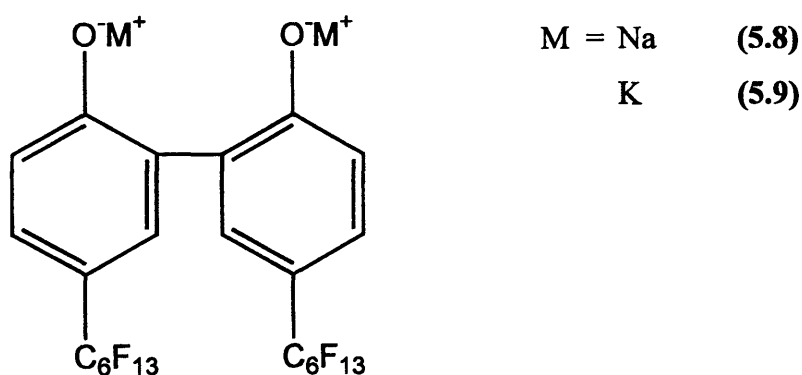
Initially, work was undertaken to prepare two fluorinated phenates by abstracting the phenolic proton, using an alkali metal hydroxide, from the phenol (5.1) bearing the directly attached perfluoroalkyl tail (Scheme 5.6).



Scheme 5.6 Attempted synthesis of fluorinated phenates (5.6) and (5.7)

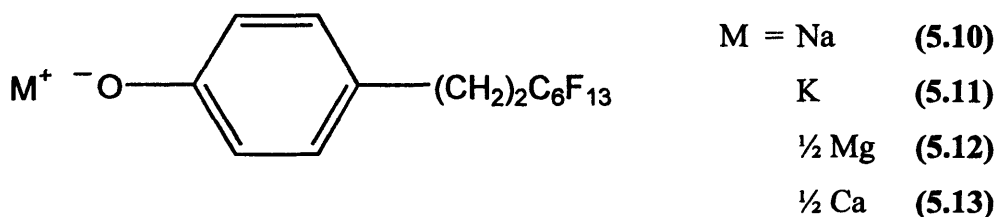
Unfortunately, the desired products could not be obtained. Apparently, during reaction, decomposition of the perfluoroalkyl tail was observed, with a number of new peaks growing in the ^{19}F NMR spectrum over time. All of the new peaks seemed to be centred around the $\alpha\text{-CF}_2$ region of the spectrum with the resonances associated with the other CF_2 groups and the CF_3 remaining unchanged. This was observed every time the reaction was repeated under a variety of different reaction conditions and in different solvents. The reaction was also repeated using metal hydrides as base in place of the metal hydroxides. Again a variable number of curious peaks were observed in the ^{19}F NMR spectrum around the region of the $\alpha\text{-CF}_2$ signal. Attempts to drive the decomposition reaction to completion to allow firm identification of the final decomposition products also proved unsuccessful.

A similar base-catalysed decomposition was also observed when attempts were made to produce (5.8) and (5.9) by analogous reactions with the perfluoroalkylated biphenol (5.3).



Decomposition of this kind has never been observed with phenates which bear hydrocarbon tails, but the instability of (5.1) and (5.3) under basic conditions made their potential use as detergents untenable. Consequently the derivatised phenol with an additional ethyl spacer group, between the perfluoroalkyl tail and the aromatic ring, which would potentially give a stable α -CH₂ whilst still retaining considerable fluorine character was synthesised.

After the formation of the derivatised phenol (5.4), it was possible to form a series of fluorinated phenate compounds (5.10-5.13) by addition of the appropriate metal hydroxide to a stirred solution of the (5.4) in 2,2,2-trifluoroethanol.



The resulting compounds were all afforded as off-white, crystalline solids, which were stable both in air and in solution, with no decomposition being observed.

The ¹H and ¹⁹F NMR spectra of the phenates (5.10-5.13) were almost identical, and were also very similar to those of the parent phenol. Numerous attempts to grow single crystals suitable for X-ray analysis were made from a variety of solvents, but all proved to be unproductive.

5.4 Chapter Conclusions

The work above describes four stable perfluoroalkyl-derivatised phenate compounds which could potentially be used as detergents in fluorocarbon oils. These compounds proved to be difficult to characterise as proton and fluorine NMR spectra were all very similar to those for the parent alcohol. Mass spectrometry failed to provide the parent ion signals while, owing to their high thermal stability, elemental analysis also proved to be inconclusive. Numerous attempts to grow crystals suitable for X-ray diffraction analysis also proved unsuccessful. Physically the phenates have

a far higher crystallinity than the parent alcohol, with a slight colour change also being observed.

If compounds of this nature were to be introduced into an additive package, a number of evaluations would have to take place regarding their compatibility with the other additives. The work reported here is primarily concerned with the formation of perfluorocarbon-soluble anti-wear and extreme pressure additives, but in some cases perfluoroalkyl-derivatised phenates could potentially be blended with compounds which are commercially available. Esters which contain long hydrocarbon tails have recently been introduced to hydrocarbon lubricants.⁸ Due to the polarity of the ester, it adsorbs onto the surface of the components in need of lubrication with the alkyl tails radiating away. This leads to the lubricant having a greater wetability, owing to the base fluids high affinity for the alkyl tails of the ester. Lubricant packages containing additives of this nature have been proven to be particularly effective for applications involving machinery which has to regularly tolerate cold starts. This principle could potentially be adapted to a fluorinated base fluid by using commercially available esters which bear long perfluoroalkyl tails.

5.5 Experimental Procedures

5.5.1 Preparation of Perfluoroalkyl-Derivatised Phenols

(4-tridecafluoro-*n*-hexyl) phenol (**5.1**) was prepared by the literature route.⁵

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.3 (d, 2H, $^3J_{\text{H-H}}$ 7.1 Hz, 2,6-ArH), 6.9 (d, 2H, $^3J_{\text{H-H}}$ 7.1 Hz, 3,5-ArH), 5.2 (s, 1H, OH); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.3 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -110.2 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, α -CF₂), -121.9 (um, 2F, β -CF₂), -122.4 (um, 2F, δ -CF₂), -123.2 (um, 2F, ε -CF₂), -126.6 (um, 2F, γ -CF₂); m/z (EI) 412 ([M]⁺).

*5,5'-bis(4-tridecafluoro-*n*-hexyl) 2,2'-acetoxybiphenol (5.2)* was prepared by the literature route.⁵

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.6 (dd, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^4J_{\text{H-H}}$ 2.1 Hz, 4,4'-ArH), 7.5 (d, 2H, $^4J_{\text{H-H}}$ 2.1 Hz, 6,6'-ArH), 7.3 (d, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, 3,3'-ArH), 2.0 (s, 6H, CH₃); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.3 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -110.8 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, α -CF₂), -121.9 (um, 2F, β -CF₂), -122.0 (um, 2F, δ -CF₂), -123.3 (um, 2F, ε -CF₂), -126.6 (um, 2F, γ -CF₂); m/z (EI) 906 ([M]⁺).

*5,5'-bis(4-tridecafluoro-*n*-hexyl) 2,2'-biphenol (5.3)* was prepared by the literature route.⁵

$\delta_{\text{H}}(d^4\text{-MeOH})$ 7.6 (dd, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^4J_{\text{H-H}}$ 2.1 Hz, 4,4'-ArH), 7.5 (d, 2H, $^4J_{\text{H-H}}$ 2.1 Hz, 6,6'-ArH), 7.3 (d, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, 3,3'-ArH), 5.0 (s, 2H, OH); $\delta_{\text{F}}(d^4\text{-MeOH})$ -83.0 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -111.0 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, α -CF₂), -122.9 (um, 2F, β -CF₂), -123.6 (um, 2F, δ -CF₂), -124.4 (um, 2F, ε -CF₂), -127.9 (um, 2F, γ -CF₂); m/z (EI) 822 ([M]⁺).

*Preparation of 4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenol (5.4)*

Bromoanisole (25.00 g, 1.34×10^{-1} mol) dissolved in 50 cm³ dry diethyl ether was added, over a period of 1 hour, to a stirred slurry of magnesium turnings (3.25 g, 1.34×10^{-1} mol) in diethyl ether (25 cm³). After addition was complete the mixture was heated to reflux for 1 hour. The Grignard solution was filtered under nitrogen before being dropped onto a solution of 1H,1H,2H,2H-perfluoro-*n*-octyl iodide (49.18 g, 1.04×10^{-1} mol) and Cu(cod)Cl (1.00×10^{-1} g, 4.83×10^{-4} mol) dissolved in THF (100 cm³). The resulting mixture was stirred at room temperature for 3 days before being heated to reflux for 4 hours. The reaction mixture was hydrolysed with 200 cm³ saturated aqueous ammonium hydroxide before the organic layer was separated, washed with water (3 x 50 cm³) and dried over Na₂SO₄ and CaCl₂. After filtering the solvent was removed *in vacuo* leaving a yellow slurry. This was subsequently distilled *in vacuo* using Kugelröhr apparatus (bp 65-70 °C, 0.05 mmHg). Boron tribromide (2.65 g, 1.06×10^{-2} mol) dissolved in dichloromethane (10 cm³) was then

dropped to a solution of the distillation product in dichloromethane (100 cm³) over 10 minutes at -70 °C. The mixture was then stirred at -70 °C for 1 hour, -15 °C for three hours then allowed to warm to room temperature overnight. After hydrolysis with water (50 cm³) diethyl ether (50 cm³) was added to solubilise the product. The organic layer was separated, washed with water (3 x 50 cm³) and dried over Na₂SO₄ before the solvent was removed *in vacuo* leaving a viscous oil which solidified over time.

$\delta_{\text{H}}(\text{CDCl}_3)$ 7.0 (dt, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^5J_{\text{H-H}}$ 2.0 Hz 2,6-ArH), 6.7 (dt, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^4J_{\text{H-H}}$ 2.5 Hz, 3,5-ArH), 2.8 (um, 2H, Ar-CH₂), 2.2 (um, 2H, R_F-CH₂); $\delta_{\text{F}}(\text{CDCl}_3)$ -81.3 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -115.0 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, α -CF₂), -122.3 (um, 2F, β -CF₂), -123.3 (um, 2F, δ -CF₂), -124.0 (um, 2F, ϵ -CF₂), -126.6 (um, 2F, γ -CF₂); *m/z* (ES) 439 ([M - H]⁻, 100 %).

5.5.2 Preparation of Perfluoroalkyl-Derivatised Phenates

*Preparation of Na{4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenate} (5.10)*

Powdered sodium hydroxide (3.90 x 10⁻² g, 9.79 x 10⁻⁴ mol) was added to a stirred solution of 4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenol (4.31 x 10⁻¹ g, 9.79 x 10⁻⁴ mol) in 2,2,2-trifluoroethanol (25 cm³). The mixture was stirred at room temperature for 10 minutes. The solvent was removed and the off-white solid product, given in quantitative yield (4.51 x 10⁻¹ g, 9.79 x 10⁻⁴ mol), was dried *in vacuo*.

$\delta_{\text{H}}(d_4\text{-MeOH})$ 7.1 (dt, 2H, $^3J_{\text{H-H}}$ 8.3 Hz, $^5J_{\text{H-H}}$ 1.9 Hz 2,6-ArH), 6.8 (dt, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^4J_{\text{H-H}}$ 2.4 Hz, 3,5-ArH), 3.0 (um, 2H, Ar-CH₂), 2.5 (um, 2H, R_F-CH₂); $\delta_{\text{F}}(d_4\text{-MeOH})$ -81.0 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -114.3 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, α -CF₂), -121.6 (um, 2F, β -CF₂), -122.5 (um, 2F, δ -CF₂), -123.1 (um, 2F, ϵ -CF₂), -125.9 (um, 2F, γ -CF₂); *m/z* (ES) 439 ([M - Na]⁻, 100 %).

Preparation of $K\{4-(1H,1H,2H,2H\text{-perfluoro-}n\text{-octyl})\text{phenate}\}$ (5.11)

Powdered potassium hydroxide (6.30×10^{-2} g, 1.12×10^{-3} mol) was added to a stirred solution of 4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenol (4.95×10^{-1} g, 1.12×10^{-3} mol) in 2,2,2-trifluoroethanol (25 cm^3). The mixture was stirred at room temperature for 10 minutes. The solvent was removed and the off-white solid product, given in quantitative yield (5.35×10^{-1} g, 1.12×10^{-3} mol), was dried *in vacuo*.

$\delta_H(d_4\text{-MeOH})$ 7.1 (dt, 2H, $^3J_{H-H}$ 8.5 Hz, $^5J_{H-H}$ 2.0 Hz 2,6-ArH), 6.8 (dt, 2H, $^3J_{H-H}$ 8.5 Hz, $^4J_{H-H}$ 2.5 Hz, 3,5-ArH), 3.0 (um, 2H, Ar-CH₂), 2.5 (um, 2H, R_F-CH₂); $\delta_F(d_4\text{-MeOH})$ -81.1 (t, 3F, $^3J_{F-F}$ 10 Hz, CF₃), -114.3 (t, $^3J_{F-F}$ 15 Hz, 2F, α -CF₂), -121.6 (um, 2F, β -CF₂), -122.5 (um, 2F, δ -CF₂), -123.1 (um, 2F, ϵ -CF₂), -126.0 (um, 2F, γ -CF₂); *m/z* (ES) 439 ([M - K]⁺, 100 %).

Preparation of $Mg\{4-(1H,1H,2H,2H\text{-perfluoro-}n\text{-octyl})\text{phenate}\}_2$ (5.12)

Powdered magnesium hydroxide (3.80×10^{-2} g, 6.51×10^{-4} mol) was added to a stirred solution of 4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenol (5.73×10^{-1} g, 1.30×10^{-3} mol) in 2,2,2-trifluoroethanol (25 cm^3). The mixture was stirred at room temperature for 10 minutes. The solvent was removed and the off-white solid product, given in quantitative yield (5.88×10^{-1} g, 6.51×10^{-4} mol), was dried *in vacuo*.

$\delta_H(d_4\text{-MeOH})$ 7.1 (dt, 2H, $^3J_{H-H}$ 8.5 Hz, $^5J_{H-H}$ 2.0 Hz 2,6-ArH), 6.8 (dt, 2H, $^3J_{H-H}$ 8.5 Hz, $^4J_{H-H}$ 2.5 Hz, 3,5-ArH), 3.0 (um, 2H, Ar-CH₂), 2.5 (um, 2H, R_F-CH₂); $\delta_F(d_4\text{-MeOH})$ -82.9 (t, 3F, $^3J_{F-F}$ 10 Hz, CF₃), -116.1 (t, $^3J_{F-F}$ 14 Hz, 2F, α -CF₂), -123.4 (um, 2F, β -CF₂), -124.4 (um, 2F, δ -CF₂), -125.0 (um, 2F, ϵ -CF₂), -127.8 (um, 2F, γ -CF₂); *m/z* (ES) 439 ([$\frac{1}{2}$ M - Mg]⁺, 100 %).

Preparation of $\text{Ca}\{4-(1\text{H},1\text{H},2\text{H},2\text{H-perfluoro-}n\text{-octyl})\text{phenate}\}_2$ (5.13)

Powdered calcium hydroxide (5.70×10^{-2} g, 7.63×10^{-4} mol) was added to a stirred solution of 4-(1H,1H,2H,2H-perfluoro-*n*-octyl) phenol (6.72×10^{-1} g, 1.53×10^{-3} mol) in 2,2,2-trifluoroethanol (25 cm^3). The mixture was stirred at room temperature for 10 minutes. The solvent was removed and the off-white solid product, given in quantitative yield (7.01×10^{-1} g, 7.63×10^{-4} mol), was dried *in vacuo*.

$\delta_{\text{H}}(d_4\text{-MeOH})$ 7.0 (dt, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^5J_{\text{H-H}}$ 2.0 Hz 2,6-ArH), 6.7 (dt, 2H, $^3J_{\text{H-H}}$ 8.5 Hz, $^4J_{\text{H-H}}$ 2.5 Hz, 3,5-ArH), 2.8 (m, 2H, Ar-CH₂), 2.3 (m, 2H, R_F-CH₂); $\delta_{\text{F}}(d_4\text{-MeOH})$ -82.9 (t, 3F, $^3J_{\text{F-F}}$ 10 Hz, CF₃), -116.2 (t, $^3J_{\text{F-F}}$ 15 Hz, 2F, $\alpha\text{-CF}_2$), -123.5 (um, 2F, $\beta\text{-CF}_2$), -124.2 (um, 2F, $\delta\text{-CF}_2$), -122.0 (um, 2F, $\varepsilon\text{-CF}_2$), -127.8 (um, 2F, $\gamma\text{-CF}_2$); *m/z* (ES) 439 ([$\frac{1}{2}$ M - Ca]⁺, 100 %).

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6.1 Introduction

The anti-wear and extreme pressure evaluation methods described in this chapter are intended to eliminate trends and allow valid comparisons to be made between the function of perfluorinated-ether-based and perfluorinated-ether-based compounds. Here, a selection of perfluorinated-ether-based compounds, both fluorinated and non-fluorinated, have been used in a mineral oil base fluid to give an overview of potential additive activity. Owing to the inavailability of conventional perfluorinated-ether-based compounds in PFPE base fluids, evaluations have to be made in mineral oil base fluids. This is a limitation, where additives allow, to provide a comparison with similar tests carried on the base fluids alone. All of the anti-wear and extreme pressure evaluations reported in this chapter were carried out in mineral oil base fluids, in accordance with the industry standard procedures.

CHAPTER SIX

Oil Additive Evaluation

6.1.1 Introduction to Additive Evaluation

Following the synthesis of potential oil additives it is essential to test them in a controlled manner to allow a comparison of their function with that of the base fluid system to be made. A number of standard tests can be employed to do this, including Four Ball¹ and SRV tests.

In the Four Ball test, a rotating ball is rotated on three identical fixed balls which are immersed in the lubricant sample. The load can be adjusted and the friction coefficient and ball scar depth can be measured. These measurements are indicative of the anti-wear and extreme pressure properties of the additive. The second testing procedure which is used is the SRV test. This is a high frequency, high pressure (3000 psi) test machine, which has been the method utilized for the evaluation of the samples in this project. Using this machine it is possible to carry out two investigations on the prospective additive dispersed in a standard base fluid:

- Friction and wear properties
- Extreme pressure properties



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6.1 Introduction

The anti-wear and extreme pressure evaluations described in this chapter are intended to illustrate trends and allow initial comparisons to be made between the function of perfluoroalkyl-derivatised and perprotio-derivatised compounds. Here, a selection metal complexes, both fluorinated and non-fluorinated, have been tested in a mineral oil base fluid to give an overview of potential additive activity. Owing to the insolubility of conventional perprotio additives in PFPE base fluids, evaluations have to be made in mineral oil to allow any direct comparison. In addition to this, a selected group of additives have been evaluated in Fomblin® PFPE lubricants, where solubilities allow, to provide a comparison with similar tests carried on the base fluids alone. All of the anti-wear and extreme pressure evaluations reported in this chapter were carried out by Castrol International Ltd. in accordance with the industry standard procedures outlined below.

6.1.1 Introduction to Additive Evaluation

Following the synthesis of potential oil additives, it is essential to test them in a controlled manner to allow a comparison of their function with that of the base fluid system to be made. A number of standard tests can be employed to do this, including Four Ball¹ and SRV tests.

In the Four Ball test, a bearing ball is rotated on three identical fixed balls which are immersed in the lubricant sample. The load can be adjusted and the friction coefficient and ball scar depths can be measured. These measurements are indicative of the anti-wear action of the additive, with small ball scar depths and low average friction coefficients representing good additive function. The second testing procedure, which has been adopted as the industry standard, uses a high frequency, linear oscillation (SRV) test machine, which has been the method utilized for the evaluation of the samples in this project. Using this machine it is possible to carry out two investigations on the prospective additive dissolved in a standard base fluid:

- Friction and wear properties
- Extreme pressure properties

For both experiments the same basic apparatus is used. This consists of a test ball oscillating under load, against a test disk with the lubricant disposed between the two (Figure 6.1). The industry standard specifies conditions such as the dimensions for test balls and disks, the stroke length and the oscillation speed but it is possible to vary these for the purposes of comparison.

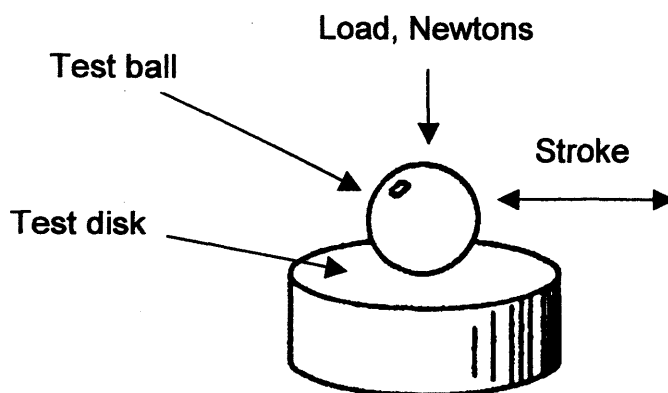


Figure 6.1 Schematic diagram of test apparatus

6.1.2 Measurement of Friction and Wear Properties²

This test is performed using a test ball which oscillates under a constant load against a test disk. The wear scar on the test ball and the coefficient of friction can be measured and directly compared to results from other lubricants tested under identical conditions. It is also possible to measure the trace wear scar on the disk to provide additional information. This test can be performed at selected temperatures and loads specified for use in particular applications.

The standard method for this test is as follows:

- 1) Set test frequency to 50 Hz and duration to 2 hours.
- 2) Place 0.1 – 0.2 g of lubricant on the test plate, and place test ball on top of this.
- 3) Load to 50 Newtons (kgms^{-2}) for break-in.
- 4) Set temperature and allow to equilibrate.
- 5) Start oscillation, and allow break-in for 30 seconds.
- 6) Load to 200 Newtons and run for 2 hours.

During the experiment a plotter shows the measured friction coefficient of the ball, while the scar measurements need to be made by physical methods at the end of the test.

6.1.3 Measurement of Extreme Pressure Properties³

This test is performed using the same apparatus as above but the test ball oscillates against a test disk under an increasing load. Here the load is increased in increments of 100 Newtons until either seizure occurs, or the system reaches a maximum of 1400 Newtons. The test can be performed at selected temperatures and provides a rapid way of comparing extreme pressure properties of different lubricants under identical conditions.

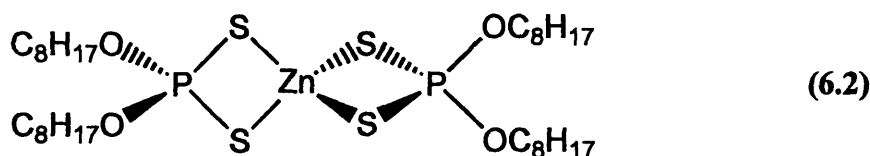
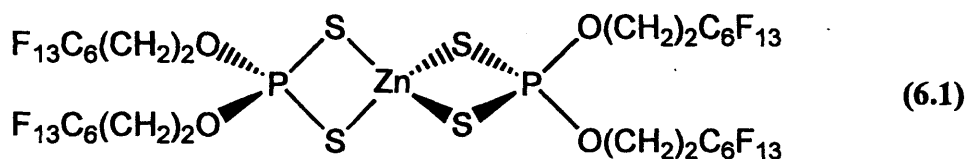
The standard method for this test is as follows:

- 1) Set test frequency to 50 Hz.
- 2) Place 0.1 – 0.2 g of lubricant on the test plate, and place test ball on top of this.
- 3) Load to 50 Newtons for break-in.
- 4) Set temperature and allow to equilibrate.
- 5) Start oscillation, and allow break-in for 30 seconds.
- 6) Increase load to 100 Newtons and maintain for 2 minutes.
- 7) Increase load by 100 Newtons every 2 minutes until 1400 Newtons is reached or failure occurs due to seizure.

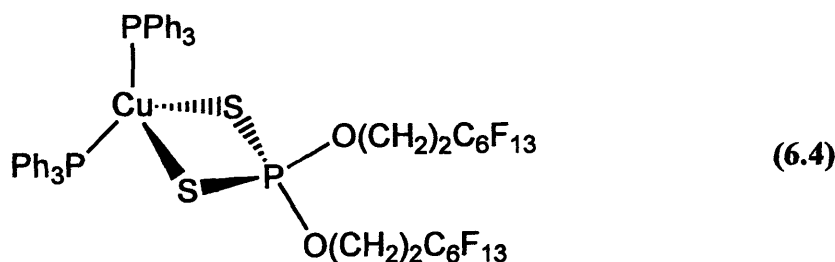
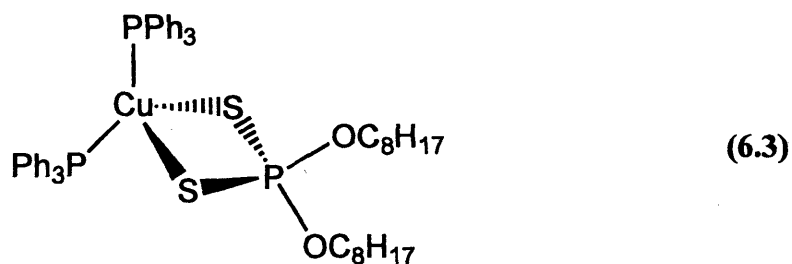
During the experiment a plotter shows the measured friction coefficient of the ball as a stepwise increase due to the increase in load. Failure can be indicated as a dramatic rise in friction coefficient, or a stoppage in the oscillation of the test machine.

6.2 Hydrocarbon Base Fluids

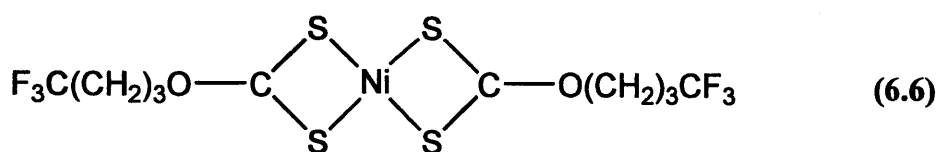
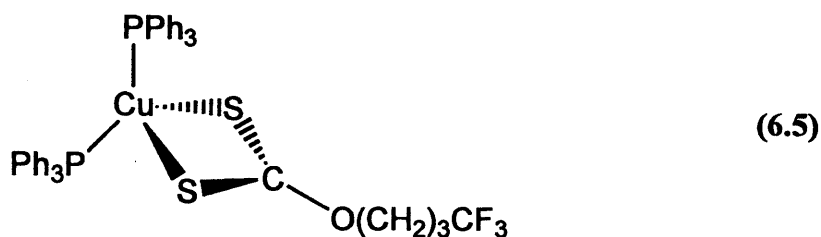
The samples were selected for this test to give a representation of a number of metal centres and both dithiophosphate and xanthate ligand systems. Firstly, conventional type zinc DTP additive (6.1) and (6.2) complexes were selected to allow a direct comparison between perfluoroalkyl and perprotio compounds.



Secondly, a copper DTP compound (6.3) and its fluorinated analogue (6.4) were chosen so as direct comparison could be made regarding the presence of the perfluoroalkyl groups in a system which is not a conventionally recognised class of oil additive.



Finally, so that a comparison between DTP and other ligand systems could be made, copper xanthate (6.5) and nickel xanthate (6.6) complexes were also considered.



All of the evaluations reported below were carried out by making up a 1 % w/w solution of the additive in 220 cSt mineral oil followed by the test procedures described in Section 6.1, above.

6.2.1 Anti-Wear Testing of Selected Compounds

The results of the friction and wear evaluations in accordance with the methods outlined above are summarised in Table 6.1.

System	Average Friction Coefficient	Ball Scar Depth / mm	Disk Scar Depth / μm
220 cSt Base Fluid	0.140	1.050	> 20
220 cSt + 1 % (6.1)	0.108	0.522	0.6
220 cSt + 1 % (6.2)	0.116	0.606	< 0.4
220 cSt + 1 % (6.3)	0.118	0.629	5.7
220 cSt + 1 % (6.4)	0.107	0.526	< 0.4
220 cSt + 1 % (6.5)	0.120	0.890	17
220 cSt + 1 % (6.6)	0.117	0.614	1.2

Table 6.1 Friction and wear test data for additives in 220 cSt mineral oil

If the results are considered generally, all additives appear to give improvement over the base fluid alone, when considering both friction coefficient and scar depths. The conventional type DTP additives give the largest improvement, with the presence of the perfluoroalkyl groups on (6.1) seemingly having a beneficial effect in comparison to the hydrocarbon groups on (6.2). The copper DTP compounds give the next best improvement, although in industrial applications copper additives are scarcely used as a result of the metal having the ability to act as a pro-oxidant to the base fluid, thus accelerating degradation of the oil. Interestingly, if the copper DTP additives (6.3) and (6.4) are considered, the fluorinated compound appears to outperform its hydrocarbon analogue in each of the three measurements taken, bringing it closer to the performance of (6.1). Finally, the xanthate compounds perform worst of all in comparison to the dithiophosphates. Although (6.6) appears to give good improvement over the base fluid, the relatively low molecular mass of the compound means that the amount of metal in a 1 % w/w solution is greatly increased. This is believed to be one of the contributory effects in the reduction of friction as a result of the possibility of a low-shear metal sulfide layer forming.⁴ If this is taken into account, the performance of (6.1) bearing four perfluoroalkyl tails, and consequently having the highest relative molecular mass, gives encouragement that the presence of fluorinated groups does not have a detrimental effect on additive action.

Often the shape of the trace of friction coefficient against time, plotted during the experiment, can give clear information about the feasibility of a potential additive. In the friction and wear test, the optimum shape would be a straight line at the lowest friction coefficient possible. The test traces (Figure 6.2) show that all compounds, perhaps with the exception of (6.5), give a significantly smoother pattern than that for the mineral oil alone, implying that lubrication between the ball and disk is more consistent.

6.2.2 Extreme Pressure Testing of Selected Compounds

All of the compounds tested above were also evaluated as extreme pressure additives in accordance with the methods outlined in Section 6.1. The seizure points for each of these assessments are summarised in Table 6.2.

System	Failure Point / N
220 cSt Base Fluid	1200
220 cSt + 1 % (6.1)	> 1400
220 cSt + 1 % (6.2)	> 1400
220 cSt + 1 % (6.3)	> 1400
220 cSt + 1 % (6.4)	1200
220 cSt + 1 % (6.5)	700
220 cSt + 1 % (6.6)	1300

Table 6.2 Extreme pressure test data for additives in 220 cSt mineral oil

The table shows that three of the DTP complexes, (6.1), (6.2) and (6.3), prolong seizure significantly to a value beyond the capability of the test apparatus, while (6.4) has no effect. The xanthate complexes, however, seem to have either a passive or detrimental effect on the failure point. As with the friction and wear tests, the trace shape can give important information. Figure 6.3 shows extreme pressure test traces for all of the compounds evaluated. In extreme pressure tests of this nature, the optimum trace shape is a smooth, stepwise increase of friction coefficient as additional load is applied. In the assessments performed on the six potential additives, all DTP compounds showed improvement over the base fluid, giving traces close to the optimum pattern. The xanthate complexes, however, when at higher loads, either seized or gave an extremely irregular pattern. This is undesirable for use in industrial applications, as large, erratic variations in friction coefficient with varying loads can cause physical damage to the components, which perhaps suggests another reason why xanthate compounds are rarely used.

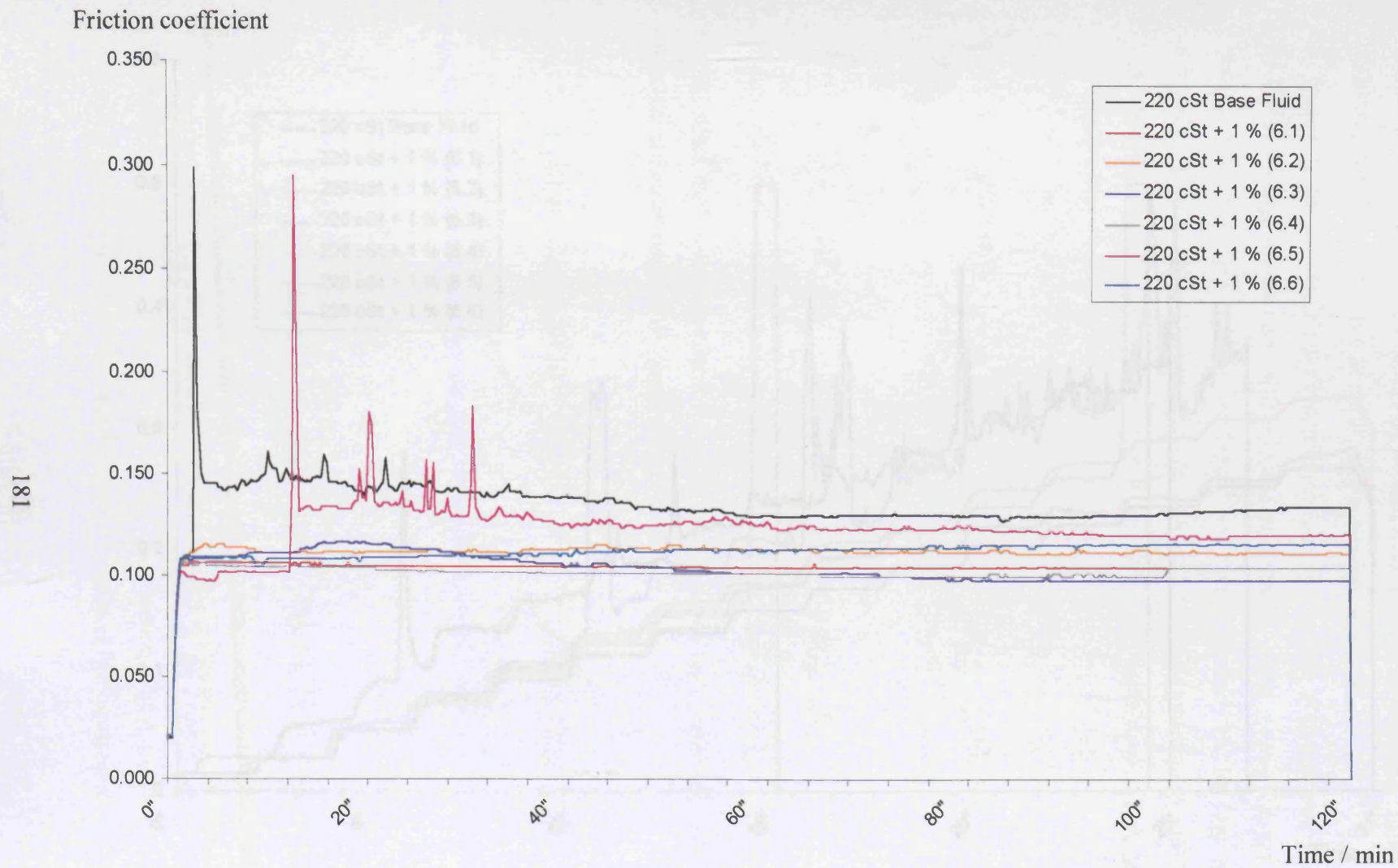


Figure 6.2 Friction and wear test traces for selected additives in 220 cSt mineral base fluid

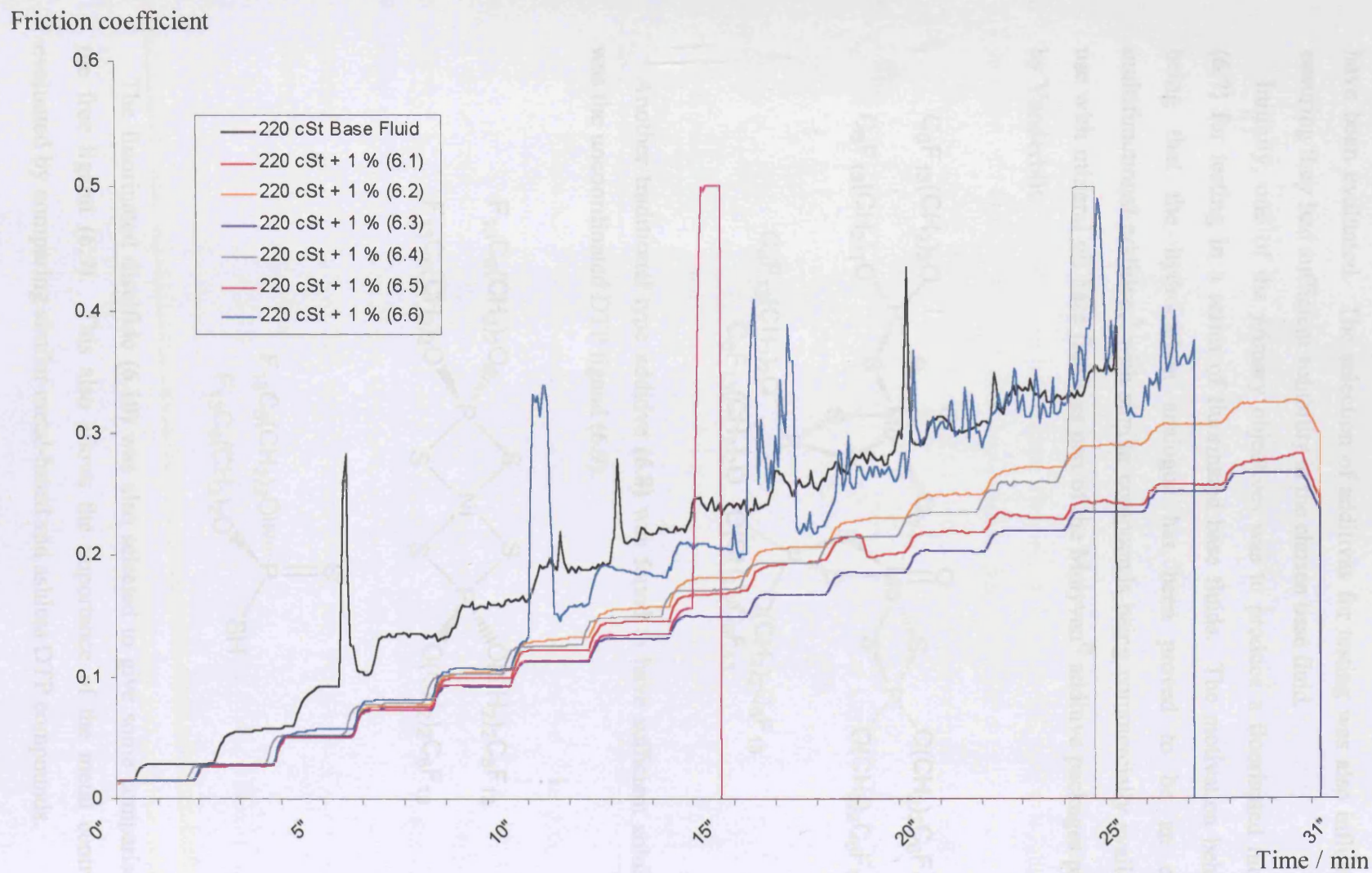
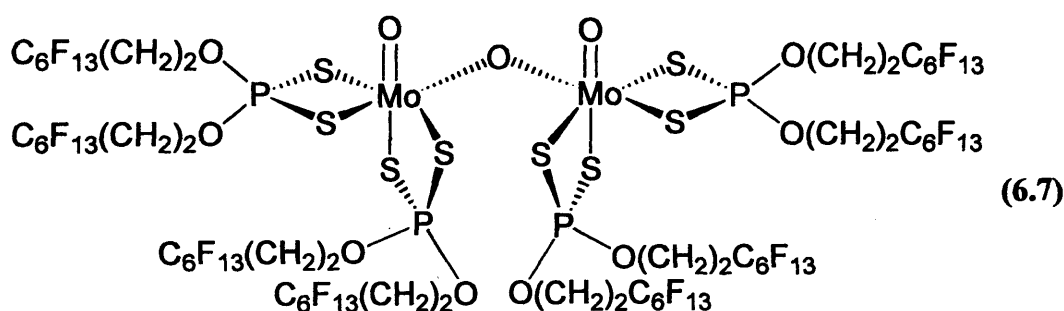


Figure 6.3 Extreme pressure test traces for selected additives in 220 cSt mineral base fluid

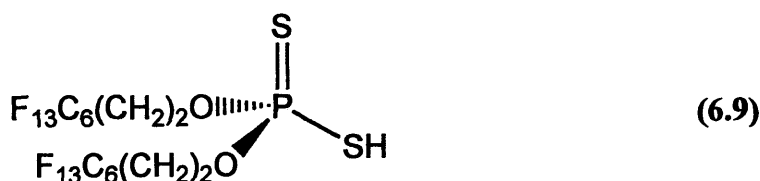
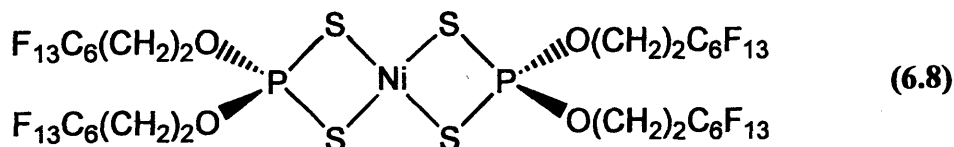
6.3 Fluorinated Base Fluids

As with the mineral oil additives, only a small number of the compounds produced have been evaluated. The selection of additives for testing was also influenced by ensuring they had sufficient solubility in the chosen base fluid.

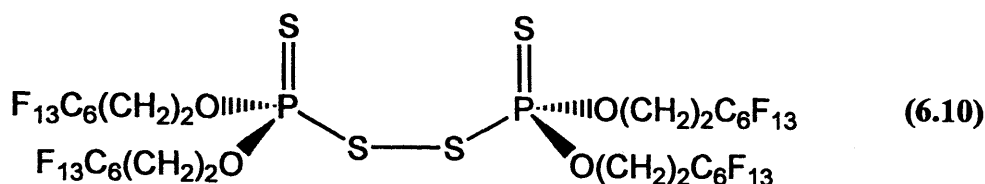
Initially, one of the primary objectives was to produce a fluorinated molybdate (6.7) for testing in a series of fluorinated base fluids. The motivation behind this being that the hydrocarbon analogue has been proved to be an effective multifunctional additive,⁵ with similar compounds being commercially available for use with mineral oil base fluids as part of the Molyvan[®] additive packages produced by Vanderbilt.



Another traditional type additive (6.8) was found to have sufficient solubility as was the uncoordinated DTP ligand (6.9).



The fluorinated disulfide (6.10) was also selected to give some comparison with the free ligand (6.9). This also allows the importance of the metal centre to be evaluated by comparing similar metal-based and ashless DTP compounds.



6.3.1 Evaluation of Fluorinated Molybdate Complex

The two perfluoropolyether base fluids used here for testing purposes, are both from the commercially available Fomblin[®] range produced by Ausimont.

Evaluation of both anti-wear and extreme pressure properties of (6.7) were carried out in accordance with the procedures outlined in Section 6.1, and conducted on a solution of 1 % w/w additive in the appropriate base fluid.

The results for the friction and wear experiments are summarised in Table 6.3.

System	Average Friction Coefficient	Ball Scar Depth / mm	Disk Scar Depth / μm
Fomblin [®] LC200	0.126	0.936	10.0
Fomblin [®] LC200 + 1 % (6.7)	0.125	0.645	7.5
Fomblin [®] Z25	0.128	0.950	8.0
Fomblin [®] Z25 + 1 % (6.7)	0.124	1.265	12.0

Table 6.3 Friction and wear test data for (6.7) in Fomblin[®] base fluids

From this it can be concluded that the presence of the additive in the Fomblin[®] LC200 base fluid reduced the wear on both the ball and the disk by almost 25 %. This constitutes a significant improvement over the base fluid alone, although the presence of the additive had very little effect on the friction coefficient measured during the two experiments.

If the other base fluid is now considered, the presence of the additive seems to have a significantly detrimental effect. Here, when 1 % of (6.7) is dissolved in Fomblin[®] Z25, the wear scar depths on both components increase by over 25 %. Again, the effect of the additive on the friction coefficient during the test was

negligible, with all four experiments giving an average friction coefficient of around 0.125.

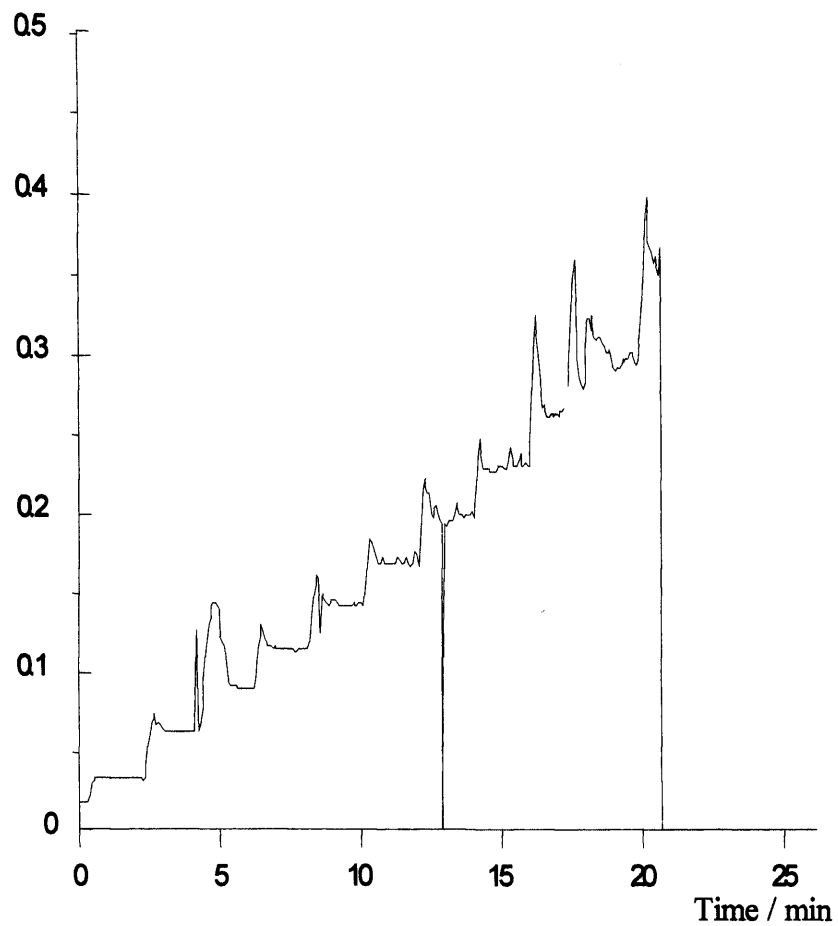
Extreme pressure tests were also performed on the same four systems, with Table 6.4 showing the seizure points for each.

System	Failure Point / N
Fomblin® LC200	1200
Fomblin® LC200 + 1 % (6.7)	1000
Fomblin® Z25	500
Fomblin® Z25 + 1 % (6.7)	500

Table 6.4 Extreme pressure test data for (6.7) in Fomblin® base fluids

From this, it can be seen that the additive had no effect on the extreme pressure properties of the Fomblin® Z25 base fluid, but it slightly reduced the load carrying capability of the Fomblin® LC200 lubricant by reducing the seizure point to a load of 1000 Newtons. What is apparent, however, is that the trace shape for the sample containing the additive is far smoother (Figure 6.4) than those for the base oils alone. As a result of (6.7) showing no positive compatibility with the Fomblin® Z25 base fluid, all further evaluation tests on other additives were performed in Fomblin® LC200 only.

Friction coefficient



Friction coefficient

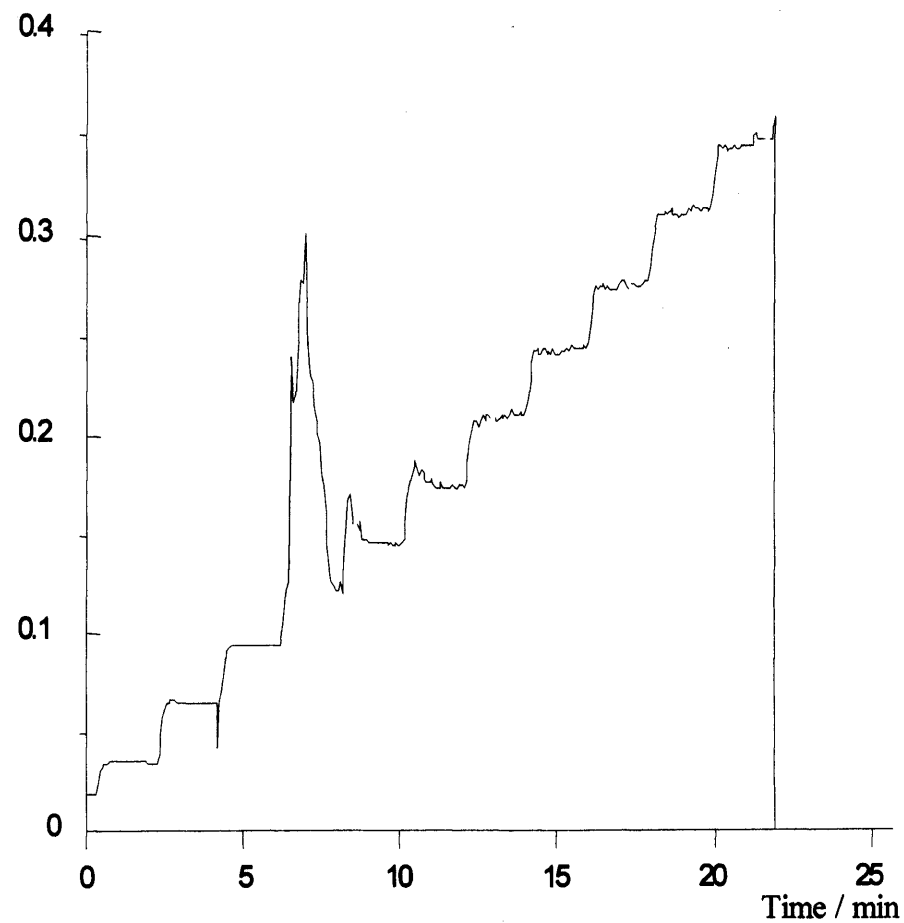


Figure 6.4 Extreme pressure test traces for Fomblin® LC200 with (right) and without (left) 1 % (6.7)

6.3.2 Anti-Wear Testing of Selected Compounds

The results of the friction and wear evaluations in accordance with the methods outlined above are summarised in Table 6.5.

System	Average Friction Coefficient	Ball Scar Depth / mm	Disk Scar Depth / μm
Fomblin [®] LC200	0.126	0.936	10.0
Fomblin [®] LC200 + 1 % (6.7)	0.125	0.645	7.5
Fomblin [®] LC200 + 1 % (6.8)	0.121	1.044	8.0
Fomblin [®] LC200 + 1 % (6.9)	0.130	0.984	10.0
Fomblin [®] LC200 + 1 % (6.10)	0.135	1.055	10.0

Table 6.5 Friction and wear test data for additives in Fomblin[®] LC200

From these results it is possible to conclude that the fluorinated analogues of traditional, metal-containing additives (6.7) and (6.8) have a positive effect on the friction and wear properties of the lubricant, with the perfluoroalkyl-derivatised molybdate (6.7) being particularly impressive. The other two compounds tested seem to have very little effect, having a passive action on both average friction coefficient and scar depths. Although not presented here, the traces of friction coefficient versus time show far more erratic plots than those seen with mineral oil base fluids. If this property is considered, the additives tested in the perfluoropolyether give no improvement over the base fluid alone.

6.3.3 Extreme Pressure Testing of Selected Compounds

The seizure points for each of the extreme pressure assessments carried out in Fomblin[®] LC200 are summarised in Table 6.6.

System	Failure Point / N
Fomblin® LC200	1200
Fomblin® LC200 + 1 % (6.7)	1000
Fomblin® LC200 + 1 % (6.8)	1200
Fomblin® LC200 + 1 % (6.9)	1000
Fomblin® LC200 + 1 % (6.10)	900

Table 6.6 Extreme pressure test data for additives in Fomblin® LC200

As with the friction and wear tests, the traditional type additives seem to have the most positive effect. Although the failure point is not improved, the test traces of the samples containing (6.7) and (6.8) do seem to be significantly smoother than that of Fomblin® LC200 alone. The evaluations of (6.9) and (6.10) appear to show a detrimental effect on the failure point and also provided no improvement in the shape of the test trace. This would suggest that the metal centre is significant in the action of anti-wear and extreme pressure oil additives of this nature.

6.4 Additive Evaluation Conclusions

In general, all of the potential additives tested in mineral oil showed improvements in friction coefficients and depths scars over those for the hydrocarbon base fluid alone. Under extreme pressure conditions all of the DTP compounds performed well, but the xanthates had a detrimental effect, possibly explaining the scarcity of test data available in the literature.

When considering the evaluation tests carried out in perfluoropolyethers, the fluorinated analogues of tried and tested compounds (6.7) and (6.8) seemed to perform well while the other compounds gave variable results. One problem which was encountered with all of the PFPE tests was associated with the trace shape. All produced far more erratic patterns than the equivalent mineral oil experiments. This could, in part, be due to the wettability of the oil with respect to the test disk. Mineral oils form thin layers across the surface, whereas, PFPE fluids have a tendency to collect into beads. This can then lead to an extremely variable friction coefficient as

the components come into contact, potentially causing seizure or other mechanical damage.

A further problem is associated with the solubility of the fluorinated additives. Perfluoropolyethers have very low polarities, leaving relatively polar metal complexes with extremely low solubilities. One approach to increasing fluorine phase solubility could be to increase the length of the perfluorinated tail, therefore, increasing the percentage of fluorine in the molecule. Another potential solution could be to add a compound of higher polarity than the base fluid, to aid the solubility of other additives.

References for Chapter Six

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5. P. C. H. Mitchell, *Wear*, 1984, **100**, 281.

CHAPTER SEVEN

General Experimental



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7.1 General Experimental Details

7.1.1 NMR Spectroscopy

^1H , $^{19}\text{F}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at the ambient temperature of the probe unless otherwise stated using deuterated solvents to provide the field/frequency lock. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally using the residual protio solvent resonance relative to TMS ($\delta = 0$ ppm). $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were referenced externally to CFCl_3 ($\delta = 0$ ppm). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced externally to 85 % H_3PO_4 ($\delta = 0$ ppm). All chemical shifts are quoted in δ (ppm) and coupling constants in Hz using the high-frequency positive convention. NMR spectra were recorded on the following spectrometers:

^1H NMR spectra; Bruker ARX 250 spectrometer at 250.13 MHz, Bruker AM 300 spectrometer at 301.37 MHz, Bruker DRX 400 spectrometer at 400.13 MHz.

$^{19}\text{F}\{^1\text{H}\}$ NMR spectra; Bruker ARX 250 spectrometer at 235.34 MHz, Bruker AM 300 spectrometer at 283.57 MHz, Bruker DRX 400 spectrometer at 376.46 MHz.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra; Bruker ARX 250 spectrometer at 101.26 MHz, Bruker AM 300 spectrometer at 121.99 MHz, Bruker DRX 400 spectrometer at 161.97 MHz.

$^{13}\text{C}\{^1\text{H}\}$ NMR spectra; Bruker DRX 400 spectrometer at 100.16 MHz.

NMR samples of air/moisture-sensitive compounds were prepared under an inert atmosphere in a dry-box using previously dried and freeze/pump/thaw degassed deuterated solvents and the spectra run using a 5 mm NMR tube fitted with a screw cap. Samples which were either insoluble in deuterated solvents, or taken directly from reaction mixtures, were run in a 5 mm tube containing a sealed capillary tube containing either D_2O or d^8 -toluene as the lock solvent.

7.1.2 Mass Spectrometry

Fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Kratos Concept 1H mass spectrometer, and were obtained in positive ion mode with 3-nitrobenzyl alcohol used as the matrix for the FAB spectra. Electrospray (ES) mass spectra were recorded on a Micromass Quattro LC spectrometer.

7.1.3 Infra-red Spectroscopy

IR spectra were recorded either as Nujol mulls between KBr plates or as KBr disks on a Digilab FTS40 Fourier transform spectrometer. All spectra were obtained using 64 scans at a resolution of 2 cm^{-1} with data processing carried out using the Bio-Rad Win-IR (v3.04) software package.

7.1.4 Elemental Analyses

Elemental analyses were performed by Butterworth Laboratories Ltd. using the following instruments: Carbon, Hydrogen and Nitrogen – PE 2400; Phosphorus – Leeman 440; Sulfur – Leco 932. Analysis of fluorine has been found, in many cases, to be inaccurate and therefore has not been included. Satisfactory elemental analyses for several compounds could not be obtained due to incomplete combustion as a result of exceptionally high thermal stability. In these cases alternative characterisation was attempted.

7.1.5 X-Ray Crystallography

X-ray crystallographic data was collected on a Siemens P4 four circle diffractometer using a Mo $K\alpha$ radiation source ($\lambda = 0.7107\text{ \AA}$) or a Bruker Apex SMART 2000 diffractometer. Crystal data and structure refinements can be found in the Appendix, whilst a complete set of tabulated data regarding atomic coordinates,

bond lengths and bond angles of structures can be found in electronic format on the accompanying CD-ROM.

7.2 Anhydrous Solvents¹

Where dried and degassed solvents were required they were prepared and stored as follows:

- Dichloromethane; Dried by heating to reflux over calcium hydride, under an atmosphere of nitrogen for 3 days and transferred under nitrogen to a closed ampoule, stored over 4 Å molecular sieves and freeze/pump/thaw degassed prior to use.
- Diethyl ether; Dried by heating to reflux over sodium metal/benzophenone, under an atmosphere of nitrogen for 3 days and transferred under nitrogen to a closed ampoule, stored over 4 Å molecular sieves and freeze/pump/thaw degassed prior to use.
- Toluene; Dried by heating to reflux over sodium metal, under an atmosphere of nitrogen for 3 days and transferred under nitrogen to a closed ampoule, stored over 4 Å molecular sieves and freeze/pump/thaw degassed prior to use.

7.3 Experimental Materials

All chemicals, unless otherwise stated, were purchased from Aldrich Chemical Co. and used as supplied. 2,2,2-trifluoroethanol was purchased from Fluorochem Ltd and used as supplied, whilst all other fluorinated alcohols were purchased from Fluorochem Ltd, and were stored over activated 4 Å molecular sieves prior to use.

Bis-triphenylphosphine copper(I) nitrate was synthesised according to the literature procedure.²

Dess-Martin periodinane was synthesised according to the literature procedure.^{3,4}

(4-tridecafluoro-*n*-hexyl) phenol was synthesised according to the literature procedure.⁵

5,5'-bis(4-tridecafluoro-*n*-hexyl) 2,2'-biphenol was synthesised according to the literature procedure.⁶

7.4 Experimental Procedures

7.4.1 Schlenk Line Procedures⁷

Due to the air- and moisture-sensitivity of some of the reagents and products involved in the synthesis of the ligands, scrupulously anhydrous conditions were maintained throughout. Synthetic procedures with these materials were carried out on a standard Schlenk line consisting of a glass, dual manifold line connected at either end to a vacuum outlet and to a nitrogen source. The vacuum was provided by an NGN PSR/2 rotary pump, protected by a liquid nitrogen trap. Vacuum, nitrogen and all other outlets were isolable by ground-glass Interkey or Young's greaseless taps. Apparatus was connected to the Schlenk line *via* thick walled Neoprene vacuum tubing connected to the outlets.

7.4.2 Glassware

All synthetic procedures were carried out in Pyrex glassware with Quickfit ground-glass joints. Due to the air- and moisture-sensitivity of some of the reagents and products involved in the synthesis of the ligands, all glassware was flame dried under vacuum before use.

7.4.3 Inert Atmosphere Dry-box

Air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere with an oxygen content of less than 5 ppm using a Faircrest auto-recirculating, positive pressure dry-box. The atmosphere was maintained by circulation through columns of molecular sieves and manganese dioxide to remove water and oxygen respectively.

References for Chapter Seven

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Appendix – Crystal Data and Structure Refinement

Table 1. Crystal data and structure refinement for (2.18).

Identification code	2020
Empirical formula	C ₃₂ H ₂₈ O ₄ CaF ₂ Cl ₂ P ₂ O ₇ ·3H ₂ O
Formula weight	1099.39
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P2 ₁
Unit cell dimensions	a = 15.131(3) Å b = 19.648(3) Å c = 19.803(3) Å
Angles	α = 90.00(16)° β = 84.728(13)° γ = 84.800(16)°
Volume	5580.3 Å ³
Z	4
Density	1.428 g cm ⁻³
Absorption	μ = 0.12 mm ⁻¹
R(001)	2024
Crystal size	0.42 × 0.42 × 0.15 mm ³
Time range for data collection	1.83 to 25.00°
Index range	−17 ≤ h ≤ 17, −23 ≤ k ≤ 23, −24 ≤ l ≤ 24
Reflections collected	21388
Independent reflections	3084 [R _{int} = 0.0428]
Completeness to θ = 25.00°	99.3%
Absorption correction	T _{min} = 0.9748
Max. and min. transmission	0.944 and 0.731
Refinement method	Full-matrix least-squares on F ²
Data / restraints / groups	3084 / 0 / 1
Goodness-of-fit on F ²	1.041
Final R indices [I > 2σ(I)]	R ₁ = 0.1461, wR ₂ = 0.3294
Largest diff. peak in hole	1.093 and −0.702 e Å ⁻³



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Appendix – Crystal Data and Structure Refinement

Table 1. Crystal data and structure refinement for (2.18).

Identification code	2026	
Empirical formula	C52 H38 Cu F26 O2 P3 S2	
Formula weight	1409.39	
Temperature	190(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P(-)1	
Unit cell dimensions	a = 15.151(2) Å	$\alpha = 87.120(10)^\circ$.
	b = 19.648(3) Å	$\beta = 82.720(10)^\circ$.
	c = 20.958(3) Å	$\gamma = 69.930(10)^\circ$.
Volume	5812.7(14) Å ³	
Z	4	
Density (calculated)	1.611 Mg/m ³	
Absorption coefficient	0.654 mm ⁻¹	
F(000)	2824	
Crystal size	0.48 x 0.42 x 0.18 mm ³	
Theta range for data collection	1.83 to 25.00°.	
Index ranges	-17 ≤ h ≤ 1, -23 ≤ k ≤ 21, -24 ≤ l ≤ 24	
Reflections collected	21588	
Independent reflections	20354 [R(int) = 0.0428]	
Completeness to theta = 25.00°	99.5 %	
Absorption correction	Psi scan	
Max. and min. transmission	0.944 and 0.737	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20354 / 0 / 1405	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2sigma(I)]	R1 = 0.0759, wR2 = 0.1702	
R indices (all data)	R1 = 0.1491, wR2 = 0.2042	
Largest diff. peak and hole	1.103 and -0.707 e.Å ⁻³	

Table 2. Crystal data and structure refinement for (2.19).

Identification code	1029	
Empirical formula	C ₅₂ H ₆₄ Cu O ₂ P ₃ S ₂	
Formula weight	941.60	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 21.8973(12) Å	α = 90°.
	b = 10.2368(6) Å	β = 110.2240(10)°.
	c = 23.5234(13) Å	γ = 90°.
Volume	4947.9(5) Å ³	
Z	4	
Density (calculated)	1.264 Mg/m ³	
Absorption coefficient	0.661 mm ⁻¹	
F(000)	1992	
Crystal size	0.15 x 0.18 x 0.45 mm ³	
Theta range for data collection	1.57 to 25.00°.	
Index ranges	-22 ≤ h ≤ 26, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27	
Reflections collected	23149	
Independent reflections	8594 [R(int) = 0.0285]	
Completeness to theta = 25.00°	98.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.762	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8594 / 0 / 543	
Goodness-of-fit on F ²	1.036	
Final R indices [I > 2σ(I)]	R1 = 0.0474, wR2 = 0.1270	
R indices (all data)	R1 = 0.0532, wR2 = 0.1308	
Largest diff. peak and hole	1.331 and -0.542 e.Å ⁻³	

Table 3. Crystal data and structure refinement for (2.20) Monomer.

Identification code	1030	
Empirical formula	C ₄₈ H ₃₈ Cu F ₁₈ O ₂ P ₃ S ₂	
Formula weight	1209.35	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 20.0826(17) Å	α = 90°.
	b = 10.1837(9) Å	β = 107.673(2)°.
	c = 26.337(2) Å	γ = 90°.
Volume	5132.1(8) Å ³	
Z	4	
Density (calculated)	1.565 Mg/m ³	
Absorption coefficient	0.705 mm ⁻¹	
F(000)	2440	
Crystal size	0.34 x 0.22 x 0.06 mm ³	
Theta range for data collection	1.62 to 25.55°.	
Index ranges	-24 ≤ h ≤ 24, -12 ≤ k ≤ 12, -31 ≤ l ≤ 31	
Reflections collected	37718	
Independent reflections	9579 [R(int) = 0.0723]	
Completeness to theta = 25.55°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	1.00 and 0.74	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9579 / 0 / 667	
Goodness-of-fit on F ²	0.813	
Final R indices [I > 2σ(I)]	R ₁ = 0.0505, wR ₂ = 0.1030	
R indices (all data)	R ₁ = 0.0978, wR ₂ = 0.1098	
Largest diff. peak and hole	1.439 and -0.588 e.Å ⁻³	

Table 4. Crystal data and structure refinement for (2.20) Dimer.

Identification code	1016	
Empirical formula	C30 H23 Cu F18 O2 P2 S2	
Formula weight	947.08	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.326(2) Å	α = 102.90(3)°.
	b = 13.737(3) Å	β = 101.72(3)°.
	c = 15.130(3) Å	γ = 110.63(3)°.
Volume	1862.2(6) Å ³	
Z	2	
Density (calculated)	1.689 Mg/m ³	
Absorption coefficient	0.904 mm ⁻¹	
F(000)	944	
Crystal size	0.12 x 0.11 x 0.07 mm ³	
Theta range for data collection	1.45 to 27.00°.	
Index ranges	-13 ≤ h ≤ 12, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	
Reflections collected	15956	
Independent reflections	8026 [R(int) = 0.0356]	
Completeness to theta = 27.00°	98.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.962 and 0.912	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8026 / 0 / 457	
Goodness-of-fit on F ²	0.955	
Final R indices [I > 2σ(I)]	R1 = 0.0720, wR2 = 0.2028	
R indices (all data)	R1 = 0.1047, wR2 = 0.2203	
Largest diff. peak and hole	1.703 and -1.187 e.Å ⁻³	

Table 5. Crystal data and structure refinement for (2.21).

Identification code	1066	
Empirical formula	C44 H42 Cu F6 O2 P3 S2	
Formula weight	937.35	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.1380(6) Å	$\alpha = 82.5060(10)^\circ$.
	b = 13.0128(7) Å	$\beta = 77.4490(10)^\circ$.
	c = 14.7399(8) Å	$\gamma = 70.5460(10)^\circ$.
Volume	2138.52(19) Å ³	
Z	2	
Density (calculated)	1.456 Mg/m ³	
Absorption coefficient	0.784 mm ⁻¹	
F(000)	964	
Crystal size	0.52 x 0.18 x 0.13 mm ³	
Theta range for data collection	1.42 to 26.50°.	
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18	
Reflections collected	17431	
Independent reflections	8739 [R(int) = 0.0164]	
Completeness to theta = 26.50°	98.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.914 and 0.725	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8739 / 0 / 523	
Goodness-of-fit on F ²	1.090	
Final R indices [I > 2sigma(I)]	R1 = 0.0812, wR2 = 0.2488	
R indices (all data)	R1 = 0.0902, wR2 = 0.2579	
Largest diff. peak and hole	1.788 and -1.090 e.Å ⁻³	

Table 6. Crystal data and structure refinement for (2.24).

Identification code	1028	
Empirical formula	C40 H34 Cu F6 O2 P3 S2	
Formula weight	881.24	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2809(4) Å	$\alpha = 76.4390(10)^\circ$.
	b = 12.9192(6) Å	$\beta = 74.6150(10)^\circ$.
	c = 16.1068(7) Å	$\gamma = 75.9050(10)^\circ$.
Volume	1967.28(15) Å ³	
Z	2	
Density (calculated)	1.488 Mg/m ³	
Absorption coefficient	0.847 mm ⁻¹	
F(000)	900	
Crystal size	0.30 x 0.27 x 0.11 mm ³	
Theta range for data collection	1.33 to 26.00°.	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19	
Reflections collected	15389	
Independent reflections	7676 [R(int) = 0.0170]	
Completeness to theta = 26.00°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.826	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7676 / 0 / 487	
Goodness-of-fit on F ²	1.083	
Final R indices [I > 2sigma(I)]	R1 = 0.0301, wR2 = 0.0858	
R indices (all data)	R1 = 0.0332, wR2 = 0.0873	
Largest diff. peak and hole	0.508 and -0.245 e.Å ⁻³	

Table 7. Crystal data and structure refinement for (2.25).

Identification code	2056	
Empirical formula	C ₄₉ H ₄₄ Cu O ₄ P ₃ S	
Formula weight	885.35	
Temperature	190(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.6690(10) Å	α = 90.230(10)°.
	b = 10.4710(10) Å	β = 90.100(10)°.
	c = 21.839(2) Å	γ = 103.350(10)°.
Volume	2151.3(4) Å ³	
Z	2	
Density (calculated)	1.367 Mg/m ³	
Absorption coefficient	0.712 mm ⁻¹	
F(000)	920	
Crystal size	0.52 x 0.44 x 0.40 mm ³	
Theta range for data collection	2.00 to 26.00°.	
Index ranges	0 ≤ h ≤ 11, -12 ≤ k ≤ 12, -26 ≤ l ≤ 26	
Reflections collected	8906	
Independent reflections	8384 [R(int) = 0.0484]	
Completeness to theta = 26.00°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.615 and 0.556	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8384 / 0 / 520	
Goodness-of-fit on F ²	1.095	
Final R indices [I > 2σ(I)]	R1 = 0.0462, wR2 = 0.1175	
R indices (all data)	R1 = 0.0612, wR2 = 0.1260	
Largest diff. peak and hole	0.624 and -0.517 e.Å ⁻³	

Table 8. Crystal data and structure refinement for (3.10).

Identification code	1067	
Empirical formula	C45 H47 Cu O P2 S2	
Formula weight	793.43	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2969(5) Å	$\alpha = 79.9780(10)^\circ$.
	b = 13.3013(6) Å	$\beta = 77.6110(10)^\circ$.
	c = 15.1633(7) Å	$\gamma = 85.0340(10)^\circ$.
Volume	1994.87(16) Å ³	
Z	2	
Density (calculated)	1.321 Mg/m ³	
Absorption coefficient	0.766 mm ⁻¹	
F(000)	832	
Crystal size	0.38 x 0.32 x 0.27 mm ³	
Theta range for data collection	1.39 to 27.00°.	
Index ranges	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -19 ≤ l ≤ 19	
Reflections collected	16581	
Independent reflections	8497 [R(int) = 0.0172]	
Completeness to theta = 27.00°	97.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.898 and 0.805	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8497 / 0 / 461	
Goodness-of-fit on F ²	1.117	
Final R indices [I > 2sigma(I)]	R1 = 0.0370, wR2 = 0.1059	
R indices (all data)	R1 = 0.0421, wR2 = 0.1083	
Largest diff. peak and hole	1.138 and -0.566 e.Å ⁻³	

Table 9. Crystal data and structure refinement for (3.14).

Identification code	1033	
Empirical formula	C41 H36 Cu F3 O P2 S2	
Formula weight	791.30	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.8112(10) Å	$\alpha = 90^\circ$.
	b = 19.9411(19) Å	$\beta = 105.546(2)^\circ$.
	c = 17.4493(17) Å	$\gamma = 90^\circ$.
Volume	3624.2(6) Å ³	
Z	4	
Density (calculated)	1.450 Mg/m ³	
Absorption coefficient	0.855 mm ⁻¹	
F(000)	1632	
Crystal size	0.19 x 0.21 x 0.28 mm ³	
Theta range for data collection	1.58 to 26.50°.	
Index ranges	-13 ≤ h ≤ 13, -25 ≤ k ≤ 25, -21 ≤ l ≤ 21	
Reflections collected	29150	
Independent reflections	7516 [R(int) = 0.0592]	
Completeness to theta = 26.50°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.88 and 0.84	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7516 / 0 / 451	
Goodness-of-fit on F ²	1.090	
Final R indices [I > 2sigma(I)]	R1 = 0.0314, wR2 = 0.0926	
R indices (all data)	R1 = 0.0353, wR2 = 0.0941	
Largest diff. peak and hole	0.633 and -0.412 e.Å ⁻³	

Table 10. Crystal data and structure refinement for (3.16).

Identification code	1057	
Empirical formula	C ₁₉ H ₃₂ Cl O Rh S ₂	
Formula weight	478.93	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.4794(3) Å	α = 73.420(1)°.
	b = 13.4425(5) Å	β = 86.859(1)°.
	c = 22.7306(9) Å	γ = 82.052(1)°.
Volume	2169.03(15) Å ³	
Z	4	
Density (calculated)	1.467 Mg/m ³	
Absorption coefficient	1.107 mm ⁻¹	
F(000)	992	
Crystal size	0.38 x 0.19 x 0.15 mm ³	
Theta range for data collection	0.93 to 26.00°.	
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -27 ≤ l ≤ 27	
Reflections collected	16918	
Independent reflections	8398 [R(int) = 0.0177]	
Completeness to theta = 26.00°	98.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.862 and 0.736	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8398 / 0 / 445	
Goodness-of-fit on F ²	1.046	
Final R indices [I > 2σ(I)]	R1 = 0.0257, wR2 = 0.0665	
R indices (all data)	R1 = 0.0291, wR2 = 0.0686	
Largest diff. peak and hole	0.754 and -0.512 e.Å ⁻³	

Table 11. Crystal data and structure refinement for (3.19).

Identification code	1026	
Empirical formula	C15 H21 Cl F3 O Rh S2	
Formula weight	476.80	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.7126(12) Å	$\alpha = 90^\circ$.
	b = 7.4689(5) Å	$\beta = 111.9350(10)^\circ$.
	c = 15.7575(11) Å	$\gamma = 90^\circ$.
Volume	1824.5(2) Å ³	
Z	4	
Density (calculated)	1.736 Mg/m ³	
Absorption coefficient	1.338 mm ⁻¹	
F(000)	960	
Crystal size	0.36 x 0.23 x 0.17 mm ³	
Theta range for data collection	1.31 to 25.03°.	
Index ranges	-19 ≤ h ≤ 19, -8 ≤ k ≤ 8, -18 ≤ l ≤ 18	
Reflections collected	12121	
Independent reflections	3218 [R(int) = 0.0186]	
Completeness to theta = 25.03°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.85 and 0.69	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3218 / 0 / 276	
Goodness-of-fit on F ²	1.073	
Final R indices [I > 2sigma(I)]	R1 = 0.0203, wR2 = 0.0528	
R indices (all data)	R1 = 0.0214, wR2 = 0.0535	
Largest diff. peak and hole	0.370 and -0.449 e.Å ⁻³	

Table 12. Crystal data and structure refinement for (3.25).

Identification code	1011	
Empirical formula	C10 H12 F6 Ni O2 S4	
Formula weight	465.15	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.1230(10) Å	$\alpha = 96.067(3)^\circ$.
	b = 7.5168(12) Å	$\beta = 95.838(3)^\circ$.
	c = 18.639(3) Å	$\gamma = 98.736(3)^\circ$.
Volume	837.1(2) Å ³	
Z	2	
Density (calculated)	1.845 Mg/m ³	
Absorption coefficient	1.719 mm ⁻¹	
F(000)	468	
Crystal size	0.02 x 0.08 x 0.31 mm ³	
Theta range for data collection	2.21 to 26.00°.	
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -22 ≤ l ≤ 22	
Reflections collected	6632	
Independent reflections	3258 [R(int) = 0.0358]	
Completeness to theta = 26.00°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3258 / 0 / 208	
Goodness-of-fit on F ²	0.807	
Final R indices [I > 2sigma(I)]	R1 = 0.0435, wR2 = 0.0748	
R indices (all data)	R1 = 0.0702, wR2 = 0.0809	
Largest diff. peak and hole	0.654 and -0.351 e.Å ⁻³	

Table 13. Crystal data and structure refinement for (4.11).

Identification code	1091	
Empirical formula	C ₂₇ H ₄₉ Cl N Rh S ₂	
Formula weight	590.15	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.0052(18) Å	α = 90°.
	b = 8.4501(10) Å	β = 106.842(2)°.
	c = 24.615(3) Å	γ = 90°.
Volume	2987.2(6) Å ³	
Z	4	
Density (calculated)	1.312 Mg/m ³	
Absorption coefficient	0.816 mm ⁻¹	
F(000)	1248	
Crystal size	0.40 x 0.12 x 0.10 mm ³	
Theta range for data collection	1.42 to 27.00°.	
Index ranges	-19 ≤ h ≤ 19, -10 ≤ k ≤ 10, -31 ≤ l ≤ 30	
Reflections collected	23661	
Independent reflections	6503 [R(int) = 0.0378]	
Completeness to theta = 27.00°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.928 and 0.758	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6503 / 0 / 296	
Goodness-of-fit on F ²	0.874	
Final R indices [I > 2σ(I)]	R1 = 0.0277, wR2 = 0.0579	
R indices (all data)	R1 = 0.0414, wR2 = 0.0595	
Largest diff. peak and hole	0.675 and -0.246 e.Å ⁻³	

Table 14. Crystal data and structure refinement for (5.1).

Identification code	1088	
Empirical formula	C ₁₂ H ₅ F ₁₃ O	
Formula weight	412.16	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 5.2414(7) Å	α = 85.147(2)°.
	b = 10.9428(14) Å	β = 88.611(2)°.
	c = 25.035(3) Å	γ = 87.639(2)°.
Volume	1429.2(3) Å ³	
Z	4	
Density (calculated)	1.915 Mg/m ³	
Absorption coefficient	0.236 mm ⁻¹	
F(000)	808	
Crystal size	0.26 x 0.15 x 0.03 mm ³	
Theta range for data collection	1.63 to 26.00°.	
Index ranges	-6 ≤ h ≤ 6, -13 ≤ k ≤ 13, -30 ≤ l ≤ 30	
Reflections collected	11051	
Independent reflections	5524 [R(int) = 0.0374]	
Completeness to theta = 26.00°	98.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.970 and 0.732	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5524 / 0 / 469	
Goodness-of-fit on F ²	0.726	
Final R indices [I > 2σ(I)]	R ₁ = 0.0421, wR ₂ = 0.0780	
R indices (all data)	R ₁ = 0.1004, wR ₂ = 0.0857	
Largest diff. peak and hole	0.466 and -0.206 e.Å ⁻³	

Table 15. Crystal data and structure refinement for (5.2).

Identification code	2036	
Empirical formula	C ₂₈ H ₁₂ F ₂₆ O ₄	
Formula weight	906.38	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 33.435(7) Å	α = 90°.
	b = 5.3317(11) Å	β = 122.461(9)°.
	c = 20.462(6) Å	γ = 90°.
Volume	3077.8(13) Å ³	
Z	4	
Density (calculated)	1.956 Mg/m ³	
Absorption coefficient	0.234 mm ⁻¹	
F(000)	1784	
Crystal size	0.40 x 0.11 x 0.05 mm ³	
Theta range for data collection	1.44 to 25.00°.	
Index ranges	-39 ≤ h ≤ 39, -6 ≤ k ≤ 6, -24 ≤ l ≤ 24	
Reflections collected	10540	
Independent reflections	2708 [R(int) = 0.0380]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.962 and 0.796	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2708 / 0 / 263	
Goodness-of-fit on F ²	0.902	
Final R indices [I > 2σ(I)]	R1 = 0.0336, wR2 = 0.0656	
R indices (all data)	R1 = 0.0498, wR2 = 0.0693	
Largest diff. peak and hole	0.211 and -0.213 e.Å ⁻³	