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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

Dedicated To My Father,

My Departed Mother,

My Wife Adlineh,

And

Our Daughter Alyssé Mariam.

Abstract

Homogeneous carbonylation and desulphurisation reactions catalysed by organometallic complexes and the synthesis of organometallic sulphur complexes are reviewed. Also included in the review are phase transfer catalysed organic reactions, organometallic synthesis and organic transformations in the presence of organometallic complexes.

The first examples of the desulphurisation of activated thiols mediated by organometallic complexes under both alkaline phase transfer and acidic biphasic conditions are described. Unlike most phase transfer catalysed reactions, organometallic complex mediated desulphurisation under alkaline PTC is not influenced by the nature of the phase transfer agent. It is also demonstrated that various thiocarbonyl compounds can be desulphurised by alkaline phase transfer catalysis in the absence of metal complexes. Also described in this thesis is an early example of acidic phase transfer catalysis. Various activated ethenes and dienes can be hydrogenated by some cobalt complexes under acidic PTC in good to excellent yields.

Synthesis of organometallic sulphur complexes under both acidic and alkaline phase transfer conditions are described. Included is the synthesis of a novel ionic complex under alkaline PTC. X-ray crystallographic studies undertaken reveals a manganese-sulphur complex in which the anion has a novel structure. Modification of the above mentioned model studies led to significant reduction in the sulphur content of crude oil and bitumen.

Carbonylation reactions are of interest and of considerable commercial value. Described herein is a new process for the homogeneous carbonylation of alcohols to esters via thiols by cobalt complexes. Also described is the first example of metal catalysed conversion of alcohols to thiols.

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Abbreviations

acac	Acetylacetonate
Aliquat 336	Tricaprylmethylammonium chloride
COD	1,5 – Cyclooctadiene
COS	Carbonyl sulphide
dasm	Bis(diphenylarsino)methane
DIOP	2,3 – *O* – Isopropylidene – 2,3 – dihydroxy – 1,4 – bis(diphenylphosphino)butane
DMAP	4 – (Dimethylamino)pyridine
dmb	Bis(dimethyl)butadiene
dpa	Diphenylacetylene
dpm	Bis(diphenylphosphino)methane
DTAB	Dodecyltrimethylammonium bromide
DTAC	Dodecyltrimethylammonium chloride
1,5 – HD	1,5 – Hexadiene
MCPBA	*m* – Chloroperbenzoic acid
NaDBS	Sodium – 4 – dodecylbenzenesulphonate
NaSH	Sodium hydrogen sulphide
PTC	Phase transfer catalysis
TBAHS	Tetrabutylammonium hydrogen sulphate
TEBAC	Benzyltriethylammonium chloride
THAB	Tetrahexylammonium bromide
THAHS	Tetrahexylammonium hydrogen sulphate

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Chapter 1

Introduction

Overlapping between the sciences is the norm these days. Many fields where rapid advances are being made lie on the border line between the major divisions of chemistry or between chemistry and other sciences. Organometallic chemistry can be viewed as a hybrid of organic and inorganic chemistry. This introductory chapter reviews some of the significant developments in organometallic chemistry relevant to the subject matter of this thesis.

1.1 Organometallic Chemistry

During the past 30 years, organometallic chemistry has become an important area of research. Although the first organometallic compound was reported in 1827, transition metal organometallic chemistry did not really get under way until the 1950's when it was spurred on by the discovery of ferrocene. Indicative of the rapid, and sustained, growth in organometallic chemistry are the ever increasing number of publications including the proliferation of books written in the last few years. Some of these books are comprehensive in nature (e.g. [1]-[5]), while others are more specialised (e.g. [6]-[11]).

The growing interest in this area is principally due to the usefulness of many

organometallic compounds for catalysing or assisting the transformation of organic substrates. Any compound containing a direct bond between a metal atom and one or more carbon atoms, may be considered to be an organometallic compound – in this thesis, and in most cases, the metal involved is a transition metal – whilst a ligand may be defined as any element or combination of elements which form(s) chemical bond(s) with a metal. Transition metals readily form linkages with most elements in the periodic table and with almost any organic molecule, resulting in a rich coordination chemistry which is especially relevant to their roles as catalysts. Transition metals are also able to form stable complexes with the metal being in a variety of formal oxidation states, to accommodate several different ligands in their coordination sphere and, perhaps more importantly, to readily interchange between oxidation states and adopt different coordination numbers during the course of a catalytic reaction.

1.1.1 Homogeneous And Heterogeneous Catalysis

Catalytic systems are conventionally divided into homogeneous and heterogeneous systems on the basis of whether a reaction takes place throughout one phase or at a phase boundary. A homogeneous reaction is defined as one in which all the constituents of the reaction, including the catalyst, are present in the same phase – generally implied to be in a common liquid phase. A heterogeneous reaction is defined as one in which one or more of the constituents are in different phases usually with the catalyst being a solid and the reactants as liquids or, more frequently, as gases. The reaction takes place at the interface, i.e. on the surface of the catalyst.

Both systems have their advantages and disadvantages. Heterogeneous catalysts can be separated much more easily from the reaction products than homogeneous catalysts and, in general, are thermally more stable. Reactions can be run under

more forcing thermal conditions, giving rise to higher reaction rates. The thermal stability of heterogeneous catalysts can be a further advantage in catalyst regeneration. In homogeneous systems, side reactions decrease the concentration of the active species by converting it to some catalytically inactive complex and requiring regeneration which cannot be done *in situ*. In heterogeneous systems, deactivation is often the result of deposition of reaction by-products on the catalyst surface and regeneration can often be accomplished by simply burning off such by-products. Homogeneous systems are generally more active (in terms of activity per metal center) and can be used under extremely mild conditions, which coupled with the ability of being "*tailored*", can lead to very high product selectivity.

It is difficult to study heterogeneous catalytic systems due to the lack of physical techniques which facilitate accurate monitoring of the reactions taking place on the catalyst surface or which allow the nature of the active site(s) to be delineated. This also hinders attempts at "*tailoring*" of catalysts used. Recently, spectroscopic techniques such as LEED, ESCA and AUGER have been used along with infrared spectroscopy to study surface reactions and active sites [12]. Homogeneous catalysts, on the other hand, are amenable to study using infrared and nuclear magnetic resonance spectroscopy thus, making it possible to study catalysed reactions as they occur. Nowadays, multinuclear (^{1}H, ^{13}C and ^{31}P) n.m.r. spectroscopy is routinely used to study the progress of homogeneous reactions, allowing a detailed evaluation of the effects of changes in ligands and/or reaction conditions during the course of the reaction. Such detailed studies aid in the "*tailoring*" of these catalysts.

During the last four decades, there has been a steady growth in the use of homogeneous catalysis [13]. Though processes using heterogeneous catalysts still account for a large proportion of the volume of *bulk* chemicals produced, systems using homogeneous catalysts make an important contribution. It is estimated that more

than 20 industrial processes employ soluble metal compounds as catalysts today. Certain organic chemicals, notably aldehydes and acetic acid are almost singularly produced using homogeneous catalysts [13]. The two major thermoplastic materials, polyethylene and polypropylene, are now exclusively produced using modified Ziegler, or Ziegler-Natta type of catalysts, which are mixtures of triethyl aluminium and titanium tetrachloride [6].

Of equal importance is the use of homogeneous catalysts to effect highly specific organic transformations for the synthesis of low–moderate volume speciality chemicals. For example, alkenes can be oligomerised by soluble nickel catalysts to give a wide variety of linear and cyclic products. Modification of the catalyst by the addition of suitable ligands lead to some highly selective catalyst systems and chemicals of potential pharmaceutical interest [14]. l-Dihydroxyphenylalanine (l-DOPA) is one of the drugs used in the treatment of Parkinson's disease and a key step in its synthesis is the asymmetric hydrogenation of α-acetamidocinnamic acid which can be effectively accomplished by using a soluble rhodium catalyst having optically active tertiary phosphine ligands [6]. There are many extensive reviews of transition metal homogeneous catalysis in the literature (e.g. [15,16]).

1.1.2 Carbonylation

One of the most versatile of all classes of homogeneously catalysed reactions are carbonylation reactions. Transition metals and their compounds have the ability to coordinate and activate carbon monoxide, thus leading to the development of some of the most important methods for the direct introduction of carbonyl groups into an organic substrate.

In recent years there has been much activity in the field of carbonylation reactions [17,18]. The carbon monoxide moiety is the most simple synthon for introduc-

ing carbonyl groups into organic molecules. Carbon monoxide is readily available from a variety of sources, including synthesis gas (a mixture of carbon monoxide and hydrogen) which in turn is available from many sources.

Carbon monoxide is an extremely effective ligand for the stabilization of low-valent metal complexes. Despite the wide use of carbon monoxide in the manufacture of organic chemicals, it is not very reactive by itself. Free carbon monoxide is susceptible to attack by strong nucleophiles, but coordination to a metal center greatly increases this susceptibility. Attack by another ligand or an external nucleophile on a coordinated CO is almost invariably a part of the mechanistic pathway leading to carbonylated organic products.

In 1938, a major breakthrough in homogeneously catalysed carbonylation reactions occured in Germany when Otto Röelen serendipitously discovered the conversion of alkenes to aldehydes by treatment with carbon monoxide and hydrogen in the presence of a cobalt catalyst at elevated temperatures and pressure. This is one of the best known carbonylation reactions and since it formally involves the addition of a formyl group (-CHO), it is known as hydroformylation.

$$R_2C{=}CR_2 + CO + H_2 \xrightarrow{Co} R_2CHCR_2CHO \qquad (1.1)$$

In the early 1940's, the second significant advance in homogeneous carbonylation reactions also occured in Germany when Reppe discovered that Group VIII metal carbonyl complexes catalysed a series of reactions in which alkenes, alkynes and alcohols were converted to carboxylic acids and their derivatives. The following are examples of 'Reppe reactions':

$$HC{\equiv}CH + CO + H_2O \longrightarrow H_2C{=}CHCOOH \qquad (1.2)$$

$$HC{\equiv}CH + CO + ROH \longrightarrow H_2C{=}CHCOOR \qquad (1.3)$$

$$RCH{=}CH_2 + CO + H_2O \longrightarrow RCH_2CH_2COOH \qquad (1.4)$$

$$RCH{=}CH_2 + CO + R'OH \longrightarrow RCH_2CH_2COOR' \quad (1.5)$$

$$RCH{=}CH_2 + CO + R'NH_2 \longrightarrow RCH_2CH_2CONHR' \quad (1.6)$$

$$RCH_2OH + CO \longrightarrow RCH_2COOH \quad (1.7)$$

The scope of Reppe reactions has expanded over the years and now represent routes to a wide variety of saturated and unsaturated acids, esters, lactones and anhydrides from different feedstocks. The large numbers of reviews and books on this subject deal with the mechanisms [14,17,19]-[24], catalysts [17,23]-[25], substrates [14,17,21]-[28], products [29], future trends [25] and economic importance of the reactions [25].

Alcohols, halides, alkenes, alkynes, diazonium ions and epoxides can be carbonylated by transition metals via mechanisms which generally involve the formation of a metal-carbon σ-bond, insertion of CO, and finally, attack on the resulting acyl ligand by an internal or external nucleophile (Nu^-) to give the products and regenerate the catalytic species.

$$[M{-}R]^{n+} \xrightarrow{CO} [M{-}C(O){-}R]^{n+} \xrightarrow{Nu^-} R{-}C(O){-}Nu + [M]^{(n-2)+} \quad (1.8)$$

The nature of the nucleophile is thus important in determining the products formed with the same catalyst being able to give different products under different conditions. Lactones, lactams, imides or cyclic anhydrides are the results of cyclisation when the R group is nucleophilic.

Carbonylation Of Alkynes

The carbonylation of unsaturated substrates to carboxylic acids is known as hydrocarboxylation. Good yields of *cis*-α,β-unsaturated acids were obtained from alkynes in the presence of nickel tetracarbonyl at 180–200°C and under 60 atm

pressure. The reaction rate decreases with increasing size of the substituent group in monosubstituted alkynes. The branched product isomer predominates with alkyl substituents [30].

$$CO + RC{\equiv}CR' + H_2O \xrightarrow{Ni(CO)_4/H^+} RC(COOH){=}CHR' + RCH{=}C(COOH)R' \quad (1.9)$$

Iron pentacarbonyl and rhodium trichloride can also be used but with reduced yields and selectivities. In a commercial process, treatment of an aqueous solution of acetylene with catalytic amounts of $Ni(CO)_4$ and haloacid, at 150°C and 30 atm of carbon monoxide, gives acrylic acid in high (90% +) selectivity [30]. A hydridonickel carbonyl species of the type $Ni(II)H(X)(CO)_4$, is thought to be the active catalytic species which is formed by the oxidative addition of HX to $Ni(CO)_4$ [6] and is preceded by the dissociation of at least one CO ligand.

$$HC{\equiv}CH + CO + H_2O \longrightarrow CH_2{=}CHCOOH \quad (1.10)$$

Acetylene can be dicarbonylated to hydroquinone and quininhydrone at 850-900 atm pressure and 100-150°C with $RhCl_3$ or $[Rh(CO)_2Cl]_2$ as catalyst [7]. Double hydrocarboxylation of acetylene to succinic acid (80% yield) occurs with $Co_2(CO)_8$ under 100–200 atm of total pressure and at 80–100°C [31]. Acrylic acid is formed at lower pressures.

Alkynes undergo simple hydroesterification, in the presence of nickel- or palladium-based catalysts, under mild conditions to give α,β-unsaturated esters. This reaction has been applied to the industrial synthesis of acrylate and methacrylate esters.

$$CH_3C{\equiv}CH + CO + MeOH \xrightarrow{Ni(CO)_4/HCl} CH_3C(COOMe){=}CH_2 \quad (1.11)$$

Alper et al. developed a process, in which alkynes could be hydroesterified selectively to mono- or di-esters under exceptionally mild conditions (1 atm of carbon

monoxide and oxygen at 25°C) by a palladium/copper catalyst system operating under acid conditions [32]. Regioselective hydroesterification of terminal alkynes led to unsaturated *cis*–diesters while internal alkynes gave *cis*–monoesters (70–80%).

Carbonylation Of Halides

Aryl halides like chloronaphthalenes or substituted bromobenzenes may be carbonylated in high yields under mild conditions with nickel tetracarbonyl as the catalyst. Dipolar aprotic solvents, such as DMSO or DMF, and an insoluble base, such as calcium hydroxide, are needed. A mechanism involving halogenotricarbonyl nickel anions $[NiX(CO)_3]^-$ has been proposed to account for the observed autocatalytic behaviour.

Reaction of alkyl halides with carbon monoxide and an alcohol in the presence of a base and $Na^+Co(CO)_4^-$ gives esters. Reactive substrates susceptible to nucleophilic substitution at the cobalt anion, e.g. iodoalkanes and benzyl halides, require very mild conditions, giving products containing an alkoxycarbonyl group.

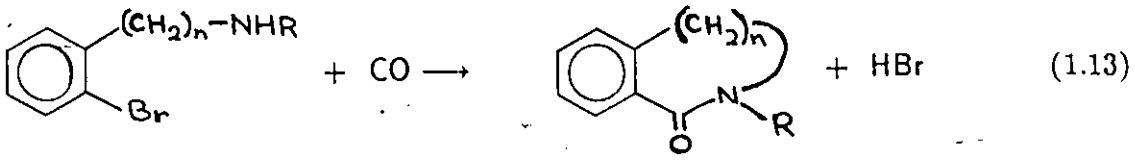
Benzyl, allyl, aryl, and vinyl halides, containing primary, secondary, or tertiary alcohol groups, can be readily carbonylated under mild conditions (1–4 atm, 25–60°C), by $Pd(CO)(PPh_3)_3$ to give four-, five-, and six-membered lactones [33].

Reactions of aryl, vinyl, or heterocyclic halides with primary or secondary amines and carbon monoxide (1 atm) at 60–100°C with $PdCl_2(PPh_3)_2$ as catalyst give high yields of amides. Added tertiary amine neutralises the HX formed in the reaction. Addition of *t*-amine becomes unnecessary if the primary or secondary amine is a sufficiently strong base. The tertiary amine is required for aniline but not for pyrrolidine. The function of the strong base could be to remove a proton from the coordinated or uncoordinated amine, and thereby increasing its nucleophilic

character significantly [34].

$$RX + CO + R'NH_2 \xrightarrow{Pd} RCONHR' + HX \qquad (1.12)$$

The above palladium catalysed amidation is the basis of a facile synthesis of benzolactams involving the carbonylation of 2-bromoamino alkyl benzenes at 100°C and 1 atm in the presence of $Pd(OAc)_2/PPh_3$. A stoichiometric amount of tertiary amine removes the hydrogen halide from the reaction, leading to five-, six-, and even seven-membered lactams in good yields [35]. This type of cyclisation has been extended to the synthesis of α-methylene-β-lactams by carbonylation of 2-bromo-3-aminopropene derivatives [9].



(1.13)

Tanaka et al. showed that palladium compounds can catalyse the synthesis of α−keto amides in good yields via the double carbonylation of organic halides in the presence of secondary amines [36]. Recently, they reported that these halides lead to α−keto esters and acids in the presence of alcohols and water with the steric nature of the alcohols and phosphine ligands being of primary importance.

$$RX + 2CO + R'OH + NR''_3 \xrightarrow{Pd} RCOCOOR' \ (+ RCOOR') + NR''_3H.X \qquad (1.14)$$

At the same time, Wolfram et al. also reported the smooth double carbonylation of simple linear and branched alkyl halides to α−keto acids, in good to excellent yields, under carbon monoxide pressures of 60 atm with $Co(CO)_4^-$ anion as the catalyst in the presence of a base. Dihaloalkanes can also be double carbonylated, at one or both halogenated centers, giving a number of products depending upon the substrate and reaction conditions [37].

Aryl, heterocyclic, and vinylic halides may be catalytically converted to aldehydes on treatment with syn gas at 80–100 atm/80–150°C, in the presence of $PdX_2(PPh_3)_2$ (X =Cl or Br) and a stoichiometric amount of a tertiary amine.

$$NR_3 + R'X + CO + H_2 \longrightarrow R'CHO + NR_3H^+X^- \qquad (1.15)$$

Alkyl halides cannot be used since they tend to dehalogenate to alkenes. Conditions vary according to the nature of the substrate — iodides being carbonylated much faster than chlorides or bromides due to the greater ease of oxidative addition of the C–I bond to the catalyst [38].

Alkoxy transfer reactions from metal alkoxides to halides, in the presence of carbon monoxide and a metal catalyst, give esters. Benzylic bromides react with borate esters and carbon monoxide in the presence of chloro(1,5-hexadiene)rhodium dimer to yield primary, secondary, or tertiary esters [39]. Potassium iodide becomes necessary for benzylic chlorides [40]. Simple alkyl mono- and di-halides can also be used, but only with a bimetallic catalyst system — $[1,5\text{-HDRhCl}]_2/Pd(PPh_3)_4$ [41]. Alkoxides of aluminium, titanium, and zirconium can be used in place of the borate esters for both the mono- and bi-metallic systems [42].

$$3\ ArCH_2Br + 3\ CO + B(OR')_3 \xrightarrow[1atm]{75^\circ C} 3\ ArCH_2COOR' + BBr_3 \qquad (1.16)$$

Potassium iodide appears to be necessary for the formation of esters from the reaction of benzylic, aryl, and alkyl halides with carbon monoxide and formate esters in the presence of $[1,5\text{-HDRhCl}]_2$. For aromatic halides as substrates, the bimetallic system mentioned above can be of particular benefit [43].

Carbonylation Of Alkenes

The carbonylation of alkenes is catalysed by a variety of transition metal complexes and these catalysts are often based on cobalt, nickel, iron, ruthenium or palladium

with the active catalytic species in most cases being a transition metal hydride. The reaction proceeds via coordination of the alkene to the metal center, insertion of this alkene moiety into the metal–hydrogen bond to give a σ-bonded alkyl species, followed by coordination of CO and its insertion into the metal–carbon bond. Product formation occurs via nucleophilic attack of the acyl–metal species with cleavage of the acyl-complex and concurrent regeneration of the metal hydride species when the nucleophile is of the type HNu. The nature of the nucleophile dictates the type of product obtained in these reactions — when HNu is water, acids are formed while esters and amides are the major products when alcohols and amines are used. Aldehydes are formed when hydrogen is the nucleophile.

The hydrocarboxylation of alkenes with carbon monoxide and water is catalysed by a variety of transition metal complexes including $Co_2(CO)_8$, $Ni(CO)_4$, and $H_2PtCl_6/SnCl_2$. The mechanism is as discussed above with water being the nucleophile. However, this route to carboxylic acids has not yet been developed into a generally useful procedure, since mixtures of products are often obtained due to the occurrence of both Markownikov and anti-Markownikov addition to the metal-hydride group of the alkene. Hydrocarboxylation of propene at 130°C/123 atm, in the presence of $HCo(CO)_4$, leads to butanoic acid (64%) and 2-methyl propanoic acid (20%). Alkene isomerisation can also occur due to the reversible nature of the reaction leading to the metal alkyl intermediate [23], and the isomerised alkene can be further hydrocarboxylated to other products. Addition of promoters such as pyridine help adjust the linear/branched product ratio to favourable levels.

$$\begin{array}{ccc} RCH_2CH{=}CH_2 & \xrightarrow{HCo(CO)_4} & RCH_2CH(CH_3)Co(CO)_4 \\ & & \Big\Downarrow \\ RCH_2CH(CH_3)Co(CO)_4 & \rightleftharpoons & RCH{=}CHCH_3 + HCo(CO)_4 \end{array} \qquad (1.17)$$

Iron compounds, e.g. $Fe(CO)_5$, may be utilised as alkene carboxylation catalysts but with modest yields [44]. Use of $PdCl_2$ as a co-catalyst with $Fe_2(CO)_9$ or $FeCl_2$ gives better yields.

The use of a bimetallic catalyst containing $H_2PtCl_6/SnCl_6$ gives increased selectivity toward linear products [45]. With 1-dodecene as the substrate in aqueous acetone at 90°C/200 atm, 68% linear acid and a total of 12% branched acids was obtained using bimetallic catalysis.

Metal catalysed hydroesterification of alkenes has been the subject of numerous patents and publications in recent years due to their potential industrial importance. Both linear (the major product in most cases) and branched chain esters are important - some of the former are of value as fatty acid ester derivatives while several of the latter are of pharmaceutical importance, e.g. ibuprofen is pharmacologically more active than aspirin.

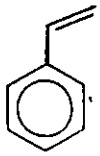
Similar to hydrocarboxylation, a mixture of products is obtained in hydroesterification reactions. Simple alkenes give saturated esters, linear and branched, the ratio between the isomers depending upon a number of factors. For example, reaction of propene with carbon monoxide and methanol in the presence of cobalt leads to methyl butanoate and methyl iso-propanoate in a 3.5:1 mole ratio [23].

$$RCH{=}CH_2 + CO + R'OH \longrightarrow RCH_2CH_2COOR' + RCH(CH_3)COOR' \quad (1.18)$$

Hydroesterification reactions can be catalysed by $Co_2(CO)_8$, palladium metal and its salts, platinum salts, and by complexes such as $PdCl_2(PPh_3)_2$ and $PtCl_2(AsPh_3)_2$. The catalytic cycle is as cited above, and Toniolo et al. provided solid evidence by isolating an intermediate butanoyl complex, *trans*-$PdCl(PPh_3)_2(COCH_2CH_2CH_3)$, from the reaction of carbon monoxide with propene in 1-butanol and obtaining its crystal structure [46]. This acyl species showed activity and selectivity identical to

the original catalyst precursor.

Palladium catalysed hydroesterification reactions have received much attention over the last ten years due to their mild conditions and consequent high selectivity. The selectivity depends on the carbon monoxide pressure, the phosphine ligand and upon the presence of additives or promoters, e.g. HCl. The importance of the phosphine ligands being evident in the hydroesterification of styrene as shown below.



$$+ \ CO + ROH \xrightarrow{PdCl_2(PPh_3)_2} H_3CCH(Ph)COOR$$

$$+ \ CO + ROH \xrightarrow{PdCl_2(Ph_2P(CH_2)_4PPh_2)_2} PhCH_2CH_2COOR \quad (1.19)$$

Mixed-metal catalysts promote improved selectivity to the linear ester. Chloroplatinic acid and tin(II) chloride gives over 80% linear isomer in many cases. Knifton has shown that ligand-stabilised bimetallic catalysts containing platinum [47] or palladium [48], and tin, can catalyse the hydroesterification of terminal alkenes, leading to very high selectivity towards the linear ester (up to 98%).

Palladium and copper comprise a much used successful combination. Palladium salts oxidatively carbonylate alkenes in stoichiometric reactions but the addition of copper(II) ions converts these reactions to catalytic ones. Copper reoxidises metallic palladium to the divalent state [49]. The presence of bases and mild conditions (25°C/3–15 atm) favour oxidative carbonylation over simple hydroesterification leading to $\alpha,\beta-$unsaturated esters, dicarboxylic acid esters or $\beta-$alkoxy esters, arising by initial attack of alkoxide on either coordinated CO or on coordinated alkene. Stille and co-workers have shown that with methanol as solvent, copper(II) chloride as reoxidant and a sodium butyrate buffer, these reactions give high yields of bis(carbomethoxylated) products [50]. A range of functionally sub-

stituted alkenes and cyclic alkenes can be used as substrates to give the diesters.

A remarkably mild, and regiospecific, palladium based process for the conversion of terminal and internal alkenes to the corresponding esters and acids, via oxidative carbonylation, was developed in 1983 by Alper and Despeyroux [51]. Bubbling carbon monoxide and oxygen through an alcoholic solution of $PdCl_2$, $CuCl_2$, HCl and alkene, at room temperature and 1 atm, yields the ester. Alkenes can also be regiospecifically hydrocarboxylated to the branched carboxylic acids in very high yields using tetrahydrofuran containing a limited amount of water as the solvent [52].

$$RCH{=}CH_2 + CO + R'OH \longrightarrow RHC(CH_3)COOR' \qquad (1.20)$$

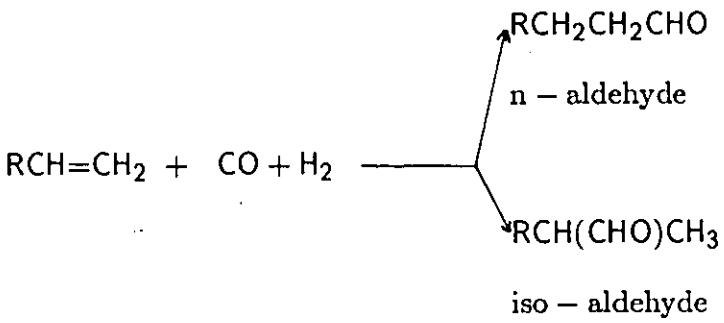
Oxidative carbonylation of alkenes to unsaturated esters has not been widely investigated. In 1979, synthesis of methyl cinnamate by carbonylation of styrene in methanol at 28°C, using a $PdCl_2$ and $MgCl_2$ catalyst system, sodium acetate as buffer, and a stoichiometric amount of $CuCl_2$ as reoxidant was reported [53]. Oxidative carbonylation of alkenes, in the presence of water, sometimes lead to $\beta-$lactones.

The cobalt or palladium catalysed hydroesterification of conjugated dienes leads to a number of products. An alkyl 3-pentanoate is obtained as the primary product of carbonylation of butadiene by $Co_2(CO)_8$ or $PdCl_2$ catalyst at 200 atm and 100°C. At higher pressure and temperature, cobalt carbonylates the second double bond to give dialkyl adipates in 50% yield. The palladium catalysed carbonylation of conjugated dienes to non-conjugated unsaturated esters is a fairly general reaction. Halide-free palladium-phosphine catalysts give diunsaturated esters e.g. 3,8-nonadionate from butadiene. These reactions possibly proceed via π-allyl intermediates [54].

Recent examples of hydroesterification of dienes include the palladium(II) catal-

ysed oxidative carbonylation of unsaturated diesters to simple β,γ-unsaturated and isomeric esters with carbon monoxide, a source of acid, alcohol, an ammonium-, phosphonium-, or arsonium salt and requiring high temperatures and pressures. Modification of the mild Pd/Cu hydroesterification system developed by Alper and co-workers, gives modest quantities of unsaturated esters [55].

Hydroformylation involves the addition of carbon monoxide and hydrogen to a carbon–carbon double bond of an alkene to afford aldehydes which have one carbon atom more than the parent alkene substrate. In terms of tonnage produced, hydroformylation represents one of the largest industrial applications of soluble transition metal catalysts.



(1.21)

Due to the industrial significance of hydroformylation, a vast amount of research has been devoted to understanding and improving this reaction. Hydroformylation has been extensively reviewed by Cornils [18,56,57], Pruitt [58], Pino et al. [23], and others [59,60].

There are three commercial processes for the hydroformylation of alkenes:

1. simple cobalt carbonyl catalysed reaction under relatively vigorous conditions;
2. tertiary phosphine ligand substituted cobalt carbonyl catalysed process; and
3. ligand modified rhodium complex catalysed system.

Until recently, cobalt carbonyl was the exclusive commercial hydroformylation catalyst and is still the dominant one. However, the rhodium catalysed process is the technology of choice for new plants.

The generally accepted mechanism for the simple cobalt carbonyl catalysed hydroformylation reaction, is based on the mechanistic sequence first elucidated by Heck and Breslow involving a series of 18 and 16 electron intermediates [61]. The important features of the mechanism are:

1. the true catalyst precursor, the 18 electron $HCo(CO)_4$, species leads to the coordinatively unsaturated, 16 electron $HCo(CO)_3$ species;

2. coordination of the alkene leads to an 18 electron π-complex and rapid hydride migration gives a 16 electron cobalt(I)–alkyl species;

3. the metal–alkyl complex is converted to an 18 electron metal–acyl species via alkyl-migration and coordination of another CO;

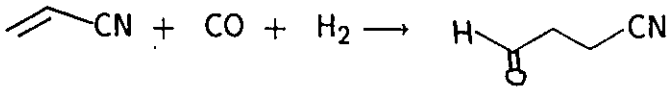
4. hydrogenolysis of the metal–acyl complex gives the aldehyde [23].

Rhodium catalysed hydroformylation was pioneered by Wilkinson and co-workers, and others, in the 1960's. The two most accepted mechanisms, associative and dissociative, for the rhodium catalysed hydroformylation of alkenes also involves a series of 18 and 16 electron intermediates. Other active hydroformylation catalysts include compounds of manganese, rhenium and platinum (with tin) [63].

Linear terminal alkenes hydroformylate more rapidly than linear internal alkenes, which in turn are more reactive than branched alkenes. The inhibiting effect of alkyl substituents increases with proximity to the double bond.

Effects of functional groups on hydroformylation have been studied extensively. Electron withdrawing groups conjugated with the double bond (e.g. $\succ$C=O, -C$\equiv$N)

promote hydrogenation and little hydroformylation which when occurs, tends to lead to addition of the formyl group at the carbon β to the substituent [64].



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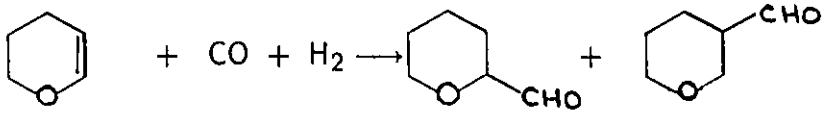
Electron donor substituents conjugated with the double bond (-OR, -NR_2, -Cl) favour addition of the formyl group at the carbon atom α to the donor group [65].



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Substituents not conjugated with the double bond have less influence than conjugated substituents, though directional effects tend to be similar.

Various chiral ligands have been incorporated to hydroformylation catalysts in attempts to achieve assymetric hydroformylation. For example, an optical yield of 32% has been achieved in the hydroformylation of isoprene to 3-methylpentanal at 95°C and 90 atm pressure with ($HRh(CO)(PPh_3)_3$+(-)-DIOP) [66]. The optical yields are typically 10–24% for the conversion of vinyl acetate to (*S*)-2-acetoxypropanal with $[Rh(CO)_2Cl)]_2$+(-)-DIOP catalyst [67].

Carbonylation Of N-Compounds

Primary, secondary and tertiary amines can be carbonylated by transition metal catalysts. Aliphatic amines can be reductively carbonylated to mainly N-formyl derivatives while aromatic amines usually afford ureas. The large difference in basicity between aromatic and aliphatic amines account for the marked distinction in behaviour between them [68]. Variation of metal catalysts can alter the selectivity, e.g. $Co_2(CO)_8$ leads to formation of substituted formamides from aliphatic amines while $Mn_2(CO)_{10}$ affords dialkylureas [68].

The mechanism for the carbonylation of amines has not been extensively investigated. A common intermediate in all of these reactions is a carbamoyl–metal

species which could arise from either an intramolecular 1,2-shift reaction involving coordinated carbon monoxide and amine, or from intermolecular attack of an amine on a carbonyl ligand [9].

Aromatic nitro compounds can be carbonylated in the presence of palladium based catalysts (e.g. $PdCl_2$/pyridine) to give the corresponding isocyanates in high yields and good selectivity.

$$4\ ArNO_2 + 3\ CO \xrightarrow{Pd} 4\ ArNCO + 2\ CO_2 \qquad (1.24)$$

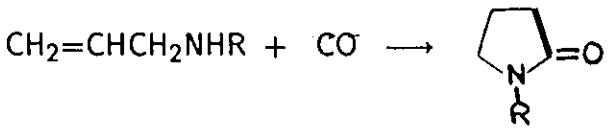
The industrial importance of isocyanates as intermediates for polyurethanes overrides the need for vigorous reaction conditions (200°C, 150 atm). Palladium(II) catalysed carbonylation of nitrobenzene in acetonitrile, at high temperature and pressure, gives phenylisocyanate in 55% yield [13]. Use of an alcohol as the solvent gives carbamate esters. Carbamates are important agricultural chemicals and can be thermally decomposed to isocyanates. This reductive carbonylation reaction has many advantages over the two-step isocyanate synthesis based on phosgene. The mechanism of the reductive carbonylation reaction is not well established.

$$ArNO_2 \xrightarrow{H_2} ArNH_2 \xrightarrow{COCl_2} ArNCO + 2\ HCl \qquad (1.25)$$

Recently, Fukuoka et al. [69,70] described the oxidative carbonylation of amines to carbamate esters catalysed by a palladium group metal deposited on carbon black and promoted by iodide ion at 83 atm and 160–170°C. Since then, a superior, extremely mild, system has been developed by Alper and Hartstock [71]. Aromatic amines can be converted to carbamate esters in fair to quantitative yields in the presence of $PdCl_2$,carbon monoxide, oxygen, hydrogen chloride and alcohols. Copper(II) chloride acts as the reoxidant. Absence of oxygen reduces the yield and addition of acid suppresses tar formation.

Numerous rhodium complexes – soluble and supported – are suitable for the carbonylation of nitrobenzenes and aromatic nitroso compounds to arylisocyanates. Reaction conditions are fairly moderate and yields are good [7].

Falbe and co-workers have described a number of intramolecular ring-closure reactions of unsaturated amides with carbon monoxide. Carbonylation of allylamine by $Co_2(CO)_8$ under forcing conditions (300 atm, 280°C) gives 2-pyrrolidone in 60% yield [72]. δ-Lactams are also accessible by this type of reaction. The carbonylation of allylic amines sometimes give γ and δ lactams. It has been postulated that initial isomerisation occurs to give a γ,δ-unsaturated amine which subsequently cyclises.



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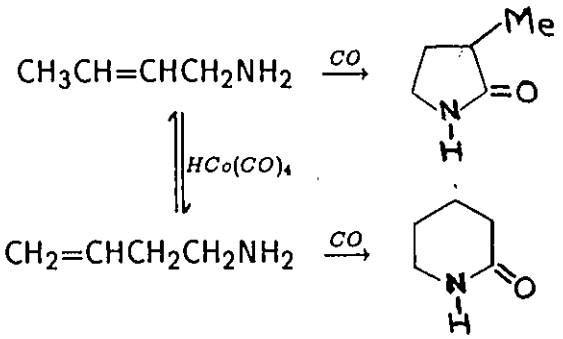
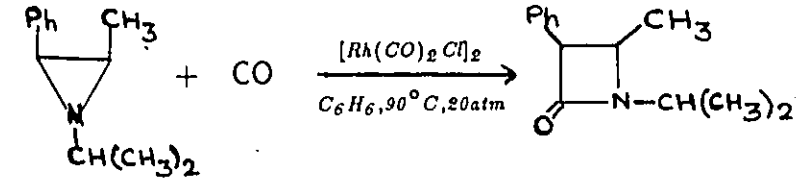


(1.27)

Succinimides were obtained in good yields in a similar carbonylation-cyclisation reaction of α,β-unsaturated amides. Crotonamide yields both 3-methylsuccinimide (68%) and glutarimide (19%) due to isomerisation [73].

Alper and co-workers have developed a novel ring expansion by carbon monoxide incorporation into a reactive nitrogen heterocycle. Monocyclic $\beta-$lactams were obtained in the chlorodicarbonyl rhodium dimer catalysed carbonylation of aziridines [74]. The reaction is both regiospecific and stereospecific with excellent yields. The reactions were run at 90°C and 20 atm in benzene.

The same catalyst (at 40°C, 1–30 atm carbon monoxide pressure, in benzene) regiospecifically carbonylates α–lactams to azetidine-2,4-diones in good yields [75]. Azirines can be carbonylated by palladium(0) ($Pd(PPh_3)_4$) to bicyclic β-lactams in a metal-induced coupling and carbonylation reaction [76].



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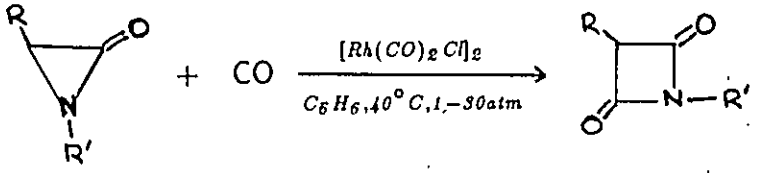

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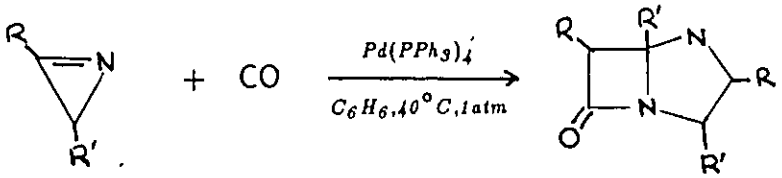


(1.30)

Carbonylation Of Alcohols

Alcohols can be carbonylated to carboxylic acids via a number of processes. Acetic acid is one of the most important industrial bulk organic intermediates and, with acetic anhydride, is used in the manufacture of vinyl acetate, cellulose acetate, pharmaceuticals, dyes and pesticides [13]. Acetic acid and its derivatives are manufactured by three homogeneous, transition metal catalysed commercial processes:

1. Oxidation of ethene via acetaldehyde – catalysed by Pd compounds;
2. Oxidation of butane or naphtha – catalysed by Co(II) compounds;
3. Carbonylation of methanol – catalysed by Co and Rh compounds.

Methanol is an important petrochemical intermediate [77]. Reppe showed that carbonyls of iron, cobalt and nickel, in the presence of halide ions, could catalyse the carbonylation of methanol to acetic acid. The carbonylation of methanol to acetic acid, catalysed by soluble rhodium and iridium carbonyl complexes under relatively mild conditions, was developed by Roth and Paulic at Monsanto Chemical Company. This represents one of the most significant industrial developments of Reppe type chemistry in recent years. A commercial process developed by BASF in 1960, utilises an iodine-promoted cobalt carbonyl catalyst and requires fairly drastic conditions for the carbonylation of methanol to acetic acid. Monsanto commercialised its rhodium catalysed methanol carbonylation process in 1970. Since then, this process has completely over-shadowed the older BASF process, becoming the technology of choice for new units. The Monsanto process has the advantage over the BASF process in working under considerably milder conditions (180°C, 35 atm compared to 230°C, 600 atm), requiring a lower catalyst concentration (10^{-3}M to 10^{-1}M), and greater product selectivity (99%+ to 90%) [78].

The mechanism for the rhodium catalysed carbonylation of methanol has been extensively studied. The active catalytic species has been postulated to be the diiododicarbonylrhodium(I) anion, $[Rh(CO)_2I_2]^-$, formed rapidly from the trihalogeno salt RhX_3 under reaction conditions via reductive carbonylation.

$$RhX_3 + 3\,CO + H_2O \longrightarrow [RhX_2(CO)_2]^- + CO_2 + 2\,H^+ + X^- \quad (1.31)$$

In the case of X not being iodo, the iodide promoter (introduced as iodomethane, hydroiodic acid (aq.) or iodine) generates the diiodo species by halide exchange. The promoter is usually added as HI which reacts with methanol to generate the more electrophilic iodomethane – the equilibrium lies well to the right.

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O \quad (1.32)$$

$$CH_3I + CO \longrightarrow CH_3COI \quad (1.33)$$

$$CH_3COI + H_2O \longrightarrow CH_3COOH + HI \quad (1.34)$$

It is the *in situ* generated iodomethane which is carbonylated, and not methanol "directly", to give acetyliodide which is quickly solvated by methanol or water to give methyl acetate or acetic acid. A series of 16 and 18 valence electron rhodium species, formed by oxidative addition and migration steps, are postulated as key intermediates in the catalytic cycle.

Carbonylation of methanol can also be effected by iridium carbonyl complexes under relatively mild conditions [79]. A comparative study of rhodium and iridium catalysts showed no major differences in gross behaviour but the Ir compounds were more sensitive to the actual ligands attached [80] and the mechanism more complicated with two possible cycles being proposed [6].

Alcohols other than methanol can also be carbonylated in the same manner. For example, benzyl alcohol can be carbonylated to phenylacetic acid in 90 minutes, 100% conversion with selectivity of 94%, by a catalyst formed from $RhCl_3.3H_2O$ in the presence of benzyl iodide under 30 atm pressure at 140°C.

The oxidative carbonylation of methanol to give dimethyl carbonate (a substitute for phosgene), dimethyl oxalate (can be reduced to ethylene glycol) and dimethyl succinate (in the presence of ethene) has been described recently [81]. A variety of oxidising agents, including dioxygen, nitrogen oxides and peroxides, can be used in tandem with copper and/or palladium catalysts. With di-*t*-butyl peroxide as oxidant, commercially valuable *t*-butanol is obtained as a by-product with no water being produced. An added dehydrating agent, e.g. orthoformate or orthoacetate ester, removes the water formed. Copper(II) chloride is used to reoxidise

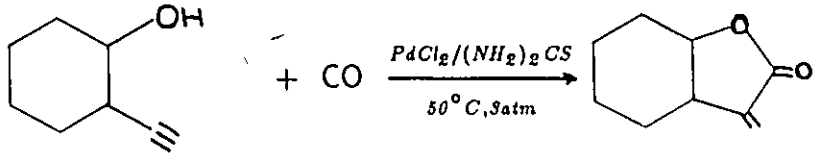
Pd(0) to Pd(II).

$$2CH_3OH + CO + [O] \xrightarrow{Pd/Cu} (COOCH_3)_2 + H_2O \quad (1.35)$$

$$2CH_3OH + CO + [O] \xrightarrow{Cu} (CH_3O)_2C{=}O + H_2O \quad (1.36)$$

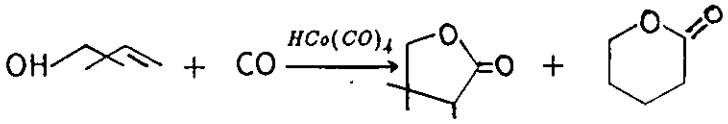
$$2CH_3OH + 2CO + CH_2{=}CH_2 + [O] \xrightarrow{Pd/Cu} CH_3OOCCH_2CH_2COOCH_3 + H_2O \quad (1.37)$$

A useful route to bicyclic α-methylene-γ-butyrolactones, some of which possess significant pharmacological activity, is the palladium-catalysed carbonylation of 3-alkyn-1-ols under mild conditions [82].



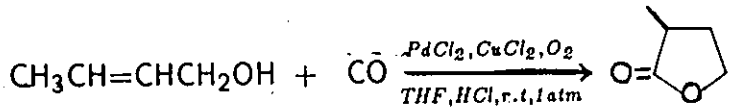
(1.38)

Unsaturated alcohols are normally isomerised to aldehydes by carbonylation catalysts, but if hydrogen migration is blocked by *gem* disubstitution, then lactones can be obtained. Carbonylation of 2,2-dimethyl-3-buten-1-ol by $HCo(CO)_4$ yields a mixture of five- and six-membered lactones, corresponding to Markownikov and anti-Markownikov addition respectively [9].



(1.39)

An extension of the already mentioned mild palladium/copper catalysed hydroesterification of unsaturated substrates by Alper and co-workers was reported for the cyclisation of unsaturated alcohols. Five membered lactones were obtained in respectable yields by the palladium catalysed reaction of primary, secondary and tertiary allylic alcohols with CO and O_2 (1 atm), hydrochloric acid and copper(II) chloride in dry tetrahydrofuran at room temperature [83].



(1.40)

Alper and Leonard also reported the synthesis of five- and six-membered lactones from alkenols under identical conditions [84]. Note that *gem* disubstitution is not required in this case.

1.1.3 Desulphurisation

Sulphur compounds are perhaps the most important non-hydrocarbon constituents of crude oil. The elemental composition of crude oil, no matter the origin, varies only slightly over very narrow limits. Despite the relatively low sulphur content of only 0.05–6.0%, there are many valid reasons for removing sulphur from petroleum fractions.

The nature, and distribution, of sulphur compounds in petroleum has been extensively studied. Organically bound sulphur accounts for most of the sulphur content of crude oils, but elemental sulphur is also present and precipitates in thermal reactions at relatively low temperatures. Organic sulphur compounds vary from the simple thiols (e.g. ethanethiol) to the simple sulphides (e.g. thiacyclohexane) and the polycyclic sulphides (e.g. 1-thiaindane). Various thiophenes (e.g. 2,3,4-trimethylthiophene) have also been isolated from a variety of crude oils while benzothiophene derivatives (e.g. dibenzothiophene) are usually present in the higher boiling petroleum fractions. On the other hand, disulphides are not regarded as being true constituents of crude oil but generally formed by oxidation of thiols during processing:

$$2R{-}SH \xrightarrow{[O]} R{-}S{-}S{-}R + H_2O \qquad (1.41)$$

Desulphurisation on a commercial scale, as currently practiced in the petroleum industry, can be achieved by:

1. thermal methods — such as the various cracking techniques which essentially concentrate the majority of the sulphur into the non-volatile products, i.e., the pitches and cokes, while the remainder of the sulphur may occur in the gases (H_2S from elemental sulphur) and as low-boiling organic sulphur compounds;
2. chemical methods — such as alkali treating (sweetening) during refining; and
3. hydrodesulphurisation — catalytic processes whereby crude oil fractions are desulphurised over a heterogeneous catalyst in the presence of hydrogen at elevated temperatures and pressures [85].

All of the commercial catalytic desulphurisation systems are heterogeneous in nature. However, there are many examples of homogeneous transition metal catalysed desulphurisation reactions on a non-commercial scale. There are also many examples of "heterogenised" systems in the literature ([86]–[89]).

Thiols are major components of the organic sulphur content of crude oils. Of the various organic sulphur compounds known, thiols and thioketones are the most susceptible to desulphurisation. Therefore, if a process for the desulphurisation of the organic sulphur component of crude oils has any potential of being successful, it is almost mandatory that such a method be applicable for the thiols and thioketones. It is, therefore, not surprising that these have been the subject of many model studies into desulphurisation reactions.

Recently, Alper et al. reported a dicobalt octacarbonyl catalysed homogeneous process for the desulphurisation of benzylic thiols and thiophenols to hydrocarbons in a benzene/water (30ml / 2ml) mixture at 185–190°C, under 60 atm of carbon monoxide pressure, in good to excellent yields [90]. Alkane thiols could not be desulphurised under these conditions. No reaction occurs in the absence of the metal catalyst or carbon monoxide and very little in the absence of water. It has

been postulated that $Co(CO)_4^-$ is the active species which is probably generated by the disproportionation of $Co_2(CO)_8$ in the presence of water [91].

$$R{-}SH + CO \xrightarrow[H_2O, C_6H_6]{Co_2(CO)_8} R{-}H + COS \qquad (1.42)$$

The same group of workers had earlier reported the desulphurisation and carbonylation of benzylic thiols to benzylic esters in fine yields under identical conditions except an ethanol/water solvent mixture (30ml / 2ml) was used. Similar limitations were in effect for both systems [92].

$$R{-}SH + CO \xrightarrow[EtOH/H_2O]{Co_2(CO)_8} RC(O)OEt + H_2S \qquad (1.43)$$

In addition, Antebi and Alper showed that thiophenols and benzylic thiols react with Schiff bases and carbon monoxide in benzene, in the presence of dicobalt octacarbonyl, to give amides as the principal products. These amides arise from cleavage of the carbon-nitrogen double bond of the reactant imine [93]. The reaction was shown to be applicable to a variety of Schiff bases (i.e. aliphatic, benzylic, aromatic).

$$\begin{array}{ccccc} RSH & + & CO & + & R'CH{=}NR'' \\ & & \begin{array}{l} 56atm \\ Co_2(CO)_8 \end{array} \Big\downarrow & \begin{array}{l} 170{-}180^\circ C \\ C_6H_6/H_2O \end{array} & \end{array}$$

$$RCONHR'' + RCON(CH_2R')R'' + R'CH{=}CHR' + COS \qquad (1.44)$$

It is known that molybdenum hexacarbonyl reacts with acetic acid to give mainly molybdenum(II) compounds such as tetrakis(acetato)dimolybdenum [94,95]. Alper and Blais reported in 1980 that these molybdenum(II) species, generated *in situ*, converted thiols into hydrocarbons at 115–120°C, and 1 atm in 3.5 hours in high yields. Different aromatic, benzylic, and aliphatic thiols were found to be suitable substrates to varying degrees. Using a supported system (heterogenised), lower yields of desulphurised products were obtained [87]. The same group of thiols

were desulphurised by transition metal chlorides (e.g. $FeCl_2$, $CoCl_2$, VCl_3) and sodium triethylhydroborate in THF at -78°C, 1 atm, in very good yields. With 2-naphthalenethiol as the substrate, 2,2′-binaphthyl was produced in 27% yield. Reaction times were short [96].

In 1981, Laycock and Alper reported that aromatic and aliphatic thioketones undergo hydrozirconation at room temperature with $Cp_2Zr(H)Cl$ (Cp = cyclopentadiene ), to give sulphur–zirconium compounds, $R_2CHSZr(Cl)Cp_2$, which upon carbonylation and bromination in alcohol (MeOH) affords the ether R_2CHOCH_3 [97].

$$R_2C{=}S \;+\; Cp_2Zr(H)Cl \xrightarrow[r.t]{C_6H_6} R_2C(H)SZr(Cl)Cp_2 \xrightarrow[MeOH]{CO,Br_2} R_2CHOCH_3 \qquad (1.45)$$

This, however, was not the first example of reaction between a thioketone and organometallic complex to give a sulphur containing complex which could subsequently be converted to a desulphurised product. In an earlier study, Alper and Chan detailed examples of sulphur-donor ligand ortho-metalated complexes of iron and of ruthenium [98,99]. Such complexes undergo desulphurisation on oxidative cleavage by 30% H_2O_2 amongst other reagents [100].

Alper also disclosed the first examples of sulphur-donor ligand ortho-metalated complexes of palladium and platinum from thiobenzophenones which could be cleaved by refluxing in alcohol to give the benzophenone in high yield [101]. In a later publication he reported the reaction of thiobenzophenone with dimanganese decacarbonyl in refluxing *n*-heptane affording tetraphenylethene in 69% yield [102].

$$2\ Ph{-}C(S){-}Ph \;+\; Mn_2(CO)_{10} \longrightarrow Ph_2C{=}CPh_2 \;+\; [SMn(CO)_3]_n \qquad (1.46)$$

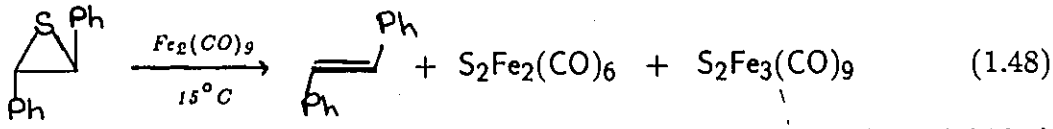
Interestingly, tetraphenylethenes were formed in good yields via the desulphurisation of thioketones by dicobalt octacarbonyl, cobalt tetracarbonyl anion (intro-

duced as $(PPh_3)_2N^+Co(CO)_4^-$), or cyclopentadienyliron dicarbonyl dimer in benzene. However, when the reaction was catalysed by hydridotetracarbonyl ferrate anion [$HFe(CO)_4^-$], generated *in situ* from $Fe(CO)_5$ and KOH, the product obtained was the hydrocarbon [103].

$$\begin{array}{l} R_2CS \quad + Fe(CO)_5 + \quad KOH \longrightarrow \quad R_2CH_2 \\ \quad {\scriptstyle C_6H_6}\downarrow{\scriptstyle cat.} \\ R_2C{=}CR_2 \end{array} \qquad (1.47)$$

Fulvenes can be synthesised with varying degrees of success by reaction of thiobenzophenones with cyclopentadienylmetal carbonyl anions [104].

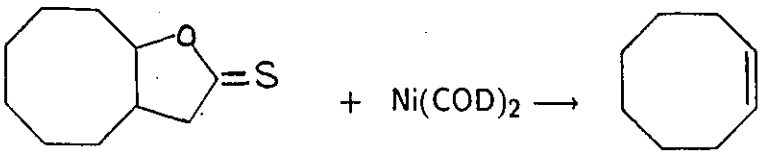
King reported the desulphurisation of cyclohexene episulphide with $Fe_3(CO)_{12}$ to give cyclohexene and $Fe_2(CO)_9S_2$ [105]. Stereoselective desulphurisation of these episulphides can also be achieved by using $Fe_2(CO)_9$ at 80°C [106] or 15°C (Alper, unpublished results), or by the use of hydridopentacarbonylmanganese [107].



$$+ \; S_2Fe_2(CO)_6 \; + \; S_2Fe_3(CO)_9 \qquad (1.48)$$

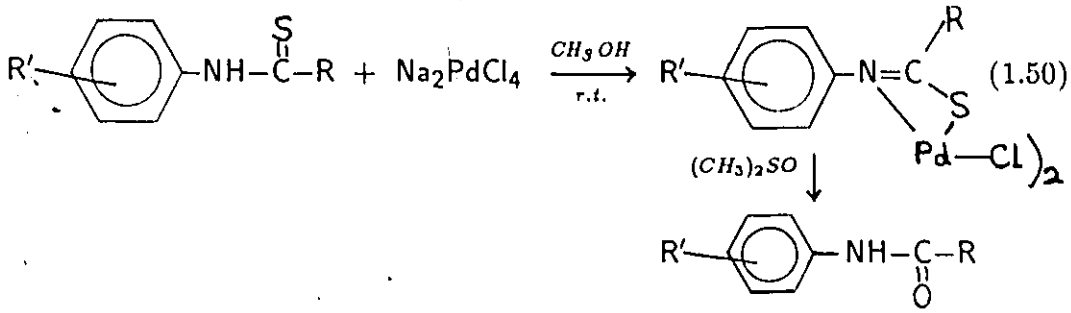
Recently, Calet and Alper developed a process by which thiiranes (episulphides) can be desulphurised in good to excellent yields by rhodium catalysts at room temperature in benzene under 26 atm carbon monoxide pressure. The most effective catalyst appears to be chlorodicarbonylrhodium(I) dimer, with $Pd(PPh_3)_4$ not very effective and $Co_2(CO)_8$ being inactive. The reaction is stereospecific and applicable to thiiranes bearing alkyl, alkoxy and carboethoxy substituents [108].

Semmelhack has shown that bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$, can stereospecifically desulphurise thionocarbonates to alkenes [109]. Use of $Fe(CO)_5$ results in non-stereospecific transformation [110,111].



(1.49)

Thioamides can be desulphurised to amines by $HFe(CO)_4^-$ [112], while use of $Fe(CO)_5$ leads to nitriles [113]. It is also possible to react thioanilides (ArNHCSR) with disodium tetrachloropalladate at room temperature to give a bidentate complex of structural type $((ArN{=}\ C(R)S)PdCl)_2$ which can be quantitatively converted to amides with wet dimethylsulphoxide at room temperature.



(1.50)

An interesting new effective desulphurisation reagent has been developed by Luh et al. Treatment of nickelocene with lithium aluminium hydride generates an active species, which reductively cleaves the C–S bond in thiols, sulphides and thioacetals in good yields at room temperature and 1 atm [114]. The same group reported the desulphurisation of certain thiols and thioesters to the hydrocarbons in respectable yields by $Mo(CO)_6$ in THF [115]. Thioketals give dimeric alkenes [116].

$$Ar(CH_2)_nSR \xrightarrow[THF]{Mo(CO)_6} Ar(CH_2)_nH \qquad (1.51)$$

(R=H, alkyl, aryl;n=0, 1)

1.1.4 Organometallic Sulphur Complexes

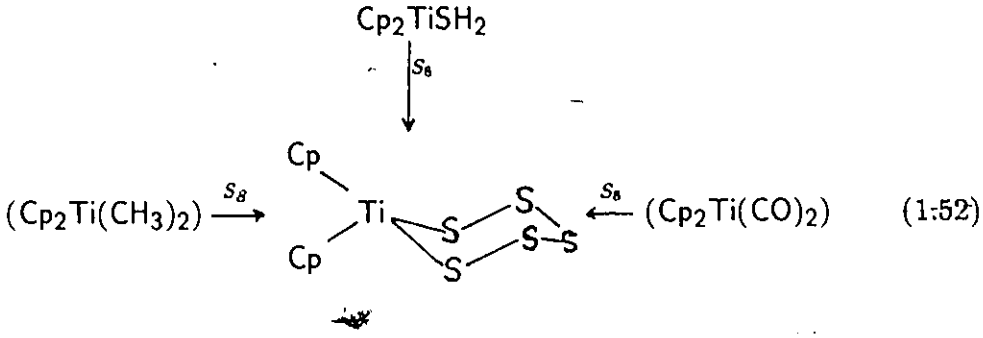
Numerous organosulphur complexes of transition metals are known to exist. Complexes containing transition metal–sulphur bonds are of biological significance since

inorganic sulphides, and possibly polysulphides, seem to be critical ligands in metalloenzymes such as ferrodoxin, nitrogenase, and the xanthine oxidase, primarily in association with iron and molybdenum [117]. Organometallic sulphur complexes are also of current interest due to their importance in the context of industrial catalysis. Inorganic sulphur (from feedstocks) is one of the most common and troublesome catalyst poisons [118]. In the broad area of metal cluster chemistry, sulphur ligands have proven to be very versatile in the synthesis of transition metal clusters, including heteronuclear clusters of potential catalytic utility [119].

The extensive development of organometallic sulphur chemistry over the last decade has resulted in the isolation and detailed characterisation of different structural types of complexes. An excellent definitive review of this subject matter has been authored by Vahrenkamp [120]. There are many examples in the literature of organometallic sulphur complexes in which elemental sulphur, S_8, is not directly involved in the synthesis. Among these are the synthesis and reactions of clusters including mixed cobalt-ruthenium-sulphur clusters [121], triiron sulphur clusters [122], chromium clusters [123] and high sulphur content clusters [124]. There are also countless examples of non-cluster organometallic complexes, ranging from sulphur-donor ligand ortho-metalated complexes [98,100], sulphur containing CO complexes of chromium [125], iron carbonyl complexes of thiourea and thioamides [126], chalcogenides as ligands in chromium, molybdenum and tungsten complexes [127], as well as products obtained by reaction with hydrogen sulphide [128] and reactions of metal–metal multiple bond complexes with organosulphur compounds giving novel complexes which display various types of bonding modes [129].

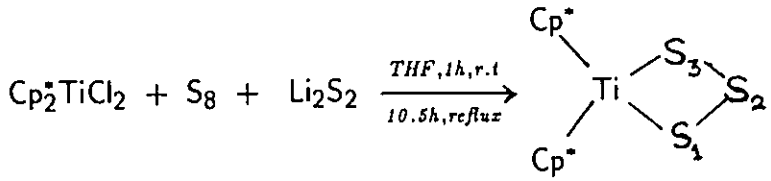
Elemental sulphur reacts with transition metal complexes in low oxidation states to give rise to a plethora of compounds. Polysulphides of the titanium and vanadium triads can be synthesised via numerous routes, several of which involve direct

participation of elemental sulphur. One of the most studied of these complexes is Cp_2TiS_5, a dark red, practically odorless, crystalline solid which is air and water stable. A simple route to Cp_2TiS_5 involves refluxing $Cp_2Ti(CO)_2$ and sulphur in hexane under nitrogen for several days. The alkyl substituted derivatives, such as the Me- and *i* Pr-C_5H_4 analogues have also been prepared. The TiS_5 ring adopts the chair conformation, even in solution, and the S–S distances and angles are within the range observed for other polysulphides, including S_8 itself [130].



(1:52)

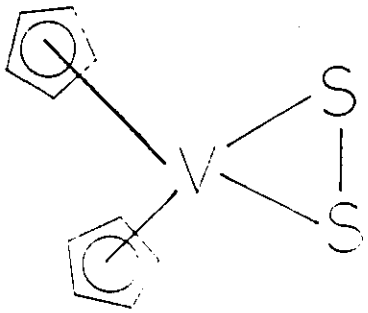
Other group IV analogues of Cp_2TiS_5 are known and they do not appear to differ structurally. Also known are $Cp^*_2TiS_3$ (where $Cp^*=C_5Me_5$) and its Zr analogue.



(1.53)

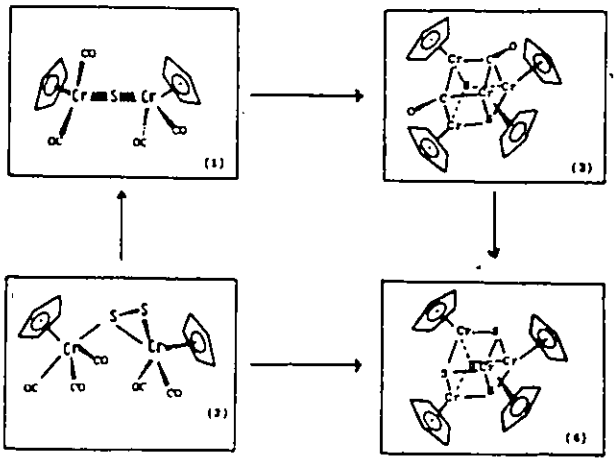
The TiS_3 ring is non-planar with S2 significantly displaced in the direction of one of the cyclopentadienyl ligands [131]. The synthesis of Cp_2VS_5 is completely analogous to that for the titanium complex. Also, $CpV(CO)_4$ reacts with elemental sulphur in refluxing toluene to give the pentasulphur complex [132], while decamethylvanadocene yields $Cp^*_2VS_2$ in THF [133]. No molecular polysulphide chelates

of niobium or tantalum have been reported thus far.



(1.54)

There has been much activity with respect to the chromium triad. An interesting reaction is that between $(CpCr(CO)_3)_2$ and varying amounts of elemental sulphur, in THF or toluene, to give $Cp_2Cr_2(CO)_4S$ (**1**) and $Cp_2Cr(CO)_5S_2$ (**2**) in high yields under inert atmosphere and ambient temperature. Both are air stable as solids [134]. Thermolysis of these two complexes in toluene gives cubane type complexes [135]. Irradiation of **1** in THF gave $Cp_2Cr_2S_4$ [136].



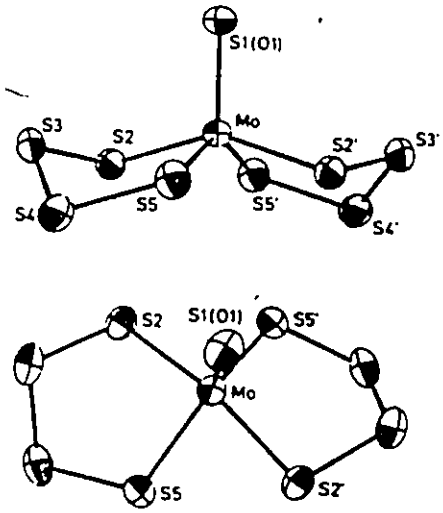
Heating $(Cp^*Cr(CO)_2)_2$ in toluene at 45°C, for 17h with S_8, yields black green

crystals of $Cp^*_2Cr_2S_5$ [137].

$$(Cp^*Cr(CO)_2)_2 + S_8 \xrightarrow[45^\circ, 17h]{toluene} Cp^*Cr\langle S_4 \rangle CrCp^* \qquad (1.55)$$

The reaction of $[MoS_4]^{2-}$ with sources of elemental sulphur affords the $[MoS_9]^{2-}$ ion. The oxo ion $[MoOS_8]^{2-}$ can be prepared by the reaction of $[MoO_2S_2]^{2-}$ or $[MoOS_3]^{2-}$ with elemental sulphur [138].

$$(Et_4N)_2MoS_4 + S_8 \xrightarrow[N_2, r.t]{CH_3CN} [MoS_9]^{2-} \qquad (1.56)$$

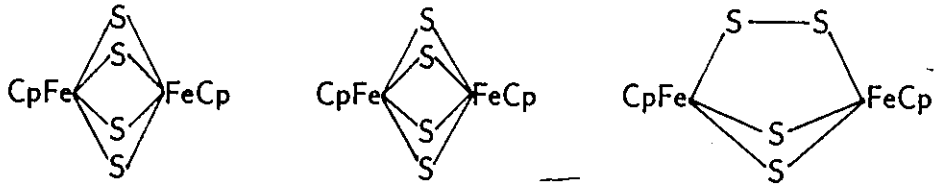


In the $[MoS_9]^{2-}$ ion, molybdenum is coordinated in a distorted square pyramidal fashion by a terminal sulphide and two bidentate S_4^{2-} ligands. The Mo–S1 distance is slightly shorter than Mo–S2.

Elemental sulphur reacts with $[Cp^*M(CO)_2]_2$ (where M=Mo, W) to give three different isomers of $Cp^*_2M_2S_4$ as well as a carbonyl containing complex, $Cp^*_2(CO)_2W_2S_3$, with the product distribution depending upon the reaction conditions. $Cp^*_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ contains three bridging sulphur ligands, one of which represents a μ-S_2 group. $Cp^*_2(CO)_2W_2S_2$ consists of a planar $W_2(\mu - S)_2$ core. The Cp^*

groups are in an anti-parallel orientation with two terminal CO's coordinated to one tungsten atom and only one terminal sulphur ligand coordinated to the other [139]. Reaction of Cp_2MH_2 or $CpM(SH)_2$ (M=Mo, W) with elemental sulphur affords the tetrasulphido complexes $CpMS_4$.

While no reports have appeared of manganese-sulphur complexes, and few of rhenium [140], some publications have described the reaction of sulphur with iron compounds, including $[CpFe(CO)_2]_2$ which affords $[CpFe(CO)_2]_2(\mu - S_3)$ [141]. When Fp_2 was photolysed in a solution of sulphur in toluene, $[CpFeS_2]_2$ was formed. Two isomers were isolated [142].



Three types of clusters can be obtained upon the reaction of strongly reducing $[Fe(SEt)_4]^{2-}$ with elemental sulphur under different conditions. In acetonitrile, at 25°C, 1.0 equiv. of sulphur gives $[Fe_2S_2(SEt)_4]^{2-}$ which upon heating to 85°C leads to $[Fe_4S_4(SEt)_4]^{2-}$. When 1.4 equiv. of sulphur in acetone was used at 25°C, $[Fe_3S_4(SEt)_4]^{3-}$ was obtained. The complex $[Fe_6S_9(SEt)_2]^{4-}$ was isolated when 1.5 equiv. of sulphur was heated to 80°C in acetonitrile with the parent iron complex. Holm et al. also reported the conversion of $[Fe(SPh)_4]^{2-}$ and $[Fe_4(SPh)_{10}]^{2-}$ with elemental sulphur in acetonitrile to $[Fe_2S_2(SPh)_4]^{2-}$ and $[Fe_4S_4(SPh)_4]^{2-}$ respectively [143].

Cyclic polysulphides are formed by the reaction of trimethylvinylsilane with elemental sulphur, in the presence of $Fe_3(CO)_{12}$. Also formed are $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$ [144].

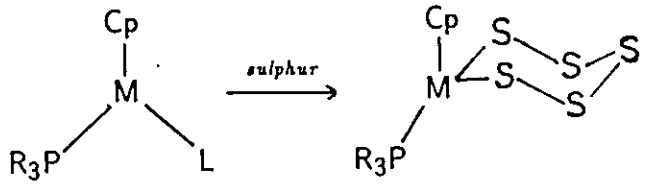
Recently, the synthesis of a new type of metal dithiolene complex was reported. Sulphur reacts with $Cp^{\dagger}_2Ru_2(CO)_4$ ($Cp^{\dagger}=\eta C_5Me_4Et$) in refluxing toluene to give

a highly soluble, air stable, intensely blue compound $Cp_2^{\dagger}Ru_2(\mu,\eta^2\text{-}S_2)$ $(\mu,\eta^1\text{-}S_2)$. Bond lengths between Ru–S are normal for the $\mu,\eta^2\text{-}S_2$, but rather short for the parallel $(\mu,\eta^1)S_2$ indicating multiple bonding between the ruthenium centers and this disulphide ligand. A minor product was identified as $Cp_4^{\dagger}Ru_4S_6$ [145].

Reaction of ruthenium and osmium phosphine complexes with S_8 initially affords $M(PMe_3)_3S_6$ which upon crystallisation gives $M(PMe_3)_3S_7$ — the only known examples of haptosulphido complexes with the S_7 ligand coordinated in a tridentate manner [146]. Elemental sulphur also reacts with $M(CO)_2(PPh_3)_3$, (M=Ru, Os), in dry, degassed benzene to give $M(S_2)(CO)_2(PPh_3)_2$ in high yields [147].

Elemental sulphur reacts with N'N'-o-phenylenebis(salicylideneaminato)cobalt(II), [Co(salophen)], in THF or pyridines to give tetrasulphidocobalt (III) complexes, [(L)(salophen)Co-S_4-Co(salophen)(L)] where L= THF or pyridine. In the presence of a sodium cation bonded by [Co(salophen)], a μ-persulphido dicobalt(III) complex, [[(THF)(salophen)Co-S_2Co(salophen)][Na(THF)]](BPh_4) was obtained [148].

Reaction of $CpM(PR_3)L$ (M=Co, R=Me, L=CS_2; M=Rh, R=Ph, L=CO) with elemental sulphur gives the oxidative addition product $CpM(PR_3S_5)$ in good yield.



(1.57)

The first structurally characterised molecular S_2 complex was prepared from $[Ir(dppe)_2]^+$ (dppe= diphenylphosphinoethane or $Ph_2PCH_2CH_2PPh_2$) and elemental sulphur to give orange air stable crystals of $[Ir(S_2)(dppe)_2]Cl$. An orange, hygroscopic sulphur complex of rhodium was obtained when $[Rh(dmpe)_2]Cl$ (dmpe=dimethylphosphinomethane) was used [149].

$$[Ir(dppe)_2]Cl + S_8 \xrightarrow[C_6H_6, CH_2Cl_2]{25^\circ C, 16h} [Ir(S_2)(dppe)_2]Cl \quad (1.58)$$

$$[Rh(dmpe)_2]Cl + S_8 \xrightarrow{C_6H_6, THF} [Rh(S_2)(dmpe)_2]Cl \xrightarrow{NH_4PF_6} [Rh(S_2)(dmpe)_2]PF_6 \quad (1.59)$$

The only known example of a metal from the nickel triad reacting with sulphur is that of $Pt(SH)_2(PPh_3)_2$ or $Pt(PPh_3)_3$ to give the well characterised square planar complex $Pt(S_4)(PPh_3)_2$ [150].

There are no examples of reaction between metals in the copper and zinc triads with sulphur.

1.2 Phase Transfer Catalysis

There are undoubtably many early examples of the phenomenon now known as phase transfer catalysis. One of the most important milestones in this field was a report by two Australian analytical chemists, Gibson and Hosking, in 1965. They discovered that triphenylmethylarsonium permanganate could be prepared, isolated and dissolved in chloroform and used as an oxidising reagent. This method could be utilised for the analysis of highly lipophilic organic substances by permanganate titration. Over the last 20 years, phase transfer catalysis (PTC) has become one of the fastest growing preparative methods in organic chemistry with over 65 different types of organic compounds being advantageously synthesised via PTC techniques. Reactions can be run at relatively low temperatures, pressures and over short reaction times while work-up and product isolation are simple. This technique allows one to bring together in the organic phase, lipophilic organic substrate and hydrophilic reagents with the aid of a particular phase transfer agent.

The most common phase transfer reactions involve liquid/liquid or solid/liquid systems. A new class of PTC reactions, gas-liquid, has recently been developed by Tundo [151]. Often used phase transfer agents are ammonium, phosphonium and arsonium salts (lipophilic quaternary salts) as well as crown ethers, cryptands and open chain polyethers (e.g. polyethylene glycols (PEG) of various molecular weights). α- and β-Cyclodextrins can act as phase transfer catalysts in the simple nucleophilic displacement between cyanide, iodide and thiocyanate ions and bromooctane in a liquid/liquid system [152]. Crown ethers and cryptands are used as phase transfer agents in solid/solid systems. New catalysts are continually being introduced, e.g. trisdioxa-3,6-heptylamine (TDA-1) for solid/liquid systems [153].

The aqueous phase of a liquid/liquid alkaline phase transfer system contains a reservoir of salt which is expected to act as a nucleophile or base, which in turn, reacts with the substrate contained in the organic phase. The phase transfer agent contains a lipophilic cation which is soluble in both phases and when in contact with the aqueous reservoir of salt, exchanges anions with the excess anion in the salt solution. The anion exchange is represented by the equilibrium 1.60.

$$Q^+X^-(aq.) + M^+Y^-(aq.) \rightleftharpoons Q^+Y^-(aq.) + M^+X^-(aq.) \qquad (1.60)$$

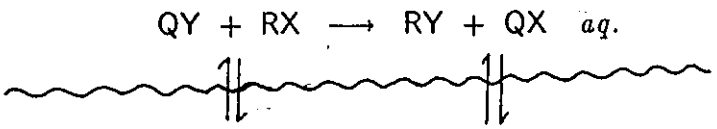
The nucleophile has to be transported across to the organic phase and a second equilibrium is set up – the phase transfer equilibrium.

$$Q^+Y^-(aq.) \rightleftharpoons Q^+Y^-(org.) \qquad (1.61)$$

Once the nucleophile is in the non-polar organic phase, reaction can take place. In the case of a nucleophilic displacement reaction, Q^+ forms the ion-pair Q^+X^- with the leaving group X^- and the above equilibrium is observed.

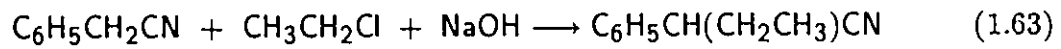
1.2.1 Organic Reactions

Simple displacement reactions involving anions such as cyanides, halides, alkoxides, thiophenoxides, carboxylates, azides and thiocyanates can be easily carried out under both liquid-liquid and solid-liquid phase transfer conditions, usually following the behaviour expected for S_N2 reactions.



(1.62)

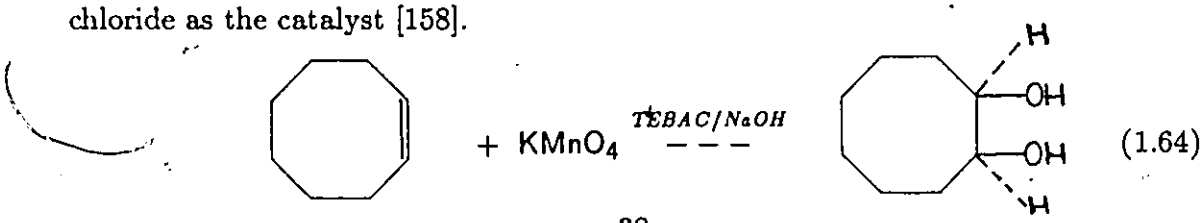
Phase transfer techniques can be applied for most types of alkylations except those with simple esters or other easily hydrolysed functional groups. It is possible to eliminate hydrolysis in the absence of the aqueous phase by utilising a solid-liquid system [154].



(1.63)

In 1984, Dolling et al. reported the first efficient, catalytic, asymmetric alkylation via chiral PTC, in high yields with up to 92% ee [155]. An interesting example of kinetic resolution by PTC has recently appeared in the literature [156]. A 1984 review lists over 60 references for polymer supported chiral PTC reactions and interest in this field continues to grow [157].

Phase transfer catalysed permanganate oxidations are usually superior to those obtained using classical methods. Under alkaline conditions good yields of *cis*-1,2-cyclooctenediol were obtained from cyclooctene with benzyltriethylammonium chloride as the catalyst [158].



(1.64)

Hypochlorite anion can be easily extracted into the organic phase in phase transfer catalysed oxidation of various functional groups (reviews [159]). The oxidation of thioureas to the corresponding carbodiimides by OCl^- under PTC conditions, as well as other heterocycles [160], and of benzyl alcohols have recently been reported [161].

Reductions can also be favourably carried out under phase transfer conditions. A variety of phase transfer agents are capable of transferring borohydride anion from an aqueous basic solution of sodium or potassium borohydride into benzene. 2-Octanone can be reduced to 2-octanol in benzene with tricaprylmethyl ammonium chloride (80% in 6.5 h), N-dodecyl-N-methylphedrinium bromide (100%,0.5 h), or N-methyl-N-dodecyl-N,N-*bis*-hydroxyethyl ammonium bromide (100%, 6.5 h) as catalyst with aqueous borohydride (see Weber and Gokel).

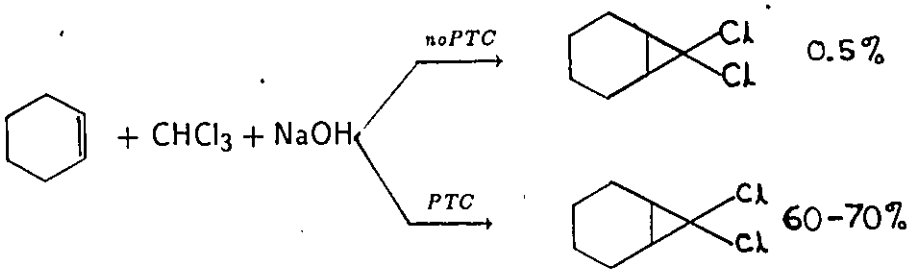
$$CH_3C(O)(CH_2)_5CH_3 \xrightarrow{Q^+BH_4^-} CH_3CH(OH)(CH_2)_5CH_3 \qquad (1.65)$$

Alkyltriphenylphosphonium salts react with aqueous sodium hydroxide to generate ylids which then yield alkenes upon reaction with aldehydes in the organic phase [162].

$$Ph_3PCH_2Ph^+Cl^- + NaOH(aq.) \xrightarrow{CH_2Cl_2} Ph_3P{=}CHPh \xrightarrow{RCHO} RCH{=}CHR + Ph_3P \qquad (1.66)$$

Dihalocarbene formation is one of the most useful phase transfer organic reactions. Chloroform reacts with cyclohexene in 25% NaOH solution to give less than 0.5% yield of the addition product in the absence of the phase transfer catalyst and

60–70% when phase transfer agents are present [163].



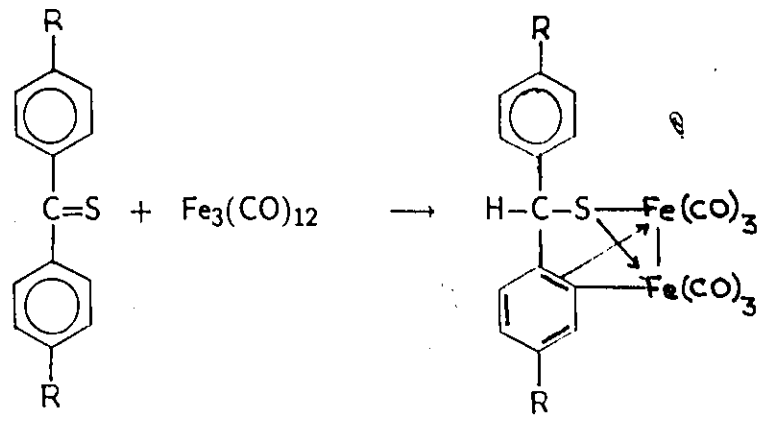
Dihalocarbenes generated by the phase transfer catalysis technique undergo insertion reactions into C–H bonds of a limited number of compounds, for example adamantane and diethyl ether [164].

Extensive use of PTC techniques have been made for monomer synthesis, polymerisation, polymer modification and free radical catalyst activation [165]. Polymer supported PTC systems have been extensively investigated and recently the first example of a new class of interfacial reactions involving polymer supports – inverse PTC – was reported [166].

The pharmaceutical industry makes extensive use of PTC techniques, including Beecham's and Astra's processes for synthetic penicillins and drugs derived from *O*- and *N*-alkylation of various heterocycles. Pesticides are also synthesised on a commercial scale by PTC processes [167].

1.2.2 Organometallic Synthesis

The first application of phase transfer to processes involving organometallic complexes was reported in 1976 by Alper and Des Roches whereby a facile synthesis of ortho-metalated complexes could be achieved starting from thioketones and triiron dodecacarbonyl.



(1.67)

The mechanism is not known, but it is possible that $HFe_3(CO)_{11}^-$ is generated under the reaction conditions, followed by nucleophilic attack on the thione group [168].

Transition metal carbonyl ligand exchange reactions under PTC conditions are assisted by the hydroxide anion. The *cis* position is postulated to be labellised in the hydroxycarbonyl intermediate and the entering ligand coordinates *cis* to the hydroxycarbonyl group. Anions such as OH^-, SH^-, S^{2-} can act as both labellising reagent and entering ligand [169].

$$M(CO)_x \xrightarrow{OH^-} (CO)_{x-1}MCOOH \xrightarrow[-OH^-,-CO]{L} (CO)_{x-1}ML \qquad (1.68)$$

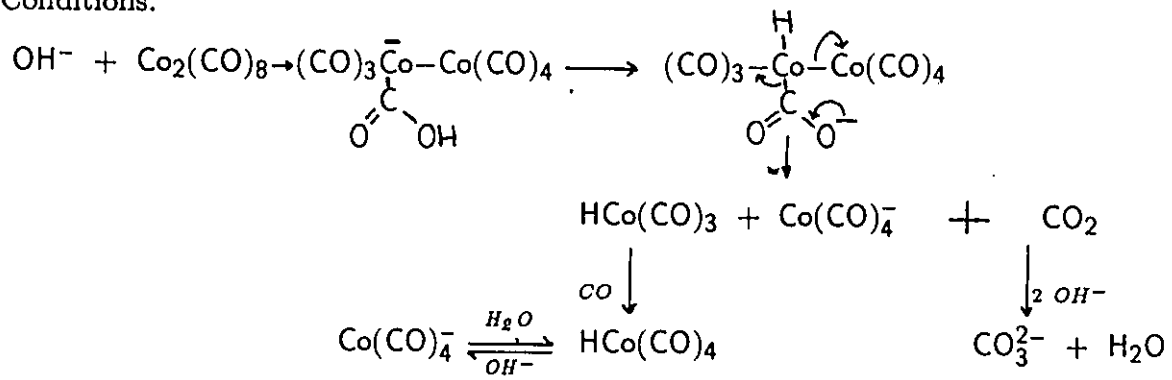
Reaction of $M(CO)_6$ (M=Cr, Mo, W) with a group V ligand and tetrabutylammonium iodide in benzene and 50% NaOH, at varying temperatures, results in the formation of ligand substituted products [170]. Ligands used include 2,2'bipyridine (dipy), triphenylarsine ($AsPh_3$) [170], and isonitriles [171]. Bridging hydroxyl complexes of platinum can be synthesised by treatment of bridging chloro complexes with aqueous potassium hydroxide and a crown ether in benzene [172].

Several metal carbonyl anions can be generated under mild conditions by utilising phase transfer catalysis. Hydroxyl and other nucleophiles (mostly borohydride) anions have been used in these reactions. Apart from the above mentioned $HFe_3(CO)_{11}^-$, $HFe(CO)_4^-$, $Co(CO)_4^-$ $CpFe(CO)_2^-$, $CpMo(CO)_3^-$, $HM(CO)_5^-$ (M=Cr,

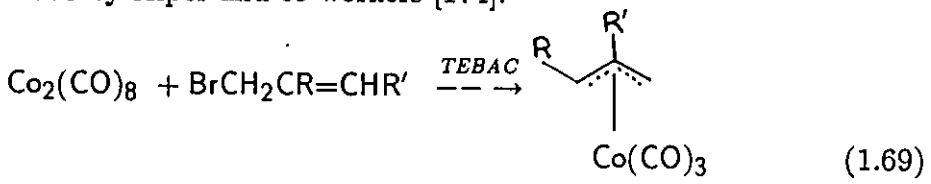
Mo, W), $Mn(CO)_5^-$ and others have been generated [104,173]. They can be used *in situ* for synthetic purposes, or isolated and fully characterised.

A possible mechanism for the generation of the mono-nuclear cobalt tetracarbonyl anion from dicobalt octacarbonyl is shown here. The key steps are the nucleophilic addition of hydroxide ion to cobalt carbonyl and the subsequent metal-metal bond cleavage of $(CO)_3CoCo(H)(CO)_3CO_2^-$.

Figure 1.1: Scheme For The Generation Of $Co(CO)_4^-$ Under Alkaline Phase Transfer Conditions.



The first example of π-allyl complexes generated under phase transfer conditions was reported in 1976 by Alper and co-workers [174].

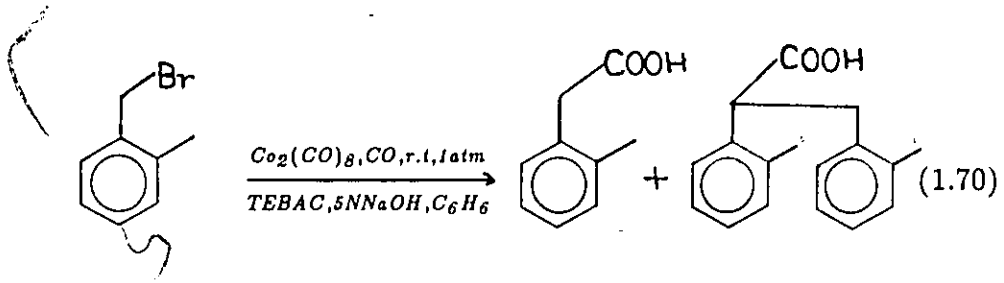


(1.69)

This has been successfully extended to other π-allyl complexes by Gibson and co-workers. They developed a useful approach to the synthesis of π and σ-allyl manganese, iron, molybdenum and ruthenium complexes by reacting metal carbonyl halides with allyl halides under PTC conditions [175,176]. Metallocenes can also be synthesised under mild conditions with a solid/liquid PTC system [177].

1.2.3 Organometallic Complex Catalysed Organic Transformations

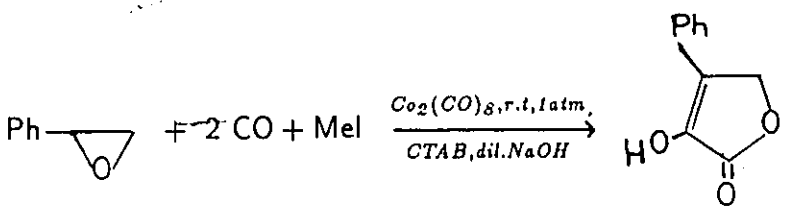
The first application of phase transfer organometallic reaction to an organic transformation was the reduction of nitro compounds, but the reaction was stoichiometric in nature with respect to triiron dodecacarbonyl [178]. Alper and co-workers later reported the catalytic reduction of nitro compounds to amines by triruthenium dodecacarbonyl in high yields (higher under carbon monoxide than nitrogen) [179]. Change of base from hydroxide to methoxide ion, and syn gas in place of carbon monoxide, leads to formamides as the principal products, while the use of $Fe_3(CO)_{12}$ results in preferential formation of carbamate esters [180]. Use of ruthenium(II) catalysts, $RuCl_2(PPh_3)_3$, also give good yields of amines. With synthesis gas, yields can double but no reactions take place under hydrogen [181]. A catalytic reduction of nitro compounds (including substituted ones) by bimetallic (dicobalt octacarbonyl and chloro(1,5-hexadiene)rhodium(I) dimer) PTC was reported in 1984 [182], but this was later found to be coincidental [183]. Benzylic halides have been carbonylated by the mononuclear cobalt tricarbonylnitrosyl complex [184], by iron pentacarbonyl [185] and $Co_2(CO)_8$ and double carbonylated under extremely mild PTC conditions [186].



(1.70)

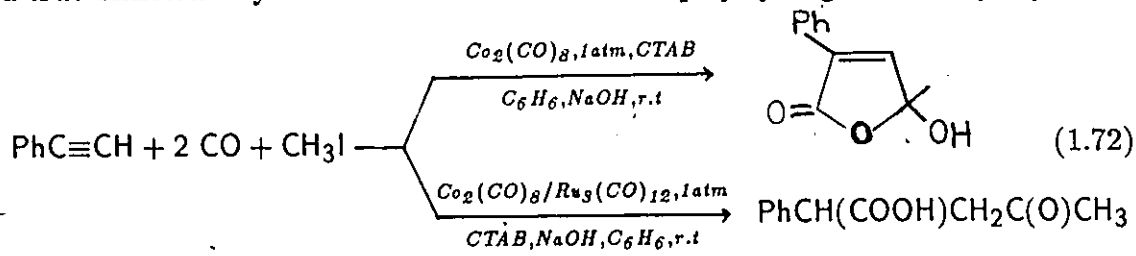
The key intermediate is thought to be an acylcobalt tetracarbonyl complex, $RCOCo(CO)_4$, which is also the case in the double carbonylation of a strained ring, like styrene oxide, in the presence of iodomethane leading to the enol of the

α-keto lactone [187]. The ability of a phenacylcobalt tetracarbonyl intermediate to undergo enolisation, thus facilitating a second carbon monoxide insertion into a vinyl cobalt-carbon bond is the driving force in these double carbonylation reactions. Kinetic studies of the mono-carbonylation reaction indicates that the cleavage of the acylcobalt tetracarbonyl by hydroxide ion is an interfacial process [188].



(1.71)

Under the same conditions, pharmacologically important 2-butenolides are formed in good yield from phenylacetylenes [189]. A bimetallic system (with $Ru_3(CO)_{12}$) leads to γ-keto acids. A mechanism involving *in situ* generation of $HRu_3(CO)_{11}^-$ and its addition to an α,β-unsaturated acylcobalt carbonyl has been proposed. This is a true bimetallic system in which the two metals play synergistic roles [190].



(1.72)

Phenyl acetic acid was the only product when benzyl bromide was used instead of iodomethane, but utilisation of a solid/liquid system, with TDA, gives 2-butenolide [191]. Alkynes can also be carbonylated to γ-butyrolactones by a regiospecific $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$ induced reaction with methyl iodide under mild PTC conditions. PEG-400 can act as the phase transfer agent [192].

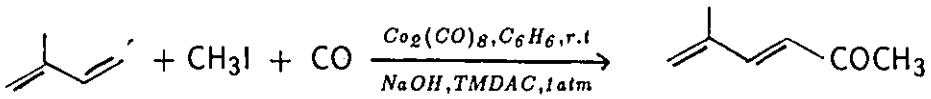
Aromatic or vinylic bromides cannot be carbonylated by $Co(CO)_4^-$ under normal PTC conditions. However, conversion of the vinylic bromides to carboxylic acids can be effected by UV irradiation at 65°C [193], while the aromatic bromides give

aryl methyl ketones and aromatic carboxylic acids in the presence of excess methyl iodide under extremely mild conditions [194].

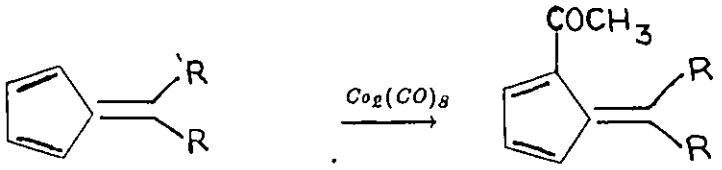
$$\mathrm{ArX} + \mathrm{MeI} + \mathrm{CO} \xrightarrow[NaOH,C_6H_6]{Co_2(CO)_8,CTAB} \mathrm{ArCOMe} + \mathrm{ArCOOH} \qquad (1.73)$$

Allyl chlorides can be transformed into mixtures of butanoic acids via nickel tetracarbonyl catalysed carbonylation under PTC conditions with polynuclear nickelates as reaction intermediates [195]. Cyanonickel catalysts can also be effective [196].

Carbonylation of dienes and trienes by dicobalt octacarbonyl under PTC conditions, in the presence of iodomethane, leads to good yields of (E)-conjugated dienones and trienones with the acylation always being at the least substituted terminal carbon of the diene unit [197]. Under the same conditions, diaryl fulvenes give 1-acylated fulvenes as the only monoketone. Dialkyl fulvenes lead to double carbonylation [198].



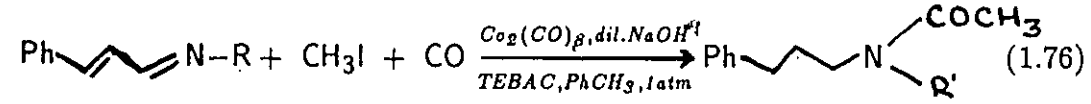
$$TMDAC = C_{12}H_{25}N(CH_3)_3Cl \qquad (1.74)$$



(1.75)

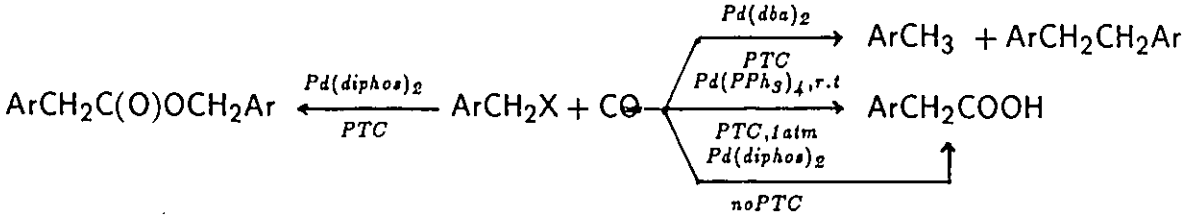
Regiospecific dicobalt octacarbonyl catalysed reaction of allenes under PTC conditions (with MeI, NaOH, C_6H_6, and CTAB), affords unsaturated hydroxy ketones [199].

Schiff bases can be reductively acylated under PTC conditions while azadienes, under identical conditions, lead to regiospecific formation of allyl amides [200].



(1.76)

Zero valent palladium complexes have been extensively used as catalysts for a variety of reactions under phase transfer conditions. Under PTC, bis(triphenylphosphine)palladium dichloride, in the presence of PPh_3 reacts with benzylic halides to give the carboxylic acids in good yields [201]. However, this is not an authentic PTC reaction [202]. Alper and co-workers have also used bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) and bis(bis-1,2-diphenylphosphino)ethane palladium(0) ($Pd(diphos)_2$) as catalysts. Coupling and dehalogenation occurs in an authentic PTC reaction with $Pd(dba)_2$. In the absence of the phase transfer agent, $Pd(diphos)_2$ gives the carboxylic acid while carbalkoxylation occurs under PTC.



Vinylic bromides can be selectively catalysed by palladium(0) to diynes, α,β-unsaturated monoacids and diacids [203]. Bromostyrenes are carbonylated to acids in good yields in a biphasic reaction with $Pd(PPh_3)_4$ and in an authentic PTC system with $Pd(diphos)_2$ [204]. Aldehydes can also be converted to the homologous acids by a two-step procedure involving initial generation of a vinylic dibromide and then its dehalogenation by $Pd(diphos)_2$ with PEG-400 as the phase transfer agent [205].

Alkenes can be oxidised to ketones by the well established homogeneous Wacker process. It is possible to do the same with Pd(0) catalysts under PTC conditions with the nature of the quaternary ammonium salt governing the course of the reaction [206]. Cyclodextrins can also be used as phase transfer agents in these reactions

[207].

$$RCH{=}CH_2 + O_2 \xrightarrow[R_4N^+X^-,C_6H_6,H_2O,80^\circ C]{PdCl_2/CuCl_2.2H_2O,1\,atm} RC(O)CH_3 \qquad (1.77)$$

β-Cyclodextrins promote the conversion of aryl alkyl ketones and aromatic aldehydes by chloro(1,5-hexadiene)rhodium(I) dimer to hydrocarbons under very mild PTC conditions [208]. Benzylic alcohols can be dehydrogenated to carbonyl compounds in the presence of chlorodicarbonylrhodium(I) dimer under PTC [209].

Water soluble alkenes can be hydrogenated by chlorotris(triphenylphosphine)-rhodium in a two-phase system. Water insoluble alkenes can also be hydrogenated by the use of a water soluble rhodium complex [210]. Conjugated dienes can also be hydrogenated to monoalkenes by a mixture of cobalt chloride, potassium cyanide and chloride, with sodium hydroxide and benzene as the two phases along with a phase transfer agent [211].

$$CH_2{=}C(CH_3)CH{=}CH_2 + H_2 \xrightarrow[Me_4N^+Cl^-,C_6H_6]{CoCl_2.6H_2O,KCN,KCl,NaOH} (CH_3)_2C{=}CHCH_3 \qquad (1.78)$$

Cobalt carbonyls induce the hydrogenation of activated alkenes under acidic PTC conditions. Benzene and 48–50% HBF_4 being the two phases and sodium-4-dodecylbenzenesulphonate acts as the phase transfer agent [212].

Reduction of α,β-unsaturated ketones and esters can be achieved with sodium formate and $RuCl_2(PPh_3)_3$ in a phase transfer system [213]. Replacing the metal catalyst with Wilkinson's catalyst and having excess formate leads to transfer hydrogenation in the presence of PPh_3 [214].

$$R_2CO + HCOONa + H_2O \xrightarrow[Aliquat366,Xylene]{Rh\ cat.,90^\circ C,1.5h} R_2CHOH \qquad (1.79)$$

The crown ether catalysed reaction of vinyl halides with KCN in the presence of $Pd(PPh_3)_4$ gives vinyl nitriles in excellent yields [215]. Cyanation of aryl halides

can be achieved with tris(triphenylphosphine)nickel(0) as the catalyst with both liquid/liquid and solid/liquid PTC systems [216].

There are of course many other examples in the literature of "classical" phase transfer catalysis, as well as those in which organometallic complexes are involved either as catalysts or as reactants.

1.3 Aims Of Research

Our goal, from the outset, was to discover and develop new processes, catalysed by organometallic complexes, for the desulphurisation and carbonylation of organic substrates under phase transfer and homogeneous conditions. We wanted to also develop a metal catalysed system for the desulphurisation of crude oil and bitumen and to this end, synthesise novel organometallic sulphur complexes.

Desulphurisation Of Thiols

The demonstrated versatility of organometallic phase transfer catalysis prompted us to investigate the possibility of applying this technique to desulphurisation — an important class of reactions which had hitherto not been the subject of such an investigation. Thiols were chosen as substrates for model desulphurisation studies, the aim being to obtain hydrocarbons as desulphurised products.

Desulphurisation Of Crude Oil And Bitumen

The sulphur content of crude oils, and bitumen, are fairly low. Nevertheless, there exists a need to lower the sulphur content of these as well as to develop new "mild" desulphurisation systems. All commercial desulphurisation processes are heterogeneous in nature and require fairly drastic operating conditions. The intent of

our investigation was to determine whether the systems developed for the desulphurisation of activated thiols could also be utilised in the case of crude oil and Athabasca bitumen. The development of a "mild" desulphurisation system would be of industrial interest.

Synthesis Of Organometallic Sulphur Complexes

Phase transfer catalysis can be a useful tool for the synthesis of organometallic complexes. There are no reported examples of the synthesis of organometallic sulphur complexes under phase transfer conditions. Our expectation was that novel organometallic sulphur complexes could be synthesised by the reaction of transition metal complexes with elemental sulphur under phase transfer conditions and that these would shed some light on the usefulness of certain complexes as desulphurisation catalysts.

Carbonylation Reactions

Carbonylation of nitro compounds to isocyanates is of industrial importance as is the hydroformylation of alkenes. Investigation of both under phase transfer conditions seemed attractive enough to be undertaken. Based on some earlier work carried out in our laboratory, it was predicted that alcohols could be carbonylated, via the corresponding thiols, to the ester in the presence of a second alcohol (e.g. ethanol) by transition metal catalysts under homogeneous conditions.

Chapter 2

Results And Discussion

The research material which forms the basis of this thesis consists of several distinct projects. The projects engaged in were neither always successful nor proceeded as anticipated. Results obtained in these projects are presented and discussed in this chapter of the thesis. Research into several diverse fields were undertaken with the utilisation of organometallic complexes being the common link. All the reactions carried out can be classified as either phase transfer or homogeneous in nature.

The projects were initiated in a logical sequence and the relevant results are presented and discussed in a more or less chronological manner.

2.1 Desulphurisation Of Organosulphur Compounds Under Alkaline Phase Transfer Conditions

Phase transfer catalysis (PTC) cannot be rivalled by any other catalytic method in organic synthesis with respect to its rapid adoption and extensive application over the last 20 years [159]. Publications in this field have increased at a remarkable pace, as has its utilisation in research laboratories and industry. The first examples of the application of phase transfer catalysis to reactions which involved organometallic complexes were reported in 1976. Since then, there have been many

interesting developments in this field [214,217]. Examples include carbonylation of halides, Schiff bases, strained heterocycles and alkynes, hydroformylation and the reduction of alkenes and nitro compounds, nucleophilic substitution and isomerisation reactions. A whole range of metal complexes under many different conditions have been used in these alkaline PTC reactions. The introductory chapter includes a review of this subject matter.

Desulphurisation reactions are important for several reasons, one being the need to reduce the sulphur content of crude oils and bitumen. Various existing desulphurisation reactions have been reviewed in the introductory chapter, ranging from heterogeneous metal catalysed commercial processes run under severe conditions to heterogenised systems as well as homogeneous metal catalysed desulphurisation reactions which are of academic interest. Thiols are major components of the organic sulphur contents of crude oils. Thiols and thioketones are two organosulphur compounds which are very susceptible to desulphurisation. Thus it is not surprising that these substrates are often the subject of model studies into new desulphurisation processes.

2.1.1 Desulphurisation Of Activated Thiols By Organometallic Complexes

Despite the demonstrated versatility of organometallic phase transfer catalysed reactions, there appeared to be no reported examples of the use of PTC for the desulphurisation of organosulphur compounds by organometallic complexes. This prompted an investigation into the possibility of developing an organometallic induced desulphurisation process under alkaline PTC. Thiols were the substrates of choice in these model studies, with the goal being to obtain high yields of hydrocarbons as desulphurised products.

A variety of activated benzylic thiols were desulphurised to hydrocarbons (as the major product) in good yields by either triiron dodecacarbonyl or dicobalt octacarbonyl under alkaline liquid/liquid phase transfer conditions. The products, and the yields, of the successful reactions are listed in Table(2.1).

$$R^1R^2R^3CSH + M_x(CO)_y \xrightarrow[5NNaOH,60^\circ]{R_4N^+X^-,C_6H_6} R^1R^2R^3CH \qquad (2.1)$$

Benzene and 5N sodium hydroxide solution (aqueous) were the two phases often used with various quaternary ammonium salts as the phase transfer agents. Most of the reactions were run at 60°C while those run at lower temperatures (e.g. room temperature), led to either lower yields of the hydrocarbon or there was no reaction. Use of lower (e.g. 3N) or higher concentrations (e.g. 25N) of the sodium hydroxide solution were also not advantageous (see Table 2.2). It has recently been shown that in the chlorobenzene/aqueous sodium hydroxide two phase system, an increase in base concentration to 25N, produces both a decrease in the extractability and an enhancement in the reactivity of the hydroxyl ion in the organic phase as quaternary ammonium hydroxide [218]. There was no reaction when 1-octane thiol, 2-naphthalenethiol and 3-toluenethiol were used as substrates under various conditions with different phase transfer agents and metal complexes.

Dicobalt octacarbonyl is slightly superior to triiron dodecacarbonyl as the metal component. Equimolar quantities of thiol and the metal complex were used in these reactions. A complex mixture of products was obtained when a catalytic amount of the metal complex was used (20:1, substrate:metal ratio). No desulphurised products were obtained in the absence of the metal carbonyls. Sulphides and disulphides were produced in these cases. Molybdenum hexacarbonyl ($Mo(CO)_6$) and tungsten hexacarbonyl ($W(CO)_6$) were shown to be ineffective under solid/liquid PTC (18-crown-6, tetrahydrofuran (THF) or hexane, at 70°C or room temperature,

Table 2.1: Desulphurisation Of Activated Thiols To Hydrocarbons Under Alkaline Phase Transfer Conditions

Thiol, $R^1R^2R^3CSH$ [a]			Products[b]	Yield(%)	
R^1	R^2	R^3		$Fe_3(CO)_{12}$	$Co_2(CO)_8$ [c]
$2\text{-}CH_3C_6H_4$	H	H	$2\text{-}CH_3C_6H_4CH_3$	87[d]	81[e]
			$(2\text{-}CH_3C_6H_4CH_2)_2S$	10	7
			$(2\text{-}CH_3C_6H_4CH_2S)_2$	3	10
$4\text{-}CH_3C_6H_4$	H	H	$4\text{-}CH_3C_6H_4CH_3$	58	79
			$(4\text{-}CH_3C_6H_4CH_2)_2S$	4	3
			$(4\text{-}CH_3C_6H_4CH_2S)_2$	5	3
$4\text{-}CH_3OC_6H_4$	H	H	$4\text{-}CH_3OC_6H_4CH_3$	73	82[f]
			$(4\text{-}CH_3OC_6H_4CH_2)_2S$	12	11[g]
$2,4\text{-}Cl_2C_6H_3$	H	H	$2,4\text{-}Cl_2C_6H_3CH_3$	95	-
Ph	Ph	H	$PhCH_2Ph$	82	84
			Ph_3CH	11	10
			$(Ph_2CH)_2S$	5	2
			$(Ph_2CHS)_2$	1	4
Ph	$4\text{-}CH_3OC_6H_4$	H	$PhCH_2C_6H_4OCH_3$	85	98
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	H	$(4\text{-}CH_3OC_6H_4)_2CH_2$	60	34
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	H	$(4\text{-}CH_3C_6H_4)_2CH_2$	80	98
Ph	Ph	Ph	Ph_3CH	65	82[h]

[a] Reaction conditions: under 1 atm N_2, at 60°C, 5N NaOH/C_6H_6 (25 ml of each), with TBAHS (1 mmol) as phase transfer agent; 2 mmols of thiol and metal complex used.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic samples. TBAHS was the phase transfer agent in most cases.

[c] 1-Octanethiol, 3-toluenethiol and 2-naphthalenethiol could not be desulphurised by either metal complexes.

[d] Use of a catalytic amount of the metal complex led to a complex product mixture.

[e] No hydrocarbons detected in the absence of phase transfer agent.

[f] $Mo(CO)_6$ is unable to desulphurise thiol under both solid/liquid and liquid conditions.

[g] With 25N NaOH, the sulphide is the major product.

[h] No desulphurisation occurs without the metal complex.

Table 2.2: Desulphurisation Of Activated Thiols To Hydrocarbons Under Alkaline Phase Transfer Conditions — Effect Of Base Concentration

Thiol, $R^1R^2R^3CSH$ [a]			PT Cat.	Base Conc.	Products[b]/% Yield		
R^1	R^2	R^3			R'H	R'SR'	R'SSR'
Ph	Ph	Ph	THAB	3N	75	10	6
"	"	"	TBAHS	5N	82	12	5
$4CH_3OC_6H_4$	H	H	"	5N	82	11	-
"	"	"	"	25N	26	66	-

[a] Reaction conditions: under 1 atm N_2, at 60°C, NaOH/C_6H_6 (25 ml of each) with 1 mmol of phase transfer catalyst; 2 mmols of thiol and metal complex ($Co_2(CO)_8$ in all cases) used.
[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic samples; R'= $R^1R^2R^3C$.

under hydrogen), as well as in liquid/liquid systems for $W(CO)_6$ (see Table 2.3).

These are authentic phase transfer reactions since no desulphurisation occured in the absence of the quaternary ammonium salt. Various quaternary ammonium salts were used as phase transfer catalysts (see Table 2.3). Tetrahexylammonium hydrogen sulphate (THAHS), benzyltriethylammonium chloride (TEBAC), dodecyltrimethylammonium chloride (DTAC), tetrahexylammonium bromide (THAB) and tetrabutylammonium hydrogen sulphate (TBAHS) were almost equally effective as phase transfer agents. The chain length of the lipophilic cation in these phase transfer agents seems to have no effect on the course of the reaction—this is not always the case in PTC reactions (e.g. Wacker oxidation of alkenes [206]). It is interesting to note that when triphenylmethane thiol was added to a solid/liquid phase transfer catalysed system, the yield of desulphurised product was almost as high as in the liquid/liquid system.

Apart from the already mentioned alkyl and aromatic thiols which could not

Table 2.3: Desulphurisation Of Activated Thiols To Hydrocarbons Under Alkaline Phase Transfer Conditions — Effect Of Phase Transfer Catalyst

Thiol, $R^1R^2R^3CSH$ [a]			Metal	PT Cat.	Yield(%) [b]		
R^1	R^2	R^3	Cat.		R'H	R'SR'	R'SSR'
Ph	Ph	Ph	$Fe_3(CO)_{12}$	TEBAC	62	12	5
"	"	"	"	TBAHS	61	14	3
"	"	"	"	THAB	65	10	6
"	"	"	"	15-Crown-5	63	10	7
2-$CH_3C_6H_4$	H	H	$Co_2(CO)_8$	TBAHS	87	4	5
"	"	"	"	THAB	87	8	3
"	"	"	"	DTAC	81	10	5
4-$CH_3OC_6H_4$	H	H	$Co_2(CO)_8$	TEBAC	69	10	5
"	"	"	"	TBAHS	82	11	-
"	"	"	"	THAB	73	12	-
"	"	"	"	THAHS	72	14	6
"	"	"	"	DTAC	73	10	4

[a] Reaction conditions: under 1 atm N_2, at 60°C, 5N NaOH/C_6H_6 (25 ml of each), with 1 mmol of phase transfer agent; 2 mmols of thiol and metal complex used.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic samples; R'=$R^1R^2R^3C$.

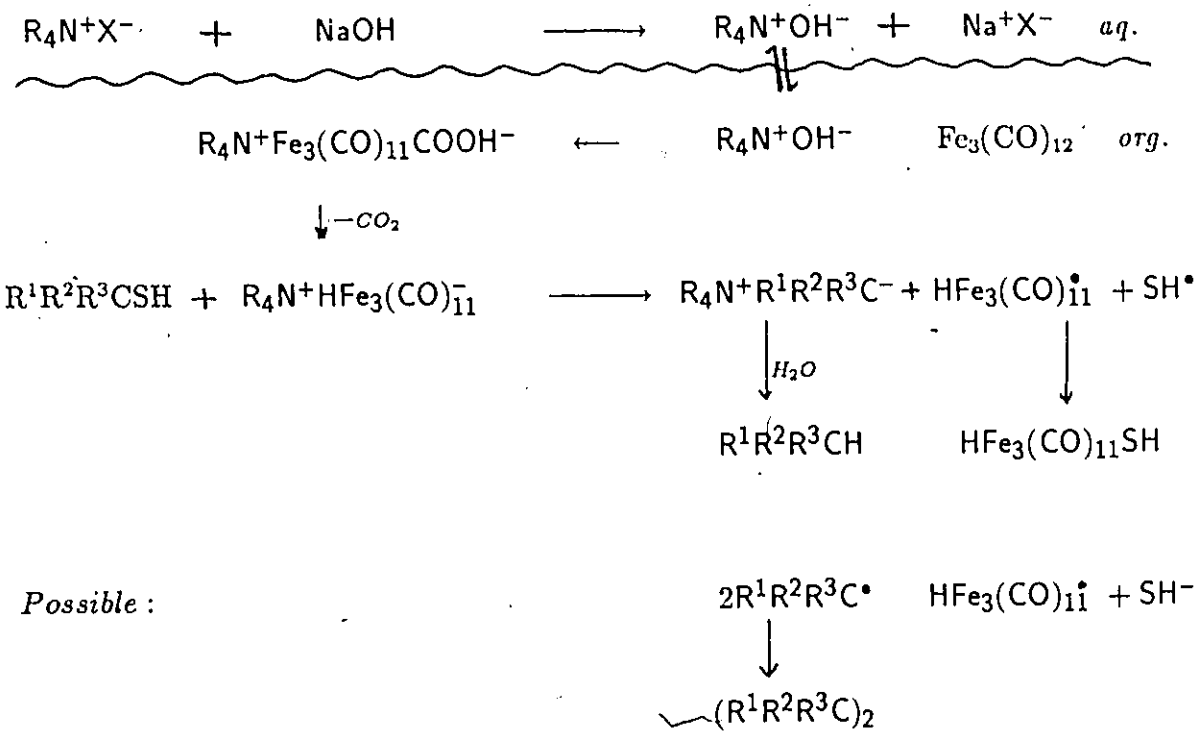
be desulphurised, nearly all the other substrates investigated, were almost equally well desulphurised by both the iron and cobalt complexes. However, there were a few exceptions. While 2,4-dichlorobenzyl thiol could be desulphurised to the hydrocarbon in very good yields by $Fe_3(CO)_{12}$, no hydrocarbon products were detected with $Co_2(CO)_8$ in the presence of neither TBAHS nor DTAC. Only the sulphide and disulphide of the dichlorobenzyl thiol were obtained when $Co_2(CO)_8$ was used as the metal complex. Due to some steric and/or electronic factor, the active cobalt species is unable to coordinate and desulphurise 2,4-dichlorobenzyl thiol to the hydrocarbon. The sulphide and disulphide must arise via a reaction in which the metal complexes do not play a part (reaction in the absence of a metal complex also gives only the mono- and di-sulphides). This is most probably a simple air oxidation of the thiol [85].

$$RSH \xrightarrow{(O)} R{-}S{-}R + R{-}S{-}S{-}R \qquad (2.2)$$

For some inexplicable reason, bis(4-methoxyphenyl)methyl thiol, gives lower yields of hydrocarbons than expected with both the metal compounds. It is interesting to note that when one of the 4-methoxyphenyl groups is replaced by a phenyl, the desulphurisation reaction proceeds very well.

A possible mechanism for the desulphurisation of activated thiols by triiron dodecacarbonyl under alkaline PTC is outlined in Figure 2.1. The quaternary ammonium salt reacts with the hydroxide ion in the aqueous phase to generate the quaternary ammonium hydroxide. This is then transferred to the organic phase where it converts triiron dodecacarbonyl to the postulated trinuclear iron hydride, $R_4N^+HFe_3(CO)_{11}^-$, after loss of CO_2 [219]. Single electron transfer reaction of the hydride with the thiol would give the carbanion $R^1R^2R^3C^-$, and radicals $HFe_3(CO)_{11}^{\bullet}$ and $SH^{\bullet}$. The carbanion is protonated to give the hydrocarbon while the two rad-

Figure 2.1: Proposed Mechanism For The Desulphurisation Of Thiols By Triiron Dodecacarbonyl Under Alkaline Phase Transfer Conditions



icals combine to give the thio complex, $HFe_3(CO)_{11}SH$. Thus, any thiol capable of generating a reasonably stable carbanion can be desulphurised via this process. It is of course possible that the electron transfer reaction could proceed so as to generate the free radicals $R^1R^2R^3C^\bullet$ and $HFe_3(CO)_{11}^\bullet$ and the anion SH^-. However, if that was true, one would expect to isolate at least small amounts of coupled products which is not the case.

When cobalt carbonyl is employed as a reactant, under basic PTC conditions, it has been shown that $Co(CO)_4^-$ is generated in a facile manner [174,214]. It is proposed that the cobalt carbonyl anion converts the thiols to hydrocarbons by a single electron transfer pathway as postulated for triiron dodecacarbonyl.

In a typical reaction, a mixture of freshly prepared 5N sodium hydroxide solution, distilled benzene and the quaternary ammonium salt,in most cases TBAHS, was degassed for 30 minutes with nitrogen bubbling through the stirred mixture. The air-sensitive metal carbonyl was added and the mixture was vigorously stirred for several hours in order to generate the active species. The generation of the active species was indicated by the change in colour of the reaction mixture. Detection of the active species was accomplished through the use of infrared spectroscopy. In the case of dicobalt octacarbonyl, the colour of the organic phase changed from dark brown to a straw yellow and an intense carbonyl stretching band was displayed in the infrared region around 1885 cm^{-1}—literature value being 1890 cm^{-1} for $[Co(CO)_4^-][PPN^+]$ [220].

The colour changed from the very deep green to dark red for triiron dodecacarbonyl, indicative of $HFe_3(CO)_{11}^-$. The infrared spectrum of the organic phase displayed the following absorption bands: 2070(w), 2002(s), 1970(m), 1945(w), 1715(m) cm^{-1} which are very close to the literature values, e.g. $Et_4N^+[HFe_3(CO)_{11}^-]$ shows stretching bands at 2070(w), 2000(vs), 1972(s), 1946(m), 1718(m) cm^{-1} [221].

No other organometallic species which may play a role in the reaction was detected or isolated.

The thiol was then added and the mixture stirred overnight at 60°C under nitrogen. The products were identified by comparison of spectral properties with those of authentic samples (analysed by infrared and proton NMR spectroscopy and by g.c.-mass spec). Fractional distillation or chromatography with silica gel were used for purification purposes. No products were ever isolated from the aqueous phase. The fate of the organometallic species is not known since we were unable to isolate any organometallic products.

Reactions in which no desulphurised products were isolated, were then repeated to confirm the results obtained in the earlier reactions. The substrates were then subjected to modified reaction conditions and these also were not successful in most cases. For example, 1-naphthalenethiol was the subject of seven different reactions, under widely differing conditions ranging from solid/liquid systems at 70°C and room temperature to a liquid/liquid system in which THAHS was the phase transfer agent, dichloromethane was the organic phase and water/sodium borohydride the aqueous phase. Dicobalt octacarbonyl was used as the metal complex for both reactions. The latter reaction was run under nitrogen at 40°C. It is interesting to note that this method for the desulphurisation of thiols with water/sodium borohydride as the aqueous phase, was successfully used to give the desulphurised product in 71% yield when applied to 4-methoxybenzyl thiol. Some of the experiments were also repeated exactly as before and under altered conditions, e.g. with different phase transfer agents, gas, or temperature. Molybdenum and tungsten hexacarbonyl were also used as metal complexes to no avail (see Table 2.4).

The desulphurisation reactions could be run equally well under carbon monoxide, synthesis gas (1:1 CO/H_2, syn gas), hydrogen or nitrogen. This is not too

Table 2.4: Attempted Desulphurisation Of 1-Naphthalenethiol Under Alkaline Phase Transfer Conditions

Metal Cat.[a]	PT Cat.	Organic Phase	Aqueous Phase	Reaction Cond.	Products
$Co_2(CO)_8$	TEBAC	C_6H_6	5N, NaOH	60°,N_2	-
"	THAHS	"	"	"	-
$W(CO)_6$	"	"	"	r.t,H_2	RSSR
$Co_2(CO)_8$	"	CH_2Cl_2	$NaBH_4$,H_2O	50°,N_2	
$Mo(CO)_6$	18-Cr-6	THF	KOH	70°,H_2	-
"	"	Hexane	"	"	-
$W(CO)_6$	"	THF	"	r.t,H_2	-

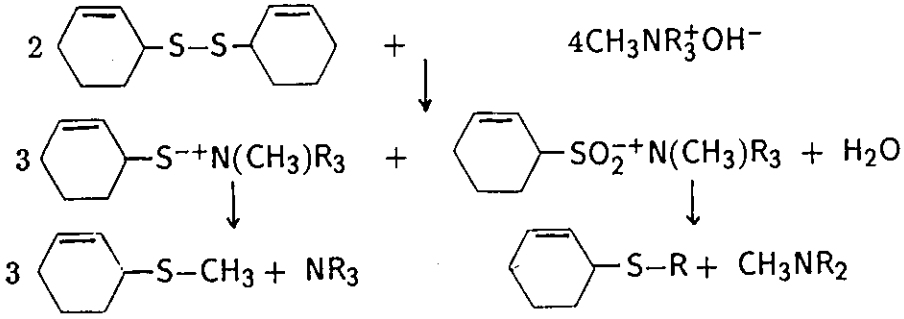
[a]Reaction conditions: under 1 atm pressure, at 50°, 60°, 70°C or room temperature, equal volumes of both phases (25 ml), 1 mmol of phase transfer agent; 2 mmols of thiol and metal complex used.

surprising since the active species can be generated under various gases as long as air is excluded from the reaction system. It is obvious that hydrogen gas is not the source of hydrogen in these reactions and this was taken into consideration in the proposed mechanism. Benzene was found to be the most suitable organic phase. Dichloromethane, tetrahydrofuran and *tert*-amyl alcohol were also tried but lower yields resulted in all cases.

The thiols used were either purchased or synthesised by converting the corresponding ketone to the thioketone by reaction with tetraphosphorus decasulphide (P_4S_{10}) [222], which was then reduced with sodium borohydride to the thiol and purified before use.

$$\begin{array}{l} RC(O)R' + P_2S_5 \longrightarrow RC(S)R' \\ \qquad\qquad\qquad\qquad\quad \downarrow NaBH_4 \\ \qquad\qquad\qquad\qquad\quad RCH(SH)R' \end{array} \qquad (2.3)$$

It is interesting to note that in 1985, workers at BF Goodrich reported on the scission of polysulphide crosslinks in rubber particles through alkaline PTC [223]. Phase transfer agents, containing a methyl group, were able to rupture the S-S bonds to give the methyl sulphides and in the process were somewhat decomposed.



Exclusive methyl transfer from the quaternary ammonium salt and no detectable

transfer of R, where R=n-C_6H_{13} or mixed C_8–C_{10} alkyl, was observed. In contrast, no methyl sulphides were detected in the thiol reactions. This is the first example of alkaline phase transfer catalysed desulphurisation of thiols to hydrocarbons aided by organometallic compounds [224].

Several attempts at desulphurisation of the above activated benzylic thiols were made with bromo(pentacarbonyl)manganese ($Mn(CO)_5Br$) and $Co_2(CO)_4(dmb)_2$ (dmb=dimethylbutadiene) as the metal complexes in the presence, and absence of iodomethane. Reactions with bromo(pentacarbonyl)manganese were carried out under nitrogen, at 40°C, with dichloromethane and 5N sodium hydroxide solution as the two phases, and TEBAC as the phase transfer agent to give only the sulphides. The substrate to metal ratio was 10:1. The cobalt complex was synthesised according to the procedure described by Winkhaus and Wilkinson [225] and used in a benzene/5N sodium hydroxide system, with TBAHS, under carbon monoxide at room temperature or 60°C, to give only the sulphides. The substrate to metal ratio was 20:1. When iodomethane was added to the reaction systems, small quantities of 4-methylanisole, the desulphurised product from 4-methylbenzyl thiol, was obtained with both complexes. It was hoped that the methyl ketones would be the desulphurised products. However, the major product was the methylsulphide (the same product was formed in the absence of the metal complex). See Table 2.5. The methyl sulphide obviously arises via an ordinary organic reaction without the metal playing any role in the reaction. This project was then abandoned since a fairly good process for the desulphurisation of activated thiols had already been developed.

A totally different approach was taken in the attempted desulphurisation of thiocarbonyl compounds.

Table 2.5: Attempted Desulphurisation Of Activated Thiols By Metal Complexes In The Presence Of Iodomethane Under Alkaline Phase Transfer Conditions

Substrate[a] $RC_6H_4CH_2SH$	Metal[b] Complex	PT Cat.	Reaction Conditions	Aqueous[c] Phase	CH_3I	Products[d],%
2-CH_3	A	TEBAC	45°,N_2	5N	-	sulphide, 42 disulphide, 56
"	"	"	40°,CO	0.5N	Yes	Me-sulphide, 65 sulphide, 10 disulphide, 15
4-CH_3	A	"	"	5N	Yes	Me-sulphide, 62 sulphide, 12 disulphide, 10
4-Cl	A	TBAHS	r.t,N_2	5N	No	sulphide, 42 disulphide, 45
4-CH_3O	A	TEBAC	40°,CO	H_2O	Yes	Complex Mix.
"	"	"	"	5N	Yes	Me-sulphide, 63 sulphide, 29
"	"	"	"	"	No	sulphide, 57 disulphide, 39
"	B	"	"	"	Yes	Me-sulphide, 16 sulphide, 49 disulphide, 27
"	-	"	"	"	Yes	Me-sulphide, 91

[a] 10 mmol of substrate, 0.5 mmol of metal complex and 1 mmol of phase transfer agent used; reactions run under 1 atm N_2.

[b] A=$Mn(CO)_5Br$; B=$Co_2(CO)_4(dmb)_2$.

[c] NaOH solution except where otherwise noted; CH_2Cl_2 was the organic phase with A, benzene with B.

[d] Products were identified by comparison of spectral properties (^{1}H NMR, mass spec) and g.c. retention times with those of authentic materials.

2.1.2 Desulphurisation Of Thiocarbonyls

Numerous methods have been reported for the conversion of thiocarbonyl to carbonyl compounds including the use of sodium peroxide [226]. Among the number of reagents and catalysts developed for converting a thiocarbonyl functional group into a carbonyl group, is a recently described process which uses clay-supported ferric nitrate ("Clayfen") [227]. This reagent is superior to many other methods but works well only for thiobenzophenones.

Despite extensive investigations, few reactions are known in which transition metal cyano complexes act as catalysts. Recently, cyanonickel (II) complexes were shown to be effective catalysts for the carbonylation of allyl chlorides and bromides under alkaline phase transfer conditions [196]. The most useful catalyst precursor was reported to be nickel cyanide ($Ni(CN)_2$). It was hoped that cyanonickel (II) complexes, in particular nickel cyanide, would be able to effectively catalyse, under basic PTC, the desulphurisation of thiocarbonyl compounds. Thus, 4,4′-dimethoxythiobenzophenone can be converted to 4,4′-dimethoxybenzophenone (40%) and 4,4′-dimethoxydiphenylmethane (5%), in the presence of $Ni(CN)_2$ with 4-methyl-2-pentanone and 5N sodium hydroxide solution as the two phases. Tetrabutylammonium hydrogen sulphate was the phase transfer agent. The reactions were run under 1 atm of carbon monoxide or synthesis gas, at room temperature or 60°C, over 1-2 hour(s) and vigorous stirring, without affecting the yield or product distribution.

$$(CH_3OC_6H_4)_2C{=}S \;+\; CO \longrightarrow (CH_3OC_6H_4)_2C{=}O \;+\; (CH_3OC_6H_4)_2CH_2 \quad (2.4)$$

It was shown at an early stage of the project, that the reaction proceeds in the absence of the metal catalyst. After a few minor modifications, a simple method was developed for the alkaline liquid/liquid phase transfer catalysed desulphurisation of

thiocarbonyls to carbonyl compounds. For example, treatment of thiobenzophenone with 3N sodium hydroxide solution/dichloromethane as the two phases and TBAHS as the phase transfer agent, under 1 atm of nitrogen for 1 hour at room temperature, and subsequent work-up, afforded benzophenone in 90% yield. This is an authentic phase transfer process since no reaction occurs in the absence of the phase transfer agent.

$$RC(S)R' \xrightarrow[TBAHS, N_2, r.t]{1-5N NaOH, CH_2Cl_2} RC(O)R' \qquad (2.5)$$

R=alkyl, aryl, amino

R'=alkyl, aryl, thioalkyl, amino.

The considerable scope of this phase transfer process was illustrated by its utilisation in the facile and efficient conversion of the thiocarbonyl group to the carbonyl function in not only thioketones, but also dienethiones, thioamides, thioureas and the thiocarbonyl function in dithioesters. However, the base concentration and reaction times had to be varied with the different substrates. Thus, a 5N sodium hydroxide solution was required in the desulphurisation of the dienethiones (thioxoandrosta-1,4-diene-3,17-dione) and for thiocamphor, thioamides and thioureas, with reaction times ranging from 2 to 8 hours (see Table 2.6). The dithioester substrates, γ-dithiobutyrolactone and ethyldithioacetate, were desulphurised to the mono-thio product in excellent yields upon treatment with 1N NaOH over several hours.

This method compares favourably with some of the other known methods for effecting the same transformations. For example, the above mentioned "Clayfen" system, which is applicable mostly to thiobenzophenones, gives a 30% yield of camphor from thiocamphor while the present phase transfer catalysed process yields 79% of the same. One of the other processes involves the treatment of a thiocarbo-

Table 2.6: Desulphurisation Of Thiocarbonyl Compounds Under Alkaline Phase Transfer Conditions

Substrate[a]	Base Conc., N	Reaction Times, h	Product[b]	Yield(%) [c]
4,4'-Dimethoxythiobenzophenone	3	40 min.	4,4'-Dimethoxybenzophenone	63[d]
Thiobenzophenone	3	1	Benzophenone	90
Thiocamphor	5	2	Camphor	79
Thioxoandrosta-1,4-diene-3,17-dione	5	8	Androsta-1,4-diene-3,17-dione	72
Ethyldithioacetate	1	7	Ethylthioacetate	99
γ-Dithiobutyrolactone	1	4	γ-Thiobutyrolactone	86
Thiobenzanilide	5	3	Benzanilide	51
Tetramethylthiourea	5	5	Tetramethylurea	75

[a]Reaction conditions: under 1 atm N_2, at room temperature, dichlomethane/NaOH (25 ml of each) as the two phases, and TBAHS as the phase transfer agent.
[b]Products were identified by comparison with IR and mass spec of authentic materials
[c]Isolated by silica gel column chromatography, when necessary.
[d]No reaction after 58 h when TEBAC used or in the absence of phase transfer agent.

nyl compound with aqueous base (potassium carbonate or triethylamine), chloroform or dichloromethane as the organic phase, bis(4-methoxyphenyl)telluride and an excess of 1,2-dibromotetrachloroethane [228]. The organotellurium compound is toxic and expensive, and thus the inexpensive and easy to handle phase transfer catalysed system is preferable.

A system that compares well with the developed PTC system was reported by Kochhar and co-workers. Primary, secondary, and tertiary thioamides, as well as a thiolactam, were efficiently converted to their carbonyl analogues in a facile manner upon reaction with *m*-chloroperbenzoic acid (MCPBA). The reactions were run at room temperature with slow addition of MCPBA to give good yields of the carbonyl products in about 2 hours [229]. Recently Lawesson and co-workers utilised the nitrosonium ion (NO^+) generated from sodium nitrite/dilute hydrochloric acid to convert a series of thiocarbonyls to the corresponding carbonyl analogues in reasonable yields [230].

Another method with which this mild phase transfer system can be favourably compared to is the halogen catalysed conversion of thiocarbonyl to carbonyl compounds using alkoxides and hydroxide ion [231]. Very strong base (25N sodium hydroxide solution), TEBAC as the phase transfer agent, and halogen are required in these reactions. Singh et al. reported the yield for the phase transfer reaction only in the case of thiobenzamide, but also mentioned that thiocamphor and benzyl dithiobenzoate afforded many products. It should be noted, that when TEBAC was used as the phase transfer agent in the attempted desulphurisation of 4,4′-dimethoxythiobenzophenone in 3N sodium hydroxide solution/dichloromethane, no reaction occured even after 58 hours. The difference in the behaviour of TEBAC and TBAHS is probably due to the relative degree of extractability, into dichloromethane, of the two active catalytic species — i.e. the quaternary ammonium

hydroxides [232]. Other phase transfer agents were not tried in this process [233].

In conclusion, a metal catalysed desulphurisation of activated thiols under alkaline phase transfer conditions was developed. It was also shown that thiocarbonyls could be converted to the carbonyl analogues under "classical", i.e. without a metal catalyst, alkaline phase transfer conditions.

2.2 Reactions Under Acidic Phase Transfer And Biphasic Conditions

There have not been many investigations into phase transfer catalysed reactions in acidic media [234,235,236]. As mentioned earlier, phase transfer catalysis is clearly a valuable synthetic method in organometallic chemistry (e.g. [173,193,217]). Prior to 1983, all of the chemistry with organometallic phase transfer catalysis had been effected under alkaline conditions. The first examples of organometallic phase transfer catalysis under acidic conditions were reported by Alper and Heveling in 1983 [212]. Diarylethenes and other activated alkenes were hydrogenated in high yields on reaction with dicobalt octacarbonyl, using sodium 4-dodecylbenzenesulphonate as the phase transfer catalyst, with benzene and 48–50% aqueous tetrafluoroboric acid as the two phases at 55°C (1 atm nitrogen, 4 hours). The reaction proceeds equally well with bis(tri-*n*-butylphosphine) dicobalt hexacarbonyl as the metal complex.

$$R_2C{=}CH_2 + \text{Metal Cat.} \xrightarrow[C_6H_6,48-50\%HBF_4]{C_{12}H_{25}C_6H_4SO_3^-Na^+} R_2CH{-}CH_3 \qquad (2.6)$$

It has been proposed that the reaction probably proceeds via a hydridocobalt carbonyl species, $HCo(CO)_3L$ (L=CO, PBu_3^n). The latter do not participate in the stoichiometric hydrogenation of arylethenes with hydridocobalt tetracarbonyl [237].

2.2.1 Phase Transfer Hydrogenation Of Activated Ethenes And Dienes By Organometallic Complexes

Hydrogenation reactions are important for various reasons including asymmetric hydrogenation which is of importance in the pharmaceutical and agrochemical industries [238]. It was desirable to extend the hydrogenation process under acidic PTC by cobalt complexes to other unsaturated substrates. With this in mind, reactions were effected on styrenes, activated dienes, and employing cobalt complexes containing chelating ligands.The hydrogenation of a series of styrenes and dienes were carried out in a benzene/48–50% fluoroboric acid (aq.) mixture under nitrogen, at 55°C with sodium 4-dodecylbenzenesulphonate as the phase transfer agent and cobalt complexes.The products and yields are listed in Table 2.7.

The order of reactivity was α-methylstyrene > styrene > 1,1-diphenylethene ≥vinylnaphthalene > 2,4-dimethylstyrene. This is somewhat different from that observed in the stoichiometric hydrogenation reactions by $HCo(CO)_4$ [237,239], where the following order is observed — 1,1-diphenylethene > vinylnaphthalene > 2,4-dimethylstyrene > α-methylstyrene > styrene. The reason for the difference in behaviour between the two systems could be the mechanisms operating in each case. For $HCo(CO)_4$, the reaction proceeds via a geminate-pair free-radical pathway. The phase transfer reaction is retarded by carbon monoxide while the homogeneous reaction is independent of carbon monoxide concentration [239,240].

Hydrogenation of 1-phenyl-1,3-butadiene under acidic PTC by $Co_2(CO)_8$, yields 1-phenyl-1-butene and 1-phenyl-2-butene in a 55:45 ratio (58% yield). Consistent with the generation of an allylic cation intermediate, no 4-phenyl-1-butene was detected. Not surprisingly, 1,4-diphenyl-1,3-butadiene gave equal amounts of the expected 1,4-diphenyl-1-butene and 1,4-diphenyl-2-butene.

Table 2.7: Hydrogenation Of Activated Ethenes And Dienes Under Acidic Phase Transfer Conditions

Substrate [a]	Cobalt Complex[b]	Reaction Temp.(°C)	Reaction Time(h)	Hydrogenated Products (%)[c]
$Ph_2C=CH_2$	A	55	4	97
	B	77	6	58
	"	"	24	-[d]
	C	"	3	97
4-$CH_3OC_6H_4C(Ph)=CH_2$	B	70	6	64
$PhCH=CH_2$	A	55	1	98
$PhC(CH_3)=CH_2$	A	55	45 min	98
	"	"	5.5	54 [e]
	B	72	6.5	58
	C	"	1	56[f]
2,4$(CH_3)_2C_6H_3CH=CH_2$	A	55	3.5	66
	C	71	2.5	100
	"	"	"	25
2-Vinylnaphthalene	A	55	2	68
$PhCH=CH-CH=CH_2$	A	55	3	58
$PhCH=CH-CH=CHPh$	A	58	3	67

[a] Equal volumes of 48–50% HBF_4 and benzene (25 ml), 0.5 mmol Na DBS, 0.5 mmol cobalt complex, 1 mmol of substrate, under 1 atm N_2.

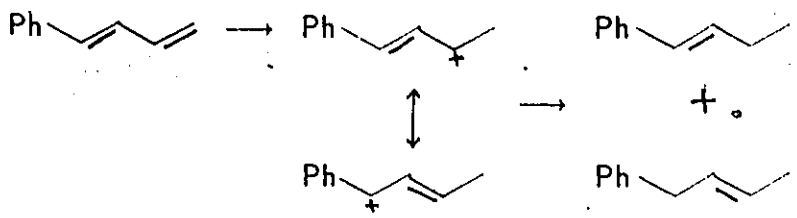
[b] A=$Co_2(CO)_8$, B=$Co_2(CO)_6$dpm, C=$Co_2(CO)_6$dasm.

[c] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those of authentic materials.

[d] No phase transfer catalyst present.

[e] Under CO atmosphere.

[f] Yield was 84% after 5 h, and 98% after 7 h.

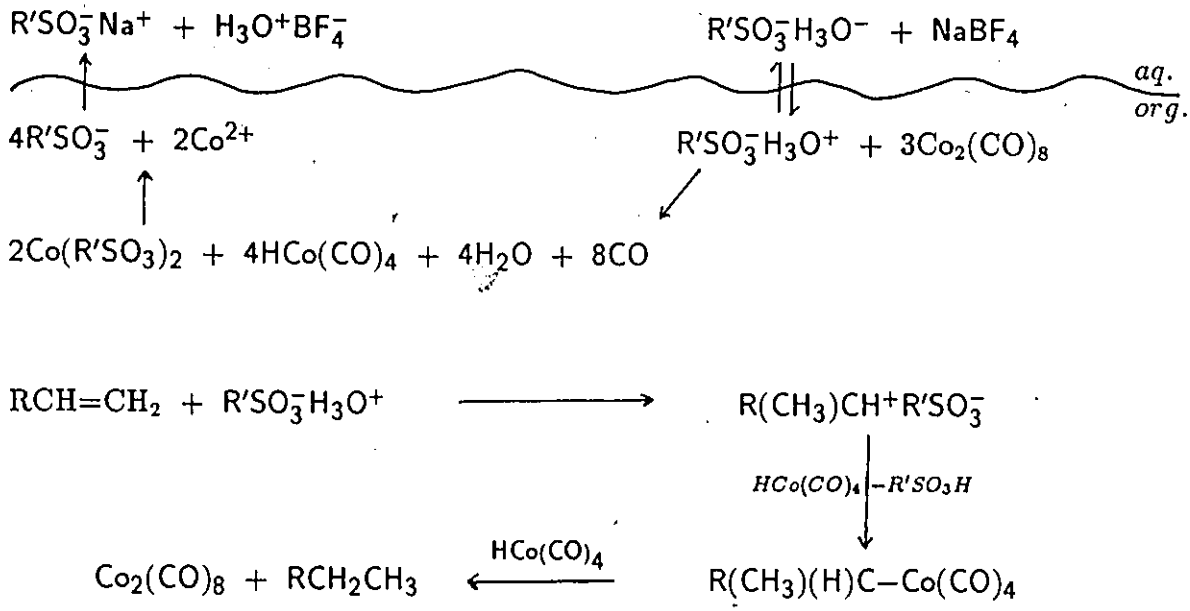


It has been shown that the reaction not only proceeds via a hydridocobalt carbonyl species but also via a carbonium ion intermediate. Therefore, two possible mechanisms can be postulated. The first (Figure 2.2) involves an initial step in which the phase transfer agent reacts with the aqueous fluoroboric acid to give $R'SO_3^-H_3O^+$ ($R'=C_{12}H_{25}C_6H_4$) [241]. This is then transferred to the organic phase where it reacts with $Co_2(CO)_8$ to give the mononuclear hydride $HCo(CO)_4$, and protonates the organic substrate to yield the carbonium ion $R(CH_3)CH^+R'S_3^-$. The carbonium ion reacts with the hydride to give the complex $RCH(CH_3)Co(CO)_4$ and subsequently RCH_2CH_3 and $Co_2(CO)_8$. The reaction is stoichiometric with respect to the metal and this is most probably due to the disproportionation which occurs in the generation of the hydride with cobalt(II) sulphonate being transferred to the aqueous phase. The source of carbon monoxide inhibition is also in the step leading to $HCo(CO)_4$.

The alternative mechanism (Figure 2.3) involves the formation of $HCo(CO)_3$ from the *in situ* generated $HCo(CO)_4$. The former then can bind the unsaturated organic substrate. The pathway may involve a π-allyl complex which would account for the observed product distribution.

The reaction can also be carried out with the bidentate complexes bis(diphenylphosphino)methane dicobalt hexacarbonyl ($Co_2(CO)_6$dpm) and bis(diphenylarsino)-methane dicobalt hexacarbonyl ($Co_2(CO)_6$dasm) (prepared according to [242]). For

Figure 2.2: Proposed Mechanism For The Hydrogenation Of Styrenes And Dienes By $Co_2(CO)_8$ Under Acidic Phase Transfer Conditions

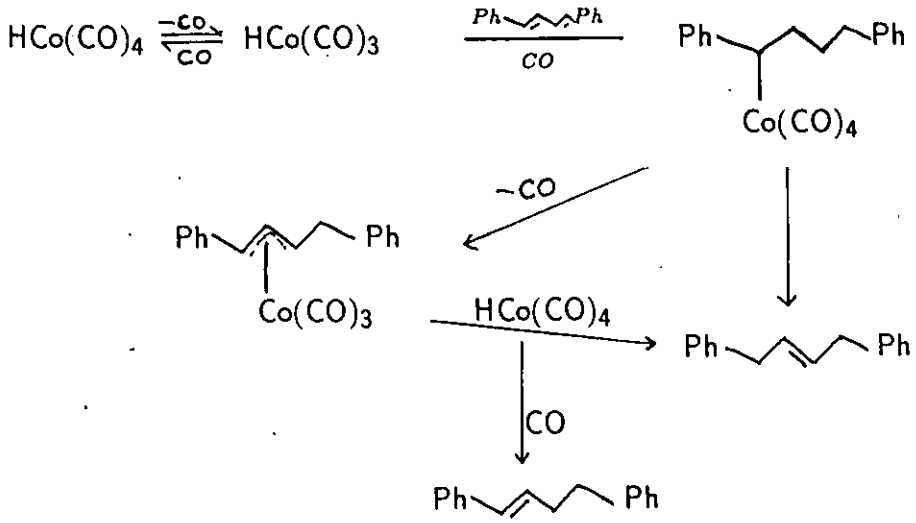


example, 1,1-diphenylethene gives the hydrogenated product in yields of 97% with $Co_2(CO)_8$, 58% with $Co_2(CO)_6$dpm, and 97% with $Co_2(CO)_6$dasm.

All the reactions are authentic phase transfer catalysed reactions since no hydrogenation occurs in the absence of the phase transfer agent. The arsine complex was more reactive than the phosphine analogue and the stoichiometry was also different (1:1 for the arsine with respect to the substrate, and 2:1 substrate:Co for the other two). The probable reason for the high reactivity of the arsine complex is that the M—As bond is much weaker than the M—P bond, and thus can generate a vacant site more easily.

A typical experiment involved a mixture of sodium 4-dodecylbenzenesulphonate, equal volumes of 48–50% HBF_4 and benzene being stirred for 30 minutes under nitrogen at room temperature. A benzene solution containing the substrate and

Figure 2.3: Alternative Mechanism For The Hydrogenation Of Dienes



dicobalt octacarbonyl was then added, the mixture was stirred vigorously for 2 hours at 55°C and samples were analysed by thin layer chromatography (TLC) as well as by gas chromatography (after 30, 60 and 105 minutes). Work up was by column chromatography [243].

The success of the hydrogenation reactions prompted an investigation into desulphurisation reactions catalysed by metal complexes under acidic PTC.

2.2.2 Phase Transfer And Biphasic Desulphurisation Of Activated Thiols By Organometallic Complexes

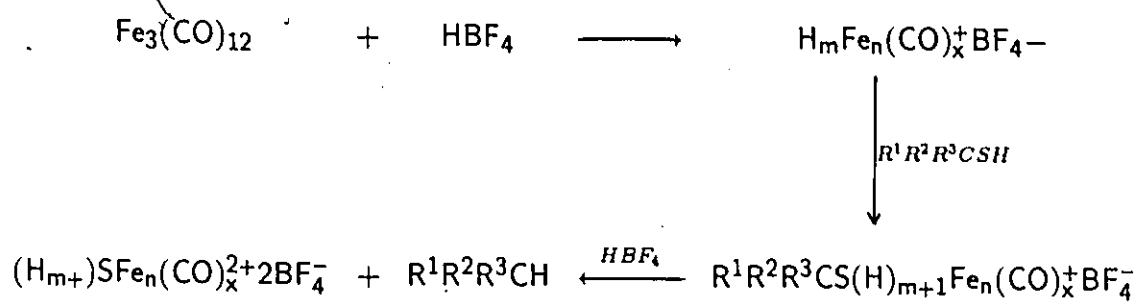
All the reported examples of organometallic phase transfer reactions in acidic media involved the use of cobalt complexes.It was hoped that the acidic PTC system could be extended to induce desulphurisation of thiols with metal complexes. Activated thiols, e.g. 4-chlorobenzyl thiol, were reacted with an equimolar amount of triiron dodecacarbonyl in benzene, 48–50% aqueous tetrafluoroboric acid (as the two phases), sodium 4-dodecylbenzenesulphonate as the phase transfer agent, at 60°C

and under 1 atm of nitrogen. This resulted in low conversion of the thiol in most cases. The major product was the sulphide (e.g. 90% when 4-methylbenzyl thiol was the substrate and 40% in the case of 4-chlorobenzyl thiol) while the desulphurised product was obtained in relatively low yield (e.g. 6% of 4-chlorotoluene and 20% *o*-xylene were formed from the corresponding thiols). However, 2,4-dichlorobenzyl thiol was desulphurised quite effectively by $Fe_3(CO)_{12}$ under acidic PTC to give 73% of 2,4-dichlorotoluene.

$$R^1R^2R^3CSH + Fe_3(CO)_{12} \xrightarrow[C_6H_6, 48-50\%\, HBF_4, N_2]{C_{12}H_{25}C_6H_4SO_3^-Na^+, 60^\circ} R^1R^2R^3CH + (R^1R^2R^3C)_2S + (R^1R^2R^3CS)_2 \quad (2.7)$$

It was clear that the desulphurisation of activated thiols cannot be effectively carried out with $Fe_3(CO)_{12}$ under acidic PTC. However, when the reactions were conducted in the absence of the phase transfer agent, i.e. in a biphasic system, significant improvement in the yields of the hydrocarbon were achieved. For example, 44% of 4-chlorotoluene was obtained under acidic biphasic conditions, while only 6% resulted under acidic PTC, when 4-chlorobenzyl thiol was subjected to the desulphurisation reaction. Further evidence indicating the superiority of the biphasic, compared to the phase transfer system, comes from the improved desulphurisations under biphasic conditions of 4-methoxybenzyl thiol (72%, up from 10% under PTC), and 4-methylbenzyl thiol (15% of *m*-xylene and 44% of the coupled product compared to 90% disulphide and no desulphurised products). The only exception to the trend was the case of 2,4-dichlorobenzyl thiol where the presence of the phase transfer catalyst did not have a detrimental effect on the desulphurisation reaction (see Table 2.8). It is difficult to rationalise this anomaly. The reaction products and yields are listed in Table 2.8. Note that bis(4-methylbenzene)methyl thiol and diphenylmethyl thiol were not subjected to the PTC reaction since by then

Figure 2.4: Proposed Mechanism For Desulphurisation Of Activated Thiols By Triiron Dodecacarbonyl In An Acidic Medium



the biphasic nature of the desulphurisation reaction had already been established.

The desulphurisation reaction is not catalytic with respect to $Fe_3(CO)_{12}$. However, a good yield of sulphide and a reasonable amount of the desulphurised coupled product was obtained when a catalytic amount of the metal carbonyl complex was reacted with 4-methylbenzyl thiol. The use of a lower concentration of tetrafluoroboric acid (25% aq.) resulted in reduced yields of hydrocarbons while no desulphurisation occured when the reaction was effected under homogeneous conditions (i.e. HBF_4 in ether in place of 48–50% HBF_4(aq.) and no phase transfer catalyst). Under homogeneous conditions, 2-methylbenzyl thiol gave ethyl 2-methylbenzyl sulphide. There was no desulphurisation in the absence of the metal carbonyl. Very little change in the product distribution was observed under carbon monoxide when compared to nitrogen.

A possible mechanism for the reaction (Figure 2.4) may involve the generation of a cationic iron hydride by reaction of the metal carbonyl with tetrafluoroboric acid. The iron hydride reacts with the thiol to give a thioiron carbonyl cation (the counter ion is BF_4^-), which may be converted to the desulphurised product by exposure to additional HBF_4. Attempts at isolating an organometallic by–product in these reactions were unsuccessful.

Table 2.8: Desulphurisation Of Activated Thiols Under Acidic Phase Transfer And Biphasic Conditions

Thiol, $R^1R^2R^3CSH$ [a]			Products[b]	Yield(%)	
R^1	R^2	R_3		Phase Transfer	Biphasic
4-ClC_6H_4	H	H	4-$ClC_6H_4CH_3$	6	44
2-CH_3 C_6H_4	H	H	*o*-xylene	20	36
4-$CH_3C_6H_4$	H	H	*p*-xylene	0	15[c]
			(4-$CH_3C_6H_4CH_2)_2$	0	49
			(4-$CH_3C_6H_4CH_2)_2S$	2	28
			(4-$CH_3C_6H_4CH_2S)_2$	90	0
4-$CH_3OC_6H_4$	H	H	4-$CH_3OC_6H_4CH_3$	10	72
			(4-$CH_3OC_6H_4CH_2)_2S$	7	4
2,4-$Cl_2C_6H_3$	H	H	2,4-$Cl_2C_6H_3CH_3$	73	74[d]
			(2,4-$Cl_2C_6H_3CH_2)_2S$	5	10
			(2,4-$Cl_2C_6H_3CH_2S)_2$	2	2
4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	H	(4-$CH_3C_6H_4)_2CH_2$	-[e]	94[f]
Ph	Ph	H	Ph_2CH_2	-	84
			$(Ph_2CH_2)_2S$		8

[a] Reaction conditions: under 1 atm N_2, at 60°C, C_6H_6/48-50% HBF_4(25 ml of each), with Na DBS (1 mmol) as the phase transfer agent; 2 mmol of the substrate and the metal complex.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials.

[c] Use of a catalytic quantity of $Fe_3(CO)_{12}$ gave *p*-xylene (3%), (4-$CH_3C_6H_4CH_2)_2$ (15%), (4-$CH_3C_6H_4CH_2)_2S$ (70%).

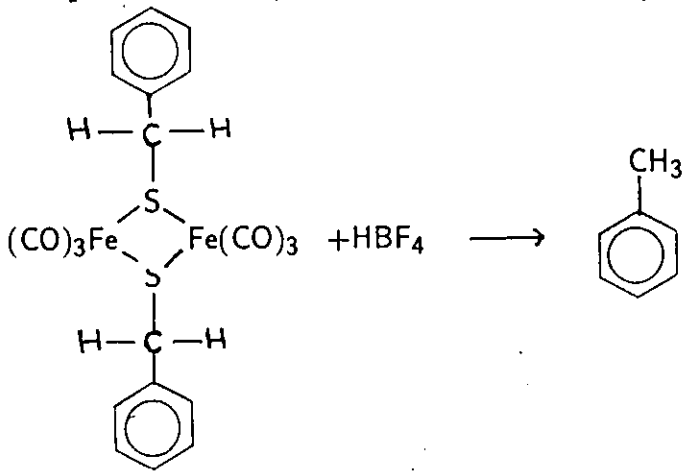
[d] Use of 25% HBF_4 as the aqueous phase resulted in 1% of the hydrocarbon and 32% sulphide.

[e] Not done.

[f] Under CO, 90% yield.

There is a possible explanation as to why the phase transfer system differs significantly in behaviour when compared to the biphasic system. It is believed that H_3O^+-4-$C_{12}H_{25}C_6H_4SO_3^-$ is transfered to the organic phase in acidic phase transfer reactions involving sodium 4-dodecylbenzenesulphonate. The sulphonate anion ion may induce disproportionation of $Fe_3(CO)_{12}$ to a mixture of carbonyl ferrates [244], which may not be able to participate in the desulphurisation reaction and thus explains the observed differences between the biphasic and phase transfer process.

It is conceivable that the desulphurisation reactions proceed via the binuclear complexes $[R^1R^2R^3CSFe(CO)_3]_2$ [245]. However, treatment of $[PhCH_2SFe(CO)_3]_2$ (prepared according to literature procedure [246,247]) with 48–50% HBF_4 under conditions identical to those described for the biphasic reactions, afforded only trace quantities of toluene as determined by gas chromatography. This may not be too surprising in light of the fact that exposure of $[R^1R^2R^3CSFe(CO)_3]_2$ to concentrated nitric acid gives a sulphonic acid rather than the hydrocarbon [247].



In a typical experiment, nitrogen was bubbled through a mixture of equal volumes of benzene and 48–50% HBF_4 — and sodium 4-dodecylbenzenesulphonate in the case of PTC reactions. Triiron dodecacarbonyl was added and the reaction

mixture was stirred under nitrogen for 4 hours at room temperature. The colour changes from the initial dark green to a very dark red, indicative of the formation of an iron hydride species. The thiol was then added and the mixture was stirred overnight at 60°C under nitrogen. Usual work-up was effected and purification was achieved by either fractional distillation or chromatography on silica gel.

It should be noted that dicobalt octacarbonyl was not useful even though the anion $Co(CO)_4^-$ was generated (as indicated by colour of the reaction mixture and infrared spectroscopy) under the reaction conditions. No products were isolated from the aqueous phase.

In conclusion, a process for the desulphurisation of activated thiols by $Fe_3(CO)_{12}$ under acidic biphasic conditions has been developed. The phase transfer catalyst used seems to inhibit desulphurisation. While several useful acidic biphasic reactions have been observed in organic chemistry (e.g. [248]), this is one of the first examples of such a reaction using organometallic reagents [249].

2.3 Synthesis Of Organometallic Sulphur Complexes Under Phase Transfer Conditions

Phase transfer catalysis is a valuable method for the synthesis of a variety of organometallic complexes. Pioneering work by Alper, Darensbourg, Gibson, Shaw and others, have established that ortho-metallation [168], ligand exchange reactions (e.g. [170,171], synthesis of π-allyl [175,176] and acyl-metal carbonyl complexes [250,251], and clusters [174] occur in a facile manner under mild alkaline PTC.

Some interesting complexes have been isolated from the reaction of sulphur with organometallic reagents under homogeneous conditions. The introductory chapter includes a review of these complexes. It was anticipated that the reaction of sulphur with organometallic compounds under phase transfer conditions may lead to unusual

complexes of potential utility as crude oil and bitumen desulphurisation catalysts since both contain "inorganic-sulphur" and "organic-sulphur" components. In light of the previously described work, it was anticipated that both basic and acidic phase transfer systems would be useful.

Gibson and co-workers reported that bromo(pentacarbonyl)manganese can be rapidly converted to the binuclear anion $Mn_2(CO)_9Br^-$ under mild alkaline phase transfer conditions [175,176]. The binuclear species was isolated as the quaternary ammonium salt in high yield and characterised spectroscopically. The anion was found to be highly soluble in dichloromethane but not in benzene. During the course of the following investigation, the anion was also shown to be highly soluble in 4-methyl-2-pentanone.

The anion could be generated very rapidly when bromo(pentacarbonyl)manganese was added, under nitrogen, to a stirred and degassed mixture of dichloromethane, 5N sodium hydroxide and benzyltriethylammonium chloride at 40°C. The generation of the anion was indicated by the change in colour of the reaction mixture, particularly the organic phase, from the initial orange to red and was confirmed by infrared spectroscopy (which matches that reported by Gibson and co-workers).

$$BrMn(CO)_5 \xrightarrow[CH_2Cl_2,5NNaOH]{TEBAC,N_2,40^\circ C} Mn_2(CO)_9Br^- \qquad (2.8)$$

$$Mn_2(CO)_9Br^- \xrightarrow{S_8} [Et_3BzN^+]_2[(Mn(CO)_3(SCS_3))_2]^{2-} \qquad (2.9)$$

The infrared spectrum of $Bz(Et)_3N^+[Br\text{-}Mn(CO)_4\text{-}Mn(CO)_5]^-$ exhibited the following carbonyl stretching bands: 2080(w), 2010(s); 1980(vs), 1970(vs), 1945(m) and 1903(m) cm^{-1} in dichloromethane. Treatment of this *in situ* generated anion with elemental sulphur at 40°C for 3 hours, under nitrogen, afforded a complex con-

taining a novel anionic species. The reaction can also be effected under CO with no change in yield. The complex displays three intense terminal metal carbonyl stretching bands in the infrared region at 1993, 1930 and 1912 cm^{-1} (in dichloromethane and after crystallisation as KBr disk). See Figure 2.5 for the IR spectrum of the complex.

The yield of the manganese-sulphur complex was 46% and orange crystals were obtained after the organic phase had been separated from the aqueous phase, dried with $MgSO_4$, filtered into a Schlenk tube, volume reduced under vacuum, and then stored in a refrigerator for several weeks with a little added hexane. Fine, orange, needle-like crystals were obtained and an elemental analysis of the product showed a significant amount of sulphur to be present. This prompted a single crystal X-ray analysis of the anticipated novel complex to be undertaken in order to unequivocally establish the structure of the complex.

X-ray analysis of the crystals showed that the unit cell contains discrete benzyltriethylammonium cations and $[(Mn(CO)_3(SCS_3))_2]^{2-}$ anions. The cation obviously arises from the phase transfer catalyst. The cation contains a tetrahedral nitrogen atom with bond lengths and angles being similar to other compounds of this type. The structure of the cation is shown in Figure 2.6.

The structure of the dianion proved to be much more interesting. The dianion is completely symmetrical, a dimer with a crystallographically imposed center of inversion. The manganese atoms are bridged by the terminal sulphur of the perthiocarbonate ligands. One of the other terminal atoms of each perthiocarbonate coordinates to an axial site on each manganese to form five-membered SSCSMn chelate rings. Carbonyl ligands complete a distorted octahedral arrangement about each manganese atom. There are no significant differences, within the precision of

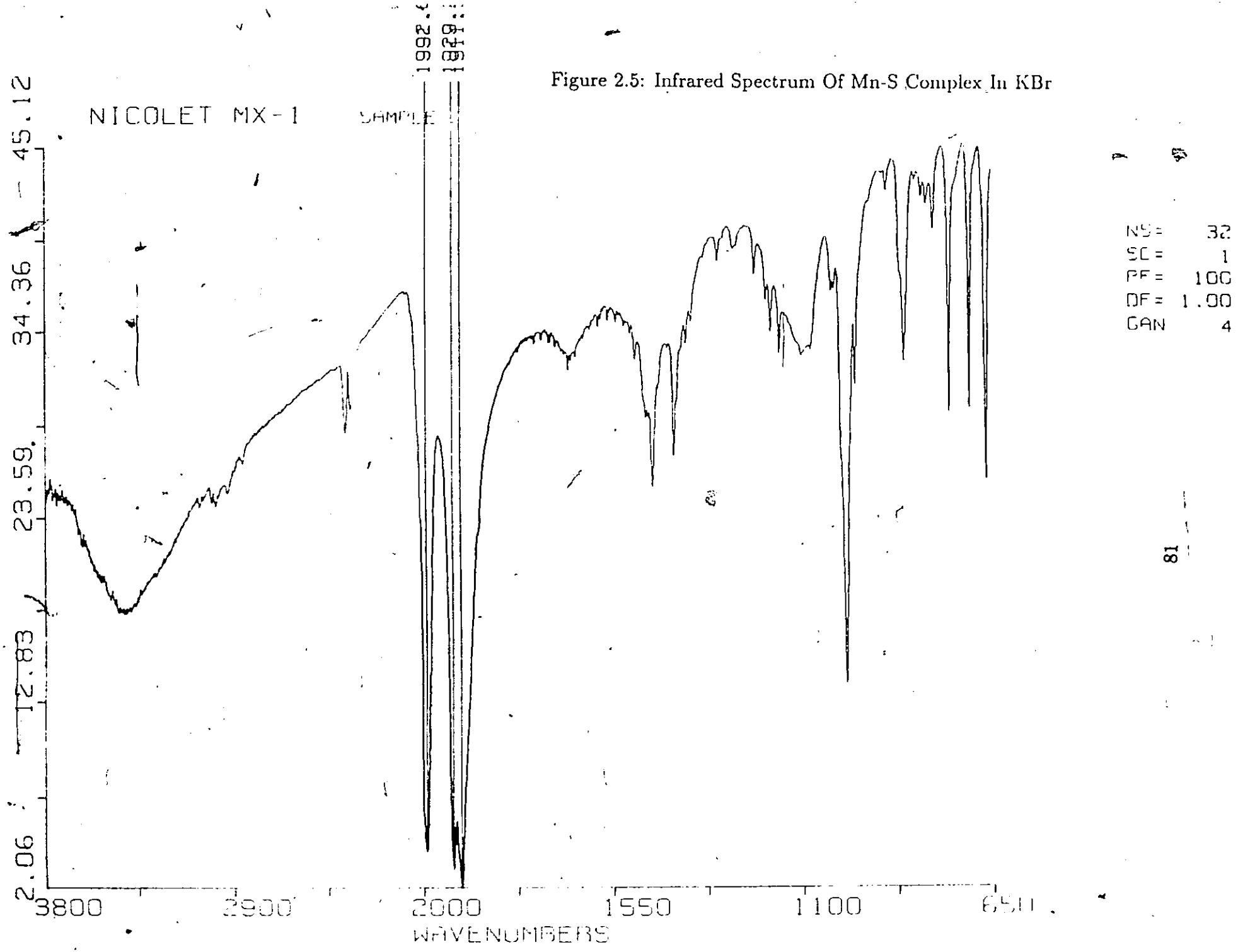
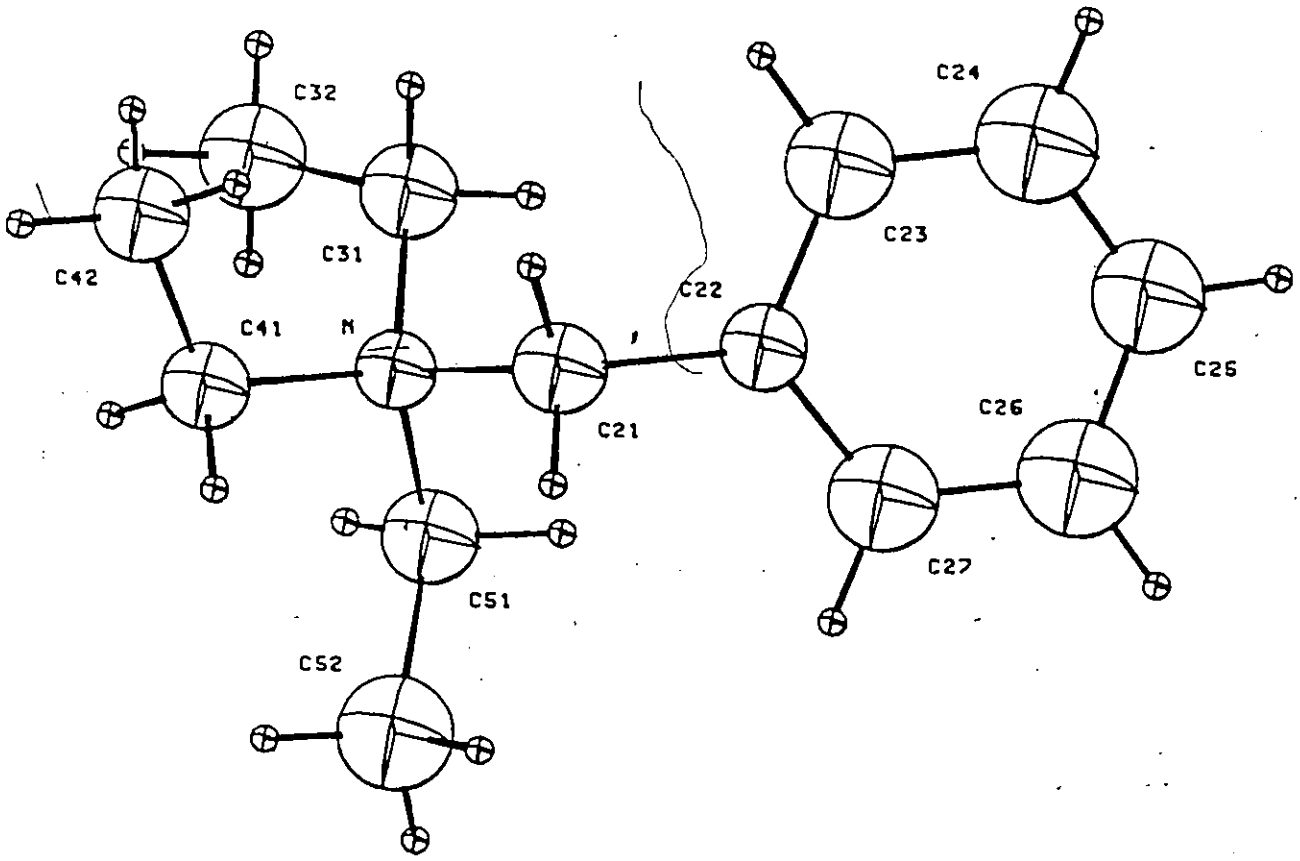


Figure 2.5: Infrared Spectrum Of Mn-S Complex In KBr

Figure 2.6: A View Of The Benzyltriethylammonium Cation



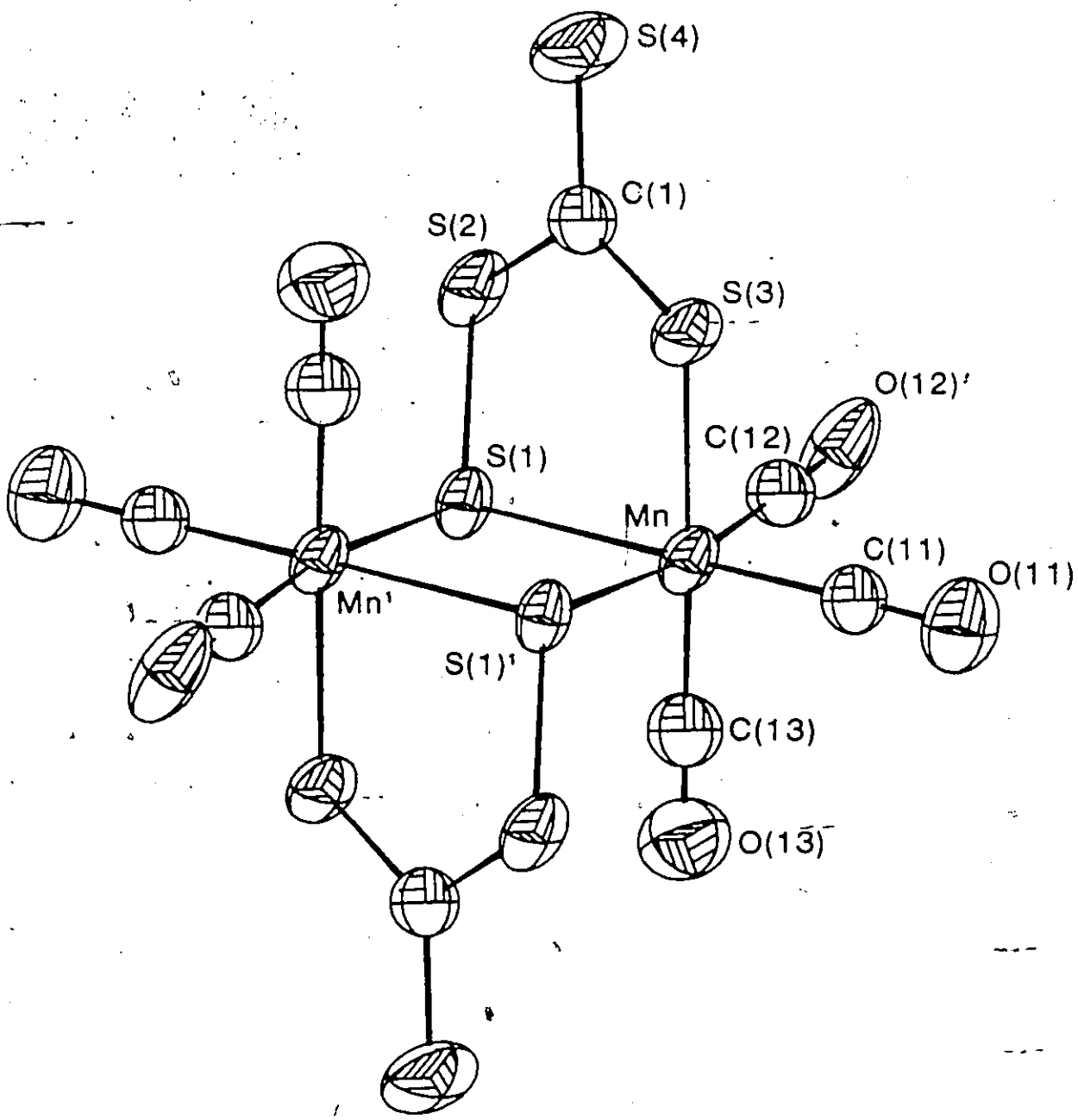
this structure analysis, in the three Mn-S bond lengths (range 2.360 (4)-2.381 (4) Å). The structure of the dianion is reproduced in Figure 2.7.

The structure of a few other perthiocarbonates, which do not have carbonyl ligands, have been reported [252]. In $[(SCS_3)_2MoS]^{2-}$ and $[(SCS_3)Mo_2S_4(SCS_3)]^{2-}$, the perthiocarbonate is bidentate with the Mo−S (perthio) bond being significantly shorter than the other Mo−S bond to this ligand (ca. 0.06 Å for the former, but only ca. 0.02 Å for the latter) [252]. Bond distances within the perthiocarbonate ligand of $[(Mn(CO)_3(SCS_3))_2]^{2-}$ closely parallel those of $[(SCS_3)_2MoS]^{2-}$: the S−S distance is somewhat long, the C−S bond to the uncoordinated sulphur is short, indicating that the double bond is largely localised here and not delocalised into the chelate ring. The C−S distances within the chelate ring are equal.

Some comparison can also be made with perthiolates [253,254,255] and S_4^{2-} [256,257] complexes as they, too, form five-membered chelate rings of the type SS(C or S)S(Metal). In these compounds the metal−S bonds may be near equal [254,256] or asymmetric [253,257], a feature which is well-known for dithiocarbamates and dithiolates [258]. Perthiolates show shorter C−S bonds within the chelate ring than perthiocarbonates as the double bond is delocalised within the ring. The structure of a copper perthiolate has been reported in which the ligating sulphur atoms bridge metal atoms [255].

It is interesting to note that the carbon atom of the SCS unit arises from a carbonyl carbon of the parent manganese complex and not from either the solvent or carbon monoxide gas. The same complex, and yield, was obtained when 4-methyl-2-pentanone was employed as the organic phase instead of dichloromethane, or when the reaction was carried out under nitrogen. The reaction was run at 70°C for 30 minutes with 4-methyl-2-pentanone as the solvent. Elemental analysis of the complex matched the calculated results.

Figure 2.7: SNOOPI Diagram Of The $[(Mn(CO)_3(SCS_3))_2]^{2-}$ Anion

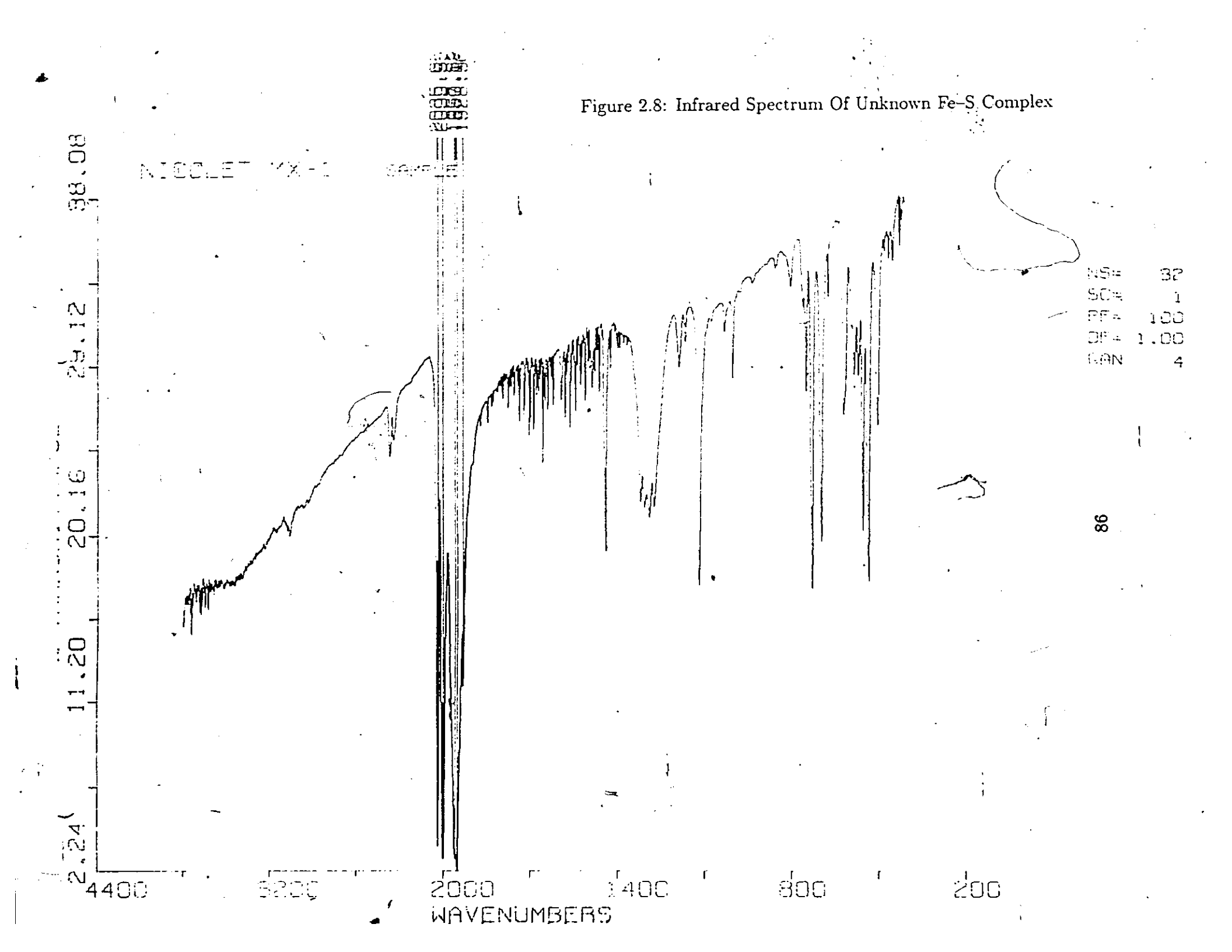


The complex was initially handled as an air sensitive material, i.e. all transfers were carried out with double-headed needles, under nitrogen, and extensive use of Schlenk tubes were made. However, it was later discovered that the complex is air-stable — both in solution and solid — and resistant to concentrated acids at room temperatures but not upon heating. Further investigation into the chemistry, and the mechanism, of this novel complex needs to be undertaken. The mechanism for the generation of the parent anion, $Mn_2(CO)_9Br^-$, has been established by Gibson and co-workers [176].

Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) is not very reactive under alkaline PTC conditions but small amounts of $Mn(CO)_5^-$ have been detected after several hours [176]. There was no reaction between $Mn_2(CO)_{10}$ and elemental sulphur under reaction conditions which supports Gibson and co-workers assertion that the binuclear anion does not arise from the direct reaction between $Mn(CO)_5^-$ (generated from $Mn(CO)_5Br$ by PTC) and $Mn(CO)_5Br$ but rather from two equivalents of $Mn(CO)_5Br$. $Mn(CO)_5^-$ was not detected in any of the reactions.

An attempt was also made to synthesise novel sulphur containing cobalt and iron complexes by reacting elemental sulphur with dicobalt octacarbonyl or tri-iron dodecacarbonyl under basic PTC conditions. The generated $Co(CO)_4^-$ anion does not react with elemental sulphur, while the iron carbonyl does give a complex on exposure to elemental sulphur. The reactions were run as usual with benzene as the organic phase. A dark purple organic phase was separated, dried and stirred under nitrogen for 4 hours at room temperature after addition of bis(triphenylphosphoranylidene)ammonium chloride. Fine needle like crystals were obtained which displayed three strong carbonyl bands in the infrared region, at 2035, 2002, and 1950 cm^{-1}, identical to the crude organic phase. Many attempts at obtaining X-ray grade crystals of this potentially novel ionic complex were un-

Figure 2.8: Infrared Spectrum Of Unknown Fe–S Complex



successful. The infrared spectrum of the complex is shown in Figure 2.8.

An elemental analysis of the product was obtained and this showed that the complex contains a fairly high amount of sulphur.

Under acidic phase transfer conditions, $Mn(CO)_5Br$ and $Co_2(CO)_8$ did not give any products with elemental sulphur, while $Fe_3(CO)_{12}$ led to almost quantitative equimolar yields of known $Fe_2(CO)_6S_2$ (IR: 2083, 2042, and 2005 cm^{-1}) and $Fe_3(CO)_9S_2$ (IR: 2086, 2067, 2051, 2030, 2014 cm^{-1}) complexes [2[illegible]].

These appear to be the first examples of the synthesis of organometallic sulphur complexes under phase transfer conditions [260]. A novel complex was obtained with manganese as the metal center under alkaline PTC, while no reaction was observed in acidic medium. Cobalt tetracarbonyl anion does not yield a sulphur complex under either alkaline or acidic PTC, but $Fe_3(CO)_{12}$ appears to give a novel ionic complex under basic conditions and known complexes under acidic conditions.

2.4 Desulphurisation Of Crude Oils And Bitumen In Acidic And Alkaline Two-Phase Systems

Despite the early recognition that hydrogenation would be effective for the simultaneous removal of nitrogen, oxygen and sulphur compounds from coal and petroleum feedstocks, hydrogenation seemed to be uneconomical for application to petroleum fractions. The high cost of hydrogen and the adequacy of the practice for meeting the demand for low-sulphur products by refining low-sulphur crude oil were two of the factors which dampened interest in hydrodesulphurisation. However, recent developments in refining technology provide substantial quantities of by-product hydrogen and a shift in supply trends to increased use of high-sulphur content crude oils as refinery feedstocks, have made hydrodesulphurisation attractive.

Included among the several reasons for removing sulphur from petroleum fractions are:

1. reduction or elimination of corrosion during refining, handling, or use of the various products;
2. production of products having an acceptable odor;
3. increasing the performance (and stability) of gasolines;
4. decreasing smoke formation in kerosenes; and
5. reduction of sulphur content in other fuel oils to a level that improves burning characteristics and its environmental acceptability.

A growing dependence on high-sulphur heavier oils and residues/bitumen has emerged as a result of continuing increases, until very recently, in the prices of the conventional crude oils coupled with their decreasing availability through the depletion of reserves in various parts of the world. Furthermore, the ever growing tendency to convert as much as possible of the lower grade feedstocks to liquid products is causing an increase in the total sulphur content in refined products.

Presently, an integral part of many refineries is the hydrodesulphurisation of petroleum fractions. The process is accomplished by the catalytic reaction of hydrogen with the organosulphur compounds in the feedstock over heterogeneous catalyst beds at elevated temperatures and pressures. Hydrogen sulphide is produced and this can be readily separated from the liquid (or gaseous) hydrocarbon products. As mentioned in the introductory chapter, all the commercial desulphurisation of crude oils and bitumen processes require drastic operating conditions [85]. Milder heterogenised processes for the desulphurisation of model compounds have been developed (e.g. [87]).

The work described earlier established that organometallic complexes can effect the desulphurisation of so-called "organic sulphur" and trap "inorganic sulphur" components of crude oils and bitumen under alkaline phase transfer and acidic biphasic conditions. Model studies with activated thiols indicate that hydrodesulphurisation can be achieved in a facile manner under basic PTC with $Co_2(CO)_8$ and $Fe_3(CO)_{12}$, the latter being also effective for acidic biphasic systems. It was also shown that thiocarbonyls can be converted to carbonyl products under "classical" PTC, i.e. without a metal complex being present. Success with these model studies, prompted attempts at desulphurising crude oils and bitumen with organometallic complexes under PTC.

2.4.1 Organometallic Desulphurisation Of Crude Oils

Significant desulphurisation of crude oils, as indicated by sulphur analysis of reacted and unreacted samples, was achieved with various phase transfer catalysts and organometallic complexes under both acidic and alkaline conditions. The metal complexes used ($Fe_3(CO)_{12}$, $Mo(CO)_6$, and $Mn(CO)_5Br$) were chosen for specific reasons. Triiron dodecacarbonyl was almost equally effective as $Co_2(CO)_8$ in desulphurising thiols in model studies under alkaline PTC conditions. It could also be used under acidic biphasic conditions. Iron-sulphur complexes were formed in reactions between $Fe_3(CO)_{12}$ and sulphur, thereby showing its potential to trap inorganic sulphur. In the model studies, $Co_2(CO)_8$ was only slightly better than $Fe_3(CO)_{12}$ as a desulphurisation agent in basic medium but proved to be ineffective in acidic medium. For this reason, $Co_2(CO)_8$ was not used in the crude oil/bitumen desulphurisation reactions. Molybdenum hexacarbonyl is an often used catalyst in desulphurisation reactions but it was not used in the model studies. However, it seemed worthwhile to try this already proven desulphurisation catalyst in the

crude oil/bitumen desulphurisation studies. Manganese pentacarbonyl bromide was shown to be effective in trapping "inorganic sulphur" in the complexation studies but not for desulphurisation of thiols. Nevertheless, this complex was also used in these reactions involving crude oils and bitumen. The results of the attempted desulphurisation of crude oil under alkaline phase transfer conditions are listed in Table 2.9.

When a catalytic amount of $Mo(CO)_6$ was added to a mixture containing equal volumes of 5N sodium hydroxide solution and crude oil (25 ml of each) and TEBAC (1 mmol), under 1 atm of hydrogen, at room temperature and heated for 10 hours at 60°C, significant reduction in the sulphur content of the crude oil was achieved. The sulphur content of the crude oil was reduced from 0.89% (0.185g or 5.8 mmol of sulphur in 25 ml of crude oil) to 0.41%, a reduction of 54% (or 3.13 mmol of sulphur was removed by 0.4 mmol of $Mo(CO)_6$). Use of 0.1 mmol of the metal complex led to 38% (2 mmol) desulphurisation. Triiron dodecacarbonyl was a fairly active desulphurisation agent. For example, when 0.4 mmol of $Fe_3(CO)_{12}$ was the complex, 53% or 3.07 mmol of sulphur was removed. With 0.6 mmol of $Mn(CO)_5Br$, 54% desulphurisation was attained (in other words, 3.1 mmol of sulphur removed). It should be mentioned that the crude oil served as the organic phase and that the proposed active species were not pre-generated. This, however, was not the case when $Mn(CO)_5Br$ was used. The perceived active species, the $Mn_2(CO)_9Br^-$ anion, was pre-generated in 2-butanone or 4-methyl-2-pentanone before crude oil was added. The phase transfer agent in all these cases was TEBAC.

Reactions were usually run under hydrogen, but no significant difference in the degree of desulphurisation was observed under nitrogen. In light of the model studies, reaction temperatures and base concentrations were not varied, except in one case when 10N sodium hydroxide solution was used and the effect was detrimental.

Table 2.9: Desulphurisation Of Crude Oil Under Alkaline Phase Transfer Conditions

Metal Complex [a] (mmol)	PT Cat. (1 mmol)	Degree of Desulphurisation		
		% S Left[b]	% S Removed[c]	S Removed(mmol)[d]
$Mo(CO)_6$(0.04)	TEBAC	0.75	15.7	0.9[e]
" (0.1)	"	0.55	38.2	2.2
" (0.4)	"	0.41	53.9	3.1
" (0.4)	TBAHS	0.57	43.8	2.5
" (0.4)	DTAB	0.63	29.2	1.7
$Fe_3(CO)_{12}$(0.4)	TEBAC	0.47	47.2	3.1
" (0.4)	TBAHS	0.50	43.8	2.5
" (0.4)	DTAB	0.53	40.5	2.3
$Mn(CO)_5Br$(0.6)	TEBAC	0.41	53.9	3.1[f]
" (0.06)	"	0.49	44.9	2.6[g]
" (0.1)	"	0.50	43.8	2.5[h]
" (0.7)	THAB	0.42	52.8	3.1
" (0.06)	Aliquat 336	0.65	27.0	1.6
" (0.06)	-	0.86	3.4	0.2
-	TEBAC	0.87	2.2	0.1

[a]Reaction conditions: under 1 atm H_2, at 60°C, 5N NaOH/crude oil (25 ml of each), 1 mmol of phase transfer catalyst; amount of metal complex as listed.

[b]Sulphur content of untreated crude oil was 0.89%; percentage of sulphur remaining in treated sample listed in this column.

[c]Relative to original sulphur content of sample.

[d]Calculated to be 5.8 mmol in untreated sample.

[e]10 N NaOH was used instead of 5N.

[f]2-Butanone was used as the organic phase at 70°C.

[g]4-Methyl-2-pentanone was the organic phase in this and the rest of the following runs at 70°C.

[h]Under N_2 instead of H_2.

Work-up was effected either by centrifuging the reaction mixture to separate the phases or by addition of benzene to aid separation of the phases in a separatory funnel, followed by washing several times with water and dilute HCl. It was then filtered through a Celite/$MgSO_4$/silica gel short column with benzene as the "eluant". Sulphur analysis was carried out after concentration. The solvent removed was checked by gas chromatography to confirm that no volatile component of the crude oil was removed with the solvent.

It is not possible to propose a mechanism for the desulphurisation process since no desulphurised products or organometallic complexes were identified. However, it can be speculated that the mechanisms proposed for the model studies may also apply to the crude oil desulphurisation. It is most likely that the inorganic sulphur in crude oils can be trapped by the formation of metal-sulphur complexes similar to that synthesised from the reaction between $Mn(CO)_5Br$ and sulphur under basic PTC. This could account for the loss of activity after several turn-overs. If the Mn–S complex is indeed formed in these reactions, it would have to be removed from the sample before sulphur analysis. In order to obtain a more accurate analysis, unreacted metal complex, as well as the formed metal-sulphur species would have to be removed from the sample. Both the Mn-S complex and the anion $Mn_2(CO)_9Br^-$ do not dissolve in benzene and it is for this reason that benzene was selected as the "eluant".

All three metal complexes were almost equally active as desulphurising agents. Use of less metal complex lowers the degree of desulphurisation achieved which is consistent with the postulation that metal-sulphur complex formation leads to deactivation. No desulphurisation occurs in the absence of the metal complex. These are authentic phase transfer reactions, similar to the model studies, since no desulphurisation occurs in the absence of the phase transfer agent. Unlike the

Table 2.10: Desulphurisation Of Crude Oil Under Acidic Phase Transfer Conditions

Metal Complex [a] (mmol)	PT Cat. (1 mmol)	Degree of Desulphurisation		
		% S Left[b]	% S Removed[c]	S Removed(mmol)[d]
$Fe_3(CO)_{12}$(0.06)	Na DBS[e]	0.77	13.5	0.8
" (0.06)	"	0.77	13.5	0.8[f]
" (0.06)	-	0.61	31.5	1.8
$Mo(CO)_6$(0.4)	Na DBS	0.47	47.2	2.7

[a]Reaction conditions: under 1 atm H_2, at 60°C, 48-50% HBF_4/crude oil (25 ml of each); with or without phase transfer agent Na DBS (1 mmol); metal catalyst as listed.
[b]Sulphur content of untreated crude oil was 0.89%; percentage of sulphur remaining in treated sample listed in this column.
[c]Relative to original sulphur content of sample.
[d]Calculated to be 5.8 mmol in untreated sample.
[e]NaDBS=Sodium-4-docecylbenzenesulphonate, 4-$C_{12}H_{25}C_6H_4SO_3^-{}^+Na$.
[f]Under N_2.

model studies, the nature of the phase transfer agent seems to have an effect on the desulphurisation process. As a generalisation, the longer the chain length of the lipophilic cation of the quaternary ammonium salt, the less active the phase transfer agent. It was anticipated that, the longer the chain of the lipophilic cation, the more soluble it would be in the crude oil and thus, the opposite of the observed phenomena should be true. However, it may be suggested that the observed difference in activity could be due to the varying degrees of extractability of the quaternary ammonium hydroxides into crude oil which is at the root of the unexpected activity of the phase transfer catalysts.

Model studies indicated that $Mn(CO)_5Br$ was inactive in acidic medium, thus only $Fe_3(CO)_{12}$ and $Mo(CO)_6$ were used in the desulphurisation of crude oils in acidic medium. Addition of $Fe_3(CO)_{12}$ to equal volumes of crude oil and 48-50% aqueous HBF_4 with sodium 4-dodecylbenzenesulphonate as the phase transfer agent,

under hydrogen at 60°C, led to 13.5% desulphurisation. This degree of desulphurisation was, in light of the model studies carried out on thiols, higher than expected. The above mentioned extractability phenomenon could be the reason behind this unexpected result, i.e. crude oil is better than benzene as the organic phase. The same result was obtained under nitrogen. However, as anticipated, the degree of desulphurisation improved significantly, to 31.5%, when the reaction was run in the absence of the phase transfer catalyst. Only one experiment was run with $Mo(CO)_6$ in acidic medium in which 47.2% desulphurisation was achieved under PTC (see Table 2.10). The biphasic system could lead to a higher level of desulphurisation with molybdenum hexacarbonyl as the metal complex. Reactions were repeated to in order to confirm the results obtained in some cases. Work-up was effected in the same way as in the basic PTC system, except that the organic phase was washed with water and dilute sodium hydroxide solution.

2.4.2 Organometallic Desulphurisation Of Bitumen

The reaction conditions which had been successfully used in the transition metal complex mediated desulphurisation of thiols and crude oil, led to a modest reduction of the sulphur content of samples of Athabasca bitumen The complex utilised in most cases was $Mn(CO)_5Br$, with a few reactions being run with $Fe_3(CO)_{12}$ and $Mo(CO)_6$ (see Table 2.11). A majority of the reactions were run under basic phase transfer conditions, but several were effected in acidic medium. The latter yielded the most promising results. Effects of the various phase transfer agents in alkaline systems were not investigated, since this had already been carried out in the thiol and crude oil desulphurisation studies.

One variation from the crude oil desulphurisation reactions, was the pre-generation of the supposed active metal species and use of an organic solvent in all cases.

For example, $Mn_2(CO)_9Br^-$ was generated in dichloromethane/5N sodium hydroxide, with TEBAC as the phase transfer agent, at 40°C under 1 atm of hydrogen from $Mn(CO)_5Br$. To this was added the highly viscous bitumen dissolved in dichloromethane. The reaction mixture was stirred for 10 hours, at 40°C under hydrogen. Work-up was effected as in the case of the crude oils. The sample was analysed for sulphur and shown to contain 32% less sulphur than the original bitumen sample (3.40% compared to 4.99%). Under nitrogen, the sulphur content was reduced by 28.7% down to 3.56%. As expected, the reaction atmosphere does not play a significant role in the desulphurisation of bitumen.

The amount of metal complex used did not seem to influence the degree of desulphurisation, indicating that after several turn-overs, the active species becomes deactivated. The speculation that one was forming a Mn-S complex of the type synthesised before, may not hold in this case, since subjecting a bitumen sample to desulphurisation twice did not increase the overall (i.e combined) degree of desulphurisation. This was unexpected, since it has been shown that when a sample of bitumen is passed through a heterogenised system more than once, the degree of desulphurisation increases with every pass up to a critical value of about 60% desulphurisation [261].

Triiron dodecacarbonyl and molybdenum hexacarbonyl were not very effective for bitumen desulphurisation under basic PTC. This was in contrast to the crude oil desulphurisation effort.

In an acidic medium, $Mo(CO)_6$ was able to effect the desulphurisation of bitumen to a reasonable degree. Thus, $Mo(CO)_6$, in a dichloromethane/40-50%HBF_4 system, with sodium 4-dodecylbenzenesulphonate as the phase transfer agent, was able to reduce the sulphur content of bitumen by 36.9%. It is interesting to note that 38.0% desulphurisation was achieved under biphasic conditions. Unlike the model studies

Table 2.11: Desulphurisation Of Bitumen Under AlkalineAnd Acidic Conditions

Metal Complex (mmol)	PT Cat. (1 mmol)	Degree of Desulphurisation	
		% S Left[a]	% S Removed[b]
$Mn(CO)_5Br$(0.5)	TEBAC	3.40	32.0[c]
" (0.5)	"	3.56	28.7[d]
" (1.0)	"	3.46	30.7
" (1.0)	"	3.49	30.1[e]
" (1.0)	"	3.38	32.2[f]
$Fe_3(CO)_{12}$(0.4)	TEBAC	4.34	13.0
$Mo(CO)_6$(0.4)	TEBAC	3.42	32.0
" (0.4)	NaDBS	3.15	36.9[g]
" (0.4)	-	3.10	38.0[h]

[a]Sulphur content of untreated bitumen was 4.99%; percentage of sulphur remaining in treated sample listed in this column.
[b]Relative to original sulphur content of sample.
[c]Perceived active species was pre-generated before addition of bitumen dissolved in the common solvent,CH_2Cl_2;5N NaOH was the aqueous phase.
[d]Under N_2.
[e]4-Methyl-2-pentanone as the organic phase.
[f]Sample subjected to two desulphurisation runs.
[g]Under acidic PTC.
[h]Under acidic biphasic conditions.

with thiols, the phase transfer agent does not retard the activity of the metal in acidic media. This is not totally consistent with the results obtained in the crude oil desulphurisation investigation. It is possible that the extractability phenomenon may again be the key. However, it should be pointed out that $Fe_3(CO)_{12}$ was the complex in the model studies and it was speculated that the phase transfer agent promotes generation of carbonyl ferrates which are incapable of desulphurising thiols.

Since the nature of the desulphurised products and the organometallic complexes remain unknown, the mode of desulphurisation, i.e. the mechanism, is not clear. Further investigation into the mechanism needs to be carried out.

An alkaline phase transfer catalysed and an acidic biphasic/phase transfer systems were developed to effectively desulphurise crude oils and bitumen to varying degrees. Several organometallic complexes were shown to be effective in most cases.

2.5 Metal Catalysed Conversion Of Benzylic Alcohols To Esters, Thiols And Hydrocarbons

Carbonylation reactions are an important class of organic reactions. The first chapter of this thesis includes a review of some of the more recent, and important, metal catalysed carbonylation processes. Some of the industrially important carbonylation reactions involve transformations utilising alkenes, alkynes, halides and alcohols, the latter being potentially the most important substrate.

Carboxylic acids and esters are valuable industrial products in their own right as solvents in lacquer, paint and varnishing applications, and as intermediates in the production of resins, plastics and coatings. Esters are generally produced on a commercial scale by the acid catalysed reaction of a carboxylic acid with an alcohol.

A particularly valuable ester is ethyl acetate obtained by the reaction of acetic acid with ethanol. Until recently, carboxylic acids (e.g. acetic acid) were produced in large quantities by the oxidation of paraffinic hydrocarbons.

Halide promoted, soluble noble metal complex catalysed carbonylation of alcohols to carboxylic acids and esters is of major industrial importance. This is demonstrated by the explosive growth, in terms of tonnage, of the Monsanto process for the carbonylation of methanol to acetic acid (see references in section 1.1.2). In 1984, Monsanto reported a combined methanol carbonylation to acetic acid production capacity, of licensees alone, totalling 1.7 million metric tonnes per annum. This accounted for 90% of all new plants coming on stream between 1973 and 1984, and for 40% of global acetic acid capacity. The halide promoter, often being added as hydrogen iodide, can lead to corrosive reaction media, thus requiring reactors constructed of highly specialised material. This need for special corrosion resistant material lends to the high capital expenditure involved in the construction of these plants. The most often used catalysts are complexes of rhodium or iridium. A recent publication describes the halide promoted carbonylation of primary alcohols by ruthenium catalysts [262]. The catalysts used in these reactions are expensive, thus, the need for a highly efficient catalyst recovery system is of paramount importance. Loss of even small amounts of the catalyst would make the operating cost prohibitively high. Therefore, it would be desirable to develop a homogeneous carbonylation process which avoids the use of expensive catalysts and "aggressive" halide promoters.

$$\mathrm{ROH} + \mathrm{CO} \xrightarrow[40atm,180^{\circ}C]{RhX_3,I^-} \mathrm{RCOOH} \qquad (2.10)$$

A recently disclosed patent describes a new route to carboxylic esters by the carbonylation of the tetrafluoroborate salt of diaromatic halides in methanol with zero-valent rhodium, ruthenium, or molybdenum complexes as the catalyst. This

process is still not any better, with respect to the corrosion factor, than the Monsanto process [263].

In 1986, the first example of carbonylation, incorporating *in situ* desulphurisation, of benzylic and aromatic thiols to esters was reported [92]. Treatment of a thiol in aqueous alcohol with a catalytic amount of $Co_2(CO)_8$ (20:1 ratio of thiol/$Co_2(CO)_8$) under high pressure of carbon monoxide and elevated temperatures, afforded carboxylic esters in 25-83% yields.

$$RSH + CO + R'OH \xrightarrow[60atm,190^\circ C,24h]{Co_2(CO)_8,H_2O} RCOOR' + H_2S \qquad (2.11)$$

Methanol, ethanol, 2-propanol and *tert*-butanol were used in these reactions. The presence of a small quantity of water was found to be critical (2 ml of water in 30 ml of alcohol) for the success of the reaction.

It has also been reported that thiols can be carbonylated to thioesters in excellent yields by $Co_2(CO)_8$ in the presence of disubstituted butadienes under high pressure of carbon monoxide, at elevated temperatures, with benzene as the solvent [264].

$$2\ RSH \ + \ 2\ CO \xrightarrow[Co_2(CO)_8,55-60atm]{Diene,185-190^\circ C} RC(O)SR \ + \ COS \qquad (2.12)$$

These reports gave credence to the possibility that benzylic alcohols could be converted to carboxylic esters via the corresponding thiol in a "one-pot" reaction. However, if the "one-pot" process was not possible, it was anticipated that a two step system could be developed which might be able to compete with the halide promoted Monsanto carbonylation process. Such a process would include a novel metal catalysed first step in which the alcohol would be transformed into the corresponding thiol. In the second step, the thiol would be desulphurised and carbonylated in the presence of a second alcohol and a small amount of water.

$$RSH \ + \ CO \xrightarrow[C_6H_6/H_2O,24h]{Co_2(CO)_8,190^\circ C} RH \ + \ COS \qquad (2.13)$$

$$ROH + Fe(CO)_5 \xrightarrow{K/HCl} RH \qquad (2.14)$$

There are no reports in the literature of metal catalysed conversion of alcohols to thiols. The dicobalt octacarbonyl catalysed conversion of thiols to hydrocarbons has recently been reported [90]. Among the few examples of metal catalysed deoxygenation of alcohols to hydrocarbons in the literature, is a report published in 1980 where iron pentacarbonyl was used as the catalyst [265].

2.5.1 Carbonylation Of Benzylic Alcohols To Esters Via Thiols

The many attempts at converting benzylic alcohols to carboxylic esters were moderately successful. A substantial amount of the alcohol was consumed in almost all reactions but selectivity to the ester was poor in most cases. The corresponding thiols and hydrocarbons were the other major products obtained. Formation of the thiols was of course expected but the degree of hydrocarbon production was surprising. It should be mentioned again, that thiols can be desulphurised to hydrocarbons by $Co_2(CO)_8$ in benzene and a little water, under 60 atm carbon monoxide at 185-190°C [90]. A representative sample of the experiments carried out and the results obtained are listed in Table 2.12 and 2.13. Examples in which very low yields of the esters were obtained are listed in Table 2.12, while those with yields over 11% are listed in Table 2.13.

Table 2.12: Carbonylation Of Benzylic Alcohols To Esters Via Thiols — Part-I

Substrate[a]	Solvent /ml		Products[b]%					
$RC_6H_4CH_2OH$	H_2O	EtOH	R'OH	R'C(O)OEt	R'SH	R'H	R'SR'	R'OEt
4-CH_3	1	10	60	1	11	16	3	-
	2	10	2	11	29	28	17	9
	2	5[c]	3	8	15	41	-	-
	2	10[d]	84	6	-	1	-	-
	"	"[e]	25	3	18	13	7	33
	"	"[f]	76	-	-	20	-	
2-CH_3	"	"	61	6	16	16	-	-
3-CH_3	"	"	84	3	5	7	-	-
H[g]	"	"	39	8	22	18	6	-
4-Cl	"	"	94	-	2	2	-	-
m-Cresol	"	"	96	-	-	-	-	-
$C_{10}H_7CH_2OH$[h]	"	"	97	-	-	-	-	-

[a] 10 mmol of substrate and 1 mmol of $Co_2(CO)_8$ was used in all cases unless stated otherwise under 13 atm H_2S and 47 atm CO at 150°C.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

[c] Methanol was used instead of ethanol.

[d] A small amount of DMAP added.

[e] A few drops of 48-50% HBF_4(aq.) added.

[f] No H_2S.

[g] 50 mmol of alcohol and 1 mmol of catalyst was used.

[h] 2-Naphthalenemethanol.

The early experiments gave only trace amounts of the desired esters. Gas chromatography was employed to detect, and in tandem with mass spectrometry to identify, the small quantities of esters produced. It was established that the presence of water was critical for the reaction to proceed (see Table 2.14), possibly in a manner similar to the carbonylation of thiols mentioned above [92]. However, it should be mentioned that small quantities of esters were formed in the absence of water in cases where the substrate seems to be highly reactive, e.g. 3,4-dimethoxybenzyl alcohol. This may be due to the small amounts of water generated *in situ*, as proposed in the mechanism for the thiolation step (see next section). Various ratios of water/ethanol were tried with added dioxane, hexane or acetonitrile. The yield of ester was lower in each case when compared to the optimal condition, where 2 ml of water and 10 ml of ethanol were used. For example, when 4-methylbenzyl alcohol was reacted in 10:1 ethanol/water mixture with $Co_2(CO)_8$ under 60 atm (13 atm hydrogen sulphide, 47 atm carbon monoxide), at 150°C for 10 hours, only trace amounts of the ethyl ester was detected. The yield of ester increased to 11% when 10:2 ethanol/water ratio was used. Use of more water was not advantageous (see Table 2.13). This is consistent with the carbonylation of thiols to carboxylic esters. Addition of a small amount of acetic acid led to formation of ester from direct reaction between the benzylic alcohol and the acid without any carbonylation being involved (see Table 2.14). Addition of a few drops of 48-50% HBF_4(aq.) led to high conversion of the benzylic alcohol to the ether ROEt accompanied with reduction in the yield of the ester (see Table 2.12). The most often used substrate to catalyst ratio was 10:1 only for convenience of measurements. Other ratios were also employed.

It is known from the literature, that enolisable acetoacetates (β-keto esters) react with primary or secondary alcohols in the presence of a catalytic amount

Table 2.13: Carbonylation Of Benzylic Alcohols To Esters Via Thiols — Part-II

Substrate[a]	Solvent /ml		Products[b]%				
$RC_6H_4CH_2OH$	H_2O	EtOH	R'OH	R'C(O)OEt	R'SH	R'H	R'SR'
4-CH_3CH_2	2	10	2	18	10	65	-
4-CH_3O	"	"	traces	23	7	67	-
	"	"	-	20	32	44	-[c]
4-CH_3CH_2O	"	"	-	22	1	62	11
3,4-CH_3O	"	"	-	58	-	40	1
	"	"[d]	-	32	-	13	-
	"	"[e]	-	15	-	64	20
	"	"	90	-	-	-	6[f]
2,4-CH_3O	"	"	-	60	-	26	6
	5	5	80	10	3	4	-
	2	10	21	37	12	20	7[g]
	"	"	97	-	-	-	2[h]

[a] 10 mmol of substrate and 1 mmol of $Co_2(CO)_8$ was used in all cases unless stated otherwise under 13 atm H_2S and 47 atm CO at 150°C.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

[c] At 120°C

[d] Methanol was used instead of ethanol; R'C(O)OMe.

[e] n-Butanol was used instead of ethanol; R'C(O)OBu .

[f] Reaction carried out at room temperature and under 1 atm.

[g] 50:1 substrate to metal catalyst used.

[h] No metal catalyst present.

Table 2.14: Carbonylation Of Benzyl Alcohol To Ester Via Thiol — Effect Of Solvent

Solvent /ml [a]			Products[b]%				
H_2O	EtOH	Others	BzOH	BzC(O)OEt	BzSH	BzH	BzSBz
-	5	-	79	1	4	6	4
2	10	-	29	8	22	18	6
-	5	10[c]	92	1	5	-	-
-	5	5	88	2.3	5.2	1.7	-
2	5	"	88	2	5	1	-
"	"	5[d]	88	3	2	1	2
"	10	0.5[e]	80	18[f]	-	-	-

[a] All reactions were run under 13 atm H_2S and 47 atm CO, at 150°C with 50:1 substrate to cobalt ratio.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; Bz= $C_6H_5CH_2$.

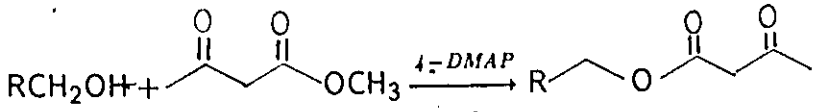
[c] Dioxane added here and in the next entry .

[d] CH_3CN added.

[e] Acetic acid added.

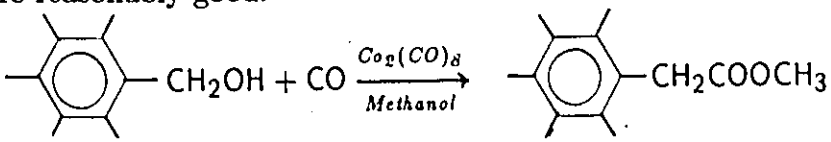
[f] Ester was from reaction with acid, $C_6H_5CH_2C(O)OCH_3$.

of 4-(dimethylamino)pyridine (4-DMAP), in toluene, at reflux by ester exchange. Addition of a nitrogen donor promoter like 4-DMAP to the reaction mixture in the attempted carbonylation process was not advantageous (see Table 2.12).



(2.15)

A recent patent claims a $Co_2(CO)_8$ catalysed carbonylation of benzylic alcohols to esters in anhydrous methanol under 200 atm of carbon monoxide at 200°C [266]. Yields are reasonably good.



(2.16)

In light of this, an attempt was made to carbonylate the benzylic alcohol in the absence of hydrogen sulphide. Hydrocarbons were the only products obtained under the prevailing reaction conditions (see Table 2.12). This adds to the speculation that the carbonylation reaction does indeed proceed via the *in situ* generated thiol. The hydrocarbons detected in the alcohol carbonylation reactions under hydrogen sulphide could arise from the direct deoxygenation of the benzylic alcohol as well as the desulphurisation of the thiol.

Ethanol was used as the solvent/reagent in most cases. Methanol and *t*-butanol were not as useful as ethanol. Steric factors can be invoked to explain why *t*-butanol was not useful as solvent/reagent. When the reaction was run at lower temperature and pressure, either lower yields of ester were obtained or no reaction occured (see Table 2.12). It is possible that the active catalytic species is generated only at relatively high temperature and pressure. A relatively high pressure of carbon monoxide may be necessary not only for the carbonylation reaction but also to "stabilise" the catalytic cobalt species in a manner analogous to the cobalt catalysed hydroformylation process. For the latter, a minimum partial pressure of carbon

monoxide is required to "stabilise" the catalytic species, $HCo(CO)_3$, in solution at a particular temperature [6].

Methoxy and ethoxy substituted benzylic alcohols appear to be the most reactive with dimethoxy substrates being the most susceptible to thiolation and subsequent desulphurisation to hydrocarbon or carbonylation to ester. Among the less reactive substrates, the 4-substituted alcohols were the most reactive with the exception of 4-chlorobenzyl alcohol. This last case could be due to the low solubility of the alcohol in the solvent system even though at elevated temperatures and pressures with vigorous stirring, one would expect the substrate to be soluble. This could also be the reason behind the apparent low reactivity of benzyl alcohol — two phases were clearly observed in this case. Unlike the carbonylation of thiols to ester process, aromatic alcohols like *m*-cresol and 2-naphthalenemethanol cannot be utilised.

The effect of the metal catalyst was extensively investigated (see Table 2.15). No reaction takes place in the absence of the metal catalyst. Only $Co_2(CO)_8$ was found to be an effective catalyst. Thus, when 3,4-dimethoxybenzyl alcohol was subjected to carbonylation in 10 ml of ethanol and 2 ml of water, under 60 atm of CO/H_2S pressure (13 atm hydrogen sulphide, 47 atm carbon monoxide) and 150°C, 58% of the ester was obtained with $Co_2(CO)_8$ as the catalyst, while the otherwise highly reactive cyclopentadienyl-1,5-cyclooctadiene cobalt, CpCo(COD), gave only traces of the desired ester. Triiron dodecacarbonyl and hexarhodium hexadecacarbonyl were not tried as catalysts since they both proved to be ineffective in the carbonylation of thiols [92]. Bimetallic systems $(Co_2(CO)_8/[Rh(CO)_2Cl]_2$ and $Co_2(CO)_8/Pd(CH_3CN)_4(BF_4)_2)$ were also ineffective as catalysts. Cobalt(II) acetate and acetyl acetonate ($Co(acac)_2$), diphenylacetylene dicobalt hexacarbonyl ($Co_2(CO)_6$dpa), diphenylphosphinomethane dicobalt hexacarbonyl ($Co_2(CO)_6$dpm) and $HRh(CO)_2(PPh_3)_2$ were not effective catalysts for the carbonylation reaction.

Table 2.15: Carbonylation Of Benzylic Alcohols To Esters Via Thiols — Effect Of Catalyst

Substrate[a] $RC_6H_4CH_2OH$	Catalyst	Products[b]%				
		R'OH	R'C(O)OEt	R'SH	R'H	R'OEt
4-CH_3	$Co_2(CO)_8$	2	11	29	28	9[c]
	$HRh(CO)_2(PPh_3)_2$	96	-	-	-	4
	Co[d]	3	1	15	54	9
	$Co(acac)_2$	78	1	6	4	8
	$Co_2(CO)_6(dpa)$	91	1	3	1	3
	$Co_2(CO)_6(dpm)$	97	trace	-	-	-
	Pd/Co[e]	65	2	7	8	15
	Co/Rh[f]	57	3	1	23	9
3,4-CH_3O	CpCo(COD)	96	-	-	-	-
	$Co_2(CO)_8$	-	58	-	40	-

[a] 10 mmol of substrate and 1 mmol of catalyst was used in all cases unless stated otherwise under 13 atm H_2S and 47 atm CO at 150°C; solvent mixture used was 2 ml water/ 10ml ethanol.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

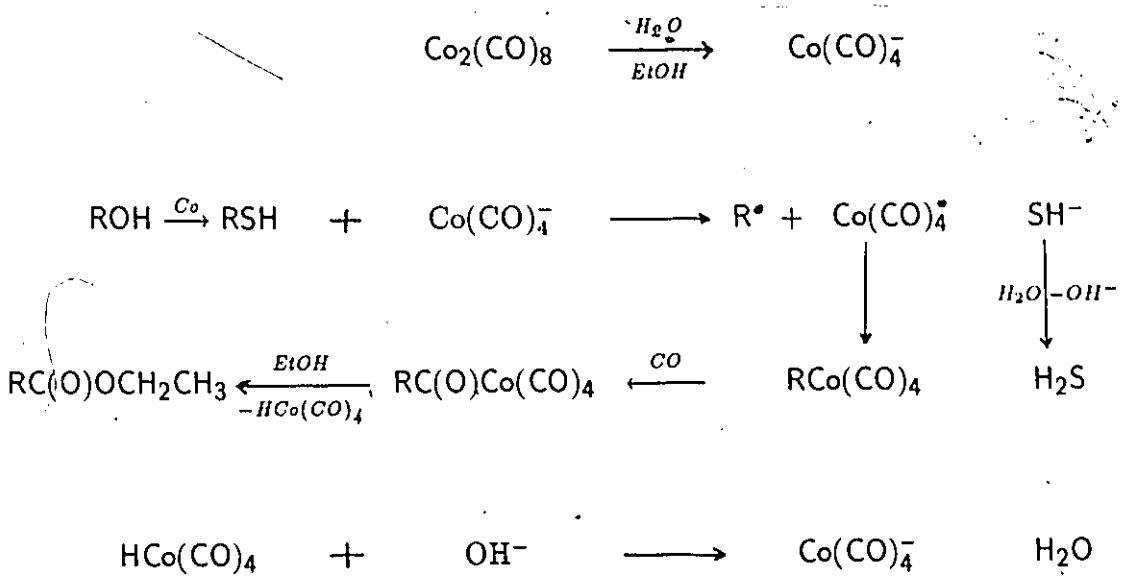
[c] 16% R'SR' formed and 0.5 mmol of catalyst used.

[d] Cobalt acetate, 19% R'SR' formed.

[e] $Pd(CH_3CN)_4(BF_4)_2$ and $Co_2(CO)_8$ as catalyst in a 1:1 ratio.

[f] $Co_2(CO)_8$ and $[Rh(CO)_2Cl]_2$, 1:1 ratio.

Figure 2.9: Proposed Mechanism For The Carbonylation Of Benzylic Alcohols To Esters Via Thiols



A proposed mechanism for the carbonylation reaction is based on the *in situ* generation of thiol (Figure 2.9). The possible mechanism for the synthesis of the thiols and the hydrocarbons will be discussed in the next section. The thiol once generated, can be either carbonylated to the ester or desulphurised to the hydrocarbon. The latter can also arise directly from the alcohol via a deoxygenation reaction. This speculation is based on the detection of small amounts of the hydrocarbon when the reaction was carried out in the absence of hydrogen sulphide.

Dicobalt octacarbonyl undergoes disproportionation in aqueous ethanol to give the cobalt tetracarbonyl anion [267]. Single electron transfer from the cobalt anion to the thiol would generate the organic radical $R^{\bullet}$, cobalt tetracarbonyl radical $Co(CO)_4^{\bullet}$, and the SH^- anion. Protonation of the latter by the solvent water liberates hydrogen sulphide. Coupling of the two radicals would give the alkyl cobalt carbonyl complex which is then carbonylated to the acyl moiety. Subsequent

reaction of the acyl species with the ethanol gives the ester and $HCo(CO)_4$. The hydridocobalt species can then react with OH^- to regenerate the active catalytic species $Co(CO)_4^-$, which would re-enter the catalytic cycle.

In conclusion, a "one-pot" process for the carbonylation of benzylic alcohols to esters via the corresponding thiols has been developed. In this process, cheap metal catalysts can be used without the need for a halide promoter being present. The reaction conditions (i.e pressure and temperature) compare favourably with the Monsanto process (40 atm, 180°C). Use of reactors constructed of special material are avoided. However, the reaction is of limited scope, being applicable to only certain types of benzylic alcohols.

2.5.2 Conversion Of Benzylic Alcohols To Thiols And Hydrocarbons

In the preceding section, attempts at developing an efficient "one-pot" process for the carbonylation of alcohols to esters via the corresponding thiol was described. This endeavour was only partially successful and thus investigation into the first transition metal catalysed conversion of alcohols to thiols was undertaken. In light of the detection of thiols (and the undesired hydrocarbons) in the attempted "one-pot" esterification of alcohols described above, it was anticipated that it would be possible to convert alcohols to the corresponding esters via a two-step esterification process. In this two-step process, alcohols would react with hydrogen sulphide in the presence of transition metal complexes to give thiols and the latter is convertible to the ester upon reaction with aqueous alcohol and carbon monoxide in the presence of $Co_2(CO)_8$ according to the known process for the esterification of thiols [92].

Thiols can be synthesised via several methods. Alkylation and arylation of simple derivatives of divalent sulphur, e.g. hydrogen sulphide, are often used as

routes to thiols. However, the danger of over alkylation leading to the formation of sulphides and sulphonium salts is always present to some extent. Side reactions resulting in elimination can also be troublesome ([268] and references therein).

$$(CH_3)_2C{=}CH_2 + H_2S \xrightarrow{H_2SO_4} (CH_3)_3CSH \qquad (2.17)$$

$$RX + H_2S \longrightarrow RSH + HX \qquad (2.18)$$

X=Halogen, OH, OTs (with H^+ or Al_2O_3)

Some other methods using simple reagents are given below. Overreaction to the sulphides remains a problem.

$$ROH + P_2S_5 \longrightarrow RSH \qquad (2.19)$$

$$ArCH_2Cl + NaBH_2S_3 \longrightarrow ArCH_2SH \qquad (2.20)$$

$$R_2C{=}O + P_4S_{10} \longrightarrow R_2C{=}S \xrightarrow{NaBH_4} R_2CHSH \qquad (2.21)$$

$$2\ ArOH \xrightarrow{ClCSCl} ArOC(S)OAr \longrightarrow ArSC(O)OAr \xrightarrow{OH^-} ArSH \qquad (2.22)$$

Therefore, it was desirable to develop a metal catalysed process for the conversion of alcohols to thiols which avoids extensive overreaction to the sulphides and which would be compatible with the known $Co_2(CO)_8$ catalysed esterification of thiols to esters. A process was developed by which benzylic alcohols can be converted to thiols, but with concomitant formation of the less desired hydrocarbons, in modest to good yields.

$$2\ ROH + H_2S + CO \xrightarrow[150^\circ C, Solvent]{Co_2(CO)_8, 10h} RSH + RH \qquad (2.23)$$

Benzylic alcohols were converted by cobalt catalysts to thiols at 150°C, under hydrogen sulphide and carbon monoxide at a combined pressure of about 60 atm. Three solvent systems were employed since no one method was equally applicable

for all substrates. Depending upon the solvent system used, significant amounts of the corresponding deoxygenated hydrocarbons were also produced (see Table 2.15). The solvent systems can be designated as follows:

1. Method A: 10 ml of hexane;
2. Method B: 5 ml of hexane and 10 ml of diethyl ether;
3. Method C: 5 ml of hexane and 10 ml of water.

From the results obtained (Tables 2.16—2.19), it is clear that the solvent system plays an important role in the product distribution. It appears that the solubility of the substrate is the critical factor. For example, 4-chlorobenzyl alcohol was soluble in hexane/ether but not in hexane alone or in hexane/water. While reaction takes place to a fair degree in the first solvent mixture, there was almost no reaction in the other two cases. Systems can be either homogeneous or biphasic. Addition of phase transfer catalysts to clearly bi-phasic examples did not improve the conversion of the alcohol.

As mentioned earlier, no one method could be applied to all substrates, but broad generalisations can be made. Solvent mixtures, i.e. hexane/water (Method C) and hexane/ether (Method B) favour thiol formation while hexane alone (Method A) leads to increased hydrocarbon formation in most cases. Apart from the above mentioned solvents, other variations, including the use of dioxane, were tried but improved selectivity toward the thiols was not achieved (see Table 2.16). Unlike the carbonylation reactions, water was not necessary for these reactions to proceed. However, it should be noted that mechanisms proposed for the thiolation and desulphurisation to the hydrocarbons, suggests *in situ* generation of water. This is necessary to explain the products formed in the reactions (see mechanisms below). When the reactions were run in the absence of a solvent, high yields of

Table 2.16: Conversion Of Benzylic Alcohols To Thiols AndHydrocarbons

Substrate[a] $RC_6H_4CH_2OH$	Method	Solvent/*ml*			Products[b], %				
		H_2O	Hexane	Ether	R'OH	R'SH	R'H	R'SR'	R'SSR'
4-Cl	A	-	10	-	98	-	-	-	-
	B	-	5	10	31	36	30	-	
	C	10	5	-	91	6	2	-	-
$C_{10}H_7CH_2OH$[c]	B	-	5	10	-	23	73	-	-
	C	10	5	-	37	9	44	-	-
H	A	-	10	-	28	44	12	11	-
	B	-	5	10	43	34	16	6	-
	C	10	5	-	91	6	1	-	-
2-CH_3	A	-	10	-	32	28	30	-	-
	B	-	5	10	12	38	39	-	-
	C	10	5	-	34	49	15	-	
3-CH_3	A	-	10	-	-	35	49	-	16
	B	-	5	10	6	53	34	-	6
	C	10	5	-	54	31	10	-	-
4-CH_3	A	-	10	-	-	30	36	-	34
	B	-	5	10	-	43	42	-	14
	C	10	5	-	4	51	21	-	19
4-CH_3CH_2	A	-	10	-	-	51	48	-	-
	B	-	5	10	-	44	26	27	-
	C	10	5	-	8	58	30	-	-
4-CH_3O	A	-	10	-	-	2	93	3	-
	B	-	5	10	-	16	83	-	-
	C	10	5	-	3	45	47	-	-

[a] 10 mmol of substrate and 0.5 mmol of $Co_2(CO)_8$ were used in all cases; autoclave pressurised to 60 atm (13 atm H_2S, 47 atm CO); temperature 150°C.

[b] Products were identified by comparison of spectral properties (NMR, mass spec) and g.c. retention times with those of authentic materials; R'= $RC_6H_4CH_2$.

[c] 2-Naphthalenemethanol, and corresponding products.

the sulphide were obtained. Thus, when 50 mmol of benzyl alcohol was reacted "neat" in the presence of 1 mmol of $Co_2(CO)_8$, white needles of dibenzyl sulphide ($C_6H_5CH_2SCH_2C_6H_5$) were isolated in 77% yield.

The effect of the gas environment was also investigated and some informative conclusions can be drawn from these experiments. Formation of hydrocarbon was also favoured by use of synthesis gas instead of carbon monoxide (see Table 2.18). It is interesting to note that, in reactions catalysed by carbonyl complexes, a carbon monoxide atmosphere was not necessary but conversion of the alcohols was slightly lower under nitrogen. The possibility exists that a certain critical pressure of gas is required to keep the metal catalyst in solution and to stabilise it. This observation is based upon the fact that no reaction took place under 1 atm of carbon monoxide pressure. Precedence for this type of behaviour comes from the need for a certain minimum partial pressure of carbon monoxide in the cobalt catalysed hydroformylation reactions. For these reactions, the active catalytic cobalt species is stabilised in solution with the critical carbon monoxide pressure being dependent upon the temperature. In the absence of hydrogen sulphide, no thiols were of course formed. However, small amounts of the hydrocarbon were detected in these reaction mixtures. This suggests that hydrocarbons arise from two sources — via direct deoxygenation/reduction of the alcohol by metal catalysts as well as via the desulphurisation of the *in situ* generated thiol. Slightly lower yields were obtained when sodium hydrogen sulphide (NaSH) was used as the sulphur source. The conversion of alcohol was also higher in this case. It should be mentioned, that 4-methoxybenzyl thiol can be desulphurised quite well under the usual reaction conditions (see Table 2.20).

Table 2.17: Conversion Of Benzylic Alcohols To Thiols And Hydrocarbons — Effect Of Solvent

Substrate[a]	Solvent /ml			Products[b]%				
$RC_6H_4CH_2OH$	H_2O	Hexane	Ether	R'OH	R'SH	R'H	R'SR'	R'SSR'
4-Cl	-	5	10	31	37	30	-	-
	-	10	-	98	-	-	-	-[c]
2-$C_{10}H_7CH_2OH$[d]	10	10	-	78	8	12	-	-
	10	5	5	65	16	17	-	-
	-	5	10	-	23	73	-	-
4-CH_3	-	-	-	42	24	18	4	14[e]
	5	5	-	3	48	25	-	21
	5	5	-	23	34	11	22	5[f]
	8	8	-	35	32	6	17	2[g]
	10	5	-	4	51	21	-	19
H	-	-	-	3	-	2	77	5
	1	-	-	54	20	9	16	-
	-	5	10	43	34	16	6	-
	-	12	3	35	32	13	11	8

[a] 10 mmol of substrate and 0.5 mmol of $Co_2(CO)_8$ was used in all cases under 13 atm H_2S and 47 atm CO at 150°C.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

[c] Substrate did not dissolve at room temperature.

[d] 2-Naphthalenemethanol and corresponding products.

[e] Dioxane (20 ml) was used as the solvent.

[f] Tetrabutylammonium hydrogen sulphate was used as the phase transfer catalyst.

[g] Benzyltriethylammonium chloride used as the phase transfer catalyst.

Table 2.18: Conversion Of Benzylic Alcohols To Thiols And Hydrocarbons — Effect Of Gas

Substrate[a] $RC_6H_4CH_2OH$	Gas[b]	Solvent /ml		Products[c]%				
		H_2O	Hexane	R'OH	R'SH	R'H	R'SR'	R'SSR'
H	CO	-	10	28	44	12	11	-
	CO/H_2	-	10	10	47	24	-	17
4-CH_3CH_2	CO	10	5	8	58	30	-	-
	N_2	10	5	52	31	12	-	
4-CH_3	CO	10	5	4	51	21	-	19
	N_2	10	5	28	50	17	-	4
	CO[d]	10	5	78	-	12	-	-
3-CH_3	CO	10	5	54	31	10	-	-
	N_2	10	5	65	27	4	-	-
2-CH_3	CO	10	5	34	49	15	-	-
	N_2	10	5	47	36	16	-	-

[a] 10 mmol of substrate and 0.5 mmol of $Co_2(CO)_8$ was used in all cases under combined pressure of 60 atm at 150°C.

[b] 13 atm of H_2S, along with 47 atm of the gas listed in the column, were used.

[c] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

[d] No H_2S.

Table 2.19: Conversion Of Benzylic Alcohols To Thiols And Hydrocarbons — Effect Of Catalyst Used

Substrate[a] $RC_6H_4CH_2OH$	Catalyst	Solvent /ml		Products[b]%				
		H_2O	Hexane	R'OH	R'SH	R'H	R'SR'	R'SSR'
H	$Co_2(CO)_8$	-	10	28	44	12	11	-
	$Co_4(CO)_{12}$	-	10	25	41	16	16	-
4-CH_3	$Co_2(CO)_8$	10	5	4	51	21	-	19
	$Co(OAc)_2$	10	5	37	40	16	-	10
	$Co(acac)_2$	10	5	41	37	14	4	-
	$Co_2(CO)_4(dmb)$	10	5	30	31	10	5	8
	$[Rh(CO)_2Cl]_2$	10	5	97	-	-	-	-
	$Rh_6(CO)_{16}$	10	5	96	-	-	-	-
	-	10	5	98	-	-	-	-

[a] 10 mmol of substrate and 0.5 mmol of catalyst was used in all cases under combined pressure of 60 atm H_2S/CO at 150°C.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

The reaction is homogeneous in most cases. A black solid precipitated from the slightly brown product mixture after exposure to air for a few minutes. This precipitate, which exhibited no carbonyl stretching bands in the infrared, could be re-used to catalyse the thiolation and deoxygenation/desulphurisation reactions, but with apparent reduced activity. However, it is possible that the lower yields were due not to reduced activity but rather to loss during filtration and transfers. These are true catalytic reactions since 50:1 substrate to catalyst ratios can be used. Most reactions were run at a 20:1 substrate to metal ratio for convenience of measurement. No reaction took place in the absence of the metal catalyst. Dicobalt octacarbonyl was found to be the most reactive, and therefore most often used metal catalyst, while tetracobalt dodecacarbonyl showed comparable reactivity. Cobalt acetate ($Co(OAc)_2$) cobalt acetylacetonate ($Co(acac)_2$) and bis(dimethylbutadiene) dicobalt tetracarbonyl ($Co_2(CO)_4(dmb)_2$) were less active. Chlorodicarbonyl rhodium dimer ($[Rh(CO)_2Cl]_2$) and hexarhodium hexadecacarbonyl ($Rh_6(CO)_{16}$) were almost totally inert (see Table 2.19). It has been reported in the literature that the addition of *tert*-butyl thiol to hydridocarbonyltris(triphenylphosphino) rhodium(I) ($HRh(CO)(PPh_3)_3$) under hydroformylation conditions, generates a much more active dinuclear species [269]. However, addition of the thiol to the reaction mixture did not improve reactivity or product selectivity under the usual reaction conditions.

A speculative mechanism for the thiolation process is given below (Figure 2.10). It is suggested that in the initial step, hydrogen sulphide reacts with $Co_2(CO)_8$ to give two active catalytic species, $HSCo(CO)_4$ and $HCo(CO)_4$, the former being involved in the thiolation and the latter in the deoxygenation processes. Recent evidence for the existence of the mercapto complex comes from publications by Milstein et al. and Puddephatt and co-workers. Milstein and co-workers reported the isolation of a cationic mercapto complex of iridium, $HIrL_4SH$, upon

Table 2.20: Conversion Of Benzylic Alcohols To Thiols And Hydrocarbons — Other Variations

Substrate[a] $RC_6H_4CH_2OH$	Variations	Solvent /ml		Products[b]%				
		H_2O	Hexane	R'OH	R'SH	R'H	R'SR'	R'SSR'
H	Usual	-	10	28	44	12	11	-
	Mild Cond.[c]	-	10	78	3	9	6	-
	NaSH[d]	-	10	33	36	11	7	10
	Reuse[e]	-	10	30	42	11	6	-
		-	10	40	30	14	8	-
	Thiol[f]	-	10	29	40	12	4	-
Thiol[g]		10	5	-	55	44	1	-

[a] 10 mmol of substrate and 0.5 mmol of $Co_2(CO)_8$ was used in all cases under combined pressure of 60 atm H_2S/CO, at 150°C.

[b] Products were identified by comparison of spectral properties (IR, NMR, mass spec) and g.c. retention times with those for authentic materials; R'= $RC_6H_4CH_2$.

[c] 5 atm H_2S pressure, 100°C, 5 h.

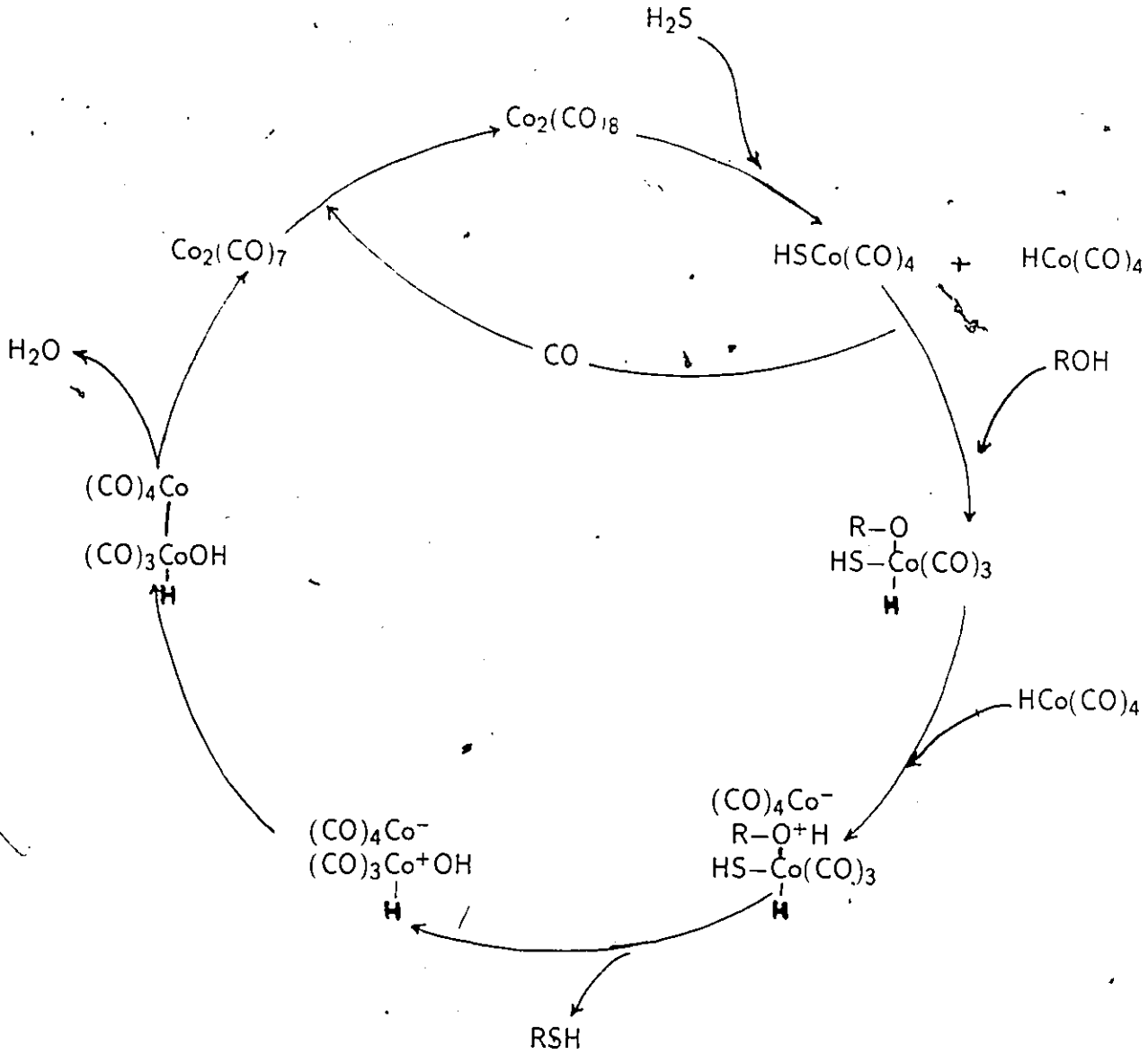
[d] Instead of H_2S as source of sulphur.

[e] Catalyst reused after filtration.

[f] A few drops of benzyl thiol was added as a "promoter".

[g] 4-Methoxybenzyl thiol was the substrate.

Figure 2.10: Proposed Mechanism For The Thiolation Of Alcohols

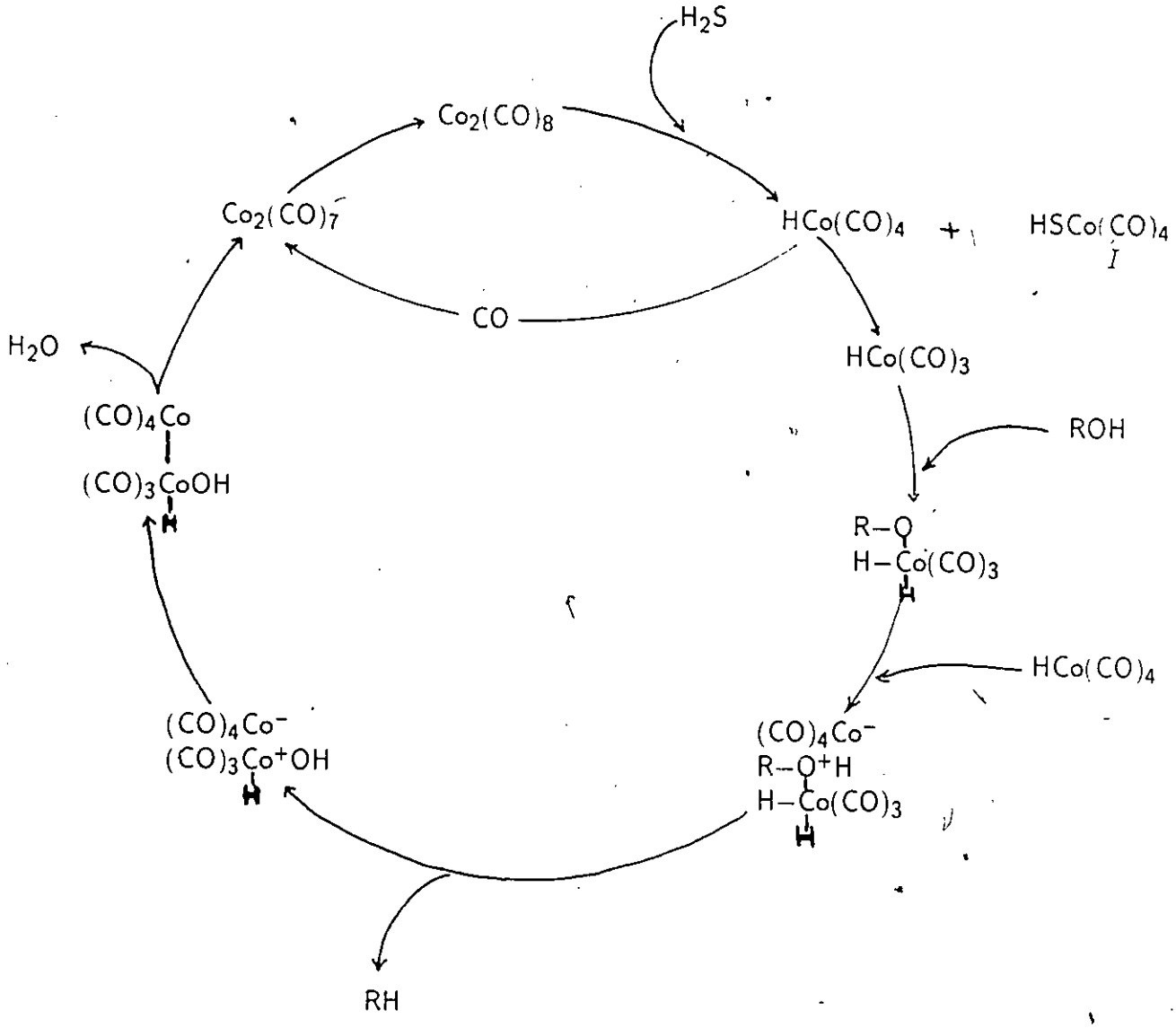


reaction between hydrogen sulphide and $IrL_4^+PF_6^-$ (where L=PMe_3) [270]. Puddephatt and co-workers also recently reported the isolation of a cationic mercapto cluster, $[Pt_3H(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, from the reaction between hydrogen sulphide and a Pt(III) surface [271]. Returning to the proposed mechanism the mercapto complex loses a carbonyl ligand and alcohol adds oxidatively to the metal center to give $HSCo(OR)(H)(CO)_3$. Hydridocobaltcarbonyl acts as a proton source to give the ionic complex with $Co(CO)_4^-$ as the counter-ion. Loss of thiol gives the cationic species which combines with cobalt tetracarbonyl anion to generate a dinuclear hydroxy complex. Reductive elimination of water gives the known dinuclear species $Co_2(CO)_7$, which then picks up carbon monoxide to form $Co_2(CO)_8$ and the catalytic cycle is closed.

It was suggested earlier, that the hydrocarbon produced in these reactions arise via two routes – the desulphurisation of the *in situ* generated thiol and the deoxygenation of the alcohol. Hence, two plausible mechanisms may be proposed.

The first mechanism (Figure 2.11), deals with the deoxygenation of the alcohol. This is very similar to that proposed for the formation of the thiols. The active species in this case being $HCo(CO)_4$ and not the mercapto complex. The latter can either be involved in the deoxygenation cycle or the thiolation cycle which may be proceeding simultaneously. Both metal species arise from the reaction between $Co_2(CO)_8$ and H_2S. Loss of a CO ligand from $HCo(CO)_4$ gives the 16 electron hydridocobalt tricarbonyl, $HCo(CO)_3$, which is, in all likelihood, the active catalytic species. The alcohol coordinates to this 16 electron species and the resultant complex is protonated by another molecule of $HCo(CO)_4$ — either from reaction between another molecule of $Co_2(CO)_8$ and hydrogen sulphide or from the acylation and subsequent loss of COS from $HSCo(CO)_4$. The ion-pair then eliminates the hydrocarbon and the dinuclear hydroxy complex is formed. Reductive elimination of

Figure 2.11: Proposed Mechanism For The Deoxygenation Of Benzylic Alcohols To Hydrocarbons



$$I \longrightarrow HSC(O)Co(CO)_3 \xrightarrow{CO} HSC(O)Co(CO)_4 \xrightarrow{-COS} HCo(CO)_4$$

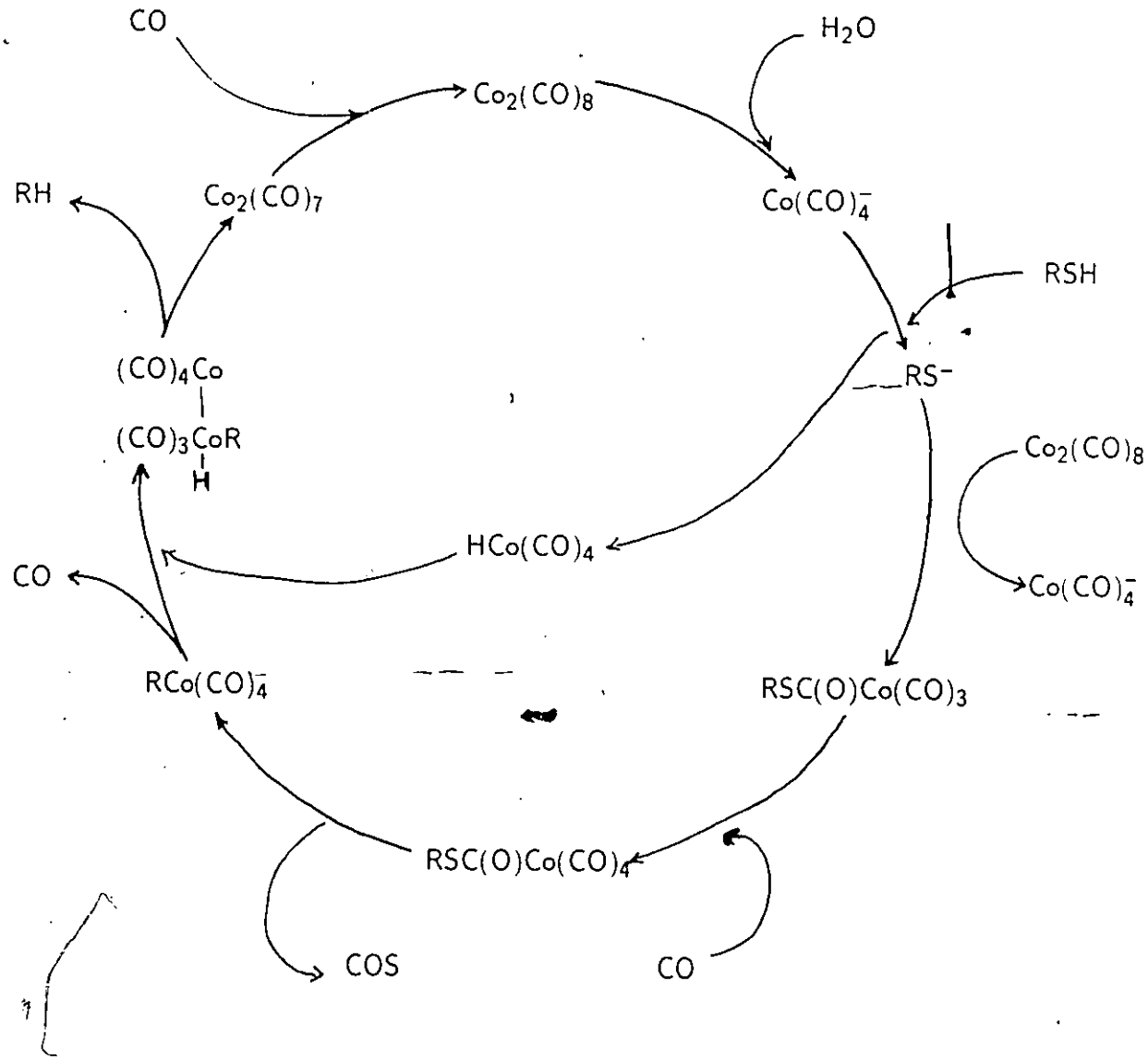
water gives the known dinuclear $Co_2(CO)_7$. The catalytic cycle is completed when this complex picks up a CO ligand and $Co_2(CO)_8$ is generated.

The second route to the hydrocarbon depends upon the presence of water which is required to generate the active desulphurisation catalyst. However, the formation of hydrocarbon can occur in the absence of added water, as was shown to be the case in reactions carried out in hexane. Yet, the reaction system is not anhydrous since the proposed mechanisms for the thiolation and the deoxygenation reactions involve water generating steps while none was consumed in either catalytic cycle. This *in situ* generation of water is pivotal with respect to the second route to the hydrocarbons (the desulphurisation of *in situ* generated thiol in the absence of external water).

Disproportionation of dicobalt octacarbonyl (Figure 2.12) with water leads to cobalt tetracarbonyl anion which is a proposed desulphurisation catalyst (see e.g. [92]). The $Co(CO)_4^-$ reacts with the thiol to give the hydridocobalt species $HCo(CO)_4$ and the RS^- anion. The RS^- anion then reacts with another molecule of $Co_2(CO)_8$ to give the acyl species and $Co(CO)_4^-$. The 16 electron $RSC(O)Co(CO)_3$ species picks up a CO ligand forming the 18 electron coordinatively saturated species which then eliminates COS affording $RCo(CO)_4$. Loss of CO and reaction with the $HCo(CO)_4$ generated in an earlier step gives the dinuclear benzylic species (R=benzylic group) from which the hydrocarbon eliminates to give the dinuclear $Co_2(CO)_7$. Addition of a carbonyl moiety regenerates $Co_2(CO)_8$.

When the system contains external water, for example hexane/water, it is expected that the desulphurisation route would be the dominant process compared to the "anhydrous" system where the generation of the active desulphurisation catalyst, $Co(CO)_4^-$, depends solely upon the *in situ* generated water. It is to be expected that the synergism between the desulphurisation and deoxygenation processes would

Figure 2.12: Proposed Mechanism For The Desulphurisation Of *in situ* Generated Thiols To Hydrocarbons



lead to enhanced hydrocarbon formation in systems with added water. But this is not so. Reactions run in hexane alone give the highest yield of hydrocarbon.

It is also difficult to rationalise the relative reactivity of the various substrates used. Relative solubilities can be a factor, as in the previously mentioned case of 4-chlorobenzyl alcohol. 2-Naphthalenemethanol appears to be very reactive, giving very high yields of 2-methylnaphthalene via direct deoxygenation and desulphurisation. The desulphurisation process in this case is probably very fast, thus accounting for the high yield of the hydrocarbon and not the thiol. Benzyl alcohol did not dissolve very well in hexane/water which could explain its low reactivity in this solvent mixture. Contrary to the trend, more benzyl thiol was generated in hexane than in hexane/ether. The three methyl substituted alcohols displayed varying degrees of reactivity in the solvent systems, but had more or less equal activity overall. 4-Ethylbenzyl alcohol demonstrated almost equal reactivity in all three solvent systems. 4-Methoxybenzyl alcohol displayed varying degrees of reactivity in the various solvent systems, and appears to be highly reactive with respect to the desulphurisation and deoxygenation reactions since 4-methylanisole was the major product in all cases.

In conclusion, a novel metal catalysed thiolation process was successfully developed, and constitute the first examples of metal catalysed conversion of alcohols to thiols. This thiolation reaction would be the first-step in a novel two-step alcohol esterification process.

Chapter 3

Experimental

3.1 General Comments

Melting point (m.p.) determinations were carried out with a Fisher-Johns apparatus and are uncorrected. Infrared spectra (IR) were obtained using a Perkin-Elmer 783 spectrometer and were calibrated with a polystyrene standard. A Nicolet MX-1 FT infrared spectrometer was utilised for recording the spectra of the pure metal complexes. Sodium chloride cells (for solutions), disks or KBr pellets were used for running the spectra. A Varian T60 or EM 360A spectrometer was employed to record the proton magnetic resonance spectra. Chemical shifts are referenced to tetramethylsilane.

Analyses by gas chromatography were carried out with programmable, Method-Controlled Varian Vista 6000 or Varian 3400 gas chromatographs equipped with flame ionisation detectors and Varian 4270 integrators. Unless otherwise stated, yields were calculated and normalised with a calibration curve. The internal standard in all cases was *n*-buthyl benzene. Glass columns (3 m) packed with 5% Carbowax 20M on Chromosorb G, AW-DMCS, 80-100 mesh and 3% OV-101 or 3% OV-17 on Chromosorb W, High Performance 80-100 mesh were utilised. Mass spectra (mass spec) were recorded with a VG Micromass 7070E spectrometer equipped

with a Digital Equipment Corporation PDP8A data system. G.C.-Mass specs were carried out with a Varian 3300 chromatograph, fitted with a Megabore DB5 capillary column (30 m), in tandem with the VG Micromass 7070E spectometer. Elemental analyses were carried out by M-H-W Laboratories, Phoenix, Arizona. Thin layer chromatographic plates (TLC plates), silica gel 60 F_{254} or neutral (Type E) aluminium oxide on aluminium sheets, were purchased from Merck as were the silica gel and active neutral aluminium oxide 90, 70-230 mesh, used for column chromatography. Also used for column chromatography were Bio-Sil A, 200-400 mesh silica gel and neutral alumina AG-7, 100-200 mesh.

The organometallic complexes used were purchased from Pressure Chemical Company or Strem Chemical Company, or synthesised according to literature procedures. The degree of care in handling these complexes was dictated by their stability in air and room temperature. Commercially available complexes were used as received in almost all cases. Triiron dodecacarbonyl was dried under vacuum to remove the added methanol "stabiliser". Most of the organic chemicals were obtained from Aldrich Chemical Company and purified before use when required. Purity was checked by gas chromatography.

Thiols were obtained from Fairfield Chemical Company or synthesised according to known literature procedures. All phase transfer catalysts were commercially available from a number of suppliers including Aldrich, Pfaltz and Bauer, and Fluka, and were used as received. Solvents were distilled and dried by standard methods. Gases were acquired from Air Products Company. High pressure reactions were carried out in 45 ml series 4700 screw cap autoclaves manufactured by Parr Instruments and constructed from either stainless steel or acid resistant INCONEL. Special stainless steel gas regulators, supplied by Air Products, had to be used for loading the autoclaves with hydrogen sulphide (H_2S). All reactions were run under

an inert atmosphere. Literature values of melting points (m.p.) are from the CRC Handbook of Chemistry and Physics or Aldrich Catalog.

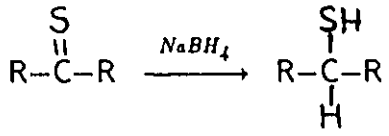
3.2 Desulphurisation Of Organosulphur Compounds Under Alkaline Phase Transfer Conditions

Desulphurisation of activated thiols under alkaline phase transfer conditions was achieved in the presence of either triiron dodecacarbonyl ($Fe_3(CO)_{12}$) or dicobalt octacarbonyl ($Co_2(CO)_8$). Some of the thiols used were not commercially available and had to be synthesised according to literature procedures. A number of thiocarbonyl compounds were desulphurised to their carbonyl analogues by "classical" alkaline phase transfer catalysis, i.e. in the absence of a metal catalyst. Most of the thiocarbonyls used in these cases were synthesised just prior to use. Reaction mixtures were stirred at a high spin rate in all cases, since kinetic studies have shown that reaction rates in PTC systems can be dependent upon the rate of stirring [188]. The complex, di-(2,3-dimethylbuta-1,3-diene) dicobalt tetracarbonyl ($Co_2(CO)_4(dmb)_2$) was synthesised according to the procedure described by Winkhaus and Wilkinson [225].

3.2.1 Synthesis Of Activated Thiols

Several routes to thiols are available in the literature. The process selected was a simple two-step one. In the initial step, the ketone was converted to the corresponding thioketone by reaction with diphosphorus pentasulphide, P_2S_5 as P_4S_{10} [222]. This was then reduced to the thiol by sodium borohydride, $NaBH_4$.

$$R-\overset{\overset{O}{\|}}{C}-R \xrightarrow[NaHCO_3]{P_2S_5} R-\overset{\overset{S}{\|}}{C}-R$$



(3.1)

(3.2)

Three of the thiols had to be synthesised from the corresponding ketones as outlined in the scheme above.

General Procedure For The Synthesis Of Thioketones

The following thioketones were synthesised according to the literature procedure cited above [222]: thiobenzophenone, 4,4-dimethylthiobenzophenone and 4-methoxythiobenzophenone.

The ketone (30 mmol) was dissolved in 65 ml of freshly distilled acetonitrile and placed in a 100 ml three necked round bottomed flask fitted with an oil trap topped condenser and gas inlet. To this solution 1.5 equivalents of tetraphosphorus decasulphide (20 g, 45 mmol) was added and the mixture turned yellow-green in colour. Sodium bicarbonate (15 g, 180 mmol) was added in batches to the vigorously stirred reaction mixture at a rate permitted by the evolution of carbon dioxide. The reaction mixture was then stirred for 3 hours under nitrogen at 30°C (oil bath temperature). A deep blue coloured solution, characteristic of these types of thioketones; was obtained. Two different methods of work-up (A and B) were applied, and the thioketones were characterised by comparison of infrared and melting point data with literature values where available, or simply by the disappearance of the characteristic $\nu_{C=O}$ of the carbonyl compound at about 1650 cm^{-1}.

Work-up:

- Method A: Diethyl ether was added to the reaction mixture which was then washed several times with aqueous sodium bicarbonate (5%) and water in a separatory funnel. After drying the organic phase with sodium sulphate

(Na_2SO_4), the solvent was removed on a rotary evaporator and a dark blue solid was obtained. This solid was dissolved in degassed benzene and chromatographed on neutral alumina under nitrogen. Elution with benzene, followed by rotary evaporation, gave blue needles of the desired thioketone.

- Method B: The reaction mixture was poured into deionised water and a dark blue solid precipitated out. The precipitate was filtered (Büchner funnel) and washed several times with water. A funnel connected to a nitrogen tank was fixed above the Büchner funnel to provide a nitrogen atmosphere. The solid was dissolved in degassed benzene, dried with magnesium sulphate ($MgSO_4$) and chromatagraphed on a short neutral alumina column under nitrogen. Using benzene as the eluant, fine deep blue needles of the thioketone were obtained.

General Procedure For The Conversion Of Thioketones To Thiols

Sodium borohydride (0.6 g, 15 mmol) was dissolved in 10 ml of anhydrous methanol or ethanol, and placed in a 100 ml three necked round bottomed flask equipped in the usual manner. The reaction temperature was lowered to 0°C (ice bath) and to this stirred mixture was added, dropwise, 15 mmol of thioketone dissolved in alcohol (10 ml) under nitrogen. After 10 hours of stirring at room temperature, the reaction mixture was exposed to air and filtered through a sintered glass funnel. The small amount of precipitate obtained was discarded. The filtrate was neutralised with dilute hydrochloric acid and a small amount of precipitate formed which dissolved when ether was added. Multiple ether extractions were carried out. The ether extracts were dried with $MgSO_4$, filtered and concentrated to give a small amount of white precipitate along with a very strongly smelling oil. The oil dissolved in hexane while the solid was not soluble. Isolation of the solid was achieved by simple

filtration and was shown by ^{1}H nmr, IR and mass spec to be the disulphide. Analysis (^{1}H nmr, IR, g.c., mass spec and TLC) showed the oil to be the pure thiol in most cases. However, when this was not the case, pure thiol was obtained by distillation under reduced pressure.

Preparation Of Diphenylmethane Thiol

Benzophenone (5.5 g) was converted to thiobenzophenone by the method described above. Thiobenzophenone was isolated according to Method A and a yield of 5.17 g (87%, 26 mmol) was obtained. The product was identified by the disappearance of the characteristic carbonyl stretch of benzophenone at 1650 cm^{-1} and by its melting point.

m.p.: 52-54°C (lit. 53-54°C)

Diphenylmethane thiol was prepared via the sodium borohydride reduction of freshly prepared thiobenzophenone. Filtration of the oily crude product mixture in hexane gave 0.36 g (6%, 0.9 mmol) of bis(diphenylmethyl)disulphide.

m.p.: 151-153°C (lit. 152-153°C);

^{1}H nmr ($CDCl_3$):δ 4.81(s, 1H), 7.11 (m, 10 H);

mass spec: m/z 398 $[M]^+$, 199 $[(C_6H_5)_2CHS]^+$(100%), 167 $[(C_6H_5)_2CH]^+$.

Analysis of the crude oily product by g.c. indicated the presence of one major and two minor products. Distillation under reduced pressure afforded 2.1 g (71%, 11 mmol) of the desired thiol as shown by g.c./mass spec.

b.p.: 97-99°C under 0.03 mm Hg (lit. 98-99°C);

^{1}H nmr ($CDCl_3$):δ 2.26 (d, 1H), 5.35 (d, 1H), 7.38 (m, 10H);

mass spec: m/z 200 $[M]^+$, 199 $[M-H]^+$, 167 $[M-SH]^+$(100%).

Preparation Of 4,4'-Dimethyldiphenylmethane Thiol

4,4'-Dimethylthiobenzophenone was prepared from 6.3 g of 4,4-dimethylbenzophenone using Method B for the purification procedure. The yield of thioketone was 5.2 g (77%, 20 mmol).

m.p.:73-75°C (lit. 72-73°C).

The thioketone (3.8 g) was smoothly converted to the corresponding thiol with sodium borohydride. Simple filtration of the oily crude product in hexane gave 3.1 g (82%, 12 mmol) of pure thiol. The purity of the product was checked by g.c. and g.c./mass spec.

^{1}H nmr ($CDCl_3$):δ 2.12 (d, 1H), 2.30 (s, 3H), 5.35 (d, 1H), 7.02 (q, 8H);

mass spec: m/z 256 $[M]^+$, 255 $[M\text{-}H]^+$, 223 $[M\text{-}SH]^+$(100%).

Preparation Of 4-Methoxydiphenylmethane Thiol

4-Methoxybenzophenone (6.36 g) was subjected to the thiolation reactions described above giving 5.8 g (85%, 25 mmol) of 4-methoxythiobenzophenone (Method B).

ν_{CO} at 1660 cm^{-1} disappears;

^{1}H nmr ($CDCl_3$):δ 3.82 (s, 3H), 7.24 (m, 9H).

The thioketone (3.4 g) was converted to the thiol by sodium borohydride reduction affording 2.7 g (77%, 12 mmol) of pure thiol.

^{1}H nmr ($CDCl_3$):δ 2.22 (d, 1H), 3.65 (s, 3H), 5.31 (d, 1H), 7.38 (m, 9H);

mass spec: m/z 230 $[M]^+$, 229 $[M\text{-}H]^+$, 197 $[M\text{-}SH]^+$(100%).

3.2.2 General Procedure For The Desulphurisation Of Activated Thiols With Organometallic Complexes

Freshly prepared 5N sodium hydroxide solution (25 ml) was placed in a 100 ml three necked round bottomed flask. Distilled benzene (25 ml) and the phase transfer cat-

alyst (1 mmol, in most cases 0.34 g of tetrabutylammonium hydrogen sulphate) were added and the mixture was stirred and degassed by bubbling nitrogen through the solution for 30 minutes at room temperature. The metal complex, triiron dodecacarbonyl (1.01 g, 2 mmol) or dicobalt octacarbonyl (0.34 g, 2 mmol) was weighed under nitrogen and then added to the reaction mixture. The mixture was stirred for 3 hours at room temperature under nitrogen. When $Fe_3(CO)_{12}$ was the metal complex used, the colour of the organic phase changed from intense green to the characteristic burgundy red colour of $HFe_3(CO)_{11}^-$ (confirmed by infrared spectroscopy [221]). The colour of the organic phase changed to straw yellow (characteristic of $Co(CO)_4^-$ and confirmed by the intense CO stretching band at 1885 cm^{-1} in the infrared [220]) from the initial brown colour when the complex used was $Co_2(CO)_8$. The thiol (2 mmol) was added to the mixture and stirred at 60°C under nitrogen for 10 hours. The following work-up was used in all cases.

The reaction mixture was cooled to room temperature and the phases were separated. The organic phase was washed with very dilute hydrochloric acid and water several times before being dried with $MgSO_4$. The aqueous phase was neutralised with dilute hydrochloric acid and extracted with diethyl ether several times. Drying and concentration of the ethereal extracts yielded no products in all cases. The dried organic phase was concentrated and the crude mixture analysed by comparing g.c. retention times with those of authentic materials, where available, and confirmed by g.c./mass spec. When the authentic materials were available, the crude samples were "spiked" with the suspected products and chromatograms were obtained. Pure products were isolated by thin layer or column chromatography on neutral alumina with 9:1 hexane/ethyl acetate as the eluant. Isolated products were identified by ^1H nmr, IR and mass spec. Disappearance of the weak SH stretch in the infrared region about 2400 cm^{-1} was also indicative of the desulphurisation process.

Desulphurisation Of 2-Methylbenzyl Thiol

2-Methylbenzyl thiol (0.28 g) was effectively desulphurised in the presence of both metal complexes. Three products were detected in the crude sample by g.c. The major product was identified as *o*-xylene, while the minor ones were the sulphide and disulphide, confirmed by g.c./mass spec. *o*-Xylene was isolated by fractional distillation and identification was achieved by ^{1}H nmr, boiling point and mass spec. *o*-Xylene was isolated in 0.18 g (87%, 1.7 mmol) yield with $Fe_3(CO)_{12}$ and in 0.17 g (81%, 1.6 mmol) with $Co_2(CO)_8$. The phase transfer catalyst in both cases was TBAHS (0.34 g, 1 mmol). When 0.43 g (1 mmol) of THAB was used with $Co_2(CO)_8$, 0.18 g (87%, 1.7 mmol) of *o*-xylene was isolated. The yield was 81% (0.17 g, 1.6 mmol) when 0.31 g (1 mmol) of DTAC was the phase transfer agent.

b.p.: 142-145°C (lit. 143-145°C);

^{1}H nmr ($CDCl_3$):δ 2.26 (s, 6H), 7.05 (m, 4H);

mass spec: m/z 106 $[M]^+$, 91 $[M\text{-}CH_3]^+$(100%).

Desulphurisation Of 4-Methylbenzyl Thiol

Both metal complexes were able to desulphurise 4-methylbenzyl thiol (0.28 g) with $Co_2(CO)_8$ being the more effective. Some unreacted thiol was detected by g.c. analysis and was confirmed by "spiking" the crude sample with the thiol and by g.c./mass spec. The same techniques were applied for identifying the major product as *p*-xylene. With $Fe_3(CO)_{12}$ as the complex, 0.12 g (58%, 1.1 mmol) of *p*-xylene was isolated while 0.17 g (79%, 1.6 mmol) of hydrocarbon was formed using $Co_2(CO)_8$. Isolation was achieved by distillation, while the sulphides were separated on TLC plates as described earlier.

b.p.: 136-138°C (lit. 138°C);

^{1}H nmr ($CDCl_3$):δ 2.30 (s, 3H), 7.00 (m, 4H);

mass spec: m/z 106 $[M]^+$, 91 $[M\text{-}CH_3]^+$(100%).

Desulphurisation Of 4-Methoxybenzyl Thiol

4-Methylanisole was isolated in excellent yield from the desulphurisation of 4-methoxybenzyl thiol (0.31 g) with both metal complexes. The only other product isolated, by TLC, was the sulphide. Using $Fe_3(CO)_{12}$, 0.18 g (73%, 1.5 mmol) of 4-methylanisole and 0.03 g (12%, 0.1 mmol) of the sulphide were formed, while $Co_2(CO)_8$ gave 0.2 g (82%, 1.6 mmol) and 0.027 g (11%, 0.1 mmol) respectively. Effect of various other phase transfer catalysts were tested with $Co_2(CO)_8$ as the metal complex:

- TEBAC (0.30 g, 1 mmol) led to 0.168 g (69%, 1.4 mmol);
- THAB (0.43 g, 1 mmol) led to 0.18 g (73%, 1.4 mmol);
- THAHS (0.46 g, 1 mmol) led to 0.17 g (72%, 1.4 mmol);
- DTAC (0.31 g, 1 mmol) led to 0.18 g (73%, 1.5 mmol)

of 4-methyl anisole. Product identification was by ^{1}H nmr and g.c./mass spec.

b.p.: 172.5-173.5°C (lit. 174°C);

^{1}H nmr ($CDCl_3$):δ 2.24 (s, 3H), 3.68 (s, 3H), 6.85 (q, 4H):

mass spec: m/z 122 $[M]^+$, 107 $[M\text{-}CH_3]^+$(100%).

Desulphurisation Of 2,4-Dichlorobenzyl Thiol

While $Fe_3(CO)_{12}$ was able to desulphurise this substrate (0.38 g) in excellent yield, 0.3 g (95%, 1.9 mmol) of hydrocarbon. $Co_2(CO)_8$ was incapable of performing the same task. The only product isolated was 2,4-dichlorotoluene and this was confirmed by g.c./mass spec and ^{1}H nmr.

^{1}H nmr ($CDCl_3$):δ 2.25 (s, 3H), 7.08 (m, 2H), 7.20 (s, 1H);
mass spec: m/z 162 $[M+2]^+$, 160 $[M]^+$, 127 $[M+2-Cl]^+$, 125 $[M-Cl]^+$(100%).

Desulphurisation Of Diphenylmethane Thiol

Both metal carbonyls were found to be effective for the desulphurisation of diphenylmethane thiol (0.4 g). Isolation by TLC (9:1 hexane/ethyl acetate) of the products from the $Fe_3(CO)_{12}$ reaction gave 0.27 g (82%, 1.6 mmol) of diphenylmethane and 0.05 g (11%, 0.2 mmol) of triphenylmethane, while the yields using $Co_2(CO)_8$ were 0.28g (84%, 1.7 mmol) and 0.04 g (10%, 0.16 mmol) respectively.

- Diphenylmethane: ^{1}H nmr ($CDCl_3$):δ 3.98 (s, 2H), 7.23 (m, 10H);
  mass spec: m/z 168 $[M]^+$.
- Triphenylmethane: ^{1}H nmr ($CDCl_3$):δ 5.56 (s, 1H), 7.22 (m, 15H);
  mass spec: m/z 244 $[M]^+$, 243 $[M-H]^+$(100%).

Desulphurisation Of 4-Methoxydiphenylmethane Thiol

Only one product was isolated in the desulphurisation of this thiol (0.46 g) in very high yields with both metal catalysts. The yield of the hydrocarbon was almost quantitative with $Co_2(CO)_8$ (0.39 g, 98%, 1.9 mmol), while 0.31 g (80%, 1.6 mmol) of 4-methoxydiphenylmethane resulted when using $Fe_3(CO)_{12}$. The ^{1}H nmr, mass spec and m.p. corroborated the identity of the product.
m.p.: 36-39°C (lit. 36-37°C);
^{1}H nmr ($CDCl_3$):δ 3.61 (s, 3H), 3.92 (s, 2H), 7.20 (m, 8H);
mass spec: m/z 198 $[M]^+$, 183 $[M-CH_3]^+$.

Desulphurisation Of 4,4'-Dimethyldiphenylmethane Thiol

Excellent yields of 4,4'-dimethyldiphenylmethane were obtained from this thiol (0.46 g) — $Fe_3(CO)_{12}$ 0.31 g (80%, 1.6 mmol), and $Co_2(CO)_8$ 0.38 g (98%, 1.9 mmol). Verification of the product, isolated by means of TLC (using 9:1 hexane/ethyl acetate as the developing solvent), was obtained with ^1H nmr and mass spec.

^1H nmr ($CDCl_3$):δ 2.26 (s, 6H), 3.97 (s, 2H), 7.21 (m, 8H);

mass spec: m/z 196 $[M]^+$, 181 $[M\text{-}CH_3]^+$.

Desulphurisation Of Triphenylmethane Thiol

$Fe_3(CO)_{12}$ afforded 0.32 g (65%, 1.3 mmol) of triphenylmethane while $Co_2(CO)_8$ gave the hydrocarbon in 0.4 g (82%, 1.6 mmol) yield. (0.55 g of the thiol was used.) Use of TEBAC led to 0.30 g (61%, 1.2 mmol) while THAB gave 0.32 g (65%, 1.3 mmol) of the hydrocarbon. Isolation was achieved with thin layer chromatography. Melting point determination, ^1H nmr and mass spec led to successful product identification.

m.p.: 91.5-94°C (lit. 92-94°C);

^1H nmr ($CDCl_3$):δ 5.56 (s, 1H), 7.22 (m, 15H);

mass spec: m/z 244 $[M]^+$, 243 $[M\text{-}H]^+$.

Attempted Desulphurisation Of Some Other Thiols

1-Octanethiol, 3-toluenethiol and 2-naphthalenethiol were not desulphurised by either metal catalysts.

3.2.3 Variations In Reaction Conditions

Several reactions were carried out under slightly modified conditions. Reactions were run exactly as usual except for the following:

1. Base concentration changed from 5N to 3N and 25N sodium hydroxide solution — work-up as usual; results recorded in Table 2.2.
2. Various phase transfer catalysts were used without any change in the procedure (see Table 2.3).
3. Molybdenum and tungsten hexacarbonyls were also used.
4. Reactions were run at various temperatures without any other variations.
5. Some reactions were run under hydrogen while others were under nitrogen, carbon monoxide or syn gas (CO/H_2).

A major variant was the use of a solid/liquid system. Among the many attempts in the desulphurisation of 1-naphthalenethiol, those made under solid/liquid conditions with molybdenum and tungsten hexacarbonyls were unsuccessful. However, an attempt at desulphurising triphenylmethane thiol with a solid-liquid system yielded results remarkably similar to the usual liquid/liquid systems.

Desulphurisation Of Triphenylmethane Thiol Under Solid/Liquid Phase Transfer Conditions

In a 100 ml three necked round bottomed flask was placed 0.108 g (2 mmol) of sodium methoxide, 1.01 g (2 mmol) of $Fe_3(CO)_{12}$ 0.44 g (2 mmol) of 15-crown-5 and dry THF (50 ml) under carbon monoxide. This mixture was stirred for 3 hours at room temperature, the thiol was added (0.553 g, 2 mmol) and the solution was then stirred for 10 hours at 60°C under carbon monoxide. Product isolation was achieved on a neutral alumina column with 9:1 hexane/ethyl acetate as eluant. Triphenylmethane (0.31 g, 63%, 1.3 mmol) was isolated and identified by ^1H nmr and mass spectrometry.

Other solid/liquid reactions involving potassium hydroxide and molybdenum or tungsten hexacarbonyl were run in the same way, but were unsuccessful.

3.2.4 General Procedure For The Attempted Desulphurisation Of Activated Thiols By $Mn(CO)_5Br$ Or $Co_2(CO)_4(dmb)_2$

To 25 ml of freshly prepared 5N sodium hydroxide in a 100 ml three necked round bottomed flask, was added dichloromethane (25 ml) and the phase transfer agent (1 mmol). The reaction mixture was degassed by bubbling nitrogen through the system for 30 minutes at room temperature. The temperature of the oil bath was raised to 40°C and 0.5 mmol of the metal catalyst was added. The mixture was stirred for about 2 hours before 1 ml of iodomethane and the thiol (10 mmol) were added in sequence under carbon monoxide. After 10 hours, the mixture was cooled to room temperature and work-up was effected in the same manner as with $Fe_3(CO)_{12}$ and $Co_2(CO)_8$.

Synthesis Of $Co_2(CO)_4(dmb)_2$

This complex was synthesised according to the procedure outlined by Winkhaus and Wilkinson [225]. Dicobalt octacarbonyl (0.86 g, 1.0 mmol) and 4.1 g (0.05 mmol) of 2,3-dimethylbuta-1,3-diene in 40 ml of hexane were refluxed under nitrogen for 2 hours (Schlenk tube). Column chromatography, under nitrogen, gave red needles of di-(2,3-dimethylbuta-1,3-diene)dicobalt tetracarbonyl (60%, 0.6 g). The complex was characterised by infrared spectroscopy. IR(CCl_4) 3060w, 2980s, 2925s, 2860m, 1485s, 1469m, 1462m, 1434m, 1403m, 1382m, 1260m cm^{-1}.

Attempted Desulphurisation Of 2-Methylbenzyl Thiol

Reaction of 2-methylbenzyl thiol (1.4 g), with $Mn(CO)_5Br$ (0.14 g), TEBAC (0.3 g) and dichloromethane/5N sodium hydroxide solution as the two phases, yielded 1.0 g (42%, 4.1 mmol) of 2-methylbenzyl sulphide and 1.5 g (56%, 5.6 mmol) of the disulphide. Product isolation was achieved by column chromatography in the usual manner.

In the presence of iodomethane, under carbon monoxide and with 0.5N sodium hydroxide solution as the aqueous phase, 0.9 g (65%, 5.9 mmol) of (2-methylbenzyl)-methyl sulphide ($2\text{-}CH_3C_6H_4CH_2SCH_3$), 0.2 g (10%, 0.8 mmol) of 2-methylbenzyl sulphide and 0.4 g (15%, 1.5 mmol) of the disulphide were isolated by thin layer chromatography using 9:1 hexane/ethyl acetate as the developer.

(2-Methylbenzyl)methyl sulphide: ^{1}H nmr($CDCl_3$):δ 2.05 (s, 3H), 2.37 (s, 3H), 3.61 (s, 2H), 7.15 (m, 4H);

mass spec: m/z 152 $[M]^+$, 105 $[M\text{-}SCH_3]^+$(100%).

Attempted Desulphurisation Of 4-Methylbenzyl Thiol

Reaction of 4-methylbenzyl thiol (1.4 g) with iodomethane in the presence of $Mn_2(CO)_9Br^-$, yielded 0.9 g (62%, 5.9 mmol) of (4-methylbenzyl)methyl sulphide ($4\text{-}CH_3C_6H_4CH_2SCH_3$), 0.3 g (12%, 1.2 mmol) of 4-methylbenzyl sulphide and 0.3 g (10%, 1.1 mmol) of the disulphide upon isolation by TLC. Product identification was via ^{1}H nmr and mass spec.

(4-Methylbenzyl)methyl sulphide: ^{1}H nmr ($CDCl_3$):δ 2.05 (s, 3H), 2.42 (s, 3H), 3.65 (s, 2H), 7.10 (m, 4H).

mass spec: m/z 152 $[M]^+$, 105 $[M\text{-}SCH_3]^+$.

Attempted Desulphurisation Of 4-Chlorobenzyl Thiol

With TBAHS (0.34 g), at room temperature, under nitrogen, in the presence of $Mn(CO)_5Br$, 1.6 g of this thiol gave only 4-chlorobenzyl sulphide (1.2 g, 42%, 4.2 mmol) and the disulphide (1.4 g, 45%, 4.5 mmol).

4-Chlorobenzyl sulphide: ^1H nmr ($CDCl_3$):δ 3.28 (s, 4H), 7.02 (m, 8H);

mass spec: m/z 284 $[M+2]^+$, 282 $[M]^+$;

Disulphide: ^1H nmr ($CDCl_3$)δ 3.73 (s, 4H), 7.23 (m, 8H);

mass spec: m/z 316 $[M+2]^+$, 314 $[M]^+$.

Attempted Desulphurisation Of 4-Methoxybenzyl Thiol

Attempted desulphurisation of 4-methoxybenzyl thiol (1.5 g) in the presence of iodomethane, TEBAC (in all cases) and $Mn(CO)_5Br$, in water at 40°C, under carbon monoxide led to a complex mixture (numerous peaks in ^1H nmr and g.c.). When this reaction was repeated with 5N sodium hydroxide solution as the aqueous phase, 1.1 g (63%, 6.3 mmol) of (4-methoxybenzyl)methyl sulphide ($4\text{-}CH_3OC_6H_4CH_2SCH_3$), and 29% of 4-methoxybenzyl disulphide were obtained. The products were isolated by TLC and identified with the aid of ^1H nmr and mass spec.

(4-Methoxybenzyl)methyl sulphide: ^1H nmr ($CDCl_3$):δ 2.01 (s, 3H), 3.82 (s, 3H), 4.50 (s, 2H), 6.97 (m, 4H);

mass spec: m/z 168 $[M]^+$, 121 $[M\text{-}SCH_3]^+$(100%).

In the absence of iodomethane, 1.6 g (57%, 5.7 mmol) of 4-methoxybenzyl sulphide and 1.2 g (39%, 3.9 mmol) of the disulphide were isolated by TLC.

With $Co_2(CO)_4(dmb)_2$ as the complex, in the presence of iodomethane, isolation of 16% (4-methoxybenzyl)methyl sulphide, 49% of the sulphide, and 27% of the disulphide was achieved. In the absence of iodomethane, the sulphide and disulphide

were the only products.

Reaction in the absence of a metal complex (with iodomethane being present) led to the isolation of 91% (4-methoxybenzyl)methyl sulphide at 40°C, under nitrogen, with 5N sodium hydroxide as the aqueous phase.

3.2.5 General Procedure For The Desulphurisation Of Thiocarbonyls

A mixture of 0.68 g (2 mmol) of tetrabutylammonium hydrogen sulphate, TBAHS, sodium hydroxide solution (25 ml) and dichloromethane (25 ml) was degassed by bubbling nitrogen through the solution for 30 minutes at room temperature. The thiocarbonyl compound, dissolved in a small volume of dichloromethane, was added to the mixture and the solution was then stirred at room temperature. The course of the reaction was monitored by TLC and by withdrawing small volumes of the organic phase, passing this through a small plug of $MgSO_4$ and recording its infrared spectrum. The appearance, and relative intensity, of the characteristic carbonyl stretch at about 1650 cm^{-1} was indicative of the formation of the carbonyl compound from the thiocarbonyl one. Work-up was effected by separating the organic phase, washing it with dilute hydrochloric acid and water before drying with $MgSO_4$ and subsequent rotary evaporation to give the product. When necessary, the crude product mixture was purified by silica gel column chromatography with 9:1 hexane/ethyl acetate as eluant.

Synthesis Of Thiocarbonyl Compounds

Thiobenzophenone and 4,4′-dimethoxythiobenzophenone were prepared via the reaction of the carbonyl compound with P_2S_5 according to procedure described earlier in this chapter [222] while thioxandrosta-1,4-diene-3,17-dione was prepared by an-

other literature procedure [272]. The other thiocarbonyl compounds were either commercially available or synthesised from the corresponding carbonyl compound upon reaction with Lawesson's reagent by Caroline Kwiatkowska [273]. Typically, a mixture containing 17-20 mmol of the carbonyl compound and 12 mmol (4.86 g) of Lawesson's reagent (the dimer of (*p*-methoxyphenyl)thionophosphine sulphide) in toluene (80 ml) was refluxed for 2 days. After concentration, the crude product was chromatographed on a silica gel column with 9:1 hexane/ether as the eluant.

Desulphurisation Of 4,4'-Dimethoxythiobenzophenone

Attempted desulphurisation of 1.3 g (5 mmol) of the thioketone with nickel cyanide (0.183 g, 1 mmol) as the metal complex, 4-methyl-2-pentanone (25 ml) and freshly prepared 5N sodium hydroxide (20 ml) as the two phases with TBAHS (0.07 g, 0.2 mmol) as the phase transfer agent, led to 0.48 g (40%, 2 mmol) of the desulphurised carbonyl compound. Work-up and isolation by TLC was effected as described above.

Under "classical" alkaline phase transfer conditions, i.e. TBAHS (0.68 g) 3N sodium hydroxide solution and dichloromethane, 0.152 g (63%, 0.63 mmol) of 4,4'-dimethoxybenzophenone was isolated from the desulphurisation of 4,4-dimethoxythiobenzophenone (0.258 g, 1 mmol). Column chromatography on a silica gel column was utilised for product isolation. When TEBAC (0.6 g) was the phase transfer agent, no reaction occured. No reaction also took place in the absence of the phase transfer catalyst. However, when TBAHS (0.68 g) was added to this reaction mixture, desulphurisation did occur. Product identification was by ^{1}H nmr, mass spec and the appearance of the carbonyl stretch in the infrared region at 1650 cm^{-1}.

m.p.: 140-142.5°C (lit. 141-143°C);

^{1}H nmr ($CDCl_3$):δ 3.90 (s, 6H), 7.40 (q, 8H);

mass spec: m/z 242 $[M]^+$.

Desulphurisation Of Thiobenzophenone

Use of thiobenzophenone (0.2 g, 1 mmol) as reactant afforded, in one hour, 0.164 g (90%, 0.9 mmol) of benzophenone. The aqueous phase was 3N sodium hydroxide solution. Purification was not necessary. Identification was by TLC, melting point determination, mass spec and infrared spectroscopy.

m.p.: 48-49°C (lit. 49-51°C);

mass spec: m/z 182 $[M]^+$.

Desulphurisation Of Thiocamphor

A tetrabutylammonium hydrogen sulphate catalysed desulphurisation reaction of thiocamphor (0.5 g, 3 mmol) with 5 N sodium hydroxide solution as the aqueous phase, gave 0.36 g (79%, 2.4 mmol) of camphor within 2 hours. Product isolation was by column chromatography and identification by TLC and IR ($\nu_{C=O}$ 1754 cm^{-1}).

Desulphurisation Of Thioxandrosta-1,4-diene-3,17-dione

After 8 hours (normality of the aqueous phase was 5), 0.04 g (72%, 0.15 mmol) of the desulphurised product was isolated in the usual way from 0.057 g (0.21 mmol) of the thiocarbonyl. Product identification was by infrared spectroscopy ($\nu_{C=O}$ 1750 and 1635 cm−1). and TLC.

Desulphurisation Of Ethyldithioacetate

This thiocarbonyl compound (0.156 g, 1.3 mmol) was very smoothly converted to the carbonyl compound over 7 hours with a 1N basic solution as the aqueous phase.

The yield of the product was 0.14 g (99%, 1.3 mmol). The product was identified by IR and the purity was confirmed by g.c.

Desulphurisation of γ-Dithiobutyrolactone

γ-Dithiobutyrolactone (.21 g, 1.8 mmol) was desulphurised using 1N sodium hydroxide (reaction time was 4 hours) and work-up gave 0.153 g (86%, 1.5 mmol) of γ-thiobutyrolactone. TLC and IR ($\nu_{C=O}$ 1680 cm^{-1}) were utilised for product identification.

Desulphurisation Of Thiobenzanilide

Benzanilide (0.08 g, 51%, 0.4 mmol) was isolated from the desulphurisation of thiobenzanilide (0.16g, 0.76 mmol). The reaction was run for 3 hours with 5N sodium hydroxide as the aqueous phase. Infrared spectroscopy and TLC were employed to identify the product.

m.p.: 160-161°C (lit. 162-164°C).

Desulphurisation Of 1,1,3,3-Tetramethylthiourea

Isolation of 0.87 g (75%, 0.75 mmol) of the carbonyl compound from 1,1,3,3-tetramethylthiourea (0.13 g, 1 mmol) was achieved in the usual manner. The aqueous phase was 5N sodium hydroxide and the reaction was run for 5 hours. Product identification was carried out in the usual manner ($\nu_{C=O}$ 1640 cm^{-1}).

3.3 Reactions Under Acidic Phase Transfer And Biphasic Conditions

The aqueous phase in almost all of these reactions, phase transfer and biphasic, was 25 ml of 48-50% tetrafluoroboric acid (HBF_4) while benzene was usually used as the

organic phase. All the activated alkenes and dienes were commercially available and used as received. The thiols used were either available commercially or synthesised according to procedure described earlier. Bis(diphenylphosphino)methane dicobalt hexacarbonyl, $Co_2(CO)_6$(dpm), and bis(diphenylarsino)methane dicobalt hexacarbonyl, $Co_2(CO)_6$(dasm), were synthesised from $Co_2(CO)_8$ via ligand substitution according to literature procedures [242]. The other metal complexes, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$, were obtained from commercial sources. The phase transfer catalyst used was the commercially available sodium 4-dodecylbenzenesulphonate.

3.3.1 Synthesis Of Organometallic Complexes

The metal complexes which were not available commercially were synthesised according to literature methods with some modifications. Products were characterised by infrared spectroscopy and checked for purity before use.

Synthesis Of $Co_2(CO)_6$(dpm) And $Co_2(CO)_6$(dasm)

Bis(diphenylphosphino)methane dicobalt hexacarbonyl, $Co_2(CO)_6$(dpm) , was synthesised according to literature procedure with some modifications [242]. In a 100 ml round bottomed flask equipped with a side arm gas adapter, and a septum stopper, 1.5 g (4.4 mmol) of dicobalt octacarbonyl was dissolved in 10 ml of degassed dichloromethane under nitrogen. A separate flask was charged with 1.7 g (4.4 mmol) of bis(diphenylphosphino)methane (dpm) dissolved in 10 ml of dichloromethane. The dpm solution was degassed with nitrogen bubbling through and then transferred via syringe to the flask containing the $Co_2(CO)_8$ solution. The reaction mixture was stirred and carbon monoxide gas evolved. The reaction was complete in 10 minutes. The mixture was cooled to -78°C and the product obtained as an orange, crystalline, air-stable solid upon addition of cold hexane. The yield was 2.5 g

(80%). Infrared spectrum matched that reported in the literature. IR (Nujol):ν_{CO} 2028(m), 1999(s), 1983(s), 1973(s), 1811(m), 1798(s) cm^{-1} (lit. 2042(m), 2000(s), 1989(s), 1975(s), 1812(m), 1799(m) cm^{-1}).

Bis(diphenylarsino)methane dicobalt hexacarbonyl, $Co_2(CO)_6$(dasm) , was prepared by Dr. V. Galamb in exactly the same way as above. The complex was a red-orange powder and relatively air-stable in the solid state but slowly decomposes upon exposure to air in solution.

Synthesis Of Benzylthioiron Tricarbonyl Dimer, $[C_6H_5CH_2SFe(CO)_3]_2$

This complex was synthesised according to the procedure described by King [246], from a mixture of $Fe_3(CO)_{12}$ (1.68 g, 1.5 mmol) and 1.3 g (3 mmol) benzyldisulphide, $(C_6H_5CH_2S)_2$, in benzene under reflux for 5.5 hours under nitrogen. The product was obtained upon removal of solvent, and characterised by infrared spectroscopy, and used without further purification.

3.3.2 Hydrogenation By Organometallic Complexes Under Acidic Phase Transfer Conditions

Typically, a mixture of sodium 4-dodecylbenzenesulphonate (0.174 g. 0.5 mmol), 48-50% HBF_4 (25 ml) and benzene (20 ml) was stirred for 30 minutes at room temperature under nitrogen. To this solution was added benzene (5 ml) containing the substrate (1 mmol) and the metal complex (0.5 mmol), and the reaction mixture was stirred at the appropriate temperature until reaction was complete. Reactions were run under nitrogen in most cases. The reactions were followed by TLC and by withdrawing small samples at various intervals which were analysed by gas chromatography. Work-up was effected by separating the phases and then concentrating the dried (with $MgSO_4$) organic phase to give the crude product.

Purification, where needed, was achieved by column chromatography on silica gel. Product identification was by ^{1}H nmr and g.c./mass spec.

Hydrogenation Of 1,1-Diphenylethene

Reaction of 0.18 g of 1,1-diphenylethene with $Co_2(CO)_8$ (0.17 g) gave 97% (0.176 g) of 1,1-diphenylethane after 4 hours of stirring under nitrogen at 55°C. This was a repeat of an experiment run with respect to another project [212]. When $Co_2(CO)_6$(dpm) (0.34 g) was used as the metal complex, the reaction was run for 6 hours at 70°C and under nitrogen, the hydrogenated product was isolated in 58% yield (0.10 g) from 0.18 g of 1,1-diphenylethene. Isolation was achieved on silica gel TLC plates with 4:1 hexane/dichloromethane as eluant. There was no reaction when the experiment was repeated in the absence of the phase transfer agent.

When bis(diphenylarsino)methane dicobalt hexacarbonyl (0.38 g) was used as the reactant with the alkene for 3 hours at 76°C, 0.176 g (97%) of the reduced product was isolated. Product identification in all cases was with ^{1}H nmr and g.c./mass spec.

^{1}H nmr ($CDCl_3$):δ 1.58 (d, 3H), 4.05 (q, 1H), 7.14 (m, 10H);

mass spec: m/z 182 $[M]^+$, 167 $[M\text{-}CH_3]^+$.

Hydrogenation Of 4-Methoxydiphenylethene

4-Methoxydiphenylethene (0.21 g) was subjected to the hydrogenation reaction under acidic phase transfer conditions with $Co_2(CO)_6$(dpm) (0.41 g) only. After 6 hours at 70°C under nitrogen, 0.14 g (64%) of the hydrogenated product was isolated by silica gel column chromatography with 4:3 hexane/dichloromethane as the eluant. Product identification was carried out as usual with ^{1}H nmr and mass spec.

^{1}H nmr ($CDCl_3$):δ 1.58 (d, 3H), 3.64 (m, 1H), 3.76 (s, 3H), 7.00 (q, 4H),

7.29 (m, 5H);

mass spec. m/z 212 $[M]^+$.

Hydrogenation Of Styrene

Styrene (0.104 g) was hydrogenated in a facile manner within 1 hour at 55°C by $Co_2(CO)_8$ (0.175 g). The liquid product ethylbenzene ($C_6H_5CH_2CH_3$) was obtained in 0.103 g (98%) yield and characterised by ^1H nmr. No other complexes were used.

^1H nmr ($CDCl_3$):δ 1.21 (t, 3H), 2.62 (q, 2H), 7.12 (s, 5H);

mass spec. m/z 106 $[M]^+$, 91 $[M\text{-}CH_3]^+$.

Hydrogenation of α-Methylstyrene

Several reactions were tried with this substrate (0.12 g) under various conditions. All were carefully monitored by g.c. Dicobalt octacarbonyl converted α-methylstyrene, almost quantitatively (0.117 g, 98%), to cumene within 45 minutes at 55°C under nitrogen. When the reaction was repeated under carbon monoxide, at the same temperature, only 54% (0.065 g) of the hydrogenated product was obtained after 5.5 hours. With $Co_2(CO)_6$(dpm) , the yield of cumene was 0.07g (58%) after 6.5 hours under nitrogen at 72°C. Once again $Co_2(CO)_6$(dasm) proved to be a more effective complex than $Co_2(CO)_6$(dpm) , giving 56% (by g.c.) of cumene after 1 hour at 72°C under nitrogen, 84% after 5 hours and 98% (0.117 g) after 7 hours. Product identified by ^1H nmr.

^1H nmr ($CDCl_3$):δ 1.20 (s, 3H), 1.30 (s, 3H), 2.91 (sep., 1H), 7.27 (m, 5H).

Hydrogenation Of 2,4-Dimethylstyrene

2,4-Dimethylphenylethane (0.09 g, 66%) was isolated from the $Co_2(CO)_8$ induced hydrogenation of 2,4-dimethylstyrene (0.13 g) at 55°C under nitrogen in 3.5 hours.

The hydrogenated product was obtained in quantitative yield in the $Co_2(CO)_6$(dasm) induced reaction (2.5 hours at 71°C). In the absence of the phase transfer agent,the hydrogenated product was isolated in 25% yield (0.044 g).

Hydrogenation Of 2-Vinylnaphthalene

A yield of 0.106 g (68%) of 2-ethylnaphthalene was obtained from the $Co_2(CO)_8$ induced hydrogenation of 2-vinylnaphthalene at 55°C in 2 hours. Product isolation was achieved by silica gel column chromatography while identification was by ^{1}H nmr.

^{1}H nmr ($CDCl_3$):δ 1.28 (t, 3H), 2.75 (q, 2H), 7.15 (m, 7H).

Hydrogenation Of 1-Phenyl-1,3-butadiene

Dicobalt octacarbonyl was effective in converting this diene at 55°C under nitrogen to give 0.075 g (58%) of hydrogenated products within 3 hours. A 55:45 ratio of 1-phenyl-1-butene/1-phenyl-2-butene was isolated on TLC plates with 5:1 hexane/dichloromethane as eluant. Product identification was by ^{1}H nmr.

trans-1-Phenyl-1-butene: ^{1}H nmr ($CDCl_3$):δ 1.07 (t, 3H), 2.18 (d, 2H), 5.95-6.5 (m, 2H), 7.16 (m, 5H);

1-Phenyl-2-butene, ^{1}H nmr ($CDCl_3$):δ 1.67 (d, 3H), 3.18 (d, 2H), 5.7 (m, 2H), 7.1 (m, 5H).

Hydrogenation Of 1,4-Diphenyl-1,3-butadiene

Reaction of 0.21 g of the substrate with $Co_2(CO)_8$ at 58°C under nitrogen for 3 hours afforded 0.14 g (67%)of the hydrogenated products (isolated by TLC with 5:1 hexane/dichloromethane as eluant).

3.3.3 Desulphurisation Of Activated Thiols Under Acidic Phase Transfer And Biphasic Conditions By Organometallic Complexes

Reactions under phase transfer and biphasic conditions were run in an identical manner except for the absence of the phase transfer agent (sodium 4-dodecylbenzenesulphonate) in the biphasic reactions. Typically, 25 ml of benzene and 25 ml of 48-50% aqueous tetrafluoroboric acid (as well as 1 mmol (0.348 g) of sodium 4-dodecylbenzenesulphonate in the phase transfer catalysed reactions) were placed in a 100 ml three necked round bottomed flask and degassed for 30 minutes with nitrogen bubbling at room temperature. Triiron dodecacarbonyl (1.01 g, 2 mmol) was then added and the dark green mixture stirred for 3 hours at room temperature under nitrogen. The colour changed to burgundy red. The thiol (2 mmol) was added and the reaction mixture was stirred for 10 hours at 60°C under nitrogen. Work-up was effected by cooling the reaction mixture to room temperature, separating the phases and washing the organic phase several times with aqueous sodium hydroxide, followed by at least four times with water. After drying with $MgSO_4$ and rotary evaporation, the residue was dissolved in hexane and purified by either fractional distillation or chromatography on silica gel or neutral alumina with 9:1 hexane/ethyl acetate as the eluant. Analysis of the product mixture was by comparison of g.c. retention times with those of authentic materials, where available, and confirmed by g.c./mass spec. Isolated products were identified by ^1H nmr, IR, and mass spec. Disappearance of the weak infrared stretch in the 2400 cm^{-1} region was also indicative of the desulphurisation process.

Desulphurisation Of 4-Chlorobenzyl Thiol

With this substrate (0.32 g), under phase transfer conditions, only 6% of 4-chlorotoluene was detected while 11% of the sulphide and 40% of the disulphide were formed. However, under biphasic conditions, the yield of 4-chlorotoluene increased to 0.11 g (44%, 0.9 mmol). The sulphide (19%) and the disulphide (6%) were also formed. Product isolation was by fractional distillation and identification was by ^{1}H nmr and g.c./mass spec.

^{1}H nmr ($CDCl_3$):δ 2.34 (s, 3H), 7.17 (m, 4H);

mass spec: m/z 128 $[M+2]^+$(33%), 126 $[M]^+$(100%).

Desulphurisation Of 2-Methylbenzyl Thiol

The phase transfer and biphasic reactions of 2-methylbenzyl thiol (0.28 g) resulted in the formation of 0.04 g (20%, 0.4 mmol) and 0.076 g (36%, 0.7 mmol) of *o*-xylene, respectively. Fractional distillation was employed for product isolation. No *o*-xylene was detected in the absence of the metal catalyst. An experiment was run under homogeneous conditions in which HBF_4 in ether was used. No desulphurised products were detected. Product identification was by boiling point and ^{1}H nmr.

Desulphurisation Of 4-Methylbenzyl Thiol

The disulphide (0.22 g, 90%, 0.9 mmol) was the only product from this thiol (0.28 g) under phase transfer conditions. Under biphasic conditions, 0.03 g (15%, 0.3 mmol) of *p*-xylene, 0.103 g (49%, 0.5 mmol) of the desulphurised dimer, $(4\text{-}CH_3C_6H_4CH_2)_2$, and 0.07 g (28%, 0.3 mmol) of the sulphide were isolated on a neutral alumina column in the usual manner. In the presence of a catalytic amount of $Fe_3(CO)_{12}$ (0.05 g, 0.1 mmol), 70% of the sulphide, 15% of the desulphurised dimer and a very

small amount of *p*-xylene were detected. Product identification was by ^{1}H nmr and g.c./mass spec.

$(4\text{-}CH_3C_6H_4CH_2)_2$: ^{1}H nmr ($CDCl_3$):$\delta$ 2.32 (s, 6H), 2.85 (s, 4H), 7.05 (s, 8H); mass spec: m/z 210 $[M]^+$, 195 $[M\text{-}CH_3]^+$.

Desulphurisation Of 4-Methoxybenzyl Thiol

When 4-methoxybenzyl thiol (0.31 g) was subjected to the desulphurisation reaction under phase transfer conditions, 0.02 g (10%, 0.2 mmol) of 4-methylanisole was formed. Some sulphide was also detected. Under biphasic conditions, 0.17 g (72%, 1.4 mmol) of the anisole was isolated by TLC in the usual way. ^{1}H nmr and g.c./mass spec were employed for product identification.

Desulphurisation Of 2,4-Dichlorobenzyl Thiol

This thiol (0.38 g) was effectively desulphurised under phase transfer and biphasic conditions giving 0.23 g (73%, 1.5 mmol) and 0.24 g (74%, 1.5 mmol) of 2,4-dichlorotoluene, respectively. Also isolated by column chromatography on neutral alumina were small amounts of the sulphide and disulphide in both cases. 2,4-Dichlorotoluene (0.09 g, 41%, 0.6 mmol) and 2,4-dichlorobenzyl sulphide (0.11 g, 32%, 0.3 mmol) were formed when 25% HBF_4 was used as the aqueous phase.

Desulphurisation of 4,4′-Dimethyldiphenylmethane Thiol

Attempts at effecting desulphurisation of this thiol (0.46 g) were restricted to those under biphasic conditions. Only one product, the expected desulphurised product, was formed in this reaction. The yield was 0.37 g (94%, 1.9 mmol). Under carbon monoxide, the yield dropped only slightly to 0.35 g (90%, 1.8 mmol).

Desulphurisation Of Diphenylmethane Thiol

Under biphasic conditions, diphenylmethane thiol (0.4 g) led to 0.28 g (84%, 1.7 mmol) of diphenylmethane and a little of the disulphide. Product isolation was by TLC and identification by ^{1}H nmr and g.c./mass spec in the usual manner.

Desulphurisation of Benzylthioiron Tricarbonyl Dimer

Treatment of the dimer (1.2 g, 2 mmol) with 48-50% HBF_4 and benzene (25 ml each) at 60°C, as described above for the biphasic reaction, afforded only trace quantities of toluene as determined by gas chromatographic analysis.

3.4 Synthesis Of Organometallic Sulphur Complexes Under Phase Transfer Conditions

Several attempts were made at synthesising metal-sulphur complexes under both acidic and alkaline phase transfer conditions. The source of sulphur in these reactions was elemental sulphur. Extensive use of infrared spectroscopy was made to monitor the course of the reactions and for characterisation of the complexes formed. A X-ray crystallographic study was undertaken in one case. Elemental analysis was carried out on new complexes.

3.4.1 Attempted Synthesis Of Mn-S Complexes

Attempts were made to synthesise novel Mn-S complexes by reacting either bromo-(pentacarbonyl)manganese ($Mn(CO)_5Br$) or dimanganese decacarbonyl ($Mn_2(CO)_{10}$) with elemental sulphur under both acidic and alkaline phase transfer conditions.

Synthesis Of A Mn-S Complex Under Alkaline Phase Transfer Conditions

In a 250 ml three necked round bottomed flask was added 50 ml of freshly prepared 5N sodium hydroxide solution, 50 ml of dichloromethane and 0.65 g (3 mmol) of TEBAC. The mixture was stirred and degassed under nitrogen for 30 minutes at room temperature. To this solution, was added 0.82 g (3 mmol) of bromo(pentacarbonyl)manganese ($Mn(CO)_5Br$) and the orange reaction mixture was stirred at 40°C for a few minutes under nitrogen. The colour changed very quickly to dark red indicating the generation of the $Mn_2(CO)_9Br^-$ anion. This was confirmed by infrared spectroscopy — IR of the organic phase matched that reported in the literature. IR (CH_2Cl_2):ν_{CO} 2080(w), 2010(s), 1980(vs), 1970(vs), 1945(m) and 1903(m) cm^{-1}. The anion was generated even more rapidly when 4-methyl-2-pentanone was employed as the organic phase at 70°C.

Elemental sulphur (0.32 g) dissolved in dichloromethane (5 ml) was added to the mixture which turned dark immediately. The mixture was stirred for 3 hours at 40°C under nitrogen. In the case of 4-methyl-2-pentanone, the reaction was over in 30 minutes. The reaction mixture was cooled to room temperature, the organic phase transferred to a Schlenk tube via a double headed needle and dried with $MgSO_4$. The red-orange solution was filtered into a second Schlenk tube under nitrogen and the IR spectrum of the organic phase was recorded. The product displayed three intense terminal stretching bands at 1993, 1930 and 1912 cm^{-1}. Thin layer chromatography of the organic phase, with 3:1 dichloromethane/hexane as the eluant, indicated the presence of only one product. The product, like the parent anion, does not dissolve in benzene. The solvent was removed under vacuum and a golden-orange sticky product was obtained. A yield of 46% was calculated

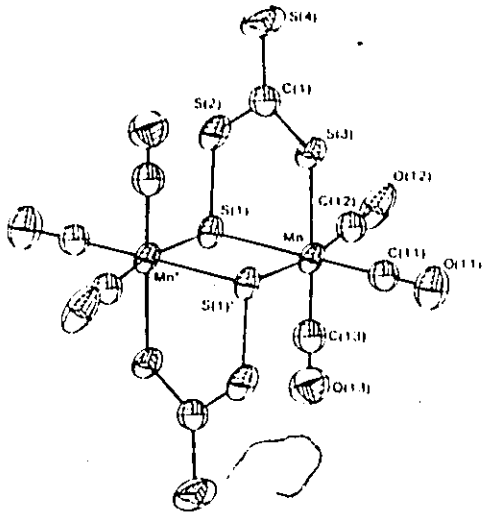
for the manganese-sulphur complex. The yield was the same when the reaction was run under carbon monoxide. The product was dissolved in a minimum volume of dichloromethane and to this a very small volume of hexane was added very carefully. After storing in the freezer for several days, fine needle-like orange coloured crystals were isolated. The IR of the crystals in KBr were identical to that obtained for the organic phase.

A X-ray structure analysis was carried out at Simon Fraser University. Crystals were triclinic of space group $P\bar{1}$ with a=9.128(9)Å, b=9.720(12)Å, c=13.308(6)Å, α=71.91(7)°, β=79.97(6)°, γ=69.86(9)°, and V=1050.8Å^3; $C_{34}H_{44}Mn_2N_2O_6S_8$; fw=943 13, ρ_{calcd}(em Z=2)=1.490 g cm^{-1}. X-ray diffraction intensity data were collected on a crystal fragment 0.39x0.28x0.02 mm on an Enraf-Nonius CAD4F diffractometer employing graphite-monochromotised Mo Kα radiation [$\lambda(\alpha_1)$=0.709 30Å]. An absorption correction (μ=10.01 cm^{-1}) was applied. Of a total of 1684 reflections with 2θ <38°, 1035 were observed [$I>2.3\sigma(I)$]. The structure was solved by MULTAN, and all non-hydrogen atoms were located by conventional methods. H coordinates were determined geometrically but were not refined. Anisotropic temperature factors were used for Mn, S_8 and O atoms and isotropic temperature factors for N and C. Full-matrix refinement (145 variables, observed reflections only) converged to R_F=0.044 and R_{wF}+0.044. The molecule possesses a crystallographic center of inversion. Selected inter-atomic distances are (Å): Mn−S(1)=2.365(4); Mn−S(3)=2.360(4); Mn−S(1)^1=2.381(4); S(1)−S(2)=2.070(4); C(1)− S(2)=1.743(10); C(1)−S(3)=1.720(10); C(1)−S(4)=1.638(11).

Selected angles(deg): S(1)−Mn−S(1)^1=82.20(14); S(1)−Mn−S(3)=87.53(13); Mn−S(1)−Mn^1=97.80(14).

Infrared spectroscopy was utilised to show that the complex is stable in air and in mineral acids at room temperature. When the complex was boiled in concentrated

Figure 3.1: SNOOPI Diagram of the $[(Mn(CO)_3(CS_3S))_2]^{2-}$ Anion



nitric acid, infrared spectroscopy showed that the complex slowly decomposed.

Elemental analysis of the product was carried out and this was in close agreement with the calculated values. Calculated for $C_{43}H_{44}Mn_2N_2O_6S_8$: C, 43.30; H, 4.70; S, 27.20. Found: C, 43.41; H, 4.61; S, 27.33.

An identical reaction in which dimanganese decacarbonyl(1.2 g, 3 mmol) was substituted for bromo(pentacarbonyl)manganese, led to no reaction as indicated by infrared spectroscopy.

Attempted Synthesis Of Mn-S Complexes Under Acidic Phase Transfer Conditions

A mixture of dichloromethane (25 ml), 48-50% HBF_4 (25 ml) and sodium 4-dodecylbenzenesulphonate (0.35 g, 1 mmol), was degassed for 30 minutes at room temperature. The temperature was raised to 40°C, and bromo(pentacarbonyl)manganese (0.82 g, 3 mmol) was added, followed ten minutes later by elemental sulphur (0.32 g). The reaction mixture was stirred for 10 hours at 40°C under nitrogen.

Work-up was effected by separating the phases, washing the organic phase with dilute sodium hydroxide solution and water before drying with $MgSO_4$. All manipulations were carried out under nitrogen. Infrared spectroscopy indicated no reaction. The same was true when the reaction was repeated in the absence of sodium 4-dodecylbenzenesulphonate.

3.4.2 Attempted Synthesis Of Co-S Complexes

Attempts at reacting cobalt tetracarbonyl anion ($Co(CO)_4^-$), generated from $Co_2(CO)_8$, with elemental sulphur to give novel Co-S complexes were made under both acidic and basic phase transfer conditions.

Attempted Synthesis of Co-S Complexes Under Alkaline Phase Transfer Conditions

The cobalt tetracarbonyl anion, $Co(CO)_4^-$, was generated by the addition of $Co_2(CO)_8$ (0.34 g, 1 mmol) to a degassed mixture of benzene (25 ml), 5N sodium hydroxide solution (25 ml) in the presence of TBAHS (0.34 g, 1 mmol) under nitrogen at room temperature and stirred for 3 hours. The presence of the anion was confirmed by IR. Elemental sulphur (0.32 g) was added and the mixture stirred at 60°C under nitrogen. After 10 hours, the infrared spectrum of the organic phase showed only the presence of $Co(CO)_4^-$, thus no reaction occured between $Co(CO)_4^-$ and elemental sulphur. When the reaction was repeated with 3N and 25N sodium hydroxide solutions, there was still no Co-S complex formation as indicated by infrared spectroscopy. There was also no reaction under carbon monoxide.

Attempted Synthesis Of Co-S Complexes Under Acidic Phase Transfer Conditions

A mixture of 48-50% HBF_4(25 ml), benzene (25 ml) and sodium 4-dodecylbenzene-sulphonate (0.35 g, 1 mmol) was degassed by nitrogen at room temperature for 30 minutes. Dicobalt octacarbonyl (0.34 g, 1 mmol) was added and the reaction mixture was stirred for 3 hours. The colour of the reaction mixture changed from the initial dark brown to a straw yellow which is indicative of the formation of $Co(CO)_4^-$ (confirmed by IR). Elemental sulphur (0.32 g) was then added and the reaction mixture was stirred at 60°C under nitrogen. An infrared spectrum of the organic phase after 10 hours only indicated the presence of $Co(CO)_4^-$. The reaction was repeated under carbon monoxide without any success.

3.4.3 Attempted Synthesis Of Fe-S Complexes

Complexation reactions between $Fe_3(CO)_{12}$ and elemental sulphur were attempted under both acidic and alkaline phase transfer conditions.

Synthesis Of A Fe-S complex Under Alkaline Phase Transfer Conditions

Freshly prepared 5N sodium hydroxide solution (25 ml), benzene (25 ml) and TBAHS (0.34 g, 1 mmol) were stirred at room temperature for 30 minutes. Triiron dodecacarbonyl (1.01 g, 2 mmol) was added and the dark green mixture was stirred for 3 hours at room temperature, and then a slurry of elemental sulphur (0.64 g) in 10 ml of hot toluene was added to the mixture. (Prior to the addition, the temperature was raised to 60°C.) The mixture was stirred for 10 hours. The dark purple organic phase was separated from the aqueous phase (yellow) and transferred into a Schlenk tube under nitrogen. This foul smelling solution was dried ($MgSO_4$) and filtered under nitrogen into a second Schlenk tube. The infrared spectrum of the

product in the organic phase displayed three strong carbonyl bands at 2035, 2002 and 1950 cm^{-1}. The sample was divided into two equal portions (by volume). The solvent was removed from one of the two samples to give a black residue whose IR was identical to the compound in the organic phase. To the other portion was added 0.6 g (1 mmol) of bis(triphenyphosphoranylidene)ammonium chloride, PPN^+Cl^-, in 5 ml of chloroform and the mixture stirred for 4 hours at room temperature. A dark precipitate was observed and so the solvent was filtered off into a Schlenk tube under nitrogen. Upon standing, fine needle-like dark crystals separated out of the filtrate which became lighter in colour. These crystals were dark purple in colour. An infrared spectrum (KBr) displayed carbonyl bands identical to the compound in the organic phase and the solid precipitates obtained above.

Elemental analysis of the solid residue indicated the presence of some sulphur. Analysis: C, 43.41; H, 3.61; s, 11.33; Fe: 28.83, ash 20.61.

Under carbon monoxide, the same results were obtained. Attempts to obtain X-ray grade crystals were unsuccessful.

Synthesis Of Fe-S Complexes Under Acidic Phase Transfer Conditions

Triiron dodecacarbonyl (1.01 g, 2 mmol) was added to a degassed mixture of benzene (25 ml), 48-50% HBF_4 (25 ml), and sodium 4-dodecylbenzenesulphonate (0.35 g, 1 mmol) under nitrogen at room temperature for 30 minutes. After 3 hours of stirring, elemental sulphur (0,64 g) was added and the reaction mixture was stirred for further 10 hours at 60°C under nitrogen. The dark organic phase was separated from the aqueous phase with a double headed needle into a Schlenk tube, dried with $MgSO_4$ and filtered into another Schlenk tube. The IR spectrum indicated the presence of $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$. The mixture was chromatographed on a neutral alumina column using benzene as the eluant. The first band gave an

orange-red solid after removal of solvent. This solid was characterised by infrared spectroscopy to be $Fe_2(CO)_6S_2$, m. p. 47,5-48°C (lit. 46°C). IR(CCl_4):ν_{CO} 2080(m), 2040(s), and 2005(s) cm^{-1} (lit. 2082, 2042, and 2005 cm^{-1}). The second purple-red band was $Fe_3(CO)_9S_2$, m.p. 114-115°C (lit. 114°C). Infrared spectrum was identical to that reported in the literature [259]. IR(CCl_4):ν_{CO} 2080(w), 2060(vs), 2050(vs), 2034(s), and 2010(m) cm^{-1} (lit. 2086(m), 2067(vs), 2051(vs), 2032(s) and 2014(s) cm^{-1}).

3.5 Desulphurisation of Crude Oil and Bitumen Under Phase Transfer Conditions

Attempts at desulphurising crude oils and bitumen were made under both acidic and alkaline phase transfer conditions. A number of metal complexes were employed in these reactions. The crude oil used contained 0.89% sulphur while the sulphur content of the bitumen was 4.99%. A 25 ml crude oil sample was calculated to contain 5.8 mmol of sulphur but the same could not be carried out for bitumen due to its very high viscosity. After work-up, crude oil and bitumen samples were sent for sulphur analysis and the degree of desulphurisation was calculated from the amount of sulphur left in the sample (expressed as both % and mmol for crude oil and just % for bitumen). Sulphur analysis was performed by M-H-W Laboratories of Phoenix, Arizona.

3.5.1 Desulphurisation of Crude Oil

Most of the attempts at reducing the sulphur content of crude oil were carried out under alkaline phase transfer conditions, while a few were under acidic phase transfer and biphasic conditions. Reaction conditions were based on earlier model studies.

Under Alkaline Phase Transfer Conditions

Three metal complexes and five phase transfer catalysts were used in these reactions. The following general procedure was utilised.

To a 100 ml round bottomed flask, 25 ml of freshly prepared 5N aqueous sodium hydroxide solution and the phase transfer catalyst (1 mmol) were added. With triiron dodecacarbonyl or molybdenum hexacarbonyl as the metal complex, 25 ml of the crude oil was then added to the base/phase transfer agent mixture followed by the metal catalyst at room temperature under hydrogen or nitrogen. In the case of bromo(pentacarbonyl)manganese, the metal complex was dissolved in a solvent (10 ml of 2-butanone or 4-methyl-2-pentanone) and added to the mixture in order to generate the perceived active species, $Mn_2(CO)_9Br^-$, by stirring the mixture at 70°C for 30 minutes under nitrogen or hydrogen prior to the addition of the crude oil. The reaction mixture was stirred for 10 hours at 60-70°C. Work-up was effected by cooling the mixture to room temperature and separating the phases by either centrifuging the sample or by adding 25 ml of benzene and allowing the sample to stand for several hours in a separatory funnel. Reasonably good separation of the phases was achieved in almost all cases. The separated "organic" phase was washed several times with water and dilute hydrochloric acid, dried with $MgSO_4$, and filtered through a short Celite/$MgSO_4$/silica gel column with benzene. The solvent was removed prior to passing the sample through the short column in the case of bromo(pentacarbonyl)manganese mediated reactions. After filtration, the eluant benzene was removed by rotary evaporation and the sample sent for sulphur analysis. The solvents removed were checked by gas chromatography.

Molybdenum Hexacarbonyl

All the reactions in this category were run according to the above general procedure with varying amounts of the metal complex and various phase transfer agents. In the presence of 0.3 g of TEBAC, under hydrogen at 60°C, 0.03 g (0.1 mmol) of $Mo(CO)_6$ led to 38% (2.2 mmol) desulphurisation. Separation of the phases was achieved by centrifugation. Reactions using 0.106 g (0.4 mmol) and 0.011 g (0.04 mmol) of the complex were carried out in an identical manner to give 53.9% (3.1 mmol) and 15.7% (0.9 mmol) of desulphurisation respectively. The aqueous phase in the latter case was 10 N sodium hydroxide. With TBAHS (0.34 g) and DTAB (0.31 g) as the phase transfer agents, 0.12 g (0.4 mmol) of $Mo(CO)_6$ led to 43.8% (2.5 mmol) and 29.2% (1.7 mmol) desulphurisation under usual conditions. Benzene was added for ease of separation of phases in the last two examples.

Triiron Dodecacarbonyl

Triiron dodecacarbonyl (0.2 g, 0.4 mmol), under conditions described above, led to the desulphurisation of crude oil to varying degrees. In the presence of TEBAC, 47.2% (3.1 mmol) of sulphur was removed, 43.8% (2.5 mmol) in the presence of TBAHS and 40.5% (2.3 mmol) in the presence of DTAB under hydrogen at 60°C. Separation of phases was aided by the addition of benzene.

Manganese Pentacarbonyl Bromide

In these reactions, the perceived active species, the $Mn_2(CO)_9Br^-$ anion, was generated in the reaction mixture prior to the addition of the crude oil. The organic solvent used was either 2-butanone or 4-methyl-2-pentanone, with 5N sodium hydroxide as the aqueous phase and the reactions were run at 70°C under hydrogen. In all the experiments, the phases were separated by centrifugation.

Sulphur analysis showed that 0.165 g (0.6 mmol) of the complex, in the presence of TEBAC, led to 53.9% (3.1 mmol) desulphurisation. The solvent used was 2-butanone. With 4-methyl-2-pentanone as the organic phase, 44.9% (2.6 mmol) desulphurisation was achieved by using 0.017 g (0.06 mmol) of the complex. Under nitrogen, use of 0.03 g (0.1 mmol) of bromo(pentacarbonyl)manganese led to 43.8% (2.5 mmol) desulphurisation. When 0.4 g of THAB was used as the phase transfer catalyst, under hydrogen, 52.8% (3.1 mmol) desulphurisation was achieved by 0.19 g (0.7 mmol) of $Mn(CO)_5Br$. Use of Aliquat 336 led to 27% (1.6 mmol) removal of sulphur, while no desulphurisation occured in the absence of the phase transfer agent. In both of these cases, 0.017 g (0.06 mmol) of the complex was used and the reactions were run under hydrogen at 70°C with 4-methyl-2-pentanone as the organic phase. There was no desulphurisation in the absence of the metal complex.

Under Acidic Phase Transfer And Biphasic Conditions

Only triiron dodecacarbonyl and molybdenum hexacarbonyl were used as the metal complexes. The phase transfer catalyst used was sodium 4-dodecylbenzenesulphonate (0.35 g, 1 mmol). In a typical experiment, 25 ml of 48-50% HBF_4 (aqueous) and the phase transfer catalyst (when needed) were placed in a 100 ml flask. To this, 25 ml of crude oil and the metal complex were added under hydrogen. The mixture was stirred for 10 hours at 60°C. The reaction mixture was cooled to room temperature, the phases separated by the addition of benzene and letting the sample stand in a separatory funnel for several hours. The organic phase was washed with dilute sodium hydroxide solution and water before being passed through a short column of Celite/$MgSO_4$/silica gel. After concentration, the sample was sent for sulphur analysis. The solvent removed was checked by gas chromatography.

Triiron Dodecacarbonyl

With 0.03 g (0.06 mmol) of $Fe_3(CO)_{12}$, in the presence of sodium 4-dodecylbenzenesulphonate, 13.5% (0.8 mmol) of sulphur was removed under both hydrogen and nitrogen. Both reactions, and work-up, were according to procedure outlined above.

In a biphasic reaction, i.e. in the absence of the phase transfer agent, 31.5% (1.8 mmol) of desulphurisation was achieved. The reaction was run under hydrogen at 60°C for 10 hours.

Molybdenum Hexacarbonyl

When 0.106 g (0.4 mmol) of $Mo(CO)_6$ was used, in the presence of sodium 4-dodecylbenzenesulphonate, a reduction of 47.2% (2.7 mmol) in the sulphur content of the crude oil was obtained. The reaction was carried out according to the procedure outlined above.

3.5.2 Desulphurisation Of Bitumen

Attempts at desulphurising Athabaska bitumen were made in both acidic and alkaline media. Reactions utilising $Mn(CO)_5Br$, $Mo(CO)_6$, and $Fe_3(CO)_{12}$ as the metal complexes were run in a manner similar to the above.

Under Alkaline Phase Transfer Conditions

The general procedure for the alkaline phase transfer catalysed reactions was similar to that described earlier. The phase transfer agent in all the reactions was TEBAC (0.3 g, 1 mmol). The solvents removed by rotary evaporation were checked by gas chromatography.

A mixture of 5N sodium hydroxide (25 ml), dichloromethane(25 ml) and TEBAC was degassed with nitrogen for 30 minutes at room temperature. To this, the metal

complex and 10 ml of bitumen dissolved in 40 ml of dichloromethane were added. The mixture was stirred for 10 hours at 40°C under hydrogen. Work-up was effected by cooling the mixture to room temperature, separating the phases and removing the solvent by rotary evaporation. The bitumen sample was dissolved in benzene, passed through a short Celite/$MgSO_4$/silica gel column and then removing the eluant benzene before being sent for sulphur analysis.

Manganese Pentacarbonyl Bromide

As with the earlier experiments, when bromo(pentacarbonyl)manganese was used as the metal complex, the perceived active species was generated before the addition of bitumen dissolved in the solvent. When 0.14 g (0.5 mmol) of $Mn(CO)_5Br$ was used, under hydrogen, 32% of sulphur was removed. Under nitrogen, 28.7% desulphurisation was achieved utilising the same parameters. Use of 0.275 g (1 mmol) of $Mn(CO)_5Br$ led to 30.7% reduction in sulphur. The degree of desulphurisation was the same when 4-methyl-2-pentanone was used as the organic phase (30.1%), even though the reaction was run at 70°C.

In a separate experiment,the same bitumen sample was run through twice. This meant that the sample, after work-up, was added to a second flask containing the 5N sodium hydroxide, dichloromethane, and TEBAC mixture and run as before. A second work-up led to a sample which showed a slight improvement in the degree of desulphurisation (32.2%).

Triiron Dodecacarbonyl

Using 0.2 g (0.4 mmol) of $Fe_3(CO)_{12}$ under alkaline phase transfer conditions, led to 10% desulphurisation. The reaction was run as described above under nitrogen but without pregeneration of the suspected active species in dichloromethane. Work-up

was carried out in the usual manner.

Molybdenum Hexacarbonyl

With 0.106 g (0.4 mmol) of $Mo(CO)_6$ as the complex, 32% desulphurisation was achieved in the usual manner. Work-up was carried out as described above.

Under Acidic Phase Transfer And Biphasic Conditions

Only one metal complex, molybdenum hexacarbonyl, was used in reactions carried out in acidic media. To a mixture of 25 ml 48-50% HBF_4 , 10 ml of bitumen dissolved in 40 ml of dichloromethane, and 0.35 g (1 mmol) of sodium 4-dodecylbenzenesulphonate in a 250 ml flask, was added 0.106 g (0.4 mmol) of $Mo(CO)_6$. The mixture was stirred for 10 hours at 40°C under hydrogen. Work-up was effected by cooling the mixture to room temperature and allowing it to stand for several hours in a separatory funnel. The phases were separated and the organic phase washed with dilute sodium hydroxide solution and water before the solvent was removed by rotary evaporation. The sample was dissolved in benzene and passed through a short Celite/$MgSO_4$/silica gel column. The eluant benzene was removed and the sample sent for analysis. Reaction under biphasic conditions, i.e. in the absence of sodium 4-dodecylbenzenesulphonate, led to only a slightly improved degree of desulphurisation (38%). The solvents removed by rotary evaporation were checked by gas chromatography in all cases.

3.6 Carbonylation Of Alcohols To Esters Via Thiols

3.6.1 General Procedure

A small magnetic stirring bar was placed in a 45 ml stainless steel or INCONEL screw cap autoclave. The benzylic alcohol (10 mmol in most cases) and solvent mixture (usually 2 ml of water and 10 ml of ethanol) were placed in the autoclave. To this mixture was added the metal catalyst (1 mmol of $Co_2(CO)_8$) and the autoclave was quickly closed, purged twice with carbon monoxide before being loaded with hydrogen sulphide (13 atm) and carbon monoxide (47 atm). The autoclave was checked for leaks and the mixture was stirred for 10 hours at 150°C (oil bath temperature). After cooling to room temperature, the autoclave gases were carefully vented in the fume hood and the autoclave opened. The pale brown homogeneous mixture was poured into a beaker and allowed to stand for a few minutes in air. The colour of the mixture changed to black with the formation of some black precipitate. Invariably, the mixture had a thiol smell. The autoclave was washed with hexane (10 ml x 3), diethyl ether (10 ml x 3) and ethanol (10 ml x 3), and the washings were added to the reaction mixture. Small amounts of Celite and $MgSO_4$ were added and filtration with ether (70 ml) and hexane (30 ml) gave a clear, colourless solution which upon concentration by rotary evaporation led to the product mixture. Analysis of the product mixture was carried out by gas chromatography aided by "spiking" with authentic materials and by g.c.-mass spec. Products were isolated, where possible, by fractional distillation or column chromatography and identified by infrared, proton NMR, and mass spectrometry.

Benzyl Alcohol

In all of these experiments, 5.4 g (50 mmol) of benzyl alcohol and 0.34 g (1 mmol) of dicobalt octacarbonyl were used. Utilising 5 ml of ethanol as the solvent, 1% of ethyl phenylacetate, 4% of benzyl thiol, 6% toluene and 4% benzyl sulphide were detected while 79% of benzyl alcohol was recovered. In 2 ml water/10 ml ethanol solvent mixture, reaction led to 8% of ester, 22% of thiol, 18% of toluene, 6% of sulphide and 29% of recovered alcohol. When 2 ml water/5 ml ethanol was used, 88% of the alcohol was recovered while 2% ester, 5% thiol and 1% toluene were detected. Similar results were obtained when 5 ml of dioxane, or acetonitrile, was added to the solvent mixture. Addition of 0.5 ml glacial acetic acid to the mixture led to 18% methyl phenylacetate and 80% recovered alcohol. With 5 ml water/10 ml dioxane, 1% ester and 5% thiol were formed while 92% alcohol was recovered.

4-Methylbenzyl Alcohol

The substrate to metal ratio was 10:1 in all cases; 1.22 g (10 mmol)of 4-methylbenzyl alcohol and 0.34 g (1 mmol) of $Co_2(CO)_8$ were used. In 1 ml water/10 ml ethanol, only 1% ethyl-4-tolylacetate, 11% 4-methylbenzyl thiol, 16% *p*-xylene and 3% 4-methylbenzyl sulphide were detected while 60% of the substrate alcohol was recovered. When the solvent mixture was changed to 2 ml water/10 ml ethanol, only 2% of methylbenzyl alcohol was recovered and the yield of ester increased to 11% , of thiol to 29% , of *p*-xylene to 28% and of the sulphide to 17% . Also detected was 9% 4-methylbenzylethyl ether, $4\text{-}CH_3C_6H_4CH_2OC_2H_5$. Addition of a small amount of 4-(dimethylamino)pryidine (DMAP) led to very little reaction — 84% of the alcohol was recovered and only 6% of the ester along with 1% of *p*-xylene were detected. Much more of the alcohol was converted when a few drops of 48-50% HBF_4 (aq.)

was added. The major product was the ether (33%), followed by 18% of thiol, 13% of *p*-xylene, 7% of sulphide, 3% of ester and 25 % recovered alcohol. The only product formed in the absence of hydrogen sulphide was *p*-xylene (20%) with 76% of the alcohol being recovered. Use of a solvent mixture containing 2 ml water and 5 ml methanol led to 8% of methyl-4-tolylacetate, 15% thiol and 41% *p*-xylene.

3,4-Dimethoxybenzyl Alcohol

Reactions were carried out according to the general procedure outlined above. The major product in the reaction of 1.68 g (10 mmol) of 3,4-dimethoxybenzyl alcohol was ethyl-3,4-dimethoxyphenylacetate (58%) while the minor product was 3,4-dimethoxytoluene (40%). Substitution of ethanol with methanol led to only 32% methyl-3,4-dimethoxyphenylacetate and 13% of the hydrocarbon. The yield of ester was even lower (15%) when *n*-butanol was used in the solvent mixture. However, 60% of 3,4-dimethoxytoluene and 20% 3,4-dimethoxybenzyl sulphide were detected. When the reaction was run at room temperature with hydrogen sulphide and carbon monoxide bubbling through the mixture, 90% of the alcohol was recovered and 6% of the sulphide was detected.

2,4-Dimethoxybenzyl Alcohol

Reaction of 1.68 g (10 mmol) of 2,4-dimethoxybenzyl alcohol, according to the procedure outlined above, led to 60% of ethyl-2,4-dimethoxyphenylacetate, 26% of 2,4-dimethoxytoluene and 6% of the sulphide. Reduction the substrate/metal ratio from 10:1 to 50:1, i.e. 4.2 g (25 mmol) of the alcohol and 0.17 g (0.5 mmol) of $Co_2(CO)_8$, afforded 37% of ester, 12% of thiol, 20% of hydrocarbon and 7% of the sulphide. Only 2% of the sulphide was detected in the absence of the metal catalyst.

Other Alcohols

These reactions were run according to the general procedure outlined above, i.e. 10 mmol of substrate alcohol was subjected to reaction in the presence of 0.34 g (1 mmol) of $Co_2(CO)_8$ under hydrogen sulphide (13 atm) and carbon monoxide (47 atm) at 150°C for 10 hours.

4-Methoxybenzyl alcohol (1.38 g, 10 mmol), gave 23% ethyl-4-methoxyphenyl-acetate, 7% 4-methoxybenzyl thiol, and 67% 4-methylanisole. When the reaction was repeated at 120°C, the yield of thiol increased to 32% while that of the ester and anisole was reduced.

4-Ethoxybenzyl alcohol(1.5 g, 10 mmol), was converted to 22% of ethyl-4-ethoxyphenylacetate, 62% of 4-ethoxytoluene and 11% of 4-ethoxybenzyl sulphide.

4-Ethylbenzyl alcohol (1.36 g, 10 mmol), led to 4-ethylbenzyl thiol in 65% yield while ethyl-4-ethylphenylacetate was formed in 18% and 4-ethyltoluene in 10% yields.

2-Methylbenzyl alcohol (1.2 g, 10 mmol), was converted to 16% of 2-methylbenzyl thiol and *o*-xylene, while the ester was formed in 6% yield with 61% of the substrate alcohol being recovered. With 3-methylbenzyl alcohol, 84% of the substrate alcohol was recovered and 3%, 5%, and 7% of the ester, thiol and hydrocarbon were detected.

There was no reaction when 1.4 g (10 mmol) of 4-chlorobenzyl alcohol, 1.1 g (10 mmol) of *m*-cresol and 1.6 g (10 mmol) of 2-naphthalenemethanol were subjected to the above mentioned reaction conditions.

Variation In Catalyst Used

All the reactions in this category were carried out in a mixture of 2 ml water/10 ml ethanol, at 150°C over 10 hours under 13 atm of hydrogen sulphide and 47 atm

of carbon monoxide pressure with 10 mmol of substrate alcohol (4-methylbenzyl alcohol (1.22 g) in all cases except for CpCo(COD) where 3,4-dimethoxybenzyl alcohol was used) and 1 mmol of catalyst. Use of cobalt acetate led to the generation of 15% 4-methylbenzyl thiol, 54% *p*-xylene and 9% 4-methylbenzylethylether while $Co_2(CO)_8/[Rh(CO)_2Cl]_2$ gave only 23% *p*-xylene and 9% of the ether. The following complexes, or mixtures, were not effective in converting the substrate alcohol to products: $Co(acac)_2$ (acac= acetylacetonate), $Co_2(CO)_6$(dpm) (dpm= di(phenylphosphino)methane), $Co_2(CO)_6$(dpa) (dpa= diphenylacetylene), CpCo(COD) (Cp= C_5H_5, COD= 1,5-cyclooctadiene), $Co_2(CO)_8/Pd(CH_3CN)_4(BF_4)_2$ and $HRh(CO)_2(PPh_3)_2$.

The commercially available complexes were used as received. The other complexes were synthesised according to literature procedure without any modifications - CpCo(COD) (ref. [274]), $Co_2(CO)_6$(dpa) (ref. [275]), and $Co_2(CO)_6$(dpm) (ref. [242]).

3.7 Conversion Of Alcohols To Thiols And Hydrocarbons

3.7.1 General Procedure

A small magnetic stirring bar was placed in a 45 ml stainless steel or INCONEL screw cap autoclave. The substrate (10 mmol in most cases) and solvent mixture were placed in the autoclave. To this mixture was added the metal catalyst (0.5 mmol of $Co_2(CO)_8$) and the autoclave was quickly closed, purged twice with carbon monoxide before being loaded with hydrogen sulphide (13 atm) and carbon monoxide (47 atm). The autoclave was checked for leaks and the mixture was stirred for 10 hours at 150°C (oil bath temperature). After cooling to room temperature, the autoclave gases were carefully vented in the fume hood and the autoclave opened.

The pale brown homogeneous mixture was poured into a beaker and allowed to stand for a few minutes in air. The colour of the mixture changed to black with the formation of some black precipitate. The autoclave was washed with hexane (10 ml x 3), diethyl ether (10 ml x 3) and ethanol (10 ml x 3), and the washings were added to the reaction mixture. Small amounts of Celite and $MgSO_4$ were added, and filtration with ether (70 ml) and hexane (30 ml) gave a clear, colourless solution which upon concentration led to the product mixture. Analysis of the product mixture was carried out by gas chromatography aided by "spiking" with authentic materials and by g.c.-mass spec. Products were isolated, where possible, by fractional distillation or column chromatography and identified by infrared spectroscopy, ^1H nmr and mass spectrometry.

The solvent system can be designated as:

1. Method A: 10 ml of hexane;
2. Method B: 5 ml of hexane and 10 ml of diethyl ether;
3. Method C: 5 ml of hexane and 10 ml of water.

All the substrate alcohols were subjected to reaction in all three solvent systems except for 2-naphthalenemethanol for which Method A was not used due to problems with solubility. The following alcohols were used in these reactions: 4-chlorobenzyl alcohol, 2-naphthalenemethanol, benzyl alcohol, 2-, 3-, and 4-methylbenzyl alcohols, 4-ethylbenzyl alcohol, and 4-methoxybenzyl alcohol. The results obtained are listed in Table 2.16.

Effect Of Solvent

These reactions were carried out in the manner described above. The results obtained are listed in Table 2.17.

2-Naphthalenemethanol

There was hardly any reaction when 1.6 g (10 mmol) of 2-naphthalenemethanol was subjected to reaction in 10 ml water/10 ml hexane — 78% of the alcohol was recovered while 8% of 2-naphthalenethiol and 12% of 2-methylnaphthalene were detected. In 10 ml water/5 ml hexane/5 ml diethyl ether, 16% of the thiol and 17% of the hydrocarbon were detected accompanied by the recovery of 65% of the substrate alcohol.

4-Methylbenzyl Alcohol

When dioxane (20 ml) was used as the solvent, 1.22 g (10 mmol) of 4-methylbenzyl alcohol led to 24% of 4-methylbenzyl thiol, 18% of *p*-xylene, 4% of the sulphide and 14% of the disulphide with 42% of the alcohol being recovered. Using 5 ml water/5 ml hexane, 48% of the thiol, 25% of *p*-xylene, and 21% of the disulphide were detected. Only 3% of the alcohol was recovered. When the reaction was repeated in the presence of 0.33g (1 mmol) of tetrabutylammonium hydrogen sulphate (TBAHS) as the phase transfer catalyst, conversion of the alcohol was lower — 29% of alcohol was recovered while 34% of the thiol, 11% of *p*-xylene, 22% of the sulphide and 5% of the disulphide were detected. Similar results were obtained with 0.28 g (1 mmol) of benzyltriethylammonium chloride (TEBAC) as the phase transfer agent.

Benzyl Alcohol

With 5.4 g (50 mmol) of benzyl alcohol run "neat", i.e. in the absence of a solvent, 3% of the alcohol was recovered; 0.34 g (1 mmol) of $Co_2(CO)_8$ was used as the catalyst. Fine white needles of benzyl sulphide were isolated in 77% yield. Also

detected were 2% of toluene and 5% of benzyl disulphide. Reaction in 12 ml hexane/3 ml diethyl ether led to 32% of the thiol, 13% of toluene, 11% of the sulphide and 8% of the disulphide; 35% of the alcohol was recovered.

Effect Of Gas

The general procedure described above was used for these reactions. However, a gas other than carbon monoxide was used. Method C was used for all cases except one where Method A was used. Results obtained in this category are listed in Table 2.18.

Under Nitrogen

Nitrogen (47 atm) was used in place of carbon monoxide while the other reaction parameters were as stated earlier.

4-Ethylbenzyl alcohol (1.36 g, 10 mmol), led to the generation of 31% of the thiol and 12% of the hydrocarbon while 52% of the alcohol was recovered. With 4-methylbenzyl alcohol (1.22 g), 50% of the thiol, 17% of *p*-xylene and 4% of the disulphide were detected; 28% of the alcohol was recovered. The amounts of thiol generated were much lower for 3-methylbenzyl alcohol (27%) and 2-methylbenzyl alcohol (36%). The former also gave 4% of the hydrocarbon while the latter gave a 16% yield. The recovered alcohols were 65% and 47% respectively.

Other Gases

Benzyl alcohol (5.4 g, 10 mmol) was reacted in 10 ml hexane (Method A) under 47 atm of synthesis gas and 13 atm of hydrogen sulphide in the presence of 0.34 g (10 mmol) of $Co_2(CO)_8$, according to the general procedure above. Benzyl thiol (47%), toluene (24%) and benzyl sulphide (17%) were generated while 10% of the

alcohol was recovered. When 4-methylbenzyl alcohol (1.22 g), in the presence of 0.17 g of $Co_2(CO)_8$, was reacted (Method C) under carbon monoxide (60 atm), in the absence of hydrogen sulphide, led to 12% of *p*-xylene and the recovery of 78% of the alcohol.

Effect Of Catalyst

These reactions were carried out according to the general procedure described above except for the catalyst used (1 mmol). One reaction was run in 10 ml hexane (Method A) while the others utilised Method B. There was no reaction in the absence of the metal catalyst. Table 2.19 lists the results obtained.

Cobalt Complexes

Reaction of 5.4 g (10 mmol) of benzyl alcohol (Method A) in the presence of 0.52 g tetracobalt dodecacarbonyl ($Co_4(CO)_{12}$) led to 41% of benzyl thiol, and 16% each of toluene and benzyl sulphide. Recovery of 28% of the alcohol was achieved.

4-Methylbenzyl alcohol (1.22 g, 10 mmol), Method C, gave 40% of 4-methylbenzyl thiol, 16% of *p*-xylene and 10% of the disulphide while 37% of the alcohol was recovered when cobalt acetate (0.25 g) was used as the catalyst. Similar results were obtained with 0.356 g cobalt $(acac)_2$. Use of $Co_2(CO)_6$(dmb) led to lower conversion of the alcohol but the ratio among the products formed was similar to the preceding catalysts.

Rhodium Complexes

There was no reaction when 1.22 g of 4-methylbenzyl alcohol (Method C), was reacted in the presence of hexarhodium hexadecacarbonyl, $Rh_6(CO)_{16}$. The alcohol was recovered almost quantitatively. The same was true for $[Rh(CO)_2Cl]_2$.

Other Variations

All of these reactions utilised benzyl alcohol (5.4 g, 50 mmol) as the substrate, $Co_2(CO)_8$ (0.34 g, 1 mmol) as the metal catalyst, and Method A (with one exception where Method C was used) as the solvent system. Reactions were run according to the general procedure above. See Table 2.20 for results.

- Mild conditions: When the reaction was run under 5 atm of hydrogen sulphide at 100°C for 5 hours, 78% of the alcohol was recovered while 8% of benzyl thiol, 9% of toluene and 6% of benzyl sulphide were formed.
- Use of NaSH as a source of sulphur: This led to 36% of the thiol, 11% of toluene, 7% of the sulphide, 10% of the disulphide while 33% of the alcohol was recovered.
- Reusing the metal complex: A reaction was run and worked-up as usual. The black precipitate was scraped off of the filter paper and reused. The "first-run" led to 42% of the thiol, 11% of toluene, 6% sulphide and 30% recovered alcohol. The "second-run" gave almost identical results.
- Benzyl thiol as promoter: A few drops of benzyl thiol was added to the reaction mixture and the reaction was run in the usual manner. Work-up led to 40% of the thiol, 12% of toluene and 4% of sulphide while 29% of the alcohol was recovered.
- Desulphurisation of benzyl thiol: Substituting benzyl thiol (1.24 g, 10 mmol) for benzyl alcohol and using 0.17 g (0.5 mmol) of $Co_2(CO)_8$ in solvent system C, resulted in 44% of toluene and 55% of the thiol being recovered.

Chapter 4

Conclusions And Recommendations

4.1 Conclusions

The research described in this thesis has resulted in the discovery of some very interesting reactions, a number of which may have potential industrial applications. Some were important as model studies which helped to establish reaction parameters for other systems.

The desulphurisation of activated thiols by triiron dodecacarbonyl and dicobalt octacarbonyl is the first example of desulphurisation by transition metal complexes under alkaline phase transfer conditions. It appears that any thiol capable of generating a reasonably stable carbanion can be desulphurised via this process. With respect to the yield of the desulphurised products, $Co_2(CO)_8$ is slightly better than $Fe_3(CO)_{12}$ as the desulphurising agent. Generation of the active species, $Co(CO)_4^-$ and $HFe_3(CO)_{11}^-$, can be achieved very easily under the reaction conditions. The type of phase transfer agent used apparently has no effect on the course of the reaction. In keeping with other phase transfer systems, work-up and product isolations are simple. This is an authentic phase transfer catalysed transition metal mediated process.

A new simple phase-transfer catalysed desulphurisation of various thiocarbonyls to carbonyl compounds was developed. This does not require the presence of a metal complex, and the yields are good to excellent. This system is superior to other processes reported in the literature for this category of reactions which include the use of clay-supported ferric nitrate and the toxic, and expensive, organotellurium compounds.

The hydrogenation of activated ethenes and dienes by various cobalt complexes under acidic phase transfer conditions (sodium 4-dodecylbenzenesulphonate is the phase transfer agent) is one of the first examples of organic transformations by metal complexes in acidic media. Yields of hydrogenised products obtained are good to excellent.

Activated thiols can be desulphurised by triiron dodecacarbonyl in acidic media. These reactions are not phase transfer catalysed but rather are biphasic in nature. This is the first example of desulphurisation in acidic media.

It has been demonstrated that the binuclear anion $Mn_2(CO)_9Br^-$ can be generated from bromo(pentacarbonyl)manganese in a facile manner under alkaline phase transfer conditions. This anion can then react with elemental sulphur to give a novel sulphur containing ionic complex. The structure of the anion is truly remarkable. Other transition metal complexes can also react with elemental sulphur under acidic and alkaline phase transfer conditions. The results obtained in the above model studies were utilised to design experiments for the attempted reduction of the sulphur content of crude oils and bitumen by transition metal complexes under both acidic and alkaline phase transfer conditions. This is a reaction of potential industrial importance.

The carbonylation of alcohols to esters via thiols is a potentially very important industrial process. This is a new transition metal catalysed route to esters which

avoids the use of highly corrosive halide promoters and very expensive rhodium catalysts.

The conversion of alcohols to thiols by cobalt complexes represents the first example of the generation of thiols from alcohols by metal complexes. Hydrocarbons are also formed and the product selectivity can be controlled to a certain degree.

4.2 Recommendations For Further Research

There are several interesting areas which this work may provide entry into. Investigations into the following may lead to unexpected and fruitful chemistry:

1. Attempts to desulphurise alkyl thiols may require changing the reaction conditions involved in the desulphurisation of benzylic thiols by transition metal complexes under alkaline phase transfer conditions. Studies involving the use of cyclodextrins and bi-metallic complexes (heteronuclear or as co-catalysts) may be useful.

2. Phase transfer catalysed reactions involving organometallic compounds in acidic media have all been carried out with surfactant type phase transfer agents. It would be interesting to use anionic phase transfer agents which would be capable of transferring electrophiles from the aqueous phase to the organic phase, i.e. the phase transfer agent would be Q^-X^+ instead of Q^+X^-.

3. Many other transition metal mediated reactions in acidic media should be investigated. A problem encountered in these reactions is the highly corrosive nature of tetrafluoroboric acid.

4. The binuclear anion $Mn_2(CO)_9Br^-$ may prove to be a very versatile complex. Not much work with respect to organic transformations has been carried out with this easy to generate species. Recently it has been used in carbonylation

reactions. It may have potential utility as a hydroformylation catalyst under alkaline phase transfer conditions.

5. Synthesis of other novel complexes under phase transfer conditions may be a very fertile area of research. Use of main group elements may be considered.

6. Some further work with molybdenum hexacarbonyl as a desulphurising agent for crude oils and bitumen needs to be carried out. Reactions under biphasic conditions may be very interesting. Use of two metal complexes as co-catalysts may lead to a greater degree of desulphurisation. Reactions using "heterogenised" systems could also be useful.

7. Further investigations into the carbonylation of alcohols to esters via thiols may involve the use of non-corrosive promoters including cyclodextrins. Transition metal complexes supported on zeolites should also tried.

8. Several different combinations of metal complexes and solvent systems could be tried in order to improve the conversion of alcohols to thiols. Here again cyclodextrins may prove to be useful.

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Appendix A

atom	x	y	z	B_{eq} or B
Mn	0.67722 (19)	0.54936 (18)	0.47090 (13)	2.85 (10)[a]
S(1)	0.5936 (3)	0.3386 (3)	0.4857 (2)	3.08 (17)[a]
S(2)	0.6348 (4)	0.3151 (3)	0.3330 (2)	3.95 (18)[a]
S(3)	0.6035 (3)	0.6438 (3)	0.2949 (2)	3.58 (18)[a]
S(4)	0.6051 (5)	0.5083 (4)	0.1218 (3)	6.05 (24)[a]
C(1)	0.6132 (12)	0.4959 (11)	0.2464 (8)	3.5 (2)
C(11)	0.7306 (12)	0.7129 (13)	0.4570 (8)	3.4 (3)
O(11)	0.7669 (9)	0.8204 (8)	0.4483 (6)	5.1 (5)[a]
C(12)	0.8680 (14)	0.4558 (12)	0.4239 (8)	3.4 (3)
O(12)	0.9899 (9)	0.3986 (9)	0.3914 (6)	5.9 (5)[a]
C(13)	0.7312 (13)	0.4727 (13)	0.6034 (10)	4.0 (3)
O(13)	0.7734 (9)	0.4174 (9)	0.6880 (7)	5.7 (5)[a]
N	0.7674 (9)	0.8704(8)	0.7907 (6)	2.59 (17)
C(21)	0.6558 (12)	0.9039 (11)	0.8870 (8)	3.4 (2)
C(22)	0.7133 (11)	0.9513 (11)	0.9646 (8)	3.1 (2)
C(23)	0.6894 (13)	1.1054 (13)	0.9511 (9)	4.8 (3)
C(24)	0.7370 (14)	1.1528 (14)	1.0259 (10)	5.8 (3)
C(25)	0.8043 (14)	1.0514 (14)	1.1108 (9)	5.3 (3)
C(26)	0.8317 (14)	0.8972 (14)	1.1269 (10)	5.8 (3)
C(27)	0.7845 (13)	0.8521 (12)	1.0523 (9)	4.8 (3)
C(31)	0.8205 (12)	1.0075 (11)	0.7332 (8)	3.7 (3)
C(32)	0.9165 (13)	1.0031 (12)	0.6314 (8)	4.5 (3)
C(41)	0.6835 (12)	0.8300 (11)	0.7223 (8)	3.2 (2)
C(42)	0.5573 (12)	0.9570 (11)	0.6647 (8)	3.8 (3)
C(51)	0.9139 (12)	0.7402 (12)	0.8283 (8)	3.7 (3)
C(52)	0.8900 (13)	0.5849(13)	0.8756 (9)	5.4 (3)

[a] B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

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PERSONAL DATA	Born: December 19, 1957, Dhaka, Bangladesh. Marital status - Married.
LANGUAGES	English, German Bengali and a little French.
EDUCATION	1973 'O'-Level (First Division), St. Joseph's High School, Dhaka, Bangladesh. 1978 'A'- Level, East Devon College, Tiverton, Devon, England. 1982 B.Sc. (Honours) in Chemistry with German, Kingston Polytechnic, Kingston-Upon-Thames, Surrey, England.
AWARDS	1978 - 1982 Local Education Authority Discretionary Award (Devon County Council, Exeter, Devon, England). 1982-83 University of Ottawa Graduate Entrance Scholarship. 1985-86 Teaching Assistant of the Year Prize, Department of Chemistry, University of Ottawa.
PROFESSIONAL ACTIVITIES	1. Graduate of The Royal Society of Chemistry, London, England. 2. Associate Member Chemical Institute of Canada. 3. Course Representative (1978 - 1982) on the Undergraduate Chemistry Course Committee, Kingston Polytechnic. 4. Executive Member, German Society, Kingston Polytechnic. 5. Executive Member, Interact (Rotary) Club, Dhaka.

EXPERIENCE

1979 August – December. Co-Op student/trainee (PRAKTIKANT) at the Institut für Erdölforschung (Institute for Petroleum Research), Hannover, Federal Republic of Germany. Involved in Enhanced Oil Recovery by Surfactant Flooding research.

1980 January – April. Praktikant at Ruhrchemie AG. Oberhausen, Federal Republic of Germany. Involved with reactions related to the Oxo-process and the synthesis of alcohols and amines. Gained experience in large scale laboratory and high pressure metal catalysed reactions, including analysis by G.C.

1982 – 1986 Fall and Winter terms. Teaching Assistant for Freshman and Second Year Organic Chemistry Laboratory Courses.

1986 Winter term. Marker for Second Year Inorganic Chemistry.

1986 January and February. Collaborative Research at Ecole Supérieure D'Ingénierie, de Pétrochimie et de Synthèse Organique Industrielle, Université D'Aix-Marseille II, Centre de Saint-Jerôme, Marseille, France.

1986 – 1987 Fall and Winter terms. Teaching Assistant Fourth Year Inorganic and Orgenometallic Laboratory Courses.

CONFERENCE PRESENTATION

9th Annual AOSTRA / University Industry Access Seminar, Banff, Alberta, September 1984.
"Heterogeneous Desulfurization of Bitumen",
H. Alper and F. Sibtain.

LIST OF PUBLICATIONS.

1. H. Alper, F. Sibtain and J. Heveling, Tetrahedron Lett., 1983, 24, 5329. Phase-Transfer Catalysed Desulfurization Reactions.

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6. H. Alper and F. Sibtain. Metal Catalysed Desulphurisation of Crude Oil and Bitumen Under Acidic and Alkaline Phase Transfer Conditions. Manuscript in preparation.

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