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LIST OF ABBREVIATIONS

IR	Infrared
vs	very strong
s	strong
ms	medium strong
NMR	Nuclear Magnetic Resonance
s	singlet
d	doublet
q	quartet
m	multiplet
MS	Mass Spectra
GC/MS	Gas Chromatography/Mass Spectra
mmol	millimole
$PdCl_2$	Palladium (II) chloride
$CuCl_2$	Copper (II) chloride
HOAc	Glacial Acetic Acid
Cp	Cyclopentadienyl
$Cp_2Mo_2(CO)_4$	Dicyclopentadienyl dimolybdenum -tetracarbonyl

ABSTRACT

The carbonylation of unsaturated and heteroatom substrates is described in Part I of this thesis. A homogeneous palladium/copper catalyst system was used to carbonylate a variety of substrates (including olefins, alkynes and allenes, as well as primary and secondary amines).

These reactions afforded fair to quantitative yields of the product esters, acids, acrylates and carbamates under conditions of unprecedented mildness. Also, it was discovered that the palladium/copper catalyst system enables a novel double carbonylation reaction to be carried out also under conditions of unprecedented mildness.

Investigations were conducted into the possibility of controlling the isomeric distribution of the products of olefin hydroesterification reactions. It was found that manipulation of carbon monoxide/oxygen ratios afforded a certain amount of control over the isomeric distribution of the product esters.

Finally, it was demonstrated that zeolites could be usefully employed in these reactions as CO_2 suppressants. As well, it was shown that acid-impregnated zeolites could be substituted for the corrosive mineral acids used in these reactions.

Part II of this thesis deals with the interaction of metal-metal multiple bonds and organo-sulfur moieties. It was demonstrated that the molybdenum triple-bond dimer was effective at promoting C-S, S-S, and P-P bond cleavage reactions. The products arising from a number of these investigations were characterized by X-Ray crystallography, and some of these were found to be quite novel compounds.

PART I

CARBONYLATION CHEMISTRY

CHAPTER 1

Introduction

The use of transition metal complexes as catalysts for the synthesis of organic compounds is of academic and industrial importance. Catalysts are conventionally divided into homogeneous and heterogeneous depending on whether they act throughout one phase, or at a phase boundary. Comparisons between the two types are inevitable. Homogeneous catalysts are easy to add into a system, but can be quite difficult to remove from the products. The catalytic effect of such materials is approximately proportional to their concentration. In heterogeneous catalysis, however, it is not the mass of catalyst available that counts, but rather its surface area. Thus, while heterogeneous catalysts often have to contend with diffusion problems, they have the great advantage of an easy separation from the reaction products. This feature, coupled with the generally higher thermal stability of such systems makes heterogeneous catalysis the most widely used form in industry.

In the last 45 years, however, there has been a steady increase in the use of homogeneous catalysis (1). This can be attributed to two facts. First, homogeneous catalysts often can be used under extremely mild conditions, allowing one to achieve a very high selectivity to the desired product. Secondly, homogeneous catalysts can be made much more reproducibly than their heterogeneous counterparts, and can be studied thoroughly the well-established techniques of physical organic chemistry and X-Ray crystallography. Most of our insights on catalysis have come

from the study of homogeneous systems.

At the present time, there are more than two dozen major industrial processes utilizing homogeneous catalysis in diverse areas (1). Homogeneously catalyzed hydrogenation, isomerization, oligomerization, polymerization, oxidation and metathesis are well known and valuable processes.

Perhaps the most versatile of all the homogeneously-catalyzed processes is the carbonylation reaction.

This is not only due to the fact that the carbon monoxide moiety is the most simple synthon for introducing a carbonyl group into an organic substrate; but also the fact that when conventional petroleum feedstocks inevitably become scarce, the use of carbon monoxide will displace many of the more traditional routes to obtain organic chemicals. This is due largely to the easy availability of carbon monoxide from many different sources (e.g. as synthesis gas).

The field of homogeneously catalyzed carbonylation reactions was initiated by two major breakthroughts which occurred in Germany in the 1930's and 1940's. First, Roelen of Ruhrchemie discovered the cobalt catalyzed carbonylation of olefins to yield aldehydes (2):

$$H_2C{=}CH_2 + CO + H_2 \xrightarrow{Co} H_3C{-}CH_2CH \quad (O)$$

This process was named the hydroformylation reaction since it involves the addition of a formyl unit to an olefin. This process has now been developed to the point where it constitutes one of the major industrial

applications of homogeneous catalysis.

The second major advance occurred when Reppe of IG Farben discovered that Group VIII metal carbonyl complexes were capable of catalyzing a whole family of carbonylation reactions involving alkenes and alkynes. These substrates give rise to carboxylic acids or esters depending on the nature of the co-reactant (3). These reactions are collectively called Reppe reactions, and a few examples are illustrated below:

$$C_2H_2 + CO + ROH \rightarrow CH_2{=}CHCOOR$$

$$C_2H_4 + CO + ROH \rightarrow CH_3CH_2COOR$$

$$R'CH_2OH + CO + ROH \rightarrow R'CH_2COOR$$

$$R, R' = H, \text{aliphatic, aromatic}$$

The area of interest examined in this thesis is Reppe-type chemistry. This includes the carbonylation of unsaturated organic compounds, as well as nitrogen-bearing substrates. A consideration of these two areas is thus in order.

Carbonylation of Unsaturated Substrates

This reaction typically results in the formation of a -C(O)OR moiety. The carbonyl group here comes from carbon monoxide. The original work done by Reppe involved a systematic examination of the metal carbonyl catalyzed reaction of unsaturated compounds with carbon monoxide and nucleophiles in the presence of a mobile H atom. In fact, Reppe was actually the one to coin the term 'carbonylation'. The original work has

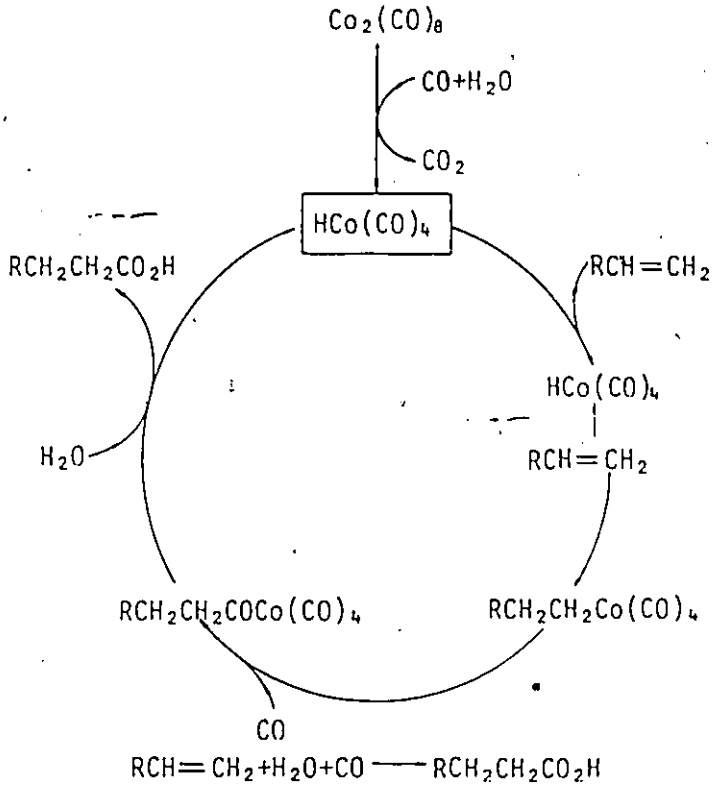
been expanded over the years to include carbon monoxide insertion into existing carbon-oxygen bonds. Thus Reppe reactions represent routes for the manufacture of a wide variety of saturated and unsaturated acids, esters, lactones and anhydrides from numerous feedstocks. Large numbers of reviews and books have been written on this subject-evidence of widespread interest and of the industrial significance of the products. These reviews cover the field from different viewpoints, such as mechanism (4-11), catalysts (3,4,10,11), different substrates (3,4,7-14), products (15), future trends (3), and economic importance of the reactions (3).

The carbonylation of alkynes, alkenes and other unsaturated species in the presence of water to produce unsaturated and saturated carboxylic acids is commonly known as a hydrocarboxylation reaction. The carbonylation of alkynes, alkenes and other unsaturated species in the presence of alcohols to produce unsaturated and saturated esters is referred to as a hydroesterification reaction.

Mechanism: The mechanism of Reppe-type carbonylations has been studied by a number of workers, most notably by Heck. The cobalt-catalyzed hydrocarboxylation of α-olefins has been carefully studied by his group, and they proposed the following mechanism:

Figure 1.1

Hydrocarboxylation Mechanism (3)



It should be noted that as the cobalt catalyst is capable of bonding to either of the olefinic carbons, two isomeric acids can result. Furthermore, as the catalyst has the ability to isomerize the double bond, other isomers are possible. It turns out, however, that for this particular cobalt-catalyzed reaction, linear acids tend to be the dominant products. In fact, even when internal olefins are used, the major products are usually linear carboxylic acids. (This selectivity can be enhanced by promoters such as pyridine.)

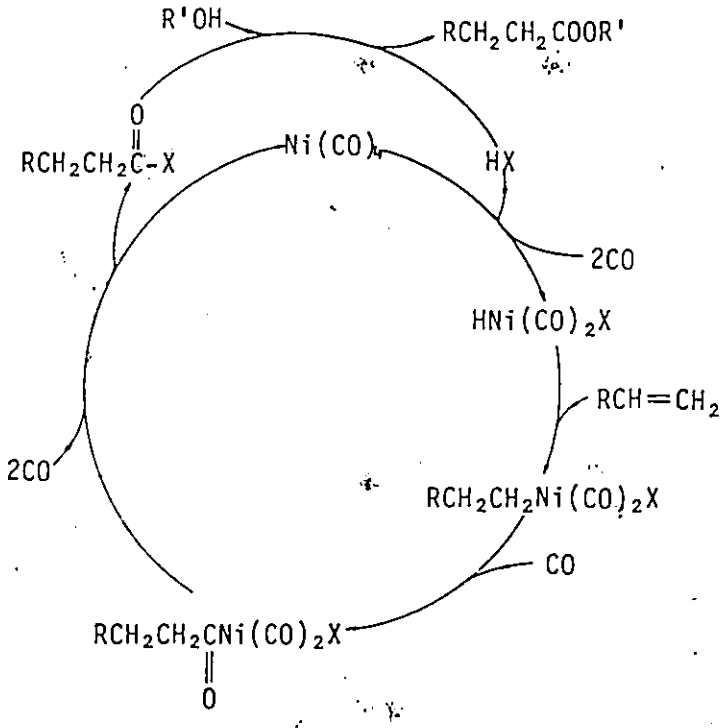
The mechanism shown in Figure 1.1 proposes initial formation of the cobalt hydride as the catalytically active species, followed by coordination of the olefinic substrate. This is followed by rearrangement to give a σ-bonded alkyl derivative. The carbon monoxide then coordinates and inserts into the cobalt-carbon bond.

Finally the attack of water on the species results in elimination of the carboxylic acid coupled with regeneration of the cobalt moiety.

Heck has also examined the nickel-catalyzed hydroesterification of olefins in the presence of traces of hydrogen halides, and has proposed a somewhat similar reaction mechanism for this case:

Figure 1.2

Hydroesterification Mechanism (3)

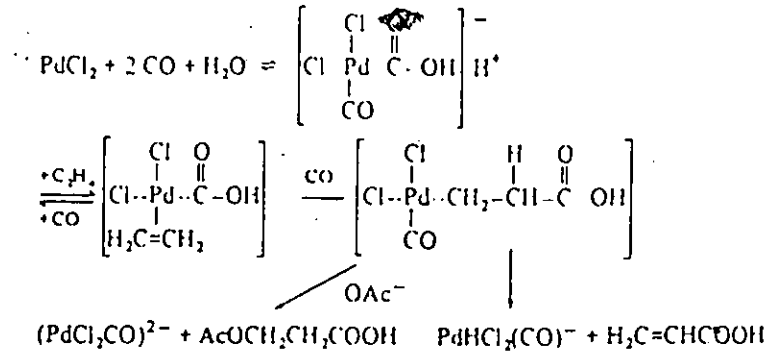


In this mechanism, the first step involves oxidative addition of the hydrogen halide to the nickel carbonyl. This is followed by coordination of the olefin, rearrangement to the σ-alkyl derivative, insertion of carbon monoxide into the nickel-carbon bond, reductive elimination of an acyl halide, and finally a reaction with alcohol to afford the ester.

The preceeding two mechanisms represent reductive carbonylations. The mechanisms of oxidative carbonylation reactions have also been examined due to their industrial potential. The following sequence represents the proposed reaction steps of a palladium-catalyzed oxidative olefin carbonylation:

Figure 1.3

Oxidative Hydrocarboxylation (3)



The suggested sequence for this reaction involves initial coordination of water and carbon monoxide to the palladium, followed by carbon monoxide insertion into the palladium-oxygen bond. Subsequent steps in the reaction mechanism include coordination of the olefin, insertion, and then collapse to the organic product.

Catalysts and Substrates

Although most Reppe catalysts are based on metal carbonyls of nickel, cobalt, rhodium, platinum, iron and palladium, other transition-metal systems based on manganese, osmium, ruthenium and copper have also been found to be applicable (3). With the appropriate choice of metal and ligand, catalysts can be obtained capable of carbonylating suitable substrates under very mild conditions. There is currently a great deal of commercial interest in producing catalysts capable of enabling carbonylation processes to occur at ambient temperature and pressure.

Generally, hydroesterification reactions are slower than the corresponding hydrocarboxylations. Moreover, in hydroesterifications, the yield of ester has been found to be inversely proportional to the molecular weight of the alcohol. Alkene carbonylation generally requires more forcing conditions than alkyne carbonylation. Moreover, while the triple bond of alkynes does not isomerize during these carbonylation reactions, the double bond of alkenes is subject to varying degrees of isomerization depending upon the catalyst.

The reactivity of alkenes and alkynes is directly related to the degree of branching and the nature of the substituent groups. For instance, for alkynes, substituent groups such as straight chain alcohols and alkyl or aryl groups promote carbonylation, whereas branched chain alcohols as well as carboxylic acid and ester substituents (-COOH and -COOR) tend to hinder the reaction.

Nickel catalysts are very suitable for the carbonylation of alkynes, whereas for alkenes cobalt, rhodium, ruthenium, platinum and palladium are

as good or better. Nickel compounds can be employed in several ways when carbonylating alkynes. When $Ni(CO)_4$ is used in stoichiometric amounts, the carbonylation reactions require only mild reaction conditions, as $Ni(CO)_4$ serves as both the (CO) source and catalyst;

$$4C_2H_2 + 4H_2O + Ni(CO)_4 + 2HCl \xrightarrow[1\ Bar]{40^\circ} 4H_2C{=}CH{-}COOH + NiCl_2$$

The $NiCl_2$ can then be recycled. This stoichiometric method has found no widespread industrial application due to the involved work-up, as well as the toxicity of $Ni(CO)_4$ (3).

The catalytic nickel processes generally take place at temperatures above 250° and at pressures up to 100 Bar, using nickel halide salts along with promoters such as phosphines or pyridine (3). Yields are about 50%. In the nickel catalyzed hydrocarboxylation of α-olefins the main products are usually branched carboxylic acids (60-70%) (3). With internal olefins, branched acids are formed almost exclusively.

Cobalt catalysts such as $Co_2(CO)_8$ can be employed to hydrocarboxylate α-olefins affording 80-90% of carboxylic acids of about a 2:1 linear:branched product content. This conversion requires up to 200°C and 250 Bar pressure (3). Internal olefins readily isomerize in the presence of cobalt catalysts, such that when β-alkenes are hydrocarboxylated, the main product is a linear acid (16). Again, promoters such as pyridine can be used to help adjust the linear/branched product ratio to more favourable levels. Catalyst systems other than cobalt carbonyl can be quite effective. For instance, for the

hydrocarboxylation of ethylene with a CoI_2-EtI system, it was found that the cobalt gave a 99% selectivity to the product (propionic acid) (17).

Finally other cobalt catalysts (Co/I_2) are used together with noble metal promoters by BASF (18) and Shell (19) to facilitate the carbonylation of methanol at lower temperatures and pressures (80-200°C, 70-300 Bar) compared to the conventional parameters of 250°C and 680 Bar (3).

Rhodium and cobalt catalysts are the most widely used agents for alcohol carbonylation, with rhodium allowing for much milder conditions than cobalt. The Monsanto methanol carbonylation process is a well-known example of the capability of rhodium catalysts.

In this case, the catalyst affords 99% selectivity to the product (acetic acid) with carbon monoxide pressures as low as 1 Bar (20). rhodium catalysts such as $RhCl_3$ have been investigated by a number of companies for hydrocarboxylation activity. It was found that these rhodium catalysts are useful olefin hydrocarboxylation catalysts requiring only fairly mild conditions (25 Bar, $<$ 200°C) and affording minimal byproducts. Although rhodium would seem to be very useful as a carbonylation catalyst, its use has been hindered by its very high cost. In fact, the economic viability of any rhodium-based process is critically dependent upon an extremely efficient catalyst recovery system.

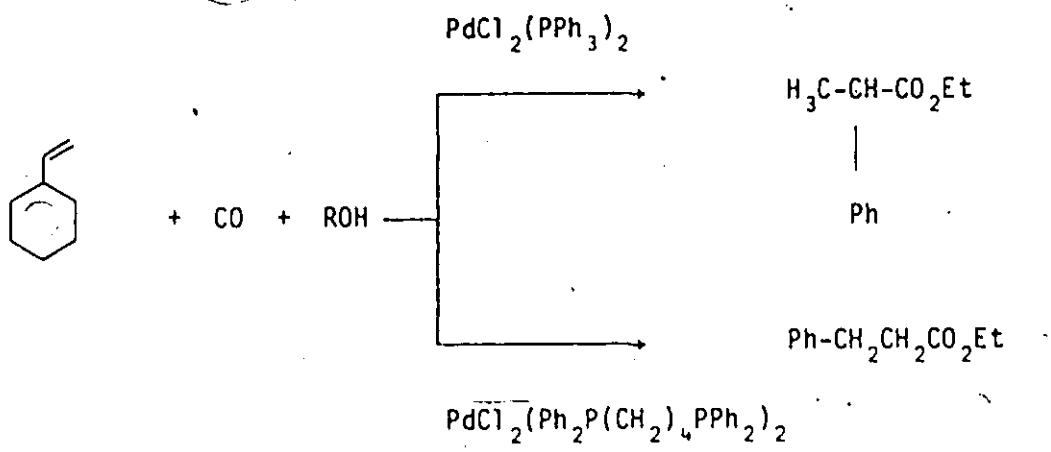
Iron catalysts such as $Fe(CO)_5$ also have activity as olefin hydrocarboxylation catalysts. However, the yields are modest (being about 30%) (21). $Fe_2(CO)_9$ or $FeCl_2$ when employed together with $PdCl_2$ as co-catalyst catalyzes the hydrocarboxylation of α-olefins such as 1-octene in (50-63%) yield with linear: branched product ratios ranging from 3:1

for $Fe_2(CO)_9$ to 4:5 for $FeCl_2$ (22). This last piece of data clearly reveals that iron shares the ability to isomerize olefins along with cobalt compounds. Finally, iron carbonyls together with halide promoters have successfully been utilized to carbonylate alcohols in modest yields.

Copper complexes such as copper(I) carbonyl catalyze the hydroesterification of olefins and alcohols in the presence of strong acids (a Koch-type reaction). The reaction conditions are very mild (25°C, 1 Bar). The major products of these reactions tend to be branched acids and esters (23,24). Copper carbonyls also afford an extremely mild hydrocarboxylation of dienes and diols to give high yield mixtures of mono- and di-acids (3).

In the final category of Reppe carbonylation catalysts, one may place platinum and palladium. Platinum catalysts allow for the hydrocarboxylation of olefins and dienes under very mild conditions (50-100°C, atmospheric pressure) (25). Probably the best known platinum catalyst is the H_2PtCl_6-$SnCl_2$ couple. This catalyst system facilitates the hydroesterification of α-olefins to produce 85% linear ester and 15% branched ester under quite mild conditions (25).

During the last decade, palladium catalyzed carbonylations have received a great deal of attention, on account of the generally mild conditions and consequent high selectivity of such reactions. It has been found that the nature of the ligands on the palladium is crucial to the type of product formed. For instance, the hydroesterification of styrene can be achieved with various palladium-phosphine complexes and the reaction is regioselective depending upon the nature of the phosphine used. This is illustrated below (26):



The carbonylation of simple olefins by palladium-phosphine complexes is often carried out under milder conditions which helps ensure minimal byproduct formation (3):

$$Pd(PPh_3)_4 + C_2H_4 + CO + H_2O \xrightarrow[135^\circ \\ 135\ Bar]{PPh_3} CH_3CH_2COOH + PPh_3$$

Another recent example is a palladium/tin cocatalyst system (27).

$$CH_2{=}CHC_5H_{11} + CO + CH_3OH \xrightarrow[70^\circ \\ 141\ Bar]{PdCl_2/SnCl_2} CH_3\text{-}\underset{\displaystyle COOCH_3}{\underset{|}{C}}HC_5H_{11} \quad (93\%)$$

A recent Dupont patent (28) has claimed that propene can be converted to the branched chain ester methyl 2-methylpropionate by a bis(triarylarsine)palladium dichloride/triarylarsine/aluminum trichloride/HCl catalyst system.

In another example, diesters were formed from the reaction of olefins with carbon monoxide, oxygen, alcohol, palladium and cupric

chloride in the presence of trialkylamine (29). Although many of these reactions occur under milder conditions than those of other catalysts, the conditions are still quite stringent, are not regiospecific and often work well only for α-olefins.

In 1983, Alper and Despeyroux (30) described a homogeneous palladium-based catalytic system which enabled a regiospecific hydroesterification of both internal and terminal olefins to occur under extremely mild conditions to give very high product yields of branched esters:

$$CH_2{=}CHC_8H_{17} + CO + CH_3OH + HCl + O_2 \xrightarrow[25^\circ \\ 1\ Bar]{PdCl_2/CuCl_2} CH_3OC(=O)\underset{CH_3}{\underset{|}{C}}HC_8H_{17} \quad 100\%$$

In a subsequent publication, Alper utilized this palladium-based system to hydrocarboxylate olefins (31). This hydrocarboxylation was also carried out at ambient temperature and pressure. The process was found to be regiospecific and it enabled one to obtain good to quantitative yields (30-100%) of branched chain carboxylic acids. A further extension of this process involved the selective hydroesterification of alkynes to mono- or diesters (32). Terminal alkynes were found to undergo regioselective hydroesterification to unsaturated cis-diesters, while cis-monoesters were obtained from internal alkynes. Yields for this reaction were variable depending upon the nature of the substrate, but generally tended to be quite good (70-80%). Finally it was also found that olefins react with diols under approximately the same conditions affording monoesters in good

to quantitative yields (56-98%) (33).

All of the above palladium-based reactions were found to be complete within two or four hours at room temperature and atmospheric pressure. The really remarkable aspect of all these reactions was that they afforded very high product yields under conditions of almost unprecedented mildness.

Industrial Applications:

There are currently a number of industrial processes based on Reppe chemistry, and there is considerable activity aimed at expanding the field. Currently the main areas of interest are: 1) acetic acid production from methanol utilizing either the drastic cobalt-based system, or the mild rhodium-based process. Current worldwide capacity is about 1.4 million tons/annum.

2) Another important area is acrylic acid and ester production. There are two catalytic processes available here - an acetylene-based process utilizes a mixture of nickel(II) and copper(II) halides in THF at 180-205°C and 40-55 Bar pressure. An alternative olefin-based process involves an oxidative carbonylation of propylene utilizing a $PdCl_2/CuCl_2$ catalyst at 95° and 70 Bar of (CO) pressure. Currently a world-wide production capacity of 350,000 tons/annum exists for acrylic acid and ester production (3).

3) Utilizing a nickel propionate catalyst, ethylene can be hydrocarboxylated to propionic acid in 95% yield. The conditions of this liquid phase reaction are 270-320°C and 200-240 Bar. This reaction is currently operated at a scale of about 30,000 tons/annum (2).

4) Butanol can be manufactured at 100°C and 15 Bar from propylene using $Fe(CO)_5$ as a catalyst, in the presence of n-propylpyrrolidine. This reaction is the basis of the BASF process and yields 85% n-butanol and 15% isobutanol. Capacity in this case is 30,000 tons/annum (34).

Carbonylation of Amines

The use of amines as promoters in hydroformylation processes led to the discovery of the insertion of carbon monoxide into N-H and N-C bonds. The types of compounds which can be obtained from the carbonylation of amines include amides, ureas, isocyanates, imides, carbamates and various heterocycles. The carbonylation of amines has been reviewed from various viewpoints, including mechanisms (10, 35), starting materials (3,35), and products (11,12).

Substrates and Products: These reactions are summarized in the following table:

TABLE 1.1

Carbonylation of Amines

i) $R^1R^2NH + CO \rightarrow HCONR^1R^2$ reductive carbonylation

ii) $R^1R^2NH + CO \rightarrow R'R^2NCONR^1R^2$ reductive carbonylation

iii) $R^1R^2NH + CO + R^3OH \rightarrow R^1R^2NCOOR^3$ oxidative carbonylation

R^1 = alkyl, aryl, R^2,R^3 = H, alkyl, aryl

Both primary and secondary amines are suitable as substrates. However, tertiary amines can be carbonylated as well. There tends to be a marked distinction in behaviour between aromatic and aliphatic amines, which is largely explained by the large difference in their basicities (2). Thus, upon reductive carbonylation, aliphatic amines yield mainly N-formyl derivatives, whereas aromatic amines usually lead to ureas (5). However, this selectivity can be altered by a careful variation of the metal catalyst and the ancillary ligands. Thus, for example, $Co_2(CO)_8$ is the catalyst of choice for the formation of substituted formamides from aliphatic amines; conversely, the use of $Mn_2(CO)_{10}$ affords dialkylureas from primary aliphatic amines (2). It should be noted that despite interest in the carbonylation of amines to obtain ureas and formamides, this method has not displaced more traditional routes to obtain these important chemicals; (this could be due to the fact that the reaction conditions for the reductive carbonylation of amines are severe: T = 150-270°C, Pressure = 300 Bar).

Carbamates are important compounds as agricultural chemicals (notably as pesticides). Moreover they are also used as precursors to isocyanates, because carbamates can be thermally decomposed to give the valuable isocyanates in good yields. The usual preparative route to carbamates involves the reaction of alcohols with isocyanates which are in turn usually prepared by treatment of the corresponding amines with phosgene (36). Relatively few methods for the high-yield catalytic conversion of amines to carbamate esters are known. For this reason, the oxidative carbonylation of amines to give carbamates is not included in many of the standard texts and reviews on the carbonylation of amines.

However, in recent years, there has been increasing interest in the oxidative carbonylation of amines to achieve carbamates, as this allows one to obtain isocyanates easily and without the use of phosgene.

Catalysts: A variety of metal complexes can be used for the reductive carbonylation of amines, with manganese, cobalt and nickel compounds being the most effective. The reaction conditions required tend to be drastic with temperatures ranging from 150-270°C and CO pressures between 100 and 300 Bar (11), affording products in a wide range of yields. For example, cyclohexylamine can be carbonylated to di-cyclohexylurea by $Mn_2(CO)_{10}$ at 180°C and 130 Bar pressure in 58% yield. In another example, n-butylamine is converted by $(RhH(CO)_3PPh_3)$ at 150°C and 70 Bar to di-n-butylurea (20%) and to n-butylformamide (40%). Dimethylamine can be converted to dimethylformamide in (34%) yield at 110°C and 60 Bar by a $Cu(CN)_2$ catalyst (3).

For the oxidative carbonylation of amines to carbamates, only a few catalytic systems are known, as interest in this alternative route to isocyanates has only developed recently.

A recent patent (37) describes the use of $PdCl_2$ and a Lewis acid (which contains metal components capable of undergoing redox reactions such as $CuCl_2$, $FeCl_3$ and FeOCl). In this case, a Wacker-type redox reaction seems to be occuring, because the catalysts have been found to be present in several oxidation states such as Pd(0), Pd(II), Fe(0) and Fe(III) during and after the reaction. Yields of 96% are claimed by this method (37).

Another catalytic system, described a number of years ago, utilized

Se and bases to oxidatively carbonylate amines to carbamate esters (38).

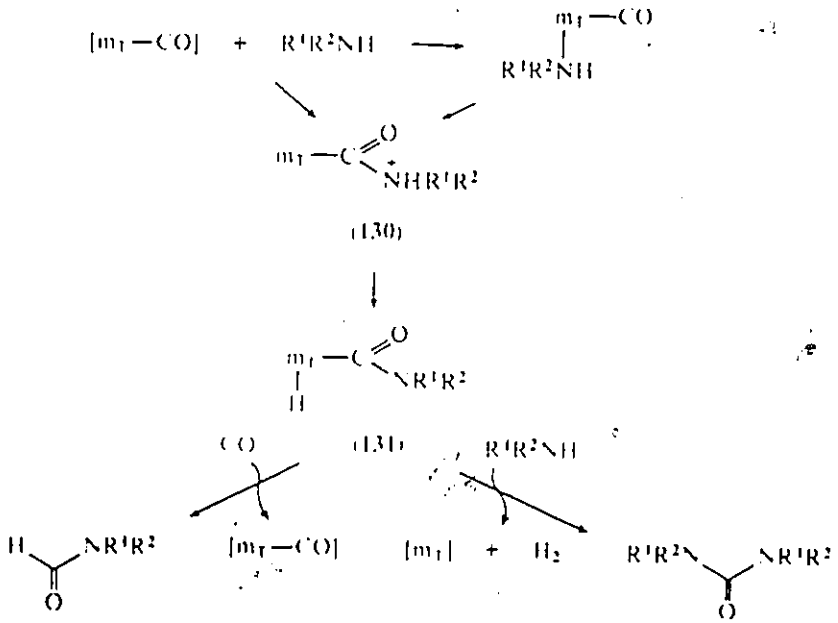
In 1984, Fukuoka's group in Japan described the conversion of amines to carbamates using noble metal catalysts deposited on carbon black (M = Ru,Rh,Ir,Pd,Pt) along with halide salts as promoters. They found that optimum results occurred for Pd with NaI as a promoter. Yields were consistently greater than 90% for this system. However the conditions required were quite drastic (temperature = 160-170°C, pressure = 86 Bar) (39,40).

Mechanism:

The mechanism of amine carbonylations has been little investigated. However, what is known (2), suggests that a common intermediate in all of these reactions is a carbamoyl-metal species. This intermediate could result from either an intramolecular 1,2 shift reaction involving coordinated (CO) and amine, or from an intermolecular attack of an amine to a carbonyl ligand. The following reaction sequence has been suggested as a plausible pathway to ureas and formamides:

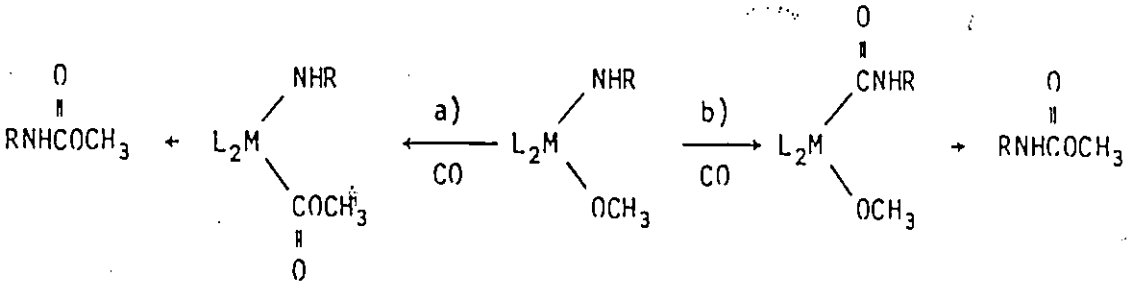
Figure 1.4 (2)

Mechanism for Reductive Carbonylation of Amines



In the preceeding sequence, the carbonyl adduct can undergo a proton shift to the metal centre, leading to a hydridocarbamoyl intermediate. From this point, reductive elimination of the amine can ensue to yield the formamide or an additional attack by an amine to yield a urea.

The oxidative conversion of amines to carbamates necessitates a different mechanism. Several potential pathways exist here, depending largely upon the relative ease of CO insertion:



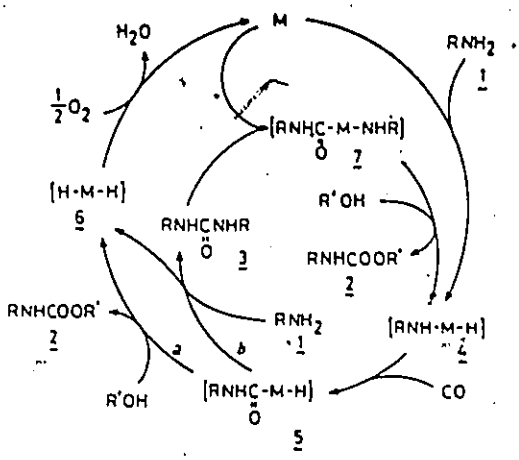
In path a) carbon monoxide inserts into a metal-oxygen bond and in path b) carbon monoxide inserts into a metal-nitrogen bond to give a carb moyl intermediate.

In several recent publications Bryndza carried out comparative studies of carbon monoxide insertion into metal-carbon, metal-oxygen and metal-nitrogen bonds (41,42). These studies support the idea of the intermediacy of a carbamoyl species as suggested in path b) above. (Bryndza found that the M-O bond is thermodynamically stonger than M-N and hence less prone to carbon monoxide insertion).

Fukuoka has proposed similar mechanistic ideas for his catalytic conversion of amines to carbamates.

Figure 1.5 (40)

Fukuoka's mechanism for Oxidative Carbonylation of Amines.



Other ligands (CO, amine) were omitted.

In this catalytic cycle , the oxidative addition of an amine 1 to the catalyst M affords the amino-metal species 4, which then can undergo insertion of coordinated (CO) to yield a carbamoyl-metal intermediate 5. From this point, two possible routes a) and b) lead to the carbamate product. In path a), the carbamoyl species 5 reacts with an alcohol to produce the carbamate 2 directly, as well as a hydrido-metal species 6.

By path b), the carbamoyl intermediate 5 can react with another amine 1, to give a urea 3 and a hydridometal species 6. Furthermore, the urea 3 adds oxidatively to the catalyst M to give an (amino) carbamoyl metal species 7 which then reacts with alcohol to produce the product carbamate 2. Finally, the hydrido-metal species is oxidized by oxygen to produce water and regenerate the original catalyst (40).

To conclude, an analysis of the carbonylation of unsaturated species and amines has been carried out in this introductory chapter. The products of these carbonylation reactions are quite valuable industrially, and clearly the use of transition metal catalysts enables one to obtain these products in a high yield and sometimes under mild conditions, provided the proper catalysts and reaction conditions are used.

The objective of this research project was to expand the extremely mild palladium-based carbonylation process discovered by Alper and Despeyroux in 1983 (30). A variety of substrates including olefins, alkynes, allenes, primary aliphatic amines, primary aromatic amines and secondary amines were subjected to the general conditions of this process. In each case, the product esters, acids or carbamates were isolated and characterized and the reaction conditions were optimized in order to maximize the yield. The primary objective of this research was to obtain esters, acids and carbamate esters in high yields utilizing the mildest possible conditions.

CHAPTER 2

Results and Discussion - Carbonylation Reactions

2.1 Carbonylation of Primary Aromatic Amines

Carbamate esters are important as precursors to the industrially valuable isocyanates and as intermediates in pesticide synthesis. Isocyanates are a convenient starting material for a variety of important chemicals, including amides, ureas, and polyurethanes (42) by simple reactions with Grignard reagents, amines and glycols respectively. Carbamates can be readily converted to broad spectrum insecticides (of general formula $RO_2CNR^1OR^2$) by reaction with anhydrides (43,44). Moreover certain carbamates (such as phenyl methyl carbamates) have direct application as insecticides due to their powerful cholinesterase inhibition activity (45).

The oxidative carbonylation of amines to give carbamate esters is an area of growing interest (36) as it offers an alternate pathway to isocyanates avoiding the use of the highly toxic phosgene commonly used in isocyanate synthesis (42).

Following the 1983 discovery by Despeyroux and Alper (30) of an exceedingly mild palladium-based hydroesterification reaction, it was reasoned that the same basic process might be capable of carbonylating amines to yield carbamate esters.

Therefore a study was conducted of the carbonylation of primary aromatic amines via the palladium/copper catalyst system shown below:

$$RNH_2 + R'OH + CO + O_2 \xrightarrow[\text{Room Temperature}\\ \text{1 Bar}]{PdCl_2/CuCl_2/HCl} RNHCOOR'$$

R = aromatic, R' = CH_3, C_2H_5

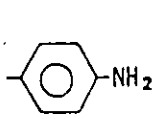
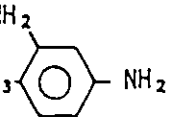
Reaction of aromatic primary amines with carbon monoxide and alcohols was found to occur at room temperature and atmospheric pressure to afford carbamate esters. A variety of substituted aromatic amines gave carbamate esters in good yields when methanol was used as the alcohol. Diamino species such as  and  failed to undergo similar reactions and afforded tars. Yields are summarized in Table 2.1.

Table 2.1

Primary Aromatic Amine Hydroesterification Yields

Reference #	Amine	Product	Yield(%)
3.2.1	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	68
3.2.2	aniline	$C_6H_5NHCOOCH_3$	99
3.2.3	p-chloroaniline	p-Cl-$C_6H_4NHCOOCH_3$	61
3.2.4	3-aminoacetophenone	m-$(CH_3CO)C_6H_4NHCOOCH_3$	99
3.2.5	2,5-dimethylaniline	2,5-$(CH_3)_2C_6H_3NHCOOCH_3$	76
3.2.6	2,6-dimethylaniline	2,6-$(CH_3)_2C_6H_3NHCOOCH_3$	16
3.2.7	3,5-dimethylaniline	3,5-$(CH_3)_2C_6H_3NHCOOCH_3$	23
3.2.8	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	34[a]
3.2.9	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	83[b]
3.2.10	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	21[c]
3.2.11	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	13[d]
3.2.12	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	71[e]
3.2.13	p-toluidine	p-$CH_3C_6H_4NHCOOCH_3$	88[f]
3.2.14	p-toluidine	p-$CH_3C_6H_4NHCOOC_2H_5$	51[g]
3.2.15	aniline	$C_6H_5NHCOOC_2H_5$	64[g]

[a] No O_2 [b] $Pd(OAc)_2/Cu(OAc)_2$ [c] HOAC [d] $Pd(CH_3CN)_42(BF_4)$

[e] 3Å sieves [f] HOAC/3Å sieves [g] ethanol

Hydroesterification could also be achieved in satisfactory yields (50-60 %) when ethanol was used as the solvent. Use of higher alcohols such as t-butanol and n-propanol as solvents in these reactions yielded azo compounds rather than carbamate esters. The usual sequence of azo compound formation in organic chemistry involves 2 steps (46): diazotization and then coupling. In this case, however, the azo compounds likely arise by an insertion/elimination reaction:

$$PdCl_2 \xrightarrow[RNH_2]{} (RNH_2)_2PdCl_2 \xrightarrow[RNH_2]{-2HCl} (RNH)_2Pd(NH_2R)_2 \xrightarrow{-H_2} (RN)_2Pd(NH_2R)_2 \longrightarrow RN{=}NR$$

Oxygen was found to be beneficial for the reaction, since in its absence, the yield of carbamate ester was quite low. For example, in the absence of oxygen, the yield of N-tolyl carbamate from p-toluidine was only 34 % (compared to the usual 68 %). With only one exception, acid is necessary for the reaction to occur (otherwise tars were formed). It was also found that acetic acid could be successfully substituted for hydrochloric acid. In this case, the high selectivity to carbamate ester was retained; however, the reaction was slower, and hence the overnight conversion of amine was low (21 %). This result demonstrated that non-halide reagents could function satisfactorily in this catalytic system thus allowing for an alternative to the use of corrosive halide reagents.

Acetates of palladium and copper can catalyze the hydroesterification of p-toluidine in excellent (> 80 %) yields. The catalyst tetrakis (acetonitrile)palladium bistetrafluoroborate is inferior to the other

palladium catalysts for the conversion of p-toluidine to N-p-tolylcarbamate. Use of this cationic palladium catalyst does not necessitate the presence of acid. The products (3.2.1-3.2.15) of these reactions were characterized by several techniques. Infrared spectra of (3.2.1-3.2.15) displayed a strong carbonyl stretching band at 1720-1700 cm^{-1}. The mass spectra of (3.2.1-3.2.15) showed the correct molecular ion peaks followed by loss of alkoxy and then carbon monoxide units. The NMR spectra were also in accord with the assigned structures, with each spectrum having the characteristic resonance for the alkoxy protons at approximately 3.6 ppm.

During the course of these experiments, it was noticed that carbon dioxide was occurring as a byproduct in large quantities. It was then reasoned that the CO_2 might arise by a concurrent water-gas shift reaction ($CO+H_2O \rightleftharpoons CO_2+H_2$). Based on this assumption, one way to suppress CO_2 formation is by the elimination of water from the reaction. These considerations led to the use of 3Å molecular sieves as a drying agent. The results of these experiments are shown in Table 2.2.

Table 2.2

CO_2 Suppression Data

Reaction	Yield Carbamate Ester	Moles CO_2/Ester Produced
p-toluidine/MeOH/HCl	68 %	14/10
p-toluidine/MeOH/HOAc	21 %	15/10
p-toluidine/MeOH/HCl/3Å sieves	71 %	0.08/10
p-toluidine/MeOH/HOAc/3Å sieves	88 %	0.3 /10

A saturated barium hydroxide solution was used to trap evolved CO_2

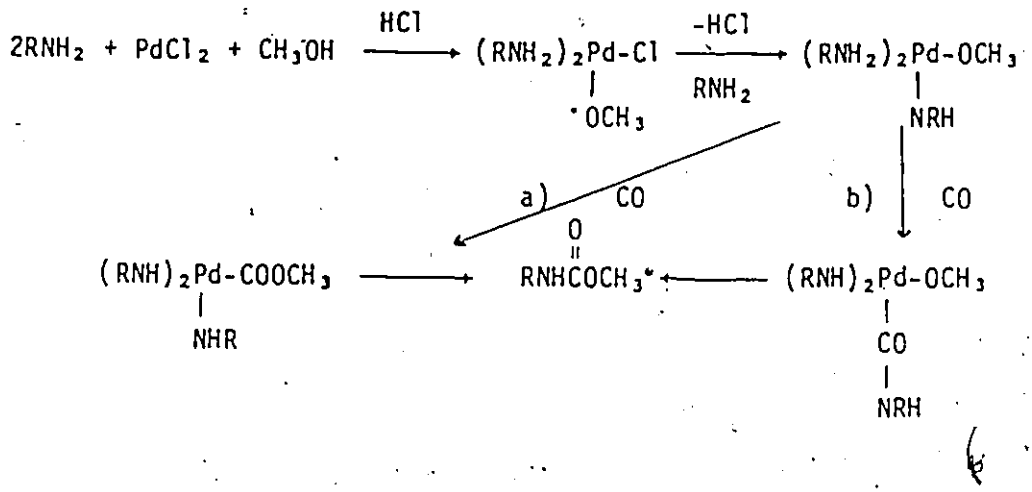
by forming barium carbonate which was then weighed to determine the number of moles of $BaCO_3$ and hence of CO_2 produced. As the data in Table 2.2 shows, the use of 3Å molecular sieves dramatically reduces the level of carbon dioxide production. Moreover, the yield of carbamate ester was also enhanced - possibly due to the availability of more catalyst for amine carbonylation once the CO_2 co-production route had been suppressed. Finally, the above data provides some corroboration for the theory that a competing water-gas shift reaction was occurring in the amine esterification process.

Gas-uptake experiments were conducted on these reactions with and without molecular sieves, in order to determine the reaction rate and the quantity of carbon monoxide utilized by the reaction. Carbonylation of 5 mmol of p-toluidine under the usual reaction conditions with hydrochloric acid but no sieves resulted in a gas uptake of 185 ml of a 1/1 CO/O_2 mixture. When 3Å sieves were present, the gas uptake was 155 ml. The reaction time to completion was essentially the same in both cases (approximately 6 hours). In conclusion, the presence of molecular sieves reduced the amount of carbon monoxide consumed in the reaction, but had no appreciable effect on the reaction rate.

The hydroesterification of amines to carbamate esters is likely to proceed via one of the pathways shown in Figure 2.1. The mechanism is similar to that of several of the amine carbonylation mechanisms described in Chapter 1. In Figure 2.1, there are two potential pathways a): involving carbon monoxide insertion into a Pd-O bond to give $-COOCH_3$ followed by elimination to afford the carbamate ester; b) insertion of carbon monoxide into a Pd-N bond to give the carbamoyl -CONRH, followed by elimination to afford the carbamate ester.

Figure 2.1

Proposed Mechanism for Amine Hydroesterification



Pd(0) recycled to Pd(II)
by $CuCl_2/O_2/HCl$

At the time that this research was originally conducted, one could not distinguish between the two pathways. However, Bryndza (8) recently compared the relative bond strengths of Pd-N and Pd-O bonds and found that the Pd-N bond was somewhat weaker than the Pd-O bond and more susceptible to CO insertion. This suggests that path (b) is the more likely pathway to occur.

The process described in this section compares favourably with the relatively few catalytic preparations of carbamates directly from amines (36,39). For instance, Fukuoka's oxidative alkoxycarbonylation of amines to carbamates using a Pd black catalyst consistently afforded yields of

greater than 90 %. However, this process required pressures of 86 Bar and temperatures of 170° (39). In another example, Yoshida's novel non-catalytic process (47) involved the reaction of carbon dioxide, an amine and an alkyl halide under 40 Bar of pressure and at 70° to give modest yields of carbamates.

The catalytic process described in Chapter 2.1 converts amines to carbamates in fair to quantitative yields at conditions of remarkable mildness and constitutes a significant advancement of methodology in this area. Moreover the problem of CO_2 byproduction was minimized by the addition of zeolites to the system as drying agents. This represented a novel use of zeolites.

2.2 Carbonylation of Primary Aliphatic Amines

The carbonylation of primary aliphatic amines was also investigated and some interesting differences were found in comparison with the behaviour of aromatic amines.

$$RNH_2 + R'OH + CO + O_2 \xrightarrow[\text{3Å sieves, Room Temperature, 1 Bar}]{PdCl_2/CuCl_2/HOAc} RNHCOOR'$$

R = aliphatic; R' = CH_3, C_2H_5, t-C_4H_9

Reaction of primary aliphatic amines with carbon monoxide, oxygen,

an alcohol, palladium and cupric chlorides, acetic acid and 3Å molecular sieves, at room temperature and atmospheric pressure afforded carbamate esters in excellent yields (see Table 2.3)

Table 2.3

Primary Aliphatic Amine Hydroesterification Yields

Reference #	Amine	Alcohol	Product	Yield(%)
3.3.1	Dodecylamine	methanol	$C_{12}H_{25}NHCOOCH_3$	99
3.3.2	Dodecylamine	ethanol	$C_{12}H_{25}NHCOOC_2H_5$	99
3.3.3	Dodecylamine	t-butanol	$C_{12}H_{25}NHCOO(C_4H_9\text{-t})$	81
3.3.4	t-Butylamine	methanol	$(t\text{-}C_4H_9)NHCOOCH_3$	99
3.3.5	t-Butylamine	t-butanol	$(t\text{-}C_4H_9)NHCOO(C_4H_9\text{-t})$	40
3.3.6	n-Butylamine	methanol	$(n\text{-}C_4H_9)NHCOOCH_3$	96
3.3.7	n-Butylamine	t-butanol	$(n\text{-}C_4H_9)NHCOO(C_4H_9\text{-t})$	66
3.3.8	n-Propylamine	methanol	$(n\text{-}C_3H_7)NHCOOCH_3$	98
3.3.9	Dodecylamine	methanol	$C_{12}H_{25}NHCOOCH_3$	95[a]
3.3.10	Dodecylamine	methanol	$C_{12}H_{25}NHCOOCH_3$	99[b]
3.3.11	Dodecylamine	t-butanol	$C_{12}H_{25}NHCOO(C_4H_9\text{-t})$	71[a]
	Dodecylamine	t-butanol	$C_{12}H_{25}NHCOO(C_4H_9\text{-t})$	64[b]
3.3.12	Dodecylamine	methanol	$C_{12}H_{25}NHCOOCH_3$	72[c]

[a]No sieves [b]No acid or sieves [c]Di-t-butyl peroxide instead of oxygen.

As Table 2.3 indicates, a variety of straight and branched chain aliphatic amines undergo facile carbonylation in methanol, ethanol or t-butanol. The latter alcohol did not afford carbamate esters in the case of aromatic amines. t-Butyl carbamates are more readily converted to isocyanates than the corresponding methyl carbamate esters, and hence are the preferred precursors to isocyanates in industry.

Another difference between the aromatic and aliphatic systems was that acid was not necessary for reaction to occur in the latter case. As products (3.3.10 and 3.3.11) indicate, excellent yields could be achieved without the presence of acid. Such differences in behaviour between aliphatic and aromatic amines are usually ascribed (2) to their large difference in basicity.

The amount of carbon dioxide produced in the aliphatic amine reaction is only about one-fifth that of the aromatic amine reaction. Furthermore, the presence of molecular sieves in the aliphatic amine reactions, had a negligible effect on CO_2 levels when compared with results in the case of aromatic amines. Finally, it is possible to use di-t-butylperoxide as the reoxidant, rather than oxygen for this reaction (last entry, Table 2.3). This was an important finding, since in industry, the use of CO/O_2 at elevated pressure must be avoided because of the explosiveness of the mixture. (This is an important drawback when dealing with moderately slow reactions such as the amine hydroesterification - where extra CO pressure would be useful in forcing a faster reaction). Thus the use of di-t-butyl-peroxide as reoxidant instead of oxygen allows one to use higher pressures if desired in order to speed up the reaction.

The products (3.3.1 - 3.3.12) of the aliphatic amine hydroesterification

reactions were characterized using spectroscopic and mass spectral analyses. Infrared spectra of (3.3.1 - 3.3.12) displayed a strong carbamate ester carbonyl stretching band at 1730 - 1710 cm^{-1}. With few exceptions, the mass spectra of (3.3.1 - 3.3.12) showed molecular ion peaks followed by the loss of alkoxy and then carbonyl groups. Two exceptions are: example (3.3.4) which gave a base peak due to $[M-CH_3]^+$, and (3.3.3) which gave a base peak due to $[M-(t-C_4H_9)]^+$. These values correspond to an unusual fragmentation of the product within the mass spectrometer. The NMR spectra were also found to be in accord with the assigned structures.

Mechanistically, this reaction can be explained satisfactorily by the mechanism for aromatic amine hydroesterification shown in Figure 2.1. What, however, cannot be easily rationalized are the differences in CO_2 co-production levels between aliphatic and aromatic amines. To summarize, this palladium-based reaction is useful for the conversion of primary aliphatic amine to carbamate esters in excellent yields, under remarkably mild conditions, using different alcohols including t-butanol.

2.3 Carbonylation of Secondary Amines

A continuation of the study of amine carbonylation reactions described in Chapter (2.1) and (2.2) led naturally to attempts to apply the reaction to secondary amines. Significant differences in reactivity and behaviour between this system and that of primary amines were noted. The general reaction scheme is described as the following:

$$R_2NH + CH_3OH + CO + O_2 \xrightarrow[\text{Room Temperature}\\ \text{1 Bar}]{PdCl_2/CuCl_2/HCl} R_2NCOOCH_3 \text{ and } R_2NCOCOOCH_3$$

Reaction of secondary amines with carbon monoxide and methanol occurs at room temperature and atmospheric pressure, affording in modest yields, the anticipated carbamate ester ($R_2NCOOCH_3$) and the unexpected oxamate ($R_2NCOCOOCH_3$), the latter arising by a novel double carbonylation reaction. (Ureas occurred as by-products in several cases). Although overnight conversion of the amine was good, the selectivity to the oxamate products was variable. The selectivity could be altered considerably by varying the ratio of CO/O_2 gas, the amounts controlled by a flowmeter. This sensitivity to the gas flow ratio was determined for dicyclohexylamine, and the results are listed below in Table 2.4.

TABLE 2.4

Variation of CO/O_2 Ratio for the Carbonylation of $(C_6H_{11})_2NH$

CO/O_2 Ratio	% Conversion Amine (GC)	% Yield (GC) R_2NCOOR'	% Yield (GC) $R_2NCOCOOR'$
5/1	64	5.8	16.0
1/2	70	2.1	25
1/3	67	10.7	7.4
1/4	80	20.0	6.4
1/5	61	7.3	3.7
1/8	nil	nil	nil

A variety of cyclic and acyclic secondary aliphatic amines were carbonylated using a CO/O_2 ratio of 1/2, and the results are presented in Table 2.5, (Tars were obtained with secondary aromatic amines).

TABLE 2.5

Secondary Amine Carbonylation Data

Reference #	Amine	% Yield (GC) Carbamate Ester	% Yield (GC) Oxamate
3.4.1	$(C_6H_{11})_2NH$	2.0	25.0
3.4.2	$(i\text{-}C_3H_7)_2NH$	12.4	2.4
3.4.3	$(C_6H_{11})NH(CH_3)$	11.6	4.3
3.4.4	$(C_2H_5)_2NH$	37.4	11.9
3.4.5	$(n\text{-}C_4H_9)_2NH$	13.0	—
3.4.6	piperidine	16.2	4.3
3.4.7	3,5-dimethyl-piperidine	37.5	1.9

Methanol was the only alcohol which afforded carbonylation products with tars resulting in the case of higher alcohols. Although the yields for this reaction are low to modest, this system is important in that it provides an example of catalytic double carbonylation. The precedents for double carbonylation are extremely limited, an example being the double carbonylation of benzyl halides using a cobalt carbonyl catalyzed phase transfer technique (48). This process appears to involve an insertion of carbon monoxide into a benzyl-cobalt bond, enolization and insertion of the second molecule of carbon monoxide to give arylpyruvic acids (49, 50):

$$ArCH_2X + Co(CO)_4^- \longrightarrow ArCH_2 - Co(CO)_4 \underset{CO}{\rightleftharpoons} ArCH_2CO - Co(CO)_4$$

$$\rightleftharpoons ArCH = CCo(CO)_4 \quad (OH) \xrightarrow{CO} ArCH = C(CO) - Co(CO)_4 \quad (OH)$$

$$\longrightarrow ArCH_2COCO - Co(CO)_4 \xrightarrow{OH^-} ArCH_2COCOOH$$

Fenton (51) found that oxalic acid derivatives could be obtained in good yields via a double carbonylation:

$$2CO + 2ROH + 1/2\ O_2 \xrightarrow[PdCl_2/CuCl_2]{125°C;\ 53\ Bar} RO_2CCO_2R + H_2O$$

Oxidative carbonylation occurred in the presence of alcohol and dehydrating agents using a palladium redox system. Interestingly the dehydrating agent was necessary in order to suppress CO_2 formation, (otherwise no oxalates were produced). This reaction required up to 67 Bar CO pressure and a temperature of 125°C.

A number of years ago, Tsuji showed that primary amines can be carbonylated to form disubstituted ureas and oxamides (RNHCOCONHR) with the co-evolution of hydrogen (52). This system simply used $PdCl_2$ and the substrates in benzene at 180° and under 100 Bar of CO pressure to afford the products.

Recently, Yamamoto's group reported that the organopalladium complexes, (trans-$PdR(X)(PMePh_2)_2$, react with CO, organic halides, and

secondary amines to give α-keto amides catalytically under fairly mild conditions (10 Bar CO, 100°C) (53, 54, 55, 56).

The infrared spectra of the carbamate and oxamic acid esters displayed strong carbonyl stretching bands in the region of 1750-1650 cm^{-1}. These were assigned by comparison with literature values (58). The carbamate ester carbonyl stretching absorption occurred at 1710 cm^{-1}. The oxamate -COOR carbonyl band occurred at 1740 cm^{-1}, and the oxamate $-CONR_2$ carbonyl stretch was at about 1660 cm^{-1}. The carbamate esters showed molecular ion peaks in the mass spectra followed by the loss of alkoxy and then carbonyl moieties. For the oxamates, mass spectral data clearly showed the molecular ion peaks followed by loss of ($COOCH_3$), and then expulsion of a second carbonyl group. The NMR spectra were also found to be in accord with the assigned structures, with the products exhibiting the characteristic $COOCH_3$ resonance at about 3.6 ppm.

In 1985, Yamamoto's group published results of a mechanistic investigation of the double carbonylation of aryl halides to α-keto amides catalyzed by organopalladium compounds (57). This mechanism consisted of three elementary steps: 1) oxidative addition of the organic halides to zerovalent palladium species; 2) CO insertion into the Pd-C bond to give an acylpalladium complex, and then 3) attack of CO and amine to produce the α-keto amide. For step 3, two possible reaction pathways exist:

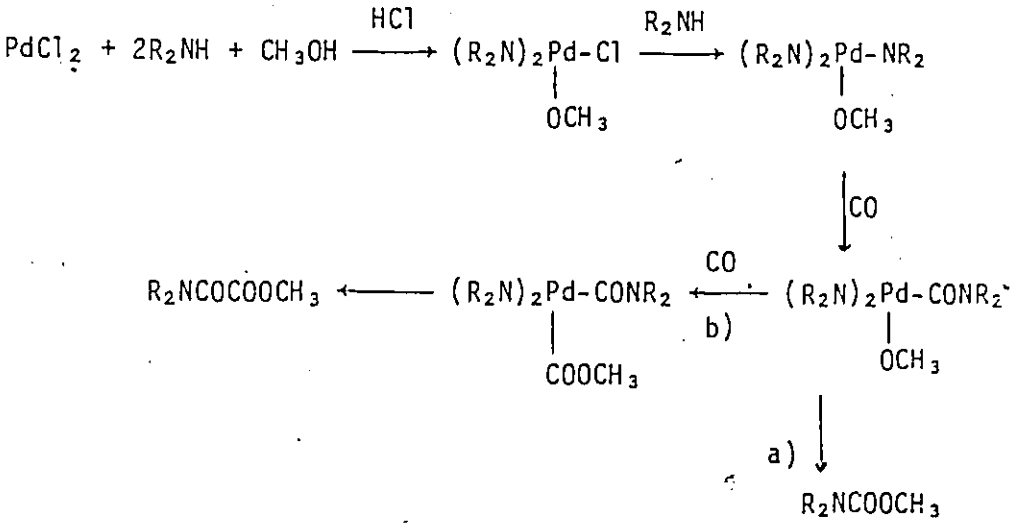
a) $$RCOPdL_n + CO + R_2NH \longrightarrow \begin{array}{c} RCOPdLn \\ | \\ CO \\ | \\ NR_2 \end{array} \longrightarrow RCOCONR_2$$

b) $RCOPdL_n + CO \longrightarrow RCOCOPdL_n \xrightarrow{NR_2H} RCOCONR_2$

Essentially path a) involves the intermediacy of a carbamoyl compound, and b) involves a consecutive CO insertion to give an alkyl glyoxyl intermediate. Yamamoto suggested that path a) was correct. This conclusion is in line with other amine carbonylation mechanisms - many of which have carbamoyl intermediates (39). Based on this work, the following mechanism is proposed for the secondary amine carbonylation described in this chapter:

FIGURE 2.2

Proposed Mechanism for
Secondary Amine Carbonylation



This mechanism involves initial coordination of the alkoxy and amine moieties by palladium, followed by CO coordination and insertion

to give the carbamoyl intermediate. At this point, path a) leads to a simple elimination affording carbamate ester. Path b) involves another CO attack and insertion into the Pd-O bond. This is then followed by elimination to afford the oxamate.

This mechanism is in accord with observed sensitivity of product yield to the CO/O_2 ratio. As Table 2.4 indicates, with decreasing CO/O_2 ratios the relative yield of oxamate to carbamate also decreases - presumably there is not enough CO present then to drive the reaction via path b), and hence most of the product is simply carbamate.

To summarize, this palladium-based carbonylation of secondary amines affords low to modest yields of carbamate esters and oxamates under very mild conditions. This reaction is important in several respects. It offers a new entry into the rarely-achieved multiple carbonylation reaction. Secondly, this process is much milder than any previously reported homogeneously-catalyzed double carbonylation. Finally, it illustrates the sensitivity of the palladium/copper catalyst system to the CO/O_2 ratio. This last fact has a substantial effect upon the olefin hydroesterification reaction (section 2.4).

2.4 Hydroesterification of 1-Decene: Induced Product Isomerization and CO_2 Suppression

Esters of carboxylic acids are chemicals of considerable industrial importance. They have large-scale usage as solvents, plasticizers and as monomers for producing important polymeric substances. Esters also have myriad specialty functions and uses ranging from defoliants to sex

hormones (59). Accordingly, there is a great deal of interest in developing improved methods of synthesis for these compounds. Typically, the hydroesterification of olefins requires high temperatures and pressures, the reaction is not highly regioselective, and esters are formed in variable yields. A typical example is shown below (60):

$$RCH=CH_2 + CO + CH_3OH \xrightarrow[\text{CO, pyridine, } 160^\circ, 160 \text{ Bar}]{Co_2(CO)_8 \text{ or CO salt}} \underset{\text{and}}{RCH_2CH_2COOCH_3} \quad RCH(CH_3)COOCH_3 \quad 75 - 95\ \%$$

The 1983 report (30) by Despeyroux and Alper of an exceedingly mild, high yield, regiospecific hydroesterification of olefins represented a significant advance in the field. Following the discovery of the sensitivity of the palladium/copper catalyst system to the CO/O_2 ratio described in Chapter 2.3, it was decided to apply this technique to the olefin hydroesterification reaction. The general reaction is described below:

$$\text{1-decene} + CH_3OH + \text{variable } CO/O_2 \xrightarrow[\text{Room Temperature, 1 Bar}]{PdCl_2/CuCl_2/HCl} RCH_2CH_2COOCH_3 + RCH(CH_3)COOCH_3$$

Reaction of 1-decene with methanol, carbon monoxide and oxygen at room

temperature and atmospheric pressure was found to give high yields of ester, but with linear/branched product ratios depending upon the CO/O_2 ratio. These data are summarized below in Table 2.6:

TABLE 2.6

Isomerization Reactions for the Hydroesterification of 1-Decene

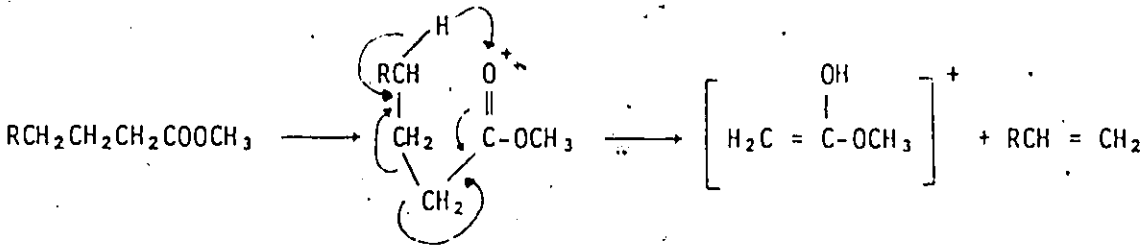
CO/O_2 Ratio	Conversion to ester	Ratio: Branched Ester / Linear Ester
20/1	92 %	8.3/1
8/1	80 %	9.0/1
1/1	93 %	4.7/1
1/2	77 %	1.5/1
1/8	30 %	1.6/1

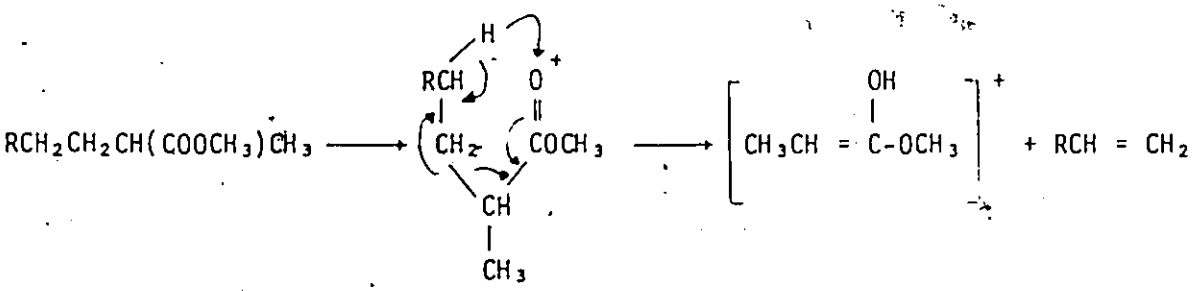
High CO/O_2 ratios were found to favour a high selectivity to branched products. Decreasing the CO/O_2 ratio increased the relative selectivity to the linear ester. (Small amounts of internal esters were also detected). A CO/O_2 ratio of 1/2 afforded a branched/linear ratio of 1.5/1.0. This seemed to be a limiting value, for the use of even lower CO/O_2 ratios could not increase the proportion of the linear ester - moreover by-product formation increased dramtically at low (cf. 1/8 : CO/O_2) ratios.

The products of these reactions were easily characterized by spectral

methods. The infrared spectra displayed intense ester carbonyl stretching bands at 1730 cm^{-1}. A singlet resonance at approximately δ 3.6 was observed in all NMR spectra, and was due to the methyl protons of the carbomethoxy group. The isomers of methyl undecanoate were best identified by gas chromatography-mass spectrometry analysis. Each isomer had the same molecular ion, however the fragmentation patterns were distinctly different.

The base peak in the mass spectrum of esters of saturated carboxylic acids in the C_6 - C_{26} range arises from β-cleavage, with transfer of a γ-hydrogen resulting in the formation of ions as shown below:





This is known as the McLafferty rearrangement. Thus different isomers of the same species will produce different base peak fragments, therefore allowing the degree of branching to be determined.

For the methyl undecanoate isomers produced in the 1-decene hydroesterification, the linear isomer $C_8H_{17}CH_2CH_2COOCH_3$ fragmented to afford the molecular ion at m/e 200, and a base peak at m/e 74 due to

$[H_2C = C(OH)OCH_3]^+$. The branched isomer $C_7H_{15}CH_2CHCH_3$ (COOCH$_3$) also resulted in the formation of a molecular ion at m/e 200, however the base peak occurred at m/e 88 due to $[CH_3\text{-}CH = C(OH)OCH_3]^+$.

The olefin hydroesterification reaction was found to have a CO_2 by-production problem similar to that described for the hydroesterification of aromatic amines. Efforts to suppress CO_2 formation in the olefin hydroesterification reaction are summarized in Table 2.7.

TABLE 2.7

CO_2 Suppression Data for the Hydroesterification of 1-Decene

CO/O_2 Ratio	Sieves	CO_2 production (mmol) per (mmols) ester produced
1/2	none	2.8/1
8/1	none	1.3/1
1/2	3Å	9.2/1
8/1	3Å	1.5/1
8/1	mordenite	3.4/1
8/1	mordenite/overnight	1.5/1

The use of zeolites was indicated by their successful utilization as CO_2 suppressants in (Chapter 2.1). As Table 2.7 indicates, 3Å molecular sieves and acid-impregnated mordenite were screened and found to have no positive impact on CO_2 formation.

For example, addition of mordenite to the reaction almost triples the amount of CO_2 produced when compared with reaction in the absence

of the zeolite. However, pre-drying of the reaction mixture overnight with mordenite resulted in 1.5 moles CO_2/mole ester produced. Unfortunately in this example, the conversion of olefin to ester dropped from the usual level of approximately 90 % to only 24 %. Clearly, therefore, there exists a trade-off between CO_2 suppression and olefin conversion when mordenite is added to the reaction.

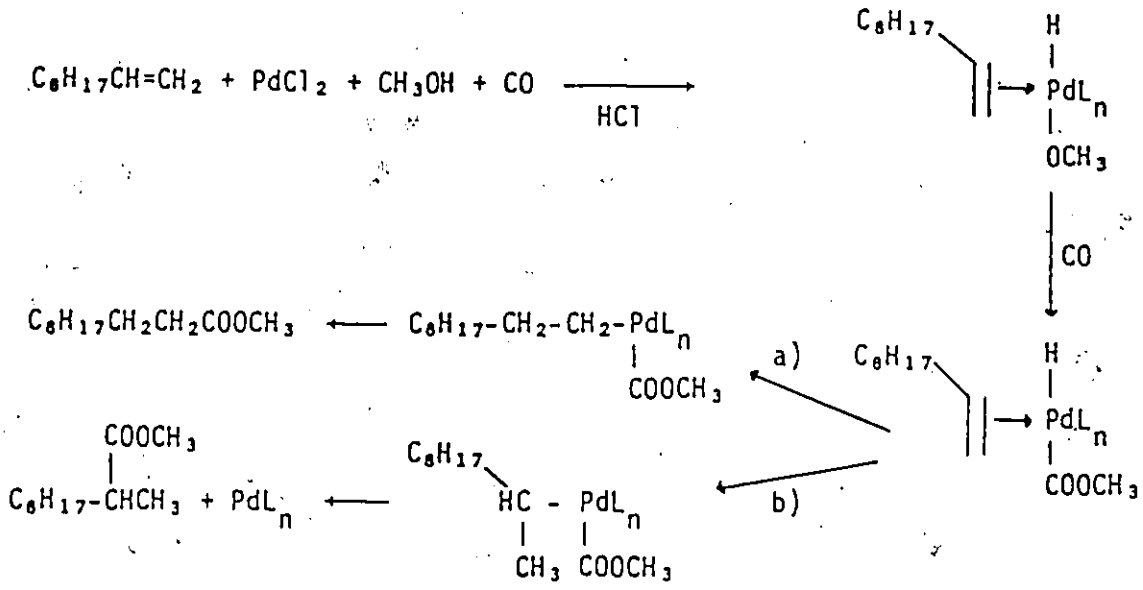
It should be noted, however, that the use of acid-impregnated mordenite was the first example of this olefin hydroesterification reaction working without the addition of hydrochloric acid. This represents an interesting observation since the use of corrosive mineral acids is unattractive from an industrial viewpoint. Clearly, zeolites influence this reaction, and although the types screened were found to have no positive impact on CO_2 formation, a study of the effect of other zeolites on this reaction would be useful.

An interesting consequence of altering the CO/O_2 ratio in order to effect an alteration in the regioselectivity of the reaction, was the suppression of CO_2 production. These data are summarized in Table 2.7.

In the absence of zeolites, a high CO/O_2 ratio suppressed CO_2 formation. For example, a 1/2 CO/O_2 ratio resulted in the formation of 2.8 moles CO_2 per mole ester. Altering the CO/O_2 ratio to 8/1 reduced CO_2 levels by more than 50 %, causing the formation of 1.3 moles CO_2 per mole ester. These observations are of relevance to the commercialization of this process. The hydroesterification of olefins to esters may proceed via the following mechanism:

Figure 2.3

Proposed Mechanism for Olefin Hydroesterification



In this mechanism, 1-decene reacts with methanol, carbon monoxide, and palladium chloride to afford an olefin-alkoxy palladium complex. Carbon monoxide then inserts into the Pd-OCH_3 bond. (Bryndza's work showed that CO inserts more readily into Pt-O bonds than into Pt-C bonds (61)). At this point, the reaction proceeds via either path a) or path b). In path a), the π-bonded olefin rearranges to a linear σ-bonded alkyl group, which then undergoes reductive elimination to the linear ester. In path b), the π-bonded olefin rearranges to a branched σ-bonded alkyl group, and the ester arises by reductive elimination. The resultant palladium (0) complex then is reoxidized to palladium (II) by a Wacker-type system ($CuCl_2/O_2/HCl$). The hydrochloric acid is also useful at the beginning of the catalytic cycle to generate a palladium-hydride - this is a well-known use for hydrochloric acid.

As mentioned previously, the product distribution can be controlled by varying the CO/O_2 ratio - increasing the relative amount of CO favours path b) and increasing the relative amount of O_2 favours path a). However, this sensitivity is difficult to rationalize.

To summarize, it was demonstrated that alteration of the CO/O_2 gasflow ratios has a significant effect on the regioselectivity of this reaction, allowing a degree of control over the isomeric distribution of the products. Moreover, an interesting consequence of this manipulation of the CO/O_2 ratio is the suppression of CO_2 byproduction levels. While zeolites examined have a negligable influence on CO_2 levels, the acid-impregnated mordenite (clay) is an effective replacement for hydrochloric acid in this reaction.

2.5 Hydroesterification of Allenes

Acrylic acid esters are of large and growing importance, especially for use in the manufacture of emulsion paints and other coatings, in polymer emulsions for textile finishing, and in acrylic fibers. Industrially, in terms of tonnage produced, the most important acrylates are the ethyl, butyl, 2-ethylhexyl and methyl esters, with methyl methacrylate being by far the most valuable (59). Other functionalized acrylates have important applications as monomers for specialty products. For instance, methyl 2-methoxymethyl methacrylate is used as the monomer for the plastic in soft contact lenses. A number of routes are available to obtain acrylates - most of which require drastic conditions.

One of the most important routes to acrylates is by the oxidation

of olefins such as propylene or isobutene, followed by esterification (59):

$$CH_2{=}CHCH_3 \xrightarrow[400\,^\circ C,\ Mo\ oxides]{H_2O/O_2} CH_2{=}CHCHO \xrightarrow[300\,^\circ C]{O_2} CH_2{=}CHCO_2H \xrightarrow{ROH} CH_2{=}CHCOOR$$

Production of acrylates at such high temperatures is complicated by polymerization problems. Another reaction is known as the Union Oil synthesis (62):

$$PdCl_2 + C_2H_4 + H_2O + CO \xrightarrow[77\ Bar]{150\,^\circ C} CH_2{=}CHCO_2H + Pd(0) + 2HCl$$

The Pd(0) is recycled by a Wacker-type process and the acrylic acid reacts with alcohols to afford acrylates.

Methyl methacrylate is also obtained by the hydrocyanation of acetone (59). The carbonylation of allene and substituted allenes is currently a subject of intense investigation. This is due to the potential to obtain acrylates and functionalized acrylates directly by the hydroesterification of allenic substrates.

Allene hydroesterification reactions can give distinctly different results depending upon the metal catalysts used. For example, use of a nickel carbonyl complex plus methacrylic acid as co-catalyst at 140°C and 23-24 Bar afforded 62 % of methyl methacrylate (63), while the same compound is formed in 50 % yield with ruthenium carbonyl complexes at 140°C and 700 Bar (64).

The unsaturated ester is also formed (40 % yield) by reaction of

allene with carbon monoxide, under drastic conditions (200°C, 980 Bar) in the presence of $H_2PtCl_2/SnCl_2$, (65).

After development of the palladium-based olefin hydroesterification process by Alper and Despeyroux (30), it was of interest to determine whether this method could be applied to allene and substituted allenes in order to obtain methyl methacrylate and other acrylates under mild conditions.

The first experiment of this series was conducted by Dr. B. Despeyroux. In this reaction, treatment of allene with carbon monoxide, oxygen, palladium and copper(II) chloride, and hydrochloric acid in methanol afforded methyl 2-methoxymethyl methacrylate in 85 % yield:

$$CH_2=C=CH_2 + CH_3OH + CO \xrightarrow[(0°)C]{PdCl_2/CuCl_2/HCl/O_2} CH_2=C(CO_2CH_3)CH_2OCH_3$$

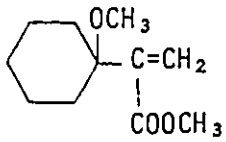
1 Bar Pressure

This reaction occurs in an ice bath and is complete in 8 - 10 hours. Methyl methacrylate is not an intermediate in this reaction, since treated methyl methacrylate was inert under identical reaction conditions as for allene.

The functionalized methacrylate obtained from this reaction had previously been synthesized in low yield by the hydroesterification of propargyl alcohol at 100°C and 97 Bar, using $PdCl_2$ and Pd on carbon as catalysts (66). This work was then extended to substituted allenes and the yields are summarized in the following table:

TABLE 2.8

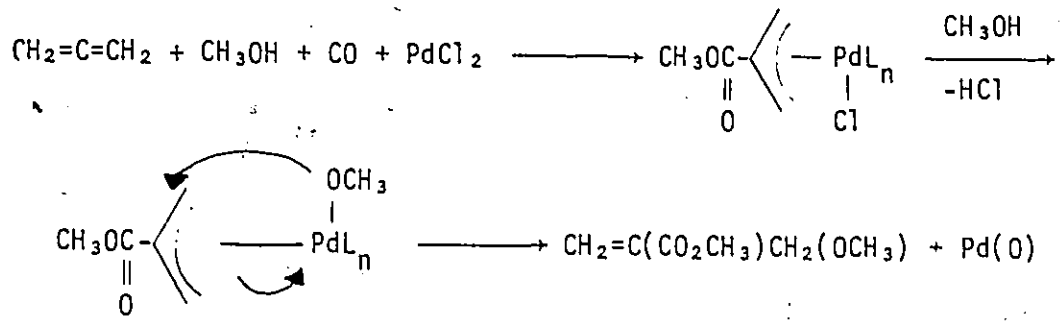
Hydroesterification of Allenes: Yields

Reference	Substrate	Products	Yields
3.6.1	Allene	$CH_2=C(CO_2CH_3)CH_2OCH_3$	85 %
3.6.2	3-Methyl-1,2-Butadiene	$(CH_3)_2C(OCH_3)C(COOCH_3)=CH_2$	19 %
		$(CH_3)_2CHC(COOCH_3)=CH_2$	12 %
3.6.3	Vinylidenecyclohexane		34 %
3.6.4	Undeca-1,2-diene	$CH_2=C(CO_2CH_3)CH(OCH_3)C_8H_{17}$	4 %
		$CH_3OCH_2C(CO_2CH_3)=CHC_8H_{17}$	6 %

The disubstituted allenes, 3-methyl-1,2-butadiene and vinylidenecyclohexane undergo hydroesterification in a manner similar to allene itself, affording methoxy unsaturated esters with the methoxy group attached to the most substituted terminal carbon of the allenic moiety. Although the product yields are modest (19-34 %), the reaction is a regiospecific one. In the case of the monosubstituted allene 1,2-undecadiene, however, two isomeric alkoxy-ester products were isolated in a low yield. The products of these reactions were characterized by spectroscopic techniques. Infrared spectra displayed an intense ester carbonyl band at 1720 cm^{-1} and a carbon-carbon double bond absorption at 1640 cm^{-1}. The mass spectra showed molecular ion peaks, and the NMR spectra obtained were in agreement with the assigned structures (see experimental section).

Figure 2.4

Proposed Mechanism for
Allene Hydroesterification



To conclude, this palladium-based process is useful for the carbonylation of allenes to obtain functionalized acrylates in low to excellent yields, under conditions of unprecedented mildness.

2.6 Hydrocarboxylation of Alkynes

In 1983 Alper and coworkers (32) described the facile regioselective hydroesterification of internal and terminal alkynes, to give mono and diesters respectively. This prompted an investigation into the possibility of hydrocarboxylating alkynes under similar conditions. The reaction is described as follows:

$$RC{\equiv}CR' + CO + H_2O + O_2 \xrightarrow[THF/HCl]{PdCl_2/CuCl_2} \underset{H\ \ COOH}{RC=CR'}$$

$$RC{\equiv}CH + CO + H_2O + O_2 \xrightarrow[THF/HCl]{PdCl_2/CuCl_2} RC(COOH)=CH(COOH)$$

Terminal alkynes react with carbon monoxide and water for two days at room temperature and atmospheric pressure, to afford 1,2-diacids in moderate yields. Cis-diacids were the major or only products formed. Overnight reactions of internal alkynes at 65° utilizing the same catalysts afforded low to moderate yields of monoesters.

A number of terminal and internal alkynes were screened and the reaction yields are summarized in Table 2.9.

TABLE 2.9

Alkyne Hydrocarboxylation Yields

Reference	Alkyne	Products	Ratio	Cis/Trans Ratio
3.7.1	1-octyne	$C_6H_{13}C(COOH)=C(H)COOH$	1/1	39
3.7.2	1-hexyne	$C_4H_9C(COOH)=C(H)COOH$	all cis	29
3.7.3	3-methyl-1-pentyne	$C_2H_5C(H)CH_3$-$C(COOH)=C(H)COOH$	3/1	20
3.7.4	4-phenyl-1-butyne	$PhCH_2CH_2C(COOH)=C(H)COOH$	all cis	18
3.7.5	2-heptyne	C_4H_9-$C(H)=C(COOH)CH_3$		6
3.7.6	2-nonyne	$C_6H_{13}C(H)=C(COOH)CH_3$		32

Infrared spectra of the products displayed a strong carboxylic acid carbonyl absorption around 1710-1700 cm^{-1}, as well as a medium strength

carbon-carbon double bond stretching band near 1640 cm^{-1}. The mass spectra gave the expected values for the molecular ion. The cis/trans isomers produced by the terminal alkyne hydrocarboxylation reaction could be distinguished by the different chemical shift of the vinylic hydrogens in the proton NMR spectrum. For example the signal for the cis vinylic hydrogen occurs at approximately 5.60 ppm, while that for the trans vinylic hydrogen is near 6.0 ppm, thus allowing for a clear distinction between the isomers, and a calculation of the relative quantities by integration.

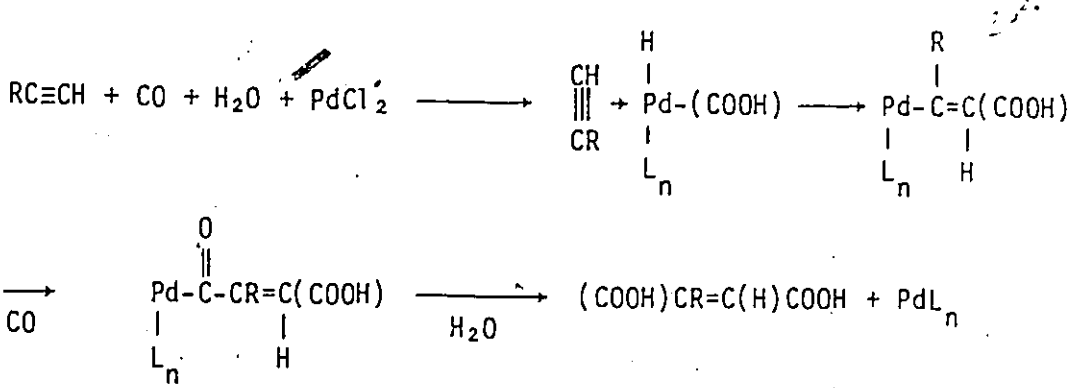
In the case of the products of the hydrocarboxylation of internal alkynes, i) $RCH_2CH=C(COOH)CH_3$ and ii) $RCH_2C(COOH)=CHCH_3$, these products could be distinguished by the multiplicity of the vinylic hydrogen signal in the NMR. The vinylic hydrogen of type i) gives a triplet signal, while that of type ii) shows a quartet for the same proton.

In terms of mechanism, this hydrocarboxylation could proceed as described in Figure 2.5:

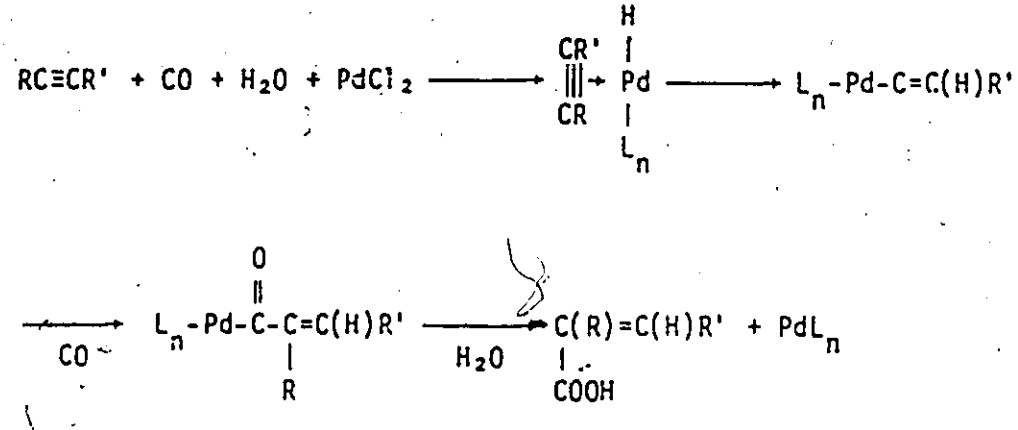
Figure 2.5

Proposed Alkyne Hydrocarboxylation Mechanism

i) Dicarbonylation of terminal alkynes



ii) Monocarbonylation of internal alkynes



This mechanism proposes separate pathways for the mono- and di-carboxylation reactions, and is similar to other proposed mono- and bis-carbonylation cycles (67).

Although the yields of this reaction are low to moderate, this methodology has several attractive features when compared to the primary and patent literature. Many of the literature processes require drastic conditions. For instance, $Ni(CO)_4$ catalyzes the conversion of acetylene to acrylic acid in 90 % yield at 200° and 40-50 Bar pressure (68). Many processes afford monoacids with a variable regioselectivity. Dicarboxylation of alkynes also requires vigorous conditions, e.g. $Co_2(CO)_8$ catalyzed dicarboxylation requires 110°C and 180 bar pressure (3).

The process described in this chapter affects carbonylation under much milder than normal conditions. Moreover, only diacids are obtained from the carbonylation of terminal alkynes with good selectivity to the cis isomers. In addition, the formation of only monoacids from internal alkynes is useful. The sensitivity of the reaction pathway (mono- versus di-carboxylation) to the position of the acetylenic bond is quite novel.

The only other comparable situation in the literature is the 1983 paper by Alper and coworkers (32), which described mono- and di-esterification of alkynes and was sensitive to the position of the acetylenic bond. The mechanism depicted in Figure 2.5 represents an attempt to rationalize this situation. It may be possible that when the terminal alkyne moiety rearranges to a σ-bonded ligand, a carboxyl group migrates to the terminal end of this ligand, followed by CO insertion into the Pd-C bond, and then reductive elimination to the diacid (see Figure 2.5). In the case of internal alkynes, following the alkyne rearrangement to a σ-bonded moiety, the carboxyl group may be inhibited from migrating by steric factors, resulting in a monoacid as the product.

CHAPTER 3

Experimental Data for Carbonylation Reactions

3.1 General Comments

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected. Infrared spectra were obtained using a Perkin-Elmer 783 spectrometer, and were calibrated with a polystyrene standard. NMR (^1H, ^{13}C) spectra were recorded on Varian EM360A, T60, FT80 or XL-300 spectrometers. Gas chromatography was carried out using Varian Vista 6000 and Varian 3400 gas chromatographs, both equipped with flame ionization detectors. Mass spectra were recorded with a VG Micromass 7070E spectrometer.

Organic chemicals were purchased from Aldrich Chemical Co., Wiley Organics Ltd., Farchan Co., and Fairfield Chemical Co., or were prepared by literature methods. Palladium (II) chloride was obtained from Johnson, Matthey Co., Aesar Co., and Strem Chemical Co. Copper (II) chloride was purchased from Aldrich Chemical Co., and Alfa Products Ltd. Molecular sieves were obtained from Strem Chemical Co., and British Petroleum. Solvents were purified and dried by standard methods. Carbon monoxide and oxygen were obtained from Air Products Co.

3.2 Hydroesterification of Primary Aromatic Amines

General Procedure

The following general procedure was used: carbon monoxide and oxygen were bubbled through methanol (60 ml) to which was added in sequence $PdCl_2$ (0.18 gm, 1.0 mmol), hydrochloric acid (0.10 ml), $CuCl_2$ (0.27 gm, 2.0 mmol), and then the amine (10.0 mmol) allowing a few minutes of induction period between each addition. The solution was stirred overnight at room temperature and atmospheric pressure. The mixture was then filtered, and the filtrate was evaporated on a rotary evaporator. The residue was extracted with acetone methylene chloride or ether, filtered and concentrated to afford the carbamate ester. Any further purification which was required, was effected by thin-layer and column chromatography on silica gel, using a mixture of hexane and ether as eluents. In those cases where CO_2 evolution was determined, a saturated $Ba(OH)_2$ solution was used as an exit bubbler to trap the evolved gas.

3.2.1 $p\text{-}CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine afforded $p\text{-}CH_3C_6H_4NHCOOCH_3$ in 68 % yield. M.Pt = 84-85°. IR $\nu_{CO}(CDCl_3)$ 1700(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s;1H,NH), 2.32(s;3H,C_6H_4-$\underline{CH_3}$), 3.76(s;3H,OCH_3), 7.10(m;4H,C_6H_4); ^{13}C NMR ($CDCl_3$) δ 20.7(CH_3), 52.3(OCH_3), 129.54, 129.63, 129.68, 129.78 (aromatic carbons), 154.3(CO); MS m/e 165$[M]^+$, 134$[M\text{-}OCH_3]^+$, 106$[M\text{-}COOCH_3]^+$. CO_2 evolution per mole amine converted: 1.4/1.0.

3.2.2 $C_6H_5NHCOOCH_3$

Carbonylation of aniline afforded $C_6H_5NHCOOCH_3$ in 99 % yield. M.Pt = 33-34°. IR ν_{CO} ($CDCl_3$) 1710(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12(s;1H,NH), 3.76(s;3H,OCH_3), 7.27(m;5H,C_6H_5); MS m/e 151$[M]^+$, 119$[M-OCH_3]^+$, 92$[M-COOCH_3]^+$.

3.2.3 $p\text{-}ClC_6H_4NHCOOCH_3$

Carbonylation of p-chloroaniline afforded $p\text{-}ClC_6H_4NHCOOCH_3$ in 61 % yield. M.Pt. = 120-122°. IR ν_{CO} ($CDCl_3$) 1720(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26(s;1H,NH), 3.74(s;3H,OCH_3), 7.31(s;4H,C_6H_4); MS m/e 185,187$[M]^+$, 157,159$[M-CO]^+$, 126,128$[M-COOCH_3]^+$.

3.2.4 $m\text{-}CH_3COC_6H_4NHCOOCH_3$

Carbonylation of 3-aminoacetophenone afforded $m\text{-}CH_3COC_6H_4NHCOOCH_3$ in 99 % yield. M.Pt. = 55-57°. IR ν_{CO} ($CDCl_3$) 1710(s) cm^{-1}; ^1H NMR δ 1.24(s;1H,NH), 2.50(s;3H,CH_3CO), 3.71(s;3H,CO_2CH_3), 6.80(m;4H,C_6H_4); MS m/e 193$[M]^+$, 162$[M-OCH_3]^+$, 134$[M-COOCH_3]^+$.

3.2.5 $2,5\text{-}(CH_3)_2C_6H_3NHCOOCH_3$

Carbonylation of 2,5-dimethylaniline gave $2,5\text{-}(CH_3)_2C_6H_3NHCOOCH_3$ in 76 % yield. M.Pt. = 58-60°. IR ν_{CO} ($CDCl_3$) 1720(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13(s;1H,NH), 2.15(s;3H,CH_3), 2.31(s;3H,CH_3), 3.75(s;3H,OCH_3),

6.94(m;3H,C_6H_3); MS m/e 179[M]$^+$, 148[M-OCH_3]$^+$, 120[M-$COOCH_3$]$^+$.

3.2.6 $2,6-(CH_3)_2C_6H_3NHCOOCH_3$

Carbonylation of 2,6-dimethylaniline afforded $2,6-(CH_3)_2C_6H_3NHCOOCH_3$ in 16 % yield. M.Pt = 63-65°. IR ν_{CO} ($CDCl_3$) 1725(ms) cm^{-1}; ^{1}H NMR ($CDCl_3$ δ 1.28(s;1H,NH), 2.18(s;3H,CH_3), 3.68(s;3H,OCH_3), 6.98(m;3H,C_6H_3); MS m/e 179[M]$^+$, 148[M-OCH_3]$^+$, 120[M-$COOCH_3$]$^+$.

3.2.7 $3,5-(CH_3)_2C_6H_3NHCOOCH_3$

Carbonylation of 3,5-dimethyaniline gave $3,5-(CH_3)_2C_6H_3NHCOOCH_3$ in 23 % yield. M.Pt. = 113-115°. IR ν_{CO} ($CDCl_3$) 1695(ms) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.02(s;1H,NH), 2.25(s;3H,CH_3), 3.70(s;3H,OCH_3), 6.93(m;3H,C_6H_3); MS m/e 179[M]$^+$, 148[M-OCH_3]$^+$, 120[M-$COOCH_3$]$^+$.

3.2.8 $p-CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine when carried as described out in (3.2) except in the absence of oxygen afforded $p-CH_3C_6H_4NHCOOCH_3$ in 34 % yield.

3.2.9 $p-CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine when carried out as described in (3.2) except for the use of $Pd(OAc)_2$ and $Cu(OAc)_2$ as catalysts gave $p-CH_3C_6H_4$

$NHCOOCH_3$ in 83 % yield. (The palladium/copper/substrate ratio was the same as that described in (3.2)).

3.2.10 $p\text{-}CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine when carried out as described in (3.2) with 0.1 ml of glacial acetic acid used instead of hydrochloric acid, afforded $p\text{-}CH_3C_6H_4NHCOOCH_3$ in 21 % yield. CO_2 evolution per mole amine converted : 1.5/1.0.

3.2.11 $p\text{-}CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine, effected using $[Pd(CH_3CN)_4]^{2+}\text{-}2[BF_4]^-$ instead of $PdCl_2$ (no acid) afforded $p\text{-}CH_3C_6H_4NHCOOCH_3$ in 13 % yield. (The catalyst/substrate ratio was the same as that described in (3.2)).

3.2.12 $p\text{-}CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine when carried out as described in (3.2) with added molecular sieves (3Å) afforded the carbamate ester in 71 % yield. CO_2 evolution per mole amine converted : 0.008/1.0 .

3.2.13 $p\text{-}CH_3C_6H_4NHCOOCH_3$

Carbonylation of p-toluidine when carried out as described in (3.2) but using 0.2 ml of HAC and added molecular sieves (3Å), resulted in the formation of $p\text{-}CH_3C_6H_4NHCOOCH_3$ in 88 % yield. CO_2 evolution per mole amine converted : 0.03/1.0 .

3.2.14 $p\text{-}CH_3C_6H_4NHCOOC_2H_5$

When p-toluidine was reacted with ethanol instead of methanol, using the procedure described in (3.2), $p\text{-}CH_3C_6H_4NHCOOC_2H_5$ was obtained in 51 % yield. M.Pt. = 74-76°. IR ν_{CO} ($CDCl_3$) 1700(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26(s;1H,NH), 2.12(t;3H,CH_3), 2.23(s;3H,CH_3), 3.98(q;2H,OCH_2R), 7.08(m;4H,C_6H_4); MS m/e 179$[M]^+$, 134$[M\text{-}OC_2H_5]^+$, 106$[M\text{-}COOC_2H_5]^+$.

3.2.15 $C_6H_5NHCOOC_2H_5$

Carbonylation of aniline in ethanol was carried out as described in (3.2), giving $C_6H_5NHCOOC_2H_5$ in 64 % yield. M.Pt. = 42-44°. IR ν_{CO} ($CDCl_3$) 1705(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27(t;3H,CH_3), 1.39(s;1H,NH), 4.17(q;2H,$\underline{OCH_2}CH_3$), 7.24(m;5H,C_6H_5); MS m/e 165$[M]^+$, 120$[M\text{-}OC_2H_5]^+$, 92$[M\text{-}COOC_2H_5]^+$.

3.3 Hydroesterification of Primary Aliphatic Amines

General Procedure

The following procedure was used: carbon monoxide and oxygen were bubbled through methanol (60 ml) (which contained 3Å molecular sieves) in a round bottom flask equipped with gas inlets, a condenser and a saturated $Ba(OH)_2$ exit bubbler to trap CO_2. To this solution was added in sequence $PdCl_2$ (0.18 gm, 1.0 mmol), glacial acetic acid (0.20 ml), $CuCl_2$ (0.27 gm, 2.0 mmol), and finally 10.0 mmol of the amine allowing

several minutes between each addition. The reaction was stirred overnight at room temperature and atmospheric pressure. The mixture was then filtered, and the filtrate was concentrated on a rotary evaporator. The residue was extracted into acetone or ether, filtered, and concentration of the filtrate afforded the carbamate ester. Any further purification, if necessary, was effected by filtration through Celite using ether, evaporation, and extraction of the residue with cold hexane. Carbon dioxide production was monitored by the use of a saturated $Ba(OH)_2$ trap as the exit bubbler.

3.3.1 $C_{12}H_{25}NHCOOCH_3$

Carbonylation of dodecylamine afforded $C_{12}H_{25}NHCOOCH_3$ in 99 % yield. M.Pt. = 40-41°. IR ν_{CO} ($CDCl_3$) 1715(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87(s;1H,NH), 1.27(m;23H,$C_{11}H_{23}$), 3.16(m;2H,$R\underline{CH_2}N$), 3.61(s;3H,OCH_3); MS m/e 243$[M]^+$, 212$[M-OCH_3]^+$, 184$[M-COOCH_3]^+$. CO_2 evolution per mole amine converted : 0.24/1.0.

3.3.2 $C_{12}H_{25}NHCOOC_2H_5$

Carbonylation of dodecylamine using ethanol as the alcohol gave $C_{12}H_{25}NHCOOC_2H_5$ in 99 % yield. IR ν_{CO} ($CDCl_3$) 1710(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s;1H,NH), 1.28(m;26H,$C_{11}H_{23}$ and $\underline{CH_3}CH_2O$), 3.11(m:2H,$R\underline{CH_2}N$), 4.07(q;2H,$CH_3\underline{CH_2}O$-); MS m/e 257$[M]^+$. CO_2 evolution per mole amine converted : 0.20/1.0.

3.3.3 $C_{12}H_{25}NHCOO(C_4H_9\text{-}t)$

Carbonylation of dodecylamine using t-butanol as the alcohol afforded $C_{12}H_{25}NHCOO(C_4H_9\text{-}t)$ in 81 % yield. IR ν_{CO} ($CDCl_3$) 1710(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (s;1H,NH), 1.27(m;23H,$C_{11}H_{23}$), 1.44(s;9H,-O(t-Bu)), 3.01(m;2H,RCH_2N); MS m/e 229$[M-(t\text{-}Bu)]^+$. CO_2 evolution per mole amine converted : 1.0/1.0.

3.3.4 $(t\text{-}C_4H_9)NHCOOCH_3$

Carbonylation of t-butylamine afforded $(t\text{-}C_4H_9)NHCOOCH_3$ as an oil in 99 % yield. IR ν_{CO} ($CDCl_3$) 1720(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84(s;1H,NH), 1.32(s;9H,(t-Bu)), 3.58(s;3H,OCH_3); MS m/e 116$[M-CH_3]^+$; ^{13}C NMR ($CDCl_3$) δ 28.7(methyls of t-butyl), 49.5(OCH_3), 74.8($R_3\underline{C}$-N), 169.7(CO). CO_2 evolution per mole amine converted : 1.4/1.0.

3.3.5 $(t\text{-}C_4H_9)NHCOO(C_4H_9\text{-}t)$

Carbonylation of t-butylamine carried out as described in (3.2) with t-butanol as the alcohol afforded $(t\text{-}C_4H_9)NHCOO(C_4H_9\text{-}t)$ in 40 % yield. M.Pt. = 35-36°. IR ν_{CO} ($CDCl_3$) 1712(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28(s;1H,NH), 1.30(s;9H,(t-Bu)), 1.42(s,9H,-O(t-Bu)); MS m/e 158$[M-CH_3]^+$. CO_2 evolution per mole amine converted : 0.88/1.0.

3.3.6 $n\text{-}C_4H_9NHCOOCH_3$

Carbonylation of n-butylamine in methanol gve $n\text{-}C_4H_9NHCOOCH_3$ as an oil in 96 % yield. IR ν_{CO} ($CDCl_3$) 1710(vs) cm^{-1}; ^1H NMR ($CDCl_3$ δ 0.51(s;1H,NH), 0.92(t;3H,CH_3), 1.43(m;4H,R-CH_2CH_2-), 3.11(m;2H,R$\underline{CH_2}$N), 3.62(s;3H,OCH_3); MS m/e 131$[M]^+$. CO_2 evolution per mole amine converted: 0.23/1.0.

3.3.7 $n\text{-}C_4H_9NHCOO(C_4H_9\text{-}t)$

Carbonylation of n-butylamine using t-butanol as the alcohol afforded the oil $n\text{-}C_4H_9NHCOO(C_4H_9\text{-}t)$, in 66 % yield. IR ν_{CO} 1705(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92(s;1H,NH), 1.48(m;16H,(C_4H_9-t) and (CH_3-$(CH_2)_2$)), 3.14(m;2H,R$\underline{CH_2}$-N); ^{13}C NMR ($CDCl_3$) δ 13.7, 13.8, 19.9, 32.1 (n-butyl carbons), 28.4 (methyls of t-Butyl), 40.5(O-$\underline{C}(CH_3)_3$) ; MS m/e 173$[M]^+$. CO_2 evolution per mole amine converted : 0.23/1.0.

3.3.8 $n\text{-}C_3H_7NHCOOCH_3$

Carbonylation of n-propylamine afforded $n\text{-}C_3H_7NHCOOCH_3$ in 98 % yield. IR ν_{CO} ($CDCl_3$) 1715(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91(t;1H,NH), 1.52(m;5H,CH_3-CH_2), 3.09(d;2H,R$\underline{CH_2}$-N), 3.61(s;3H,OCH_3); MS m/e 117$[M]^+$. CO_2 evolution per mole amine converted : 0.68/1.0.

3.3.9 $C_{12}H_{25}NHCOOCH_3$

Repetition of experiment (3.3.1) in the absence of molecular sieves gave $C_{12}H_{25}NHCOOCH_3$ in 95 % yield. CO_2 evolution per mole amine converted : 0.23/1.0.

3.3.10 $C_{12}H_{25}NHCOOCH_3$

Repetition of experiment (3.3.1) in the absence of both molecular sieves and acid afforded $C_{12}H_{25}NHCOOCH_3$ in 99 % yield. CO_2 evolution per mole amine converted : 0.32/1.0.

3.3.11 $C_{12}H_{25}NHCOO(C_4H_9\text{-}t)$

Repetition of experiment (3.3.3) without molecular sieves gave $C_{12}H_{25}NHCOO(C_4H_9\text{-}t)$ in 71 % yield. The yield decreased to 64 % when both acid and molecular sieves were absent.

3.3.12 $C_{12}H_{25}NHCOOCH_3$

Carbonylation of dodecylamine was carried out as described in (3.3), except that 10 mmol t-butylperoxide was used as the reoxidant instead of oxygen. (The peroxide : amine ratio was 1:1). The carbamate ester, $C_{12}H_{25}NHCOOCH_3$, was obtained in 72 % yield.

3.4 Carbonylation of Secondary Amines

General Procedure

The following general procedure was used : methanol (60 ml) was placed into a round flask equipped with a condenser and a gas inlet. The gas flow was monitored with a flowmeter, to enable adjustments to be made to the CO/O_2 gas ratio. Carbon monoxide and oxygen were bubbled through the solution at a known rate and ratio. Then $PdCl_2$(0.090 gm, 0.51 mmol), hydrochloric acid (0.10 ml), and $CuCl_2$(0.135 gm, 1.0 mmol) were added in sequence, to form a greenish-brown solution. Finally, after an induction period of several minutes, 5.0 mmol of the substrate was added, and the reaction was run overnight at room temperature and atmospheric presure. The mixture was then filtered, concentrated by rotary evaporation, and extracted into acetone to afford the product. Two products were obtained from these reactions; one was a carbamate ester (R_2NCOOR') and the other was an oxamate ester ($R_2NCOCOOR'$). A by-product of these reactions was often urea (R_2NCONR_2). Product yields were sensitive to the CO/O_2 gas ratio. This ratio was optimized for dicyclohexylamine as the substrate, as shown in Table 2.4. Attempts to further purify the products by preparative gas chromatography failed, owing to the thermal sensitivity of the compounds.

3.4.1 (a) $(C_6H_{11})_2NCOOCH_3$ and (b) $(C_6H_{11})_2NCOCOOCH_3$

Carbonylation of dicyclohexylamine as described in (3.4) using a 1/2 : CO/O_2 ratio afforded:

(a) $(C_6H_{11})_2NCOOCH_3$ in 2 % yield. IR ν_{CO} ($CDCl_3$) 1710(s) cm^{-1}; ^1H NMR($CDCl_3$) δ 0.97-2.26(m;20H,methylene protons), 3.40(m;2H,two $R_2\underline{C}HN$),

3.87(s;3H,$CO_2\underline{CH_3}$); MS m/e 239[M]$^+$, 198[M-OCH_3]$^+$;

(b) $(C_6H_{11})_2NCOCOOCH_3$ in 25 % yield. IR ($CDCl_3$) ν_{COOR} 1745(s), ν_{CONR_2} 1650(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97-2.26(m;20H, methylene protons), 3.40(m;2H,two $R_2\underline{CH}N$), 3.87(s;3H,$CO_2\underline{CH_3}$); MS m/e 267[M]$^+$, 208[M-$COOCH_3$]$^+$, 180[M-$COCOOCH_3$]$^+$; ^{13}C NMR ($CDCl_3$) δ 157.8(CO).

3.4.2 (a) $(i\text{-}C_3H_7)_2NCOCOOCH_3$ and (b) $(i\text{-}C_3H_7)_2NCOOCH_3$

Carbonylation of diisopropylamine using a 1/2 : CO/O_2 ratio afforded: (a) $(i\text{-}C_3H_7)_2NCOOCH_3$ in 12 % yield. IR ($CDCl_3$) ν_{CO} 1710(ms) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50(d;12H,methyls of isopropyls), 3.36 (m;2H,two[$(CH_3)_2\ \underline{CH}]_2N$), 3.74(s;3H,$OCH_3$); MS m/e 159 [M]$^+$.
(b) $(i\text{-}C_3H_7)_2NCOCOOCH_3$ in 2 % yield. IR ($CDCl_3$) ν_{COOR} 1750(s), ν_{CONR_2} 1655(ms) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50(d;12H,methyls of isopropyls), 3.36(m;2H,two[$(CH_3)_2\underline{CH}]_2N$), 3.74(s;3H,$OCH_3$); MS m/e 187[M]$^+$, 128[M-$COOCH_3$]$^+$, 100[M-$COCOOCH_3$]$^+$.

3.4.3 (a) $C_6H_{11}N(CH_3)COOCH_3$ and (b) $C_6H_{11}N(CH_3)COCOOCH_3$

Carbonylation of N-methylcyclohexylamine using a 1/2 : CO/O_2 ratio afforded : (a) $C_6H_{11}N(CH_3)COOCH_3$ in 12 % yield. IR ν_{CO} ($CDCl_3$) 1710(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84-1.93(m;10H,C_6H_{10}), 2.68(s;3H,CH_3N), 3.19(m;1H,$R_2\underline{CH}N$), 3.61(s;3H,OCH_3); MS m/e 171[M]$^+$, 140[M-OCH_3]$^+$, 112[M-$COOCH_3$]$^+$; (b) $C_6H_{11}N(CH_3)COCOOCH_3$ in 4 % yield. IR ($CDCl_3$) ν_{COOR} 1740(ms), ν_{CONR_2} 1675(s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84-1.93(m;10H,C_6H_{10}), 2.68(s;3H,CH_3N), 3.19(m;1H,$R_2\underline{CH}N$), 3.61(s;3H,OCH_3); MS m/e 199[M]$^+$, 140[M-$COOCH_3$]$^+$, 112[M-$COCOOCH_3$]$^+$.

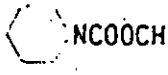
3.4.4 (a) $(C_2H_5)_2NCOOCH_3$ and (b) $(C_2H_5)_2NCOCOOCH_3$

Carbonylation of diethylamine using a 1/2 : CO/O_2 ratio afforded : (a) $Et_2NCOOCH_3$ in 37 % yield. IR ν_{CO} ($CDCl_3$) 1710(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48(t;6H,two methyls), 3.02(m;4H,two $\underline{RCH_2}N$), 3.50(s;3H,OCH_3); MS m/e 131$[M]^+$, 100$[M-OCH_3]^+$, 72$[M-COOCH_3]^+$.

(b) $Et_2NCOCOOCH_3$ in 12 % yield. IR ($CDCl_3$) ν_{COOR} 1710(ms), ν_{CONR_2} 1630(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48(t;6H,two methyls), 3.02(m;4H,two $\underline{RCH_2}N$), 3.50(s;3H,OCH_3); MS m/e 159$[M]^+$, 100$[M-COOCH_3]^+$, 72$[M-COCOOCH_3]^+$.

3.4.5 $(n\text{-}C_4H_9)_2NCOOCH_3$

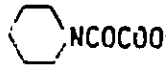
Carbonylation of di-n-butylamine using a 1/2 : CO/O_2 ratio gave $(n\text{-}C_4H_9)_2NCOOCH_3$ in 13 % yield. IR ν_{CO} ($CDCl_3$) 1680(ms) cm^{-1}; ^1H NMR($CDCl_3$) δ 1.00-2.12 (m;14H,two($CH_3CH_2CH_2$-)), 3.02(m;4H,two $\underline{RCH_2}N$), 3.58(s;3H,OCH_3); MS m/e 187$[M]^+$, 156$[M-OCH_3]^+$, 128$[M-COOCH_3]^+$.

3.4.6 (a) 

and (b) 

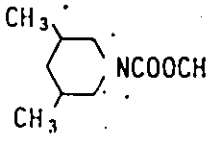
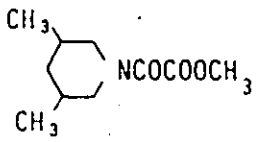
Carbonylation of piperidine using a 1/2 : CO/O_2 ratio gave : (a) 

in 16 % yield. IR ν_{CO} ($CDCl_3$) 1710(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16-2.12(m;6H,three CH_2), 2.83-3.77(m;4H,two $\underline{RCH_2}N$), 3.80(s;3H,OCH_3), MS m/e 143$[M]^+$, 112$[M-OCH_3]^+$, 84$[M-COOCH_3]^+$;

(b) 

in 4 % yield. IR ($CDCl_3$) ν_{COOR} 1745(ms), ν_{CONR_2} 1680(s) cm^{-1}; ^1H NMR($CDCl_3$) δ 1.16-2.12 (m;6H,three CH_2),

2.83-3.77(m;4H,two $\underline{RCH_2}N$), 3.80(s;3H,OCH_3), MS m/e 171$[M]^+$, 112$[M-COOCH_3]^+$, 84$[M-COCOOCH_3]^+$.

3.4.7 (a)  and (b) 

Carbonylation of 3,5-dimethylpiperidine using a 1/2 ; CO/O_2 ratio gave : (a) the carbamate ester in 38 % yield. IR ν_{CO} ($CDCl_3$) 1710(vs); ^1H NMR ($CDCl_3$) δ 0.86(m;4H,CH cyclic), 2.21(m;6H,two CH_3), 2.94(m;4H,two $\underline{RCH_2}N$), 3.63(s;3H,OCH_3); MS 171$[M]^+$, 140$[M-OCH_3]^+$, 112$[M-COOCH_3]^+$; (b) the oxamate in 2 % yield. IR ($CDCl_3$) ν_{COOR} 1745(ms), ν_{CONR_2} 1685(vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86(m;4H,(CH)cyclic), 2.21(m;6H,two CH_3), 2.94(m;4H,two $\underline{RCH_2}N$), 3.63(s;3H,OCH_3); MS m/e 199$[M]^+$, 140$[M-COOCH_3]^+$, 112$[M-COCOOCH_3]^+$.

3.5 Hydroesterification of 1-Decene: Induced Product Isomerization and CO_2 Suppression

General Procedure:

Methanol (60 ml) was placed into a round bottom flask equipped with a condenser, gas inlets and a gas-measuring flowmeter. A saturated $Ba(OH)_2$ exit bubbler was set up to trap escaping CO_2. Carbon monoxide was bubbled through the alcohol at a known rate. The following were then added in sequence: $PdCl_2$ (0.09 gm, 0.51 mmol), hydrochloric acid (0.10 ml), $CuCl_2$ (0.54 gm, 4.0 mmol). Oxygen was bubbled through the solution at a known rate. Finally, the olefin (5.0 mmol) was added, as well as 3A molecular sieves (if any). Several minutes were allowed between each addition as an induction period. The reaction was then stirred overnight

at room temperature and atmospheric pressure. Work-up was effected by rotary evaporation, extraction into hexane, rotary evaporation, treatment of the residue with carbon tetrachloride, filtration and evaporation to yield the product esters. See Tables (2.6) and (2.7) for data. No further purification was conducted.

3.5.1 $C_8H_{17}\underset{\underset{COOCH_3}{|}}{C(H)}CH_3$ and $C_8H_{17}CH_2CH_2COOCH_3$

Carbonylation of 1-decene as described in (3.5) afforded linear and branched esters, which were isolated as yellow oils. IR ν_{CO} ($CDCl_3$) 1730(s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 - 1.28(m;aliphatic protons), 2.09 - 2.58(m;($R\underline{CH}$-C(=O)-) and (RCH_2-C(=O)-); 3.61(s;3H,$COOCH_3$); GC/MS ($C_8H_{17}C(H)(COOCH_3)CH_3$): m/e 200$[M]^+$, 99$[CH_3CH{=}\underset{\underset{OH}{|}}{C}\text{-}OCH_3]^+$; GC/MS ($C_8H_{17}CH_2CH_2(COOCH_3)$): m/e 200$[M]^+$, 74$[CH_2{=}\underset{\underset{OH}{|}}{C}\text{-}OCH_3]^+$. The isomers fragmented according to the McLafferty rearrangement pattern. (See Chapter 2.4 for discussion).

3.6 Hydroesterification of Allenes

General Procedure:

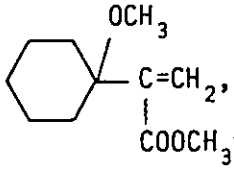
Carbon monoxide was slowly bubbled through an ice-cold solution of methanol (60 ml). $PdCl_2$ (0.178 gm, 1.0 mmol), hydrochloric acid (1.0 ml) and $CuCl_2$ (1.08 gm, 8.0 mmol) were added in sequence, allowing a few minutes of induction between each addition. Oxygen was then slowly bubbled through the solution, and 10.0 mmol of the allene was

added. The reaction was stirred for 4-6 hours at ice-bath temperature. Work-up then consisted of extraction into hexane, rotary evaporation, treatment of the residue with carbon tetrachloride, filtration and evaporation of the filtrate to afford the product esters. During both reaction and work-up, the temperature was kept low to suppress polymerization of the product.

3.6.1 3-Methyl-1,2-Butadiene

Hydroesterification of 3-methyl-1,2-butadiene afforded $(CH_3)_2C(OCH_3)C(COOCH_3)=CH_2$ in 19 % yield. This alkoxy ester was isolated as an oil. IR ν_{CO} (neat) 1724(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43(s;6H,CH_3 groups), 3.15(s;3H,OCH_3), 3.72(s;3H,CO_2CH_3), 5.70(s;1H,CH_2=), 6.02(s;1H,CH_2=); MS m/e 158$[M]^+$. The byproduct of this reaction, $(CH_3)_2CHC(COOCH_3)=CH_2$ was characterized by the following data: IR ν_{CO} (neat) 1724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90(m;1H,$(CH_3)_2\underline{CH}$), 1.38(d;6H,methyls), 3.59(s;3H,CO_2CH_3), 5.50(s;1H,CH_2=), 5.80(s;1H,CH_2=); MS m/e 128$[M]^+$.

3.6.2 Vinylidenecyclohexane

Hydroesterification of vinylidenecyclohexane when carried out as described in (3.6) (except that the reaction time was 20 hours) afforded (0.68 gm, 34 %) of  , which was isolated as a viscous yellow oil. ^1H NMR ($CDCl_3$) δ 1.3 - 2.0(m;10H,$(CH_2)_5$), 3.09(s;3H,OCH_3),

3.70(s;3H,CO_2CH_3), 5.57(s;1H,CH_2=), 5.93(s;1H,CH_2=); ^{13}C NMR ($CDCl_3$) δ 21.62,25.47,26.24,28.36,33.21((CH_2)$_5$), 49.6(OCH_3), 51.7(CO_2CH_3), 77.1(saturated quaternary carbon), 123.6(CH_2=), 145.6(R_2C=), 168.1(CO); MS m/e 198$[M]^+$.

3.6.3 Undeca-1,2-diene

Hydroesterification of undeca-1,2-diene (except that the reagent quantities were halved) afforded 0.12 gm (10 %) of a yellow oil containing a 4:3 mixture of two products:

i) CH_2=C(CO_2CH_3)-CH(OCH_3)C_8H_{17}; ^1H NMR ($CDCl_3$) δ 0.87(t;1H,CH(OCH_3)C_8H_{17}), 1.30(m,17H,C_8H_{17}), 3.24(s;3H,OCH_3), 3.77(s;3H,CO_2CH_3), 5.77(s;1H,CH_2=), 6.27(s;1H,CH_2=);

ii) $CH_2(OCH_3)$-C(CO_2CH_3)=CHC_8H_{17}; ^1H NMR($CDCl_3$) δ 1.30(m;17H,C_8H_{17}), 3.24(s;3H,OCH_3), 3.75(s;3H,CO_2CH_3), 4.32(s:2H,$CH_2(OCH_3)$-), 6.96(t;1H,C_8H_{17}CH=).

3.7 Alkyne Hydrocarboxylation Reactions

General Procedure

Into a round-bottom flask, equipped with gas inlets and a condenser, containing THF (60 ml), was bubbled carbon monoxide and oxygen. Water (0.11 ml) was added, followed by $PdCl_2$ (0.178 gm, 1.0 mmol), hydrochloric acid (0.1 ml), $CuCl_2$ (0.269 gm, 2.0 mmol), and then the substrate (10.0 mmol). An induction period of several minutes was allowed between each addition. The reaction mixture was stirred at room

temperature and atmospheric pressure for two days. Work-up consisted of extraction with 1M NaOH, washing with ether, and acidification with concentrated hydrochloric acid. The product was then extracted with ether, dried ($MgSO_4$), and removal of the solvent afforded the unsaturated acid. Any further purification which was required was carried out using thin layer silica plates with pure hexane as the eluent.

3.7.1 $C_6H_{13}-\underset{\underset{COOH}{|}}{C}=CHCOOH$

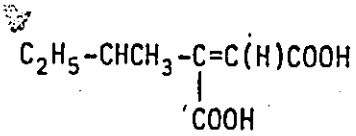
Hydrocarboxylation of 1-octyne afforded 0.78 gm (39 %) of $C_6H_{13}-\underset{\underset{COOH}{|}}{C}=CHCOOH$, isolated as an oil. The product was determined by ^1H NMR to be a 1:1 cis:trans mixture. IR $\nu_{CO}(CDCl_3)$ 1700(s); $\nu_{C=C}$ 1640(ms)cm^{-1}; ^1H NMR($CDCl_3$) δ 0.83(t;6H,CH_3), 1.31(m;16H,$(CH_2)_4$), 2.38(m;4H,$R\underline{CH_2}$-CH=), 5.78(s;1H,RCH=, (cis)), 6.74(s;1H,RCH=, (trans)), 9.69(s;4H,two COOH); ^{13}C NMR ($CDCl_3$) δ 14.04(CH_3), 22.52,25.98,28.7,29.2,31.5$(CH_2)_5$; 127.2(RCH=,(cis)), 128.5(RCH=,(trans)), 153.79(R_2C=,(cis)), 153.89(R_2C=,(trans)), 170.7(COOH), 171.9(COOH); MS m/e 200$[M]^+$.

3.7.2 $cis\text{-}C_4H_9-\underset{\underset{COOH}{|}}{C}=CHCOOH$

Hydrocarboxylation of 1-hexyne afforded 0.50 gm (29 %) of $C_4H_9-\underset{\underset{COOH}{|}}{C}=CHCOOH$ isolated as an oil. IR ν_{CO} ($CDCl_3$) 1705, $\nu_{C=C}$ 1640(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94(t;3H,CH_3), 1.15-1.83(m;4H,$(CH_2)_2$-),

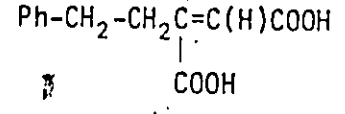
2.45(t;2H,$\underline{RCH_2}CH$=), 6.03(s;1H,RCH=), 11.50(s;2H,COOH); ^{13}C NMR($CDCl_3$) δ 17.32(CH_3), 21.69,29.30,41.28(CH_2 carbons), 121.70(RCH=), 142.0(R_2C=), 153.75(COOH), 168.95(COOH).

3.7.3



Hydrocarboxylation of 3-methyl-1-pentyne afforded 0.34 gm (20 %) of C_2H_5-CH(CH_3)-C(COOH)=CH(COOH), isolated as an oil. The product was determined by ^1H NMR to be a 3:1 cis:trans mixture. IR ν_{CO}($CDCl_3$) 1700(s) cm^{-1}; $\nu_{C=C}$ 1637(ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 - 1.79(m;16H,CH_3CH_2-C(CH_3); cis and trans), 2.38(m;2H,$C_2H_5\underline{CH}CH_3$, cis and trans), 5.65(s;1H,RCH=,cis), 5.92(s;1H,RCH=,trans), 9.23(s;4H,COOH).

3.7.4



Hydrocarboxylation of 4-phenyl-1-butyne was conducted in a variation of the general procedure described in (3.7). In this reaction, (30 ml) THF and (1 ml) H_2O were placed in a flask together with (0.054 gm, 0.30 mmol) $PdCl_2$, (0.1 ml) hydrochloric acid, (0.087 gm, 0.64 mmol) $CuCl_2$, and (0.39 gm, 3.0 mmol) of the alkyne. The reaction was conducted for 3 hours at 0°, then worked up in the usual manner.

This reaction afforded 0.12 gm (18 %) of $PhCH_2CH_2C(COOH)=CHCOOH$, isolated as an off-white waxy product. IR ν_{CO}($CDCl_3$) 1700(ms); $\nu_{C=C}$ 1640(ms)

cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.72(m;4H,$(CH_2)_2$), 5.75(s;1H,RCH=), 7.16(s;5H,C_6H_5), 10.90(s;2H,COOH); ^{13}C NMR (DMSO-d_6) δ 29.2(CH_2), 34.6(CH_2), 125.89(RCH=), 127.33,128.03,128.19,128.21(aromatic carbons), 146.17(R_2C=), 166.5(COOH), 167.69(COOH).

3.7.5 C_4H_9-CH=C(CH_3)COOH

Hydrocarboxylation of 2-heptyne was effected as described in (3.7) (except that the reaction temperature was 65° and the reaction was left overnight) to give 0.17 gm (12 %) of an oily product. IR ν_{CO}($CDCl_3$) 1710(ms); $\nu_{C=C}$ 1640(ms) cm^{-1}; ^1H NMR ($CDCl_3$ δ 0.92-2.35(m;12H,$\underline{CH_3}(\underline{CH_2})_3$-C=C-$\underline{CH_3}$)), 6.88(t;1H,RC$\underline{H_2}$CH=); 11.85(s;1H,COOH).

3.7.6 $C_6H_{13}CH{=}C(CH_3)COOH$

Hydrocarboxylation of 2-nonyne as described in (3.7) (except that the reaction time was overnight) afforded 0.40 gm (32 %) of an oil, which was found by NMR to be all $C_6H_{13}CH{=}C(COOH)CH_3$. IR ν_{CO}($CDCl_3$) 1690(vs); $\nu_{C=C}$ 1640(m)cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 - 2.28(m;16H,$\underline{C_6H_{13}}$-C=C-CH_3), 6.91(t;1H,$C_6H_{13}\underline{CH}$=), 11.78(s;1H,COOH); ^{13}C NMR ($CDCl_3$) δ 11.9(CH_3), 14.1(CH_3), 22.6,28.4,28.9,29.1,31.7($(CH_2)_5$), 139.9(RCH=), 145.5(R_2C=), 173.8(COOH); MS m/e 170$[M]^+$.

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PART II

METAL-METAL TRIPLE BOND CHEMISTRY

Chapter 4

Introduction:

Classical coordination chemistry, as originally developed by Werner underwent a major evolutionary step in the first half of the 1960's. At this time, an entirely new and previously unknown form of transition-metal chemistry was recognized. Werner's concept of transition metal chemistry can be essentially defined as one-centre coordination chemistry - in other words, a single metal ion, surrounded by a set of ligands. The non-Wernerian transition metal chemistry which developed in the period 1963-1965 can be essentially defined as multi-centre chemistry - or in other words, the chemistry of direct metal-metal bonds.

The discovery of metal-metal bonds of order greater than one was first made by Cotton in 1963 (1). Though such compounds had been in existence for several years previous to that time, Cotton was the first to rationalize their structure and bonding (2). Since then, a large number of complexes containing metal-metal multiple bonds have been prepared, and a number of books and reviews have been published (3-10). Bond orders of 2,3 and 4 between metal atoms are no longer unusual. Rhenium, molybdenum, tungsten and chromium are capable of forming the widest range of metal-metal multiple bonded complexes, while technetium; osmium, ruthenium, platinum, iron and vanadium are also known to exhibit the phenomenon. The characteristic common to all these compounds is an extremely short metal-metal bond distance - often considerably shorter than the metal-metal distance in the pure metals. X-ray crystallography

is extensively used in order to accurately measure the bond distances, and hence to aid in bond order determinations.

One of the most widely examined of multiple bond systems is the triply-bonded carbonyl family of general formula $L_2M_2(CO)_4$, (L = Cp, C_5Me_5, Cp-Me), (M = Cr, Mo, W). These complexes are straightforward to synthesize, exhibit a fascinating and varied reactivity and are easy to analyze by X-Ray crystallography (as they tend to crystallize readily).

Synthesis and Structure of $L_2M_2(CO)_4$:

These compound can be obtained by a variety of ways. The first member of the family was $(\eta^5\text{-}C_5Me_5)Mo_2(CO)_4$. This was obtained by refluxing $Mo(CO)_6$ together with C_5Me_5H in 2,2,5-trimethylhexane (11). A photochemical conversion of $Cp_2Cr_2(CO)_6$ to $Cp_2Cr_2(CO)_4$ has also been used to generate the triple bond (12). The preparative method of choice, however, is a simple thermal decarbonylation reaction. Commercially available $Cp_2Mo_2(CO)_6$ is simply refluxed in toluene, xylene or diglyme. This yields the triply-bonded dimer $Cp_2Mo_2(CO)_4$ in situ. The rate of formation of the triple-bond dimer is qualitatively Cr > Mo>> W. Apparently the thermal and photochemical routes to the triple-bonded dimer follow a sequence of preliminary metal-metal bond cleavage steps (13).

$$Cp_2Mo_2(CO)_6 \rightleftharpoons 2CpMo(CO)_3 \rightleftharpoons 2CpMo(CO)_2$$

$$2CpMo(CO)_2 \longrightarrow Cp_2Mo_2(CO)_4$$

Once the above sequence was recognized, it was realized that

mixed-metal species would be easy to obtain. For instance refluxing a 1:1 mixture of $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$ in diglyme produced statistical mixtures of $Cp_2Mo_2(CO)_4$, $Cp_2W_2(CO)_4$ and $Cp_2MoW(CO)_4$ (8).

X-Ray crystal structures have been obtained for $Cp_2Cr_2(CO)_4$ and $Cp_2Mo_2(CO)_4$. Although they revealed the expected similarity in gross structure, they exhibited some interesting differences in fine detail. The crystal structures are shown in the following figures (8):

Figure 4.1a
Crystal Structure of $Cp_2Cr_2(CO)_4$

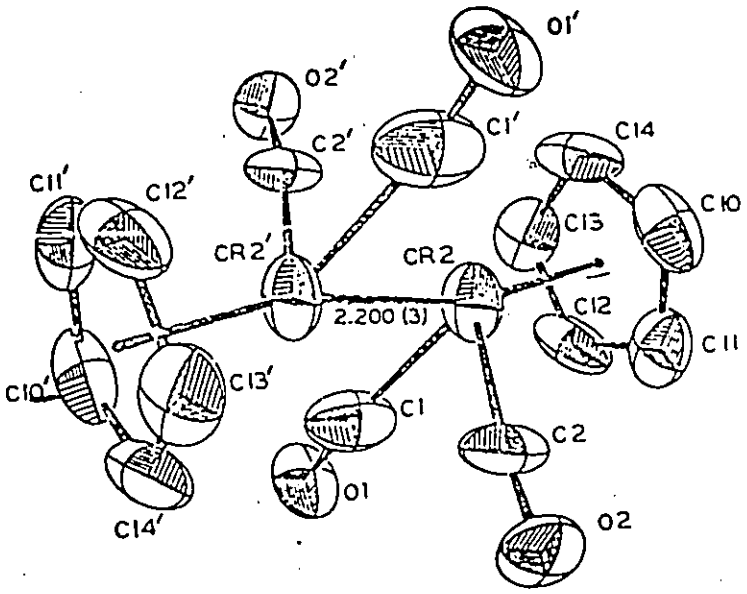
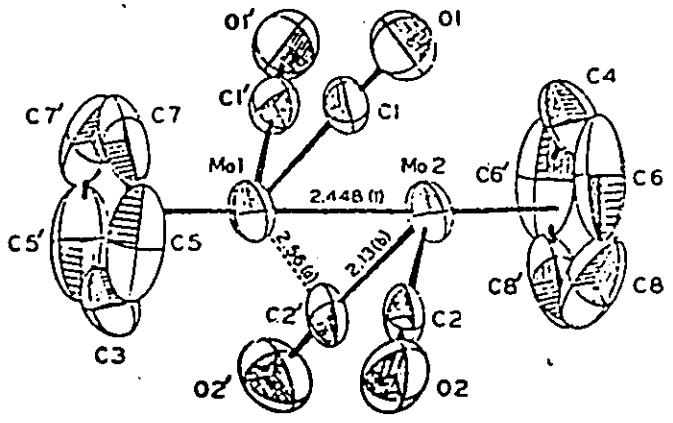


Figure 4.1b
Crystal Structure of $Cp_2Mo_2(CO)_4$



The chromium dimer has a very short Cr-Cr distance (2.23Å) and a non-linear Cp-Cr-Cr-Cp axis which is usually observed for Cp_2M_2 compounds. The carbonyls are bent back over the Cr-Cr-CO bond at angles of 75°. The molybdenum dimer also has a short metal-metal distance (2.44Å). In this case, the carbonyls are bent back even more (Mo-Mo-CO=67°) ! Finally, the Cp-Mo-Mo-Cp axis has an unprecedented linear shape. In both cases, the CO ligands may be viewed as acting as four-electron donors. This $\sigma+\pi$ bonding mode has been cited by Curtis (14) as a reflection of the susceptibility of these dimers to nucleophilic attack. In line with this obervation, it has been noted (9) that the chromium dimer with its larger angle is less reactive than the molybdenum analogs with the smaller angles. Another interesting effect of the carbonyl ligands is on the internuclear distance. The metal-metal distance of the molybdenum dimer is considerably longer than that found in non-carbonyl triple-bond dimers. For instance, Chisholm has synthesized complexes of the type $X_3Mo{\equiv}MoX_3$ which have metal-metal distances of about 2.21Å. It has been suggested (8) that the semi-bridging carbonyls are responsible for this by donating π electron density into Mo≡Mo antibonding orbitals, hence weakening the triple bond.

General Reactivity Patterns of $Cp_2M_2(CO)_4$ Compounds:

In organic chemistry, multiple bonds are important functional groups. The π bonds of alkynes are rich in electron density, and are easily polarizable. They are reactive towards electrophiles and are displaced by nucleophiles (as in Michael additions). These reactivity

modes are shown below:

1) $C\equiv C + E^+ \rightarrow E - C=C^+$

2) $C\equiv C + N:^- \rightarrow N - C=C:^-$

With unsaturated metal dimers, there are some interesting differences in reactivity. For instance, as depicted in equation 2), the displacement of a π-bond by a nucleophile renders the remote carbon nucleophilic due to its lone pair; in the case of an unsaturated metal dimer, however, the displacement of the π bonds renders the remote metal electrophilic:

3) $M\equiv M_1 + N:^- \rightarrow N-M-M_1^+$

The rupture of two of the metal-metal bonds above leaves M_1 two electrons short and coordinatively unsaturated, and hence electrophilic. Thus, from equation 3) one can predict that, in general, when the triple bond is reacted with two or four electron donors, the following reactions will occur:

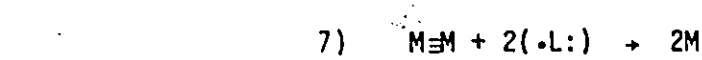
4) $M\equiv M_1 + 2L: \rightarrow L-M-M_1-L$

5) $M\equiv M_1 + :L: \rightarrow M-M_1$ (with L bridging)

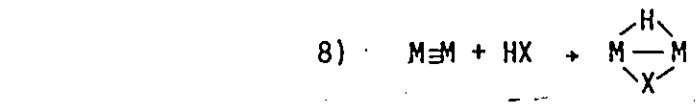
Other general patterns of interaction between nucleophiles and the triple-bond dimer have been found. For instance, carbenoid (two-electron donor) species can react by displacing only one π bond, giving a bridged M=M double bond:

6) $M\equiv M_1 + :C \rightarrow M=M$ (with C bridging)

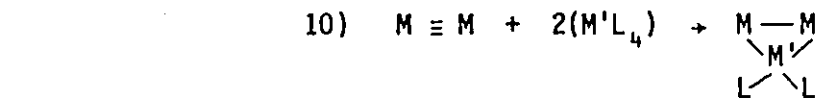
Finally, the interaction of certain donors can completely rupture the metal-metal triple bond. Three electron donors such as NO are particularly effective in this regard:



Oxidative addition reactions to the triple bond by electrophilic reagents are fairly well known:



Finally, the metal-metal multiple bond can undergo an oligomerization reaction with other multiply-bonded species, or simply with other transition metal compounds to form clusters:



As the preceeding general discussion shows, unsaturated metal carbonyl complexes undergo a wide variety of reactions. It has been found convenient to classify these general reactions into five catagories. These are i) reactions with nucleophiles (L) leading to a reduction of the bond order, and formation of $Cp_2M_2(CO)_4L_2$; ii) reactions

with small unsaturated organic molecules; iii) oxidative addition reactions with electrophiles and mild oxidizing agents; iv) metal-metal bond cleavage reactions; v) cluster formation.

i) The simplest reaction of the first type is the reaction of CO with $Cp_2M_2(CO)_4$ to form $Cp_2M_2(CO)_6$. Wrighton (15) found that when M = Mo,W, the complexes take up CO at ambient temperature and pressure while for M = Cr, a pressure of 100 Bar is required. The reaction of $Cp_2Mo_2(CO)_4$ with phosphorus-bearing nucleophiles such as trimethylphosphite and triphenylphosphine gives 1,2 addition products of type $Cp_2Mo_2(CO)_4L_2$ (13). Interestingly, the reactivity of $Cp_2Mo_2(CO)_4$ complexes can be sharply contrasted against the apparent inertness of $(C_5Me_5)Mo_2(CO)_4$ towards phosphines and phosphites. This disparity in behaviour is not well understood, although some suggestions (9) have been made that the lack of reactivity of the pentamethyl derivatives may partly arise from a blocking of the metal sites to attack by bulky nucleophiles. $Cp_2Mo_2(CO)_4$ fails to react with many hard bases such as aliphatic amines, pyridine, esters or alcohols.

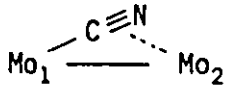
An interesting example of a comparatively rare 1,1 nucleophilic addition is shown below (16):

$$Cp_2Mo_2(CO)_4 + 2Ph_3PS \rightarrow \begin{matrix} & & Cp & \\ & & | & \\ Ph_3PS & \diagdown & Mo & — Mo(CO)_3Cp \\ Ph_3PS & \diagup & | & \\ & & CO & \end{matrix}$$

It is possible that this unusual product occurs as a rearrangement product of the more normal 1,2 addition instead of a direct 1,1 addition,

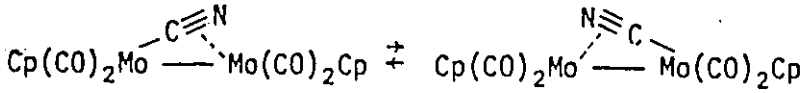
however this is still uncertain.

Another different type of nucleophilic attack occurs upon reaction of $Cp_2Mo_2(CO)_4$ with KCN (13). This facile reaction produces not the expected terminally-bound ligand, but a novel fluxional σ-π derivative:

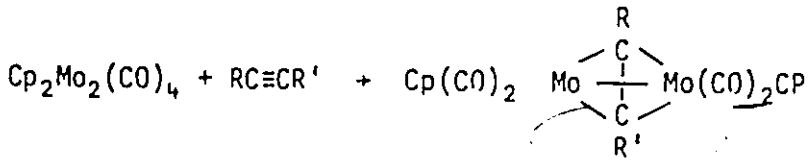


Mo_1-Mo_2 = 3.14 Å

Here the CN^- formally behaves as a four-electron donor with two electrons being donated to Mo_1 from the σ lone pair and two more donated to Mo_2 from the cyanide π orbital. A further point of interest is the "windshield wiper" fluxionality of the cyanide. This fluxionality has been followed by NMR (17) and can be frozen out at about -60°:



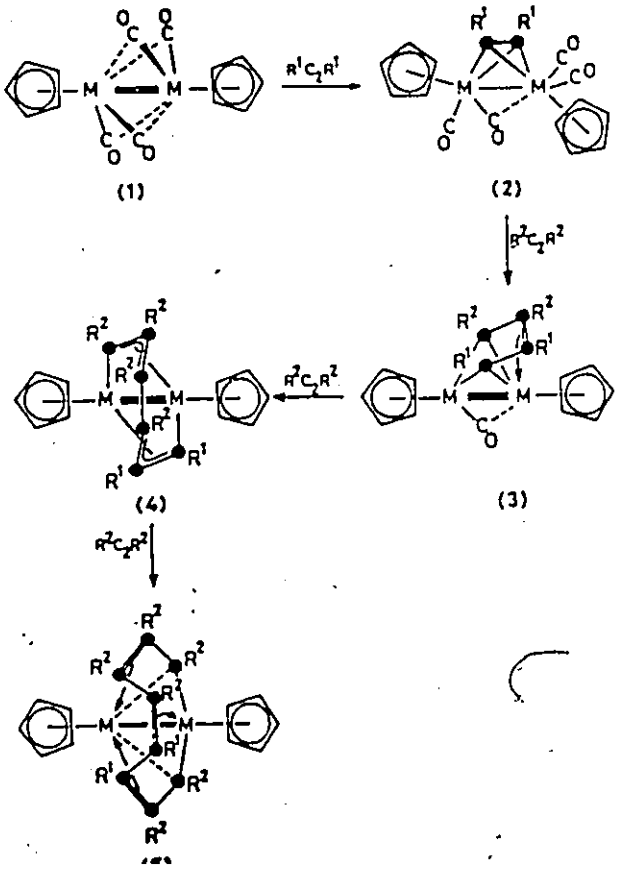
ii) Study of the reaction of triple-bond dimers with small unsaturated organic molecules has been dominated by systems involving acetylenic ligands ($RC{\equiv}CR'$; R,R'=H,CH_3,Ph,CF_3,C_3H_7,CH_2OH,CH_2CH_2OH,CO_2CH_3) (9). These ligands all react either at room temperature, or under the influence of U.V. irradiation to give dimetallatetrahedrane complexes:



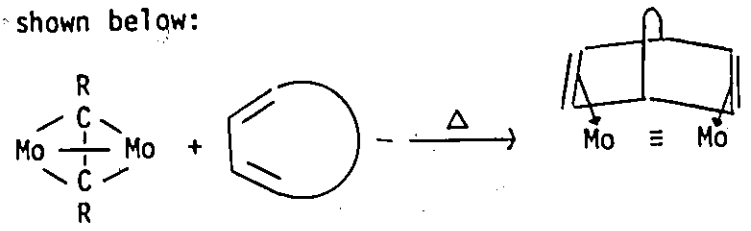
Numerous structural determinations on these derivatives have been carried out. Common features to all the structures are metal-metal bond lengths of ca. 2.98Å and C-$C_{acet.}$ lengths of 1.33Å. (The latter is consistent with an internal acetylene bond order of approximately 1.4). Moreover the bound acetylenes appear to be fluxional. This dynamic behaviour has led to some fascinating chemistry. For instance, it has been found that these complexes undergo acetylene exchange at about 110° (8). Furthermore, these complexes react with H_2 to regenerate the triple bond and produce cis-olefins exclusively. In the presence of excess acetylene, the process has been found to become catalytic.

Knox and Stone have found that this cross-bound acetylene is activated towards oligomerization as shown below:

Figure 4.2 (9)
Scheme showing the sequence of reactions leading to the cyclotetramerization of acetylenes at a dimetal centre

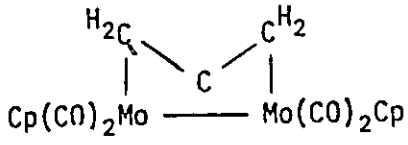


The extent of this reaction has been found to depend on the nature of the acetylene ligand and the metal used. Stone (18) has also reported the activation of a complexed acetylene towards a Diels-Alder type reaction. In these reactions, the complexed acetylene reacts with cyclic-1,3 dienes as shown below:



In contrast with its ready reaction with alkynes, $Cp_2Mo_2(CO)_4$ does not react with simple olefins or dienes, such as ethylene, butadiene or norbornadiene (8).

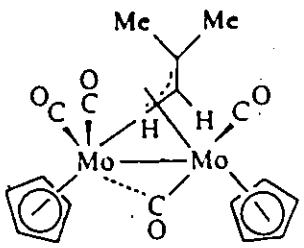
Allenes react with $Cp_2Mo_2(CO)_4$ cleanly to form bridged species. For instance, allene itself reacts with the triple-bond dimer at room temperature to give (19):



Reactions with higher allenes such as $MeCH=C=CH_2$ and MeCH=C=CHMe require more forcing conditions (sealed tube at 80°) to give the same product. The above structure shows allene as a V shaped symmetrical bridge between two metal atoms. The Mo-Mo distance of 3.117Å is longer than that in the acetylene derivative discussed previously. Moreover, the carbonyl ligands are not semi-bridging as in the acetylene case. Cotton (9) has suggested that these differences are due to an optimum overlap of the

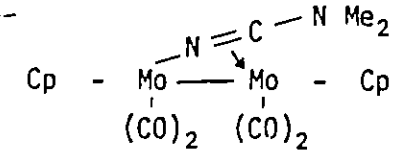
ligand π electrons without the necessity of such a close approach of the metal atoms.

An interesting allyl-bridged species is formed upon prolonged reaction of 3,3-dimethylcyclopropene with $Cp_2Mo_2(CO)_4$ (20):



This product is noteworthy in two ways. First, the 2,3 carbon bond of the cyclopropene has been cleaved during the course of the reaction. Secondly, this represents a rare case of an olefinic ligand reacting with $Cp_2Mo_2(CO)_4$.

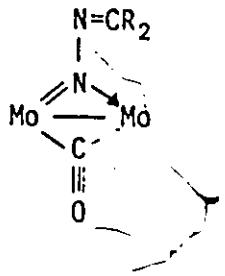
A number of interactions of $Cp_2Mo_2(CO)_4$ with unsaturated hetero-atom compounds are now known and these have revealed some fascinating chemistry. For instance, it has been found that $Cp_2Mo_2(CO)_4$ reacts with aminocyanamides R_2NCN (R=H or CH_3) (21) to give products which resemble the μ-cyano derivative discussed previously:



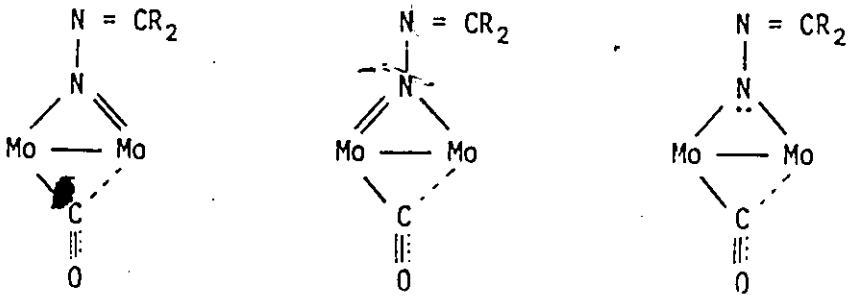
Mo - Mo = 3.056Å

In this case, however, the unsymmetrical bridging ligand is not fluxional.

The triple bond dimers have also been found to react with diazoalkanes to produce novel diazoalkane adducts which lose nitrogen under mild conditions to produce compounds containing bridging alkylidene complexes. Diphenyl or ditolyl-diazomethane react at room temperature to produce the following bridged species (22):

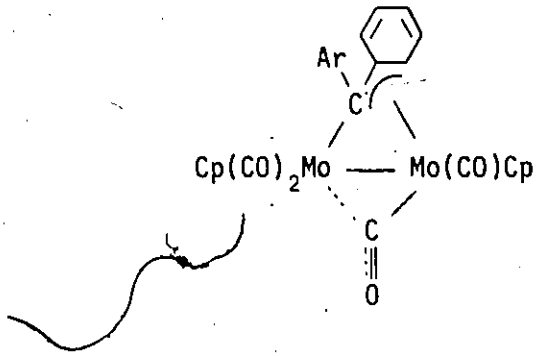


The actual structure may be described as a hybrid since the R_2CN_2 ligand can act as either a 4-electron or 2-electron donor:



The somewhat shorter Mo-Mo distance than that found for $Cp_2Mo_2(CO)_2L_2$ complexes might be due to the contribution of the hybrid

form c) above. These compounds are stable indefinitely as solids under N_2. In solution, however, the compounds lose N_2 at temperature dependent rates to give an alkylidene product, $Cp_2Mo_2(CO)_2(CAr_2)$. X-Ray analysis has revealed that the structure of the product is not the expected carbenoid product but rather one in which one aryl group interacts with one metal to form a π-allyl type of ligand, the other end of which is σ-bonded to the second metal (8):



Mo-Mo = 3.08 Å

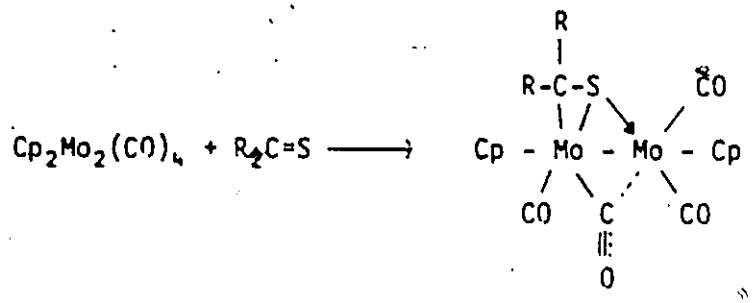
The Mo-Mo distance of this compound is in the range expected for a single bond. This alkylidene ligand has been found to be activated towards interaction with several small molecules. For instance, the addition of dihydrogen to the compound resulted in alkylidene cleavage from the metals as shown below (8):

$$Cp_2Mo_2(CO)_4(CPh_2) + H_2 \xrightarrow[45\ psi]{50^\circ} Cp_2Mo_2(CO)_6 + Ph_2CH_2$$

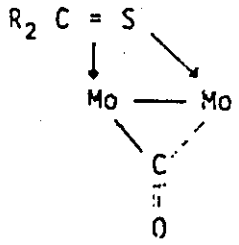
Carbonylation of the alkylidene compound afforded a ketene and regenerated the original single-bond dimer (8):

$$Cp_2Mo_2(CO)_4(CPh_2) + CO \xrightarrow{50^\circ} Cp_2Mo_2(CO)_6 + Ph_2C{=}C{=}O$$

There has been a great deal of interest recently in the interaction of $Cp_2Mo_2(CO)_4$ with unsaturated thio compounds. For instance, thioketones react with the triple-bond dimer under mild conditions to produce 1:1 adducts without displacement of (CO) (23). The structure of the complex is shown below:

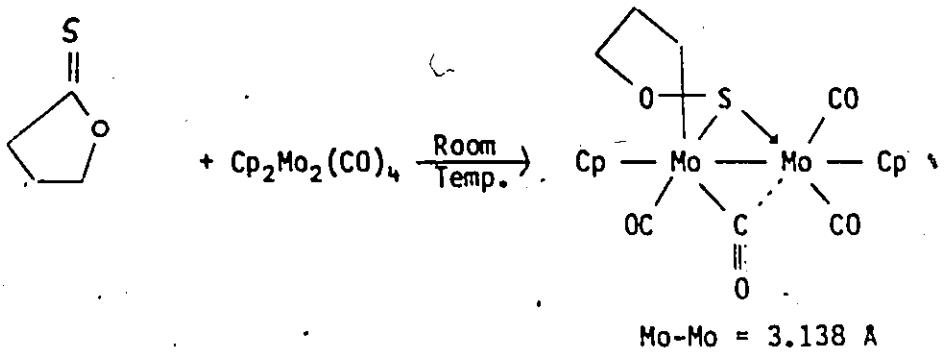


The structure of this complex reveals that a key structural unit here is:

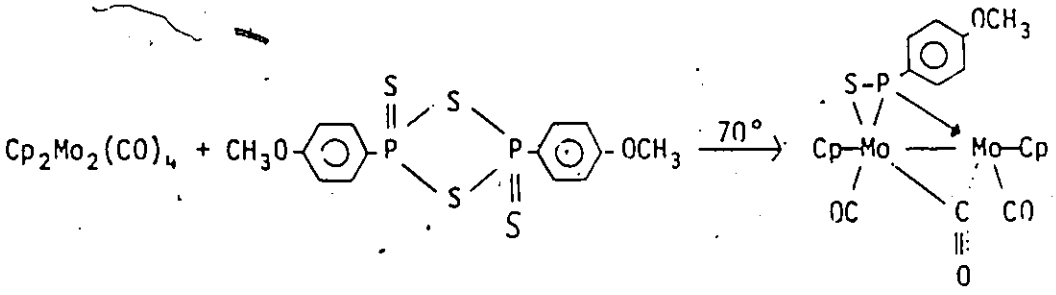


Here the π electron density from the thione fragment is being donated to one molybdenum and the other sulfur lone pair to the other molybdenum. Steric crowding is probably responsible for the semi-bridging carbonyl. The Mo-Mo distance of 3.145 Å is in the range expected for a Mo-Mo single bond.

Treatment of thioesters and thiolactones (RC(=S)OR') with $Cp_2Mo_2(CO)_4$ forms structurally similar complexes (24):



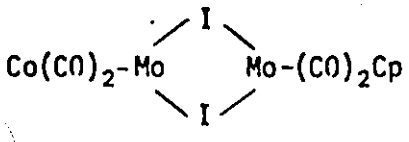
The reaction of $Cp_2Mo_2(CO)_4$ with the dimer of (p-methoxyphenyl) thionophosphine sulfide (Lawesson's reagent) proved to yield an interesting class of complexes (25):



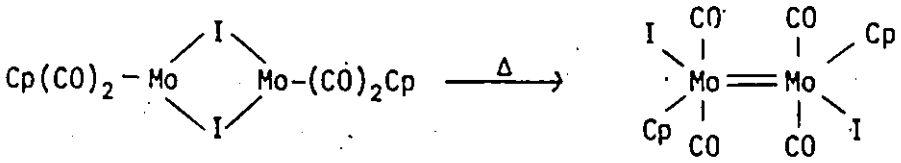
This complex contains a novel bridging phosphinothioylidene moiety. An unusual feature here is the use of the phosphorus atom as the bridge instead of the sulfur atom. The molecule also contains a semi-bridging carbonyl unit. The Mo-Mo distance of 3.245 A indicates single bond order, however is slightly shorter than in most related compounds with a bridging ligand. As one can observe, the reactivity of the Mo≡Mo triple bond towards unsaturated moieties shows interesting diversity.

iii/ The triple bond in $Cp_2Mo_2(CO)_4$ componds has been found to be active towards mild oxidizing agents and electrophiles. This is principally due to the high electron density between the two metal centres. The

triple-bond dimer reacts with I_2, even at -78°, to produce an iodo-bridged dimer(8):

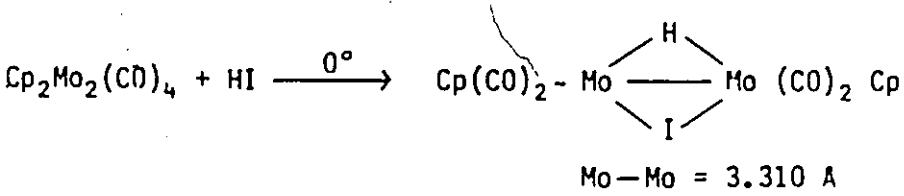


There is no metal-metal bond as the Mo-Mo distance is 4.441 Å, which is well outside the bonding range. This compound is quite readily oxidized to give $CpMo(CO)_3I$ as the major product. The dimer also readily rearranges in solution at elevated temperatures:



This novel isomerization has been followed by NMR but has not been confirmed by X-Ray studies due to some crystal growth problems associated with the product.

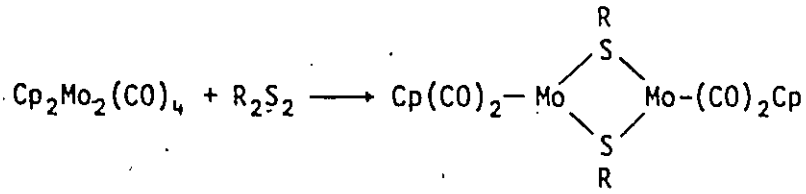
Hydrogen halides react rapidly with the triple-bond dimer even at well below room temperature (8):



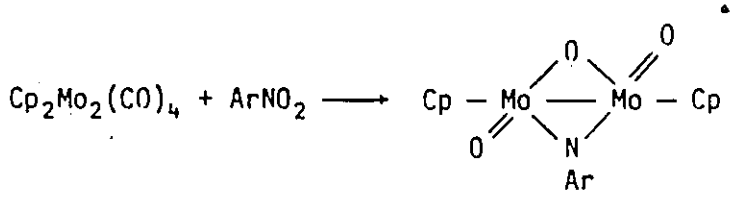
Mo—Mo = 3.310 Å

Interestingly, this compound can also be obtained by reacting hydride donors with the di-iodo bridged compound described at the beginning of this section.

Other formal oxidative addition reactions result by reacting $Cp_2Mo_2(CO)_4$ with disulfides R_2S_2 (R=CH_3,Ph). These disulfides behave as pseudohalogens to give products with no metal-metal bond (8):



The reaction of nitro compounds with the triple-bond dimer gives a novel class of dinuclear complexes (26):



The short Mo-Mo distance of 2.649 A is consistent with a metal-metal single bond and a Mo(V) oxidation state. This reaction is noteworthy since it involves a complete decarbonylation of $Cp_2Mo_2(CO)_4$, plus the trapping of a bridging nitrene ligand.

iv) Metal-metal bonds in the multiply-bonded complexes can be cleaved by a variety of reagents. For instance, Alper and Petrignani recently reported cleavage induced by organic halides (27):

$$Cp_2Mo_2(CO)_4 + RCOCH_2X \longrightarrow RCOCH_3 + CpMo(CO)_3X$$

Other examples of metal-metal bond cleavage reactions include treatment with sodium amalgam followed by nitric oxide to give $CpMo(CO)_2NO$ (28), and with $HgPh_2$ affording $[CpMo(CO)_3]_2$ Hg (9). Finally, a fascinating disproportionation reaction occurs between elemental sulfur and $Cp_2Mo_2(CO)_4$ in acetone, resulting in the formation of:

$$[Cp_3Mo_3(CO)_6(\mu_3\text{-}S)]^+[CpMo(CO)_3]^- \qquad (29)$$

v) Cluster formation may be achieved in a variety of ways using $Cp_2Mo_2(CO)_4$. For instance, refluxing the dimer with $Mn_2(CO)_{10}$ produces a mixed metal complex: $CpMo(CO)_3Mn(CO)_5$ (13). Treatment of $Cp_2Mo_2(CO)_4$ with $Pt(PPh_3)_4$ produces $[Mo_2Cp_2(CO)_4]Pt(PPh_3)_2$ which is believed to contain a bridging $Pt(PPh_3)_2$ (13).

Refluxing a mixture of $Cp_2Mo_2(CO)_4$ and $Co_2(CO)_8$ in toluene produces $CpMo(CO)_3Co(CO)_4$ (13). Finally, the reaction of iron carbonyl with $Cp_2Mo_2(CO)_4I_2$ affords another metal bridged cluster: $[Cp_2Mo_2(CO)_4][Fe(CO)_4]$ (13).

An examination of some of the reactions of triply-bonded metal carbonyl compounds has been considered in this introductory section. These species exhibit a fascinating and diverse reactivity.

Objectives of this research:

The prinicipal objective of this research was to expand the chemistry of the triple-bond compounds with unsaturated heteroatom moieties.

The first systems to be examined were the reactions between dithioesters, and dithiolactones and the Mo≡Mo triple bond. Predictions that the products of these reactions would be similar to the thioester/thiolactone molybdenum triple-bond products proved to be only partially correct, and several novel products were to be characterized. Furthermore, the reaction between the molybdenum triple-bond dimer and potentially chelating thio-ligands such as the $R_2NC(=S)-S-S-C(=S)NR_2$ and $R_2-P(=S)-P(=S)-R_2$ systems was explored. These ligands were found to experience cleavage and bind to molybdenum in a novel fashion.

CHAPTER 5

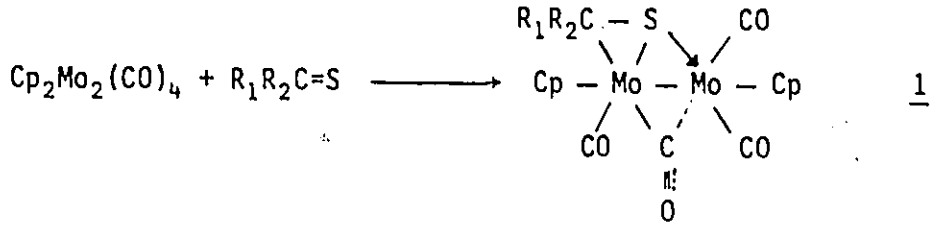
Results and Discussion - Triple Bond Reactions

5.1 Introduction

There is currently a considerable amount of interest in discovering new reactivity pathways for multiply-bonded metal compounds. This interest stems from several viewpoints. For example, since carbon-carbon multiply-bonded functionalities are of fundamental importance in organic chemistry, it is of interest to determine whether the comparable metal-metal multiple bonds can react in a similar fashion. Secondly, only a modest number of reactivity patterns for metal-metal multiply bonded compounds have been systemized. Third metal-metal multiply bonded dimers are the smallest examples of unsaturated metal cluster compounds and they provide building blocks for the systematic synthesis of polynuclear cluster compounds. Finally, the organometallic reaction schemes of binuclear systems can serve as useful models for surface-catalyzed organic reactions.

One of the most widely investigated class of unsaturated metal compounds is the cyclopentadienyl molybdenum dicarbonyl dimer and related complexes. The metal-metal bond of such complexes undergoes a variety of intriguing reactions. The reaction of this class of compound with organosulfur moieties has been the subject of a number of investigations (30, 31, 32, 33).

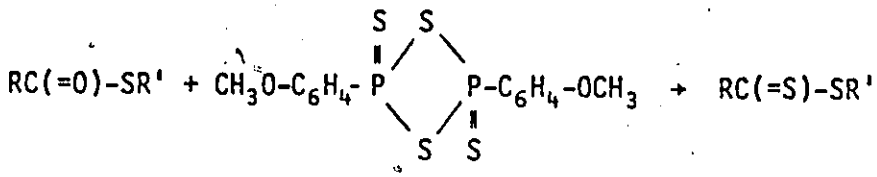
As described in the introduction, treatment of $Cp_2Mo_2(CO)_4$ with thioketones in xylene or toluene at room temperature gave the novel class of bridging thione complex (structure 1):



(Reaction of $Cp_2Mo_2(CO)_4$ with thioesters gave complexes structurally similar to the thioketone products, but with interesting differences in fine detail). This led to an interest in the possibility of reacting dithioesters with the triple bond complex.

5.2 Reaction of Acyclic Dithioesters with $(C_5H_4R)_2M_2(CO)_4$ Compounds

The reaction of dithioesters with metals has been extensively investigated (34). Complexes have been isolated in which one or both sulfur atoms are coordinated to the metal. It was of interest to determine whether simple analogs of the thioketone complexes would arise on reaction of the dithioester with compounds containing a metal-metal triple bond, or novel types of organometallics would arise from such an investigation. The dithioesters utilized for these reactions were prepared by treatment of thioesters with Lawesson's reagent in refluxing toluene (35):



Treatment of $(C_5H_4R)_2M_2(CO)_4$ $(R=CH_3)$,$(M=Mo)$ with ethyl dithioacetate in refluxing toluene afforded red $[(C_5H_4CH_3)_2Mo_2(CO)_2(CH_3CS)(SC_2H_5)]$ in 14% yield. This product was characterized by analytical, spectral, and X-Ray techniques. The X-Ray crystal structure revealed the compound to have structure 2, shown in Figure 5.1. Tables 5.1-5.4 list crystal data, data collection information, atomic coordinates, and selected bond lengths and bond angles.

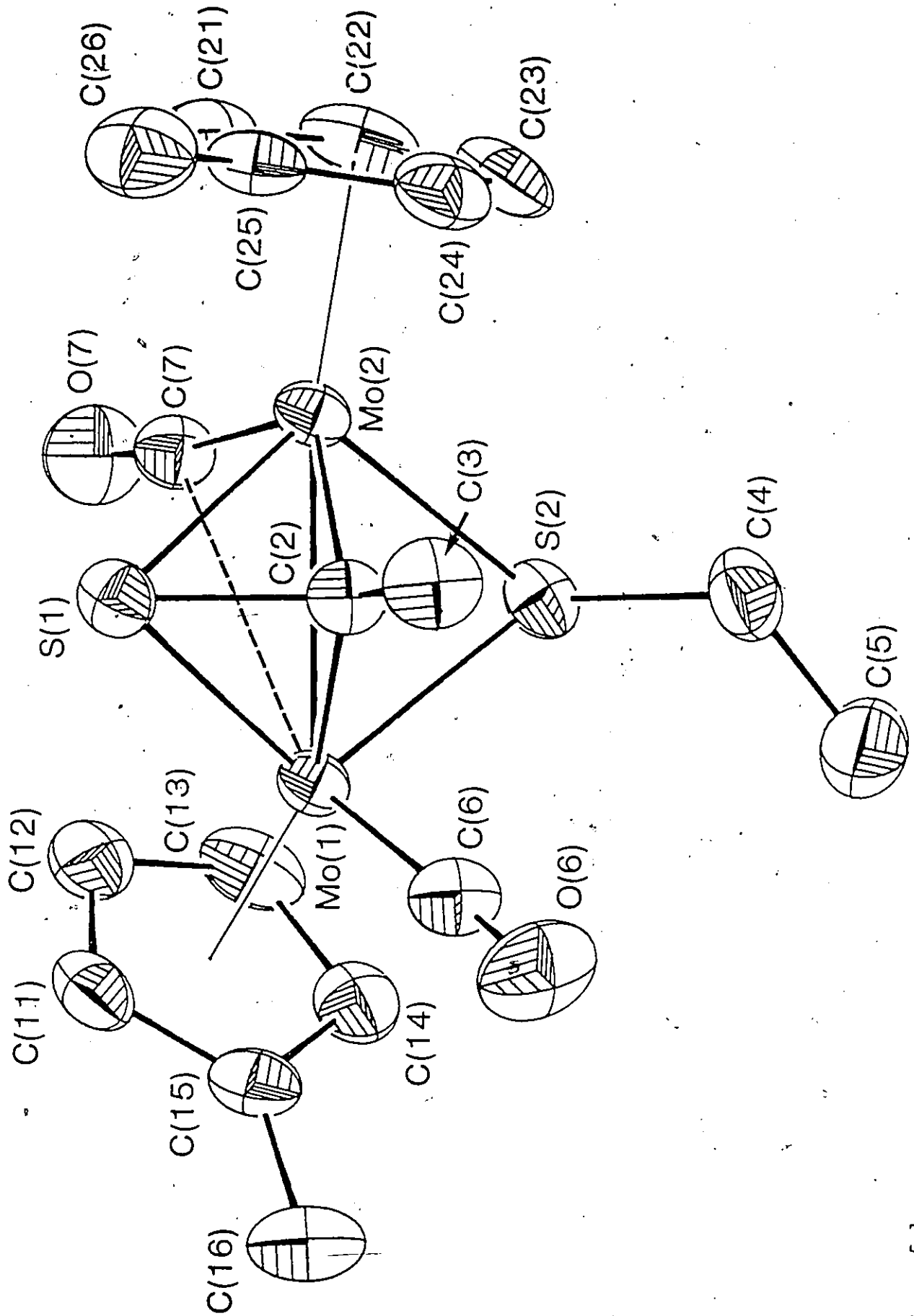


Figure 5.1 Structure 2: ORTEP diagram of $[(C_5H_4CH_3)_2Mo_2(CO)_2(CH_3CS)(SC_2H_5)]$

TABLE 5.1

Crystal Data for Structure 2 and Structure 3

	2	3
Formula	$C_{18}H_{22}Mo_2O_2S_2$	$C_{19}H_{22}Mo_2O_5S_2 \cdot 0.5CH_2Cl_2$
fw	526.38	628.86
cryst system	monoclinic	orthorhombic
space group	$P2_1/c$	Pbcn
a, Å	14.067 (1)	25.380 (2)
b, Å	9.864 (1)	12.747 (4)
c, Å	14.948 (2)	14.394 (2)
β, deg	111.851 (8)	
V, $Å^3$ [a]	1925.09	4656.8
Z	4	8
ρ_{calcd}, g cm^{-3}	1.816	1.794
ρ_{obsd}, [b] g cm^{-3}	1.80	1.72 [c]
μ, cm^{-1}	14.89	13.67

[a] At 18 ± 1 °C. [b] Flotation in aqueous $ZnBr_2$ solution. [c] Crystals used in the density determination had been stored under dry N_2 for several months. The low observed density suggests that they lost some CH_2Cl_2 solvate during this time. $\rho_{calcd}(C_{19}H_{22}Mo_2O_5S_2)$ = 1.673 g cm^{-3}.

TABLE 5.2

Data Collection and Refinement for Structure 2 and Structure 3

diffractometer	Nonius CAD4F
radiation	Mo Kα[a]
scan mode	coupled ω-2θ

	2	3
scan width,[b,c] deg in ω	0.55	0.70
scan speed,[d] deg in ω	4.02-0.44	4.02-0.69
2θ range, deg	0-50	0-45
total no. of reflns	3380	3045
no. of obsd reins[e]	3140	2082
no. of variables	306	256
final R_1[f]	0.019	0.045
final R_2[g]	0.030	0.054
final GOF[h]	1.32	1.47

[a]Graphite monochromator, λ = 0.70930 A (α_1), 0.71359 A (α_2). [b]Also corrected for $K\alpha_1$-$K\alpha_2$ dispersion. [c]Scan extended by 25% on each side for background measurement. [d]Variable scan speed determined from intensity of reflection obtained in prescan. [e]Reflections where I $2.3\sigma(I)$. [f]$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [g]$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}$. [h]$GOF = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$; m = no. of observations, n = no. of variables.

TABLE 5.3

Final Atomic Coordinates for Structure 2

atom	x	y	z	B_{iso}/B^a
Mo(1)	0.27789 (1)	0.17131 (2)	0.23587 (1)	2.115 (10)
Mo(2)	0.21902 (1)	-0.05548 (2)	0.11432 (1)	2.171 (10)
S(1)	0.39127 (4)	0.04462 (6)	0.17644 (4)	2.83 (3)
C(2)	0.3367 (2)	-0.0307 (2)	0.2521 (2)	2.50 (9)
C(3)	0.3927 (2)	-0.1299 (3)	0.3304 (2)	3.38 (12)
S(2)	0.11867 (4)	0.04578 (6)	0.19809 (4)	2.67 (3)
C(4)	0.1167 (2)	-0.0617 (3)	0.2974 (2)	3.93 (14)
C(5)	0.0851 (4)	0.0178 (4)	0.3669 (3)	5.82 (23)
C(6)	0.3383 (2)	0.1354 (3)	0.3722 (2)	3.33 (12)
O(6)	0.3758 (2)	0.1176 (2)	0.4547 (1)	4.99 (13)
C(7)	0.1641 (2)	0.0880 (2)	0.0168 (2)	2.79 (10)
O(7)	0.1291 (2)	0.1602 (2)	-0.0471 (1)	4.16 (11)
C(11)	0.3451 (2)	0.3843 (2)	0.2191 (2)	3.36 (12)
C(12)	0.2626 (2)	0.3551 (2)	0.1323 (2)	3.56 (14)
C(13)	0.1735 (2)	0.3499 (2)	0.1526 (2)	3.18 (13)
C(14)	0.2006 (2)	0.3747 (3)	0.2516 (2)	3.50 (13)
C(15)	0.3077 (2)	0.3993 (2)	0.2934 (2)	3.16 (11)
C(16)	0.3673 (3)	0.4447 (4)	0.3947 (3)	4.74 (18)
C(21)	0.2027 (2)	-0.1982 (3)	-0.0105 (2)	3.56 (14)
C(22)	0.1073 (2)	-0.1946 (3)	0.0010 (2)	3.61 (14)
C(23)	0.1211 (2)	-0.2527 (3)	0.0905 (2)	4.13 (16)
C(24)	0.2244 (2)	-0.2929 (3)	0.1338 (2)	3.58 (14)
C(25)	0.2759 (2)	-0.2601 (2)	0.0714 (2)	3.21 (11)
C(26)	0.3842 (3)	-0.2948 (4)	0.0870 (3)	4.82 (19)
H(3A)	0.419 (2)	-0.209 (3)	0.305 (2)	3.9 (6)
H(3B)	0.350 (2)	-0.163 (3)	0.369 (2)	4.6 (7)
H(3C)	0.456 (2)	-0.084 (3)	0.381 (2)	5.0 (7)
H(4A)	0.189 (3)	-0.089 (4)	0.335 (3)	8.1 (11)
H(4B)	0.074 (3)	-0.140 (4)	0.269 (2)	5.7 (8)
H(5A)	0.073 (3)	-0.039 (4)	0.409 (3)	8.3 (12)
H(5B)	0.025 (3)	0.062 (4)	0.336 (3)	6.8 (11)
H(5C)	0.134 (3)	0.090 (5)	0.392 (3)	7.4 (11)
H(11A)	0.414 (2)	0.394 (3)	0.225 (2)	4.2 (6)
H(12A)	0.268 (2)	0.346 (3)	0.073 (2)	4.6 (7)
H(13A)	0.106 (2)	0.331 (3)	0.105 (2)	4.4 (7)
H(14A)	0.163 (2)	0.378 (3)	0.281 (2)	4.2 (7)
H(16A)	0.435 (5)	0.426 (6)	0.422 (4)	11.5 (17)
H(16B)	0.340 (3)	0.415 (4)	0.446 (3)	6.5 (9)
H(16C)	0.381 (4)	0.545 (5)	0.398 (4)	10.5 (15)
H(21A)	0.215 (2)	-0.171 (3)	-0.064 (2)	3.9 (7)
H(22A)	0.045 (3)	-0.160 (4)	-0.037 (2)	6.2 (9)
H(23A)	0.077 (2)	-0.265 (3)	0.117 (2)	4.1 (7)
H(24A)	0.251 (2)	-0.336 (3)	0.188 (2)	4.1 (7)
H(26A)	0.411 (2)	-0.232 (3)	0.056 (2)	4.5 (7)
H(26B)	0.417 (3)	-0.296 (4)	0.150 (3)	6.7 (10)
H(26C)	0.387 (3)	-0.383 (5)	0.063 (3)	8.2 (11)

$^a B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$ for non-hydrogen atoms.

TABLE 5.4

Selected Interatomic Distances (A) and Angles (deg) for Structure 2

Mo(1)-Mo(2)	2.8056 (3)		
Mo(1)-S(1)	2.4391 (6)	Mo(2)-S(1)	2.4563 (6)
Mo(1)-S(2)	2.4345 (6)	Mo(2)-S(2)	2.4236 (6)
Mo(1)-C(2)	2.136 (2)	Mo(2)-C(2)	2.122 (2)
Mo(1)-C(6)	1.927 (3)	Mo(2)-C(7)	1.971 (2)
Mo(1)-C(11)	2.355 (2)	Mo(2)-C(21)	2.280 (3)
Mo(1)-C(12)	2.341 (3)	Mo(2)-C(22)	2.289 (3)
Mo(1)-C(13)	2.334 (2)	Mo(2)-C(23)	2.333 (3)
Mo(1)-C(14)	2.334 (3)	Mo(2)-C(24)	2.358 (3)
Mo(1)-C(15)	2.388 (2)	Mo(2)-C(25)	2.347 (2)
Mo(1) C(7)	3.171 (2)		
S(1)-C(2)	1.751 (2)	S(2)-C(4)	1.834 (2)
C(2)-C(3)	1.505 (3)	C(4)-C(5)	1.494 (4)
C(6)-O(6)	1.161 (3)	C(7)-O(7)	1.146 (3)
(C15)-C(11)	1.402 (4)	C(25)-C(21)	1.411 (4)
C(11)-C(12)	1.411 (4)	C(21)-C(22)	1.415 (5)
C(12)-C(13)	1.395 (4)	C(22)-C(23)	1.401 (5)
C(13)-C(14)	1.404 (4)	C(23)-C(24)	1.409 (4)
C(14)-C(15)	1.420 (4)	C(24)-C(25)	1.416 (4)
C(15)-C(16)	1.501 (4)	C(25)-C(26)	1.493 (4)
Mo(2)-Mo(1)-S(1)	55.32 (2)	Mo(1)-Mo(2)-S(1)	54.75 (2)
Mo(2)-Mo(1)-S(2)	54.54 (2)	Mo(1)-Mo(2)-S(2)	54.91 (1)
Mo(2)-Mo(1)-C(2)	48.56 (6)	Mo(1)-Mo(2)-C(2)	49.01 (6)
Mo(2)-Mo(1)-C(6)	116.51 (8)	Mo(1)-Mo(2)-C(7)	81.15 (7)
Mo(2)-Mo(1)-Cp(1)	132.19	Mo(1)-Mo(2)-Cp(2)	166.52
S(1)-Mo(1)-S(2)	108.95 (2)	S(1)-Mo(2)-S(2)	108.74 (2)
S(1)-Mo(1)-C(2)	44.39 (6)	S(1)-Mo(2)-C(2)	44.23 (6)
S(1)-Mo(1)-C(6)	101.55 (8)	S(1)-Mo(2)-C(7)	92.92 (7)
S(1)-Mo(1)-Cp(1)	119.71	S(1)-Mo(2)-Cp(2)	124.62
S(2)-Mo(1)-C(2)	80.55 (6)	S(2)-Mo(2)-C(2)	81.09 (6)
S(2)-Mo(1)-C(6)	99.08 (8)	S(2)-Mo(2)-C(7)	86.70 (7)
S(2)-Mo(1)-Cp(1)	113.87	S(2)-Mo(2)-Cp(2)	120.81
C(2)-Mo(1)-C(6)	73.08 (10)	C(2)-Mo(2)-C(7)	125.75 (9)
C(2)-Mo(1)-Cp(1)	163.25	C(2)-Mo(2)-Cp(2)	119.62
C(6)-Mo(1)-Cp(1)	111.04	C(7)-Mo(2)-Cp(2)	112.01
Mo(1)-S(1)-Mo(2)	69.93 (2)	Mo(1)-C(2)-Mo(2)	82.43 (8)
Mo(1)-S(1)-C(2)	58.59 (8)	Mo(2)-S(1)-C(2)	57.69 (7)
Mo(1)-C(2)-S(1)	77.02 (9)	Mo(2)-C(2)-S(1)	78.08 (9)
Mo(1)-C(2)-C(3)	139.8 (2)	Mo(2)-C(2)-C(3)	132.4 (2)
Mo(1)-S(2)-Mo(2)	70.55 (2)		
Mo(1)-S(2)-C(4)	113.35 (11)	Mo(2)-S(2)-C(4)	111.57 (9)
S(1)-C(2)-C(3)	123.3 (2)	S(2)-C(4)-C(5)	110.9 (2)
Mo(1)-C(6)-O(6)	178.1 (2)	Mo(2)-C(7)-O(7)	172.5 (2)
C(15)-C(11)-C(12)	109.1(2)	C(25)-C(21)-C(22)	108.9 (3)
C(11)-C(12)-C(13)	107.7 (2)	C(21)-C(22)-C23)	107.8 (3)
C(12)-C(13)-C(14)	108.0 (2)	C(22)-C(23)-C(24)	107.8 (3)
C(15)-C(14)-C(15)	108.7 (2)	C(23)-C(24)-(25)	109.0 (3)
C(14)-C(15)-C(11)	106.4 (2)	C(24)-C(25)-C(21)	106.4 (2)
C(14)-C(15)-C(16)	126.7 (3)	C(24)-C(25)-C(26)	126.0 (3)
C(11)-C(15)-C(16)	126.7 (3)	C(21)-C25)-C(26)	127.4 (3)

This complex was found to contain an unusual symmetrically-bridged thioacyl function, as well as a bridging thioalkyl group. These thio-ligands were due to induced carbon-sulfur bond cleavage of the dithioester.

Structure 2 is revealed in Figure 5.1 to have a $(C_5H_4CH_3)(CO)Mo\text{-}Mo(CO)(C_5H_4CH_3)$ skeleton with two different, sulfur-containing ligands bridging across the metal-metal bond.

The thioacyl moiety $(CH_3CS)^{3-}$ is located perpendicular to the metal-metal bond axis with both the S and α C atoms bonded to each molybdenum. For the thioethyl ligand, the sulfur atom is a bridge to the molybdenum atoms. All four Mo-S distances are similar: [Mo(1)-S(1)=2.439Å, Mo(2)-S(1)=2.456Å, Mo(1)-S(2)=2.435Å, Mo(2)-S(2)=2.424Å]. From a purely crystallographic viewpoint, there are significant differences in these Mo-S distances; however, from a chemical point of view, both S atoms can be regarded as being symmetrically bound. The $(CH_3CS)^{3-}$ group may be regarded as a five electron donor. The very short S(1)-C(2) distance of 1.751(2)Å suggests significant double bond character, and therefore, a $(\sigma+\pi)$ bonding arrangement must be considered along with a pure σ-bonded resonance form. The S(2)-C(4) distance of the thioethyl ligand of 1.834(2)Å, indicates a conventional σ bond between S and C for this ligand.

The Mo-Mo distance of 2.8056(3)Å is shorter than values which have been reported for related metal carbonyl compounds (10,23,24,36-40), which range from 2.95-3.25Å. The C(7)-O(7) carbonyl is not a true semi-bridging carbonyl. This is indicated by the very long Mo(1)---C(7) distance of 3.171(2)(Å).

Three carbonyl bonds (at 1891, 1882 and 1859 cm^{-1}) instead of the expected two bonds were observed in the IR spectra of 2. However, ^{13}C NMR signals (∂234.9, 286.3) for the carbonyls. ^1H NMR signals for the $(C_5H_4CH_3)$, (SC_2H_5) and $(CH_3C(S))$ groups are in accord with the assigned structure. The mass spectrum revealed a molecular ion at the expected value of m/e $[526]^+$.

Two other examples of structure 2 were prepared. Reaction of $CH_3(S)SC_2H_5$ with $(C_5H_4R)_2Mo_2(CO)_4$ (R=H) in refluxing toluene afforded a 17 % yield of red $[(C_5H_5)_2Mo_2(CO)_2(CH_3C(S))(SC_2H_5)]$; and $(p\text{-}CH_3O\text{-}C_6H_4)CH_2S\text{-}C(S)CH_2P$ reacted with the same metal complex reactant to give a 4 % yield of red $[(C_5H_5)_2Mo_2(CO)_2(PhCH_2C(S))(SCH_2\text{-}C_6H_4\text{-}pOCH_3)]$. These compounds were characterized by IR and ^1H NMR spectroscopy (see experimental section). These two products were suggested to have structure 2, even though their IR frequencies were not an exact match. This was considered possible since the fingerprint pattern of the IR bands was very similar. It is well known that shifts in carbonyl frequencies can occur as the result of changing electron density on a metal centre. Furthermore, though group theory may predict the total number of IR bands, it cannot rule out the possibility of superimposed or very weak bands. Moreover, it is possible that conformational isomers may exist - again altering the expected bands.

Treatment of $(C_5H_4R)_2M_2(CO)_4$, (R=H, M=Mo) with $CH_3C(S)SC_2H_5$ in toluene at room temperature afforded a 13 % yield of brown $[(C_5H_5)_2Mo_2(CO)_4(CH_3C(S)SC_2H_5)]$.

An X-Ray crystal structure of this complex showed it to have structure 3; an ORTEP diagram of which is illustrated in Figure 5.2, with pertinent crystal data, data collection information, atomic coordinates and selected bond lengths and bond angles listed in Tables 5.1,5.2,5.5,5.6.

Figure 5.2

Structure 3: ORTEP diagram of $[(C_5H_5)_2Mo_2(CO)_4(CH_3C(S)SC_2H_5)]$.

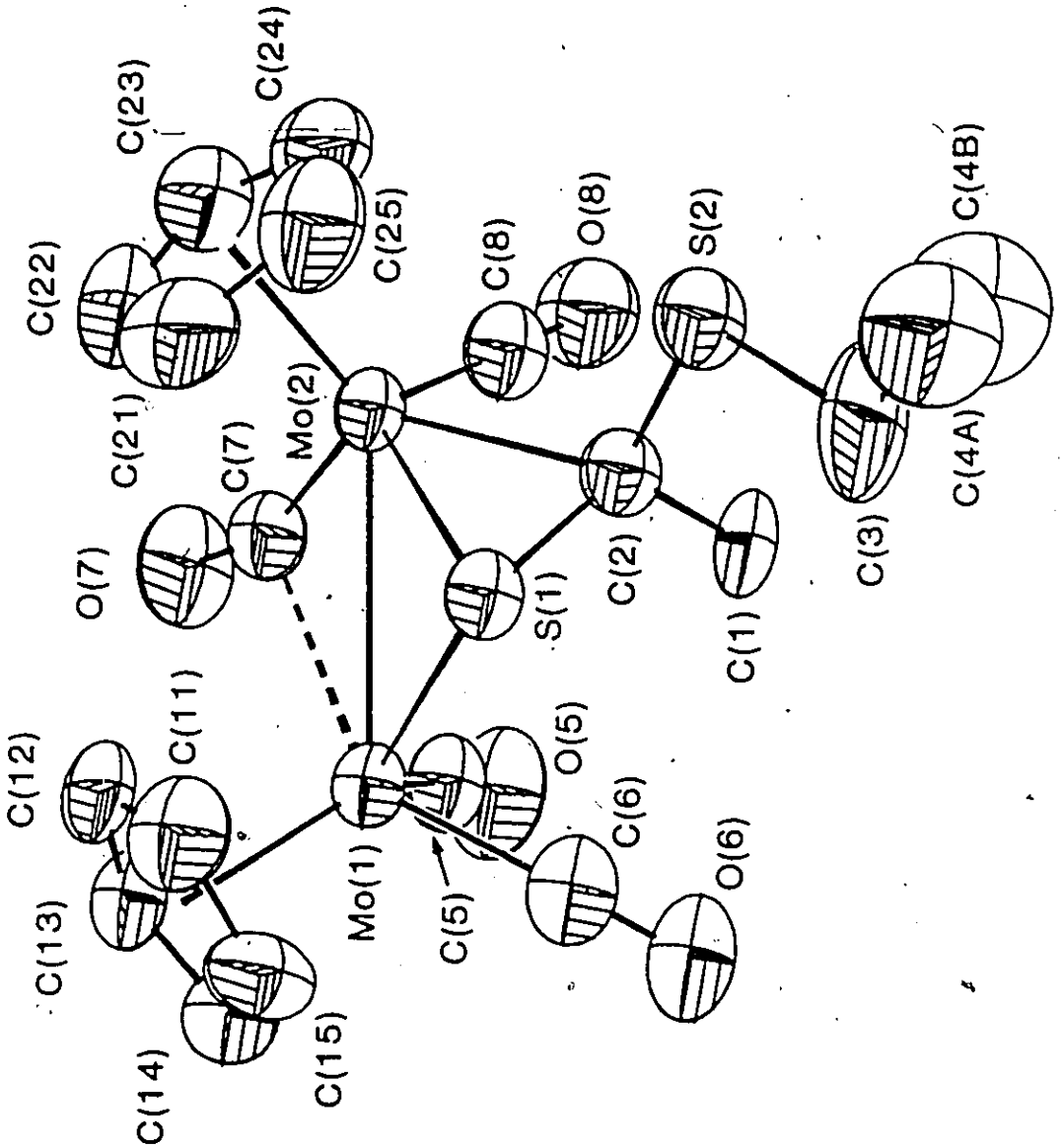


TABLE 5.5

Final Atomic Coordinates of 3

atom	x	y	z	B_{iso}/B^a
Mo(1)	0.26141 (4)	0.09598 (8)	0.21768 (6)	3.45 (5)
Mo(2)	0.38107 (4)	0.13819 (8)	0.16884 (6)	3.45 (5)
S(1)	0.31562 (12)	0.24868 (22)	0.23413 (19)	3.8 (1)
S(2)	0.41416 (14)	0.33004 (28)	0.31536 (24)	5.6 (2)
C(1)	0.3618 (5)	0.1673 (10)	0.3997 (7)	5.2 (8)
C(2)	0.3705 (5)	0.2204 (9)	0.3081 (7)	4.0 (6)
C(3)	0.3831 (8)	0.4101 (16)	0.4104 (12)	10.4 (15)
C(4A)[b]	0.4079 (15)	0.5078 (35)	0.4220 (28)	12.2 (10)
C(4B)[b]	0.4289 (31)	0.4310 (68)	0.4640 (53)	15.9 (24)
C(5)	0.2820 (5)	-0.0258 (10)	0.2904 (8)	4.4 (7)
O(5)	0.2916 (4)	-0.0993 (7)	0.3354 (6)	6.6 (7)
C(6)	0.2385 (5)	0.1340 (9)	0.3415 (9)	4.7 (8)
O(6)	0.2235 (4)	0.1525 (7)	0.4155 (6)	6.9 (7)
C(7)	0.3470 (5)	0.0009 (11)	0.1487 (8)	4.7 (7)
O(7)	0.3411 (4)	-0.0843 (7)	0.1210 (6)	6.5 (6)
C(8)	0.4205 (5)	0.0587 (10)	0.2614 (9)	4.7 (7)
O(8)	0.4448 (4)	0.0130 (8)	0.3145 (6)	6.6 (6)
C(11)	0.2196 (6)	0.1799 (12)	0.0943 (11)	6.0 (10)
C(12)	0.2383 (6)	0.0859 (15)	0.0596 (8)	6.2 (12)
C(13)	0.2150 (5)	0.0028 (11)	0.1069 (8)	5.0 (7)
C(14)	0.1796 (5)	0.0456 (11)	0.1704 (9)	4.9 (8)
C(15)	0.1825 (5)	0.1553 (12)	0.1606 (10)	5.6 (9)
C(21)	0.3801 (7)	0.2292 (22)	0.0254 (12)	7.9 (15)
C(22)	0.3963 (9)	0.1271 (19)	0.0088 (10)	7.6 (14)
C(23)	0.4422 (9)	0.1110 (16)	0.0531 (13)	7.8 (13)
C(24)	0.4569 (7)	0.1969 (23)	0.0993 (11)	7.5 (15)
C(25)	0.4202 (11)	0.2736 (14)	0.0842 (13)	8.0 (15)
C(71)[c]	0.0412 (14)	0.2874 (30)	0.1224 (27)	14.2
C(72)[c]	0.0282 (19)	0.2722 (42)	0.2001 (44)	14.2
C(73)[c]	0.0103 (20)	0.1978 (49)	0.1399 (37)	14.2
C(74)[c]	0.0000	0.1394 (64)	0.2500	14.2
C(75)[c]	0.0431 (20)	0.2224 (39)	0.2782 (34)	14.2
C(76)[c]	0.0316 (24)	0.0873 (52)	0.1634 (43)	14.2

[a] $B_{iso} = 8\pi^2(U_{11} + U_{22} + U_{33}/3$ (in A^2). [b] Fixed partial occupancies: C(4A), 0.62; C(4B), 0.38. [c] Refined occupancies: C(71), 0.82 (5); C(72), 0.62 (5); C(73), 0.53 (4); C(74), 0.51 (6); C(75), 0.60 (4); C(76), 0.53 (4).

TABLE 5.6

Selected Bond Lengths (A) and Bond Angles (deg.) for 3

Mo(1)-Mo(2)	3.1633 (14)	Mo(2)-C(2)	2.178 (10)
Mo(1)-S(1)	2.395 (3)	Mo(2)-S(1)	2.372 (3)
Mo(1)-C(5)	1.944 (13)	Mo(2)-C(7)	1.974 (15)
Mo(1)-C(6)	1.937 (13)	Mo(2)-C(8)	1.951 (13)
Mo(1)-C(11)	2.330 (13)	Mo(2)-C(21)	2.369 (13)
Mo(1)-C(12)	2.353 (12)	Mo(2)-C(22)	2.340 (14)
Mo(1)-C(13)	2.311 (11)	Mo(2)-C(23)	2.304 (13)
Mo(1)-C(14)	2.278 (12)	Mo(2)-C(24)	2.295 (14)
Mo(1)-C(15)	2.294 (12)	Mo(2)-C(25)	2.335 (14)
Mo(1) C(7)	2.678 (12)		
S(1)-C(2)	1.790 (11)	S(2)-C(3)	1.879 (17)
C(2)-C(1)	1.50 (2)	C(3)-C(4A)	1.41 (5)
C(2)-S(2)	1.786 (12)	C(3)-C(4B)	1.42 (8)
C(5)-O(5)	1.16 (2)	C(7)-O(7)	1.17 (2)
C(6)-O(6)	1.16 (2)	C(8)-O(8)	1.14 (2)
C(11)-C(12)	1.38 (3)	C(21)-C(22)	1.39 (4)
C(12)-C(13)	1.39 (2)	C(22)-C(23)	1.34 (3)
C(13)-C(14)	1.39 (2)	C(23)-C(24)	1.33 (4)
C(14)-C(15)	1.41 (2)	C(24)-C(25)	1.37 (4)
C(15)-C(11)	1.38 (2)	C(25)-C(21)	1.44 (4)
Mo(2)-Mo(1)-S(1)	48.1 (7)	Mo(1)-Mo(2)-S(1)	48.75 (8)
		Mo(1)-Mo(2)-C(2)	76.7 (3)
Mo(2)-Mo(1)-C(5)	89.8 (4)	Mo(1)-Mo(2)-C(7)	57.4 (3)
Mo(2)-Mo(1)-C(6)	116.7 (4)	Mo(1)-Mo(2)-C(8)	104.6 (4)
S(1)-Mo(1)-Cp(1)	120.6	Mo(1)-Mo(2)-Cp(2)	134.1
		S(1)-Mo(2)-C(2)	45.2 (3)
S(1)-Mo(1)-C(5)	116.2 (4)	S(1)-Mo(2)-C(7)	106.1 (4)
S(1)-Mo(1)-C(6)	83.0 (4)	S(1)-Mo(2)-C(8)	113.4 (4)
S(1)-Mo(1)-Cp(1)	118.8	S(1)-Mo(2)-Cp(2)	118.4
		C(2)-Mo(2)-C(7)	119.1 (5)
		C(2)-Mo(2)-C(8)	72.5 (4)
		C(2)-Mo(2)-Cp(2)	129.3
C(5)-Mo(1)-C(6)	77.6 (5)	C(7)-Mo(2)-C(8)	82.2 (5)
C(5)-Mo(1)-Cp(1)	124.3	C(7)-Mo(2)-Cp(2)	111.5
C(6)-Mo(1)-Cp(1)	117.2	C(8)-Mo(2)-Cp(2)	118.4
Mo(1)-S(1)-Mo(2)	83.14 (10)		
Mo(1)-S(1)-C(2)	110.0 (4)	Mo(2)-S(1)-C(2)	64.6 (4)
S(1)-C(2)-C(1)	119.9 (9)	Mo(2)-C(2)-S(1)	70.2 (4)
S(1)-C(2)-S(2)	111.1 (6)	Mo(2)-C(2)-S(2)	109.8 (5)
C(1)-C(2)-S(2)	113.2 (8)	Mo(2)-C(2)-C(1)	125.7 (8)
C(2)-S(2)-C(3)	102.0 (7)	S(2)-C(3)-C(4A)	112 (2)
		S(2)-C(3)-C(4B)	99 (3)
Mo(1)-C(5)-O(5)	176 (1)	Mo(1)-C(7)-O(7)	159 (1)
Mo(1)-C(6)-O(6)	177 (1)	Mo(1)-C(8)-O(8)	178 (1)
C(15)-C(11)-C(12)	106.7 (12)	C(25)-C(21)-C(22)	105.1 (16)
C(11)-C(12)-C(13)	109.7 (12)	C(21)-C(22)-C(23)	108.6 (17)
C(12)-C(13)-C(14)	107.3 (13)	C(22)-C(23)-C(24)	110.7 (18)
C(13)-C(14)-C(15)	106.8 (12)	C(23)-C(24)-C(25)	108.5 (17)
C(14)-C(15)-C(11)	109.4 (12)	C(24)-C(25)-C(21)	107.1 (17)

The dithioester moiety remains intact on complexation to give 3 and acts as a bridge across the metal atoms. S(1) is bonded to both Mo(1) and Mo(2) and C(2) is bound only to Mo(2). Thus the gross structure of 3 resembles the thiocamphor (32) 1 and thiolactone (33) complexes previously prepared. The Mo-S bond lengths of the latter complexes are comparable to these of 3. However, the Mo(2)-C(2) distance in structure 3 of 2.178(10)A is considerably shorter than that of the thiocamphor (2.235(6)A) and thiolactone (2.364(9)A) derivatives. This difference could be due to a delocalization of electron density throughout the S(1)-C(2)-S(2) portion of the ligand. This idea is supported by the nearly identical C(2)-S(1) and C(2)-S(2) bond lengths of 1.790(11)A and 1.786(12)A respectively.

The Mo(1)-Mo(2) distance of structure 3 was 3.163(1)A, and is similar to that of the thiocamphor (3.145(1)A) and thiolactone (3.138(1)A) derivatives. As the metal-metal distance of such dimers is sensitive to the nature, arrangement and number of bridging ligands, one can conclude that there must be strong parallels in the bonding arrangement of these three complexes.

Finally, structure 3 also contains a carbonyl C(7)-O(7) which is semi-bridging in nature. (The Mo(1)---C(7) interaction here is 2.678(12)A which is typical for the asymmetric M-C bond in semi-bridging compounds) (14).

An infrared (KBr) spectrum of this compound revealed five carbonyl peaks (1960, 1940, 1918, 1841 and 1806 cm^{-1}) instead of the expected four. ^1H NMR analysis agrees with the assigned structure, and satisfactory C and H analyses were obtained (see experimental).

Several other examples of compounds having the same structure as 3

were prepared. For example, reaction of $CH_3C(S)SC_2H_5$ with $(C_5H_4CH_3)_2Mo_2(CO)_4$ in toluene at room temperature afforded a 14 % yield of brown $[(C_5H_4CH_3)_2Mo_2(CO)_2(CH_3C(S)SC_2H_5)]$. In another example, $CH_3C(S)SC_2H_5$ when reacted at room temperature in xylene with $(C_5H_5)_2W_2(CO)_4$ afforded an 8 % yield of brown $[(C_5H_5)_2W_2(CO)_2(CH_3C(S)SC_2H_5)]$.

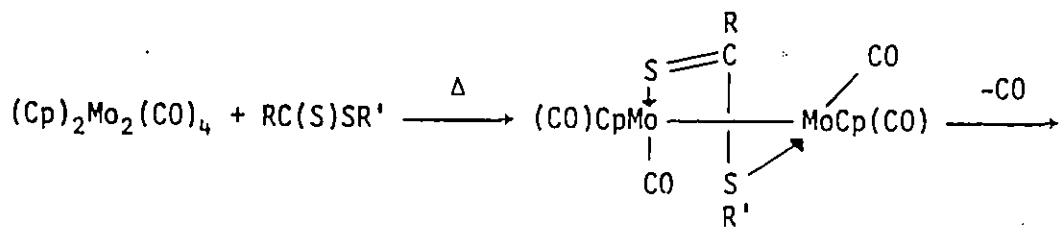
These two compounds were characterized spectroscopically (see experimental).

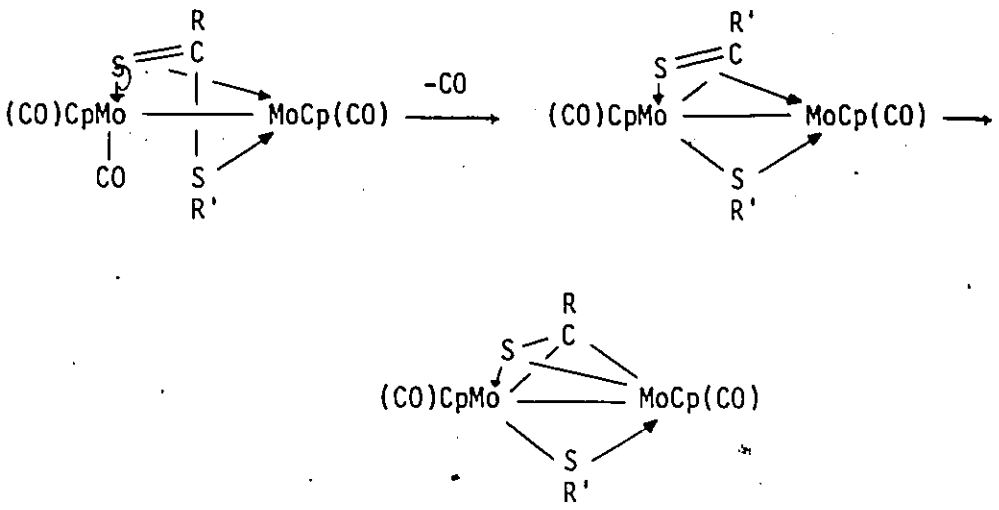
Complex 3 is not a precursor to complex 2, since none of the latter was detected on heating 3 in refluxing xylene. Thus, these two structures probably form by different mechanistic routes.

Structure 3 probably arises by a simple addition reaction: $(L + (C_5H_4R)_2M_2(CO)_4 \rightarrow (C_5H_4R)_2M_2(CO)_4L)$. The unusual nature of structure 2 necessitates a somewhat more complex path which might be the following:

Figure 5.4

Proposed Mechanism to Obtain Structure 2



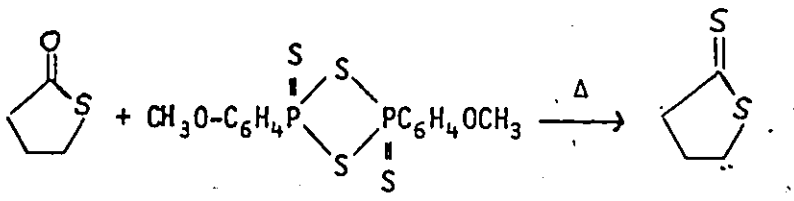


To conclude, acyclic dithioesters react with metal-metal triply bonded dimers to give the expected addition products (structure 3) and a truly novel bridged structure (structure 2), the latter containing a symmetrically bridged thioacyl unit and a bridging thioalkyl moiety.

5.3 Reaction of a Cyclic Dithioester with $(C_5H_4R)_2Mo_2(CO)_4$ (R=H, CH_3)

The interesting C-S bond cleavage reactions and the resulting novel thioacyl/thioalkyl products described in Chapter 5.2, provided impetus for a study of the reactions described in this chapter. It was of interest to react a dithiolactone with a metal-metal triple bond dimer to determine if it were possible to induce ring opening by C-S bond cleavage and, if this occurred, to see what effect the connecting alkyl chain has on the structure of the product.

The thiolactone used for this reaction (dithiobutyrolactone) was prepared by treatment of thiobutyrolactone with Lawesson's reagent in refluxing toluene:



Treatment of dithiobutyrolactone with $(C_5H_4R)_2M_2(CO)_4$ (R = CH_3, M = Mo) in refluxing toluene afforded red $[(C_5H_4CH_3)_2Mo_2(CO)_2(SC(CH_2)_3S)]$ in 38 % yield. This compound was characterized by analytical, spectral and X-Ray structural data, and was found to exist as structure 4, an ORTEP of which is shown in Figure 5.5; with crystal data, data collection information, final atomic coordinates and bond lengths and bond angles listed in Tables 5.7 - 5.10.

Table 5.7

Crystal Data for 4

formula	$C_{18}H_{20}Mo_2O_2S_2$	V, A^3	1849.8
cryst system	monoclinic	Z	4
space group	$P2_1/c$	fw	524.36
a, A	8.057 (1)	ρ_{obs} g cm^{-3}	1.86[a]
b, A	29.857 (2)	ρ_{calc} g cm^{-3}	1.883
c, A	7.992 (3)	μ, cm^{-1}	15.50
β, deg	105.80 (2)		

[a]By flotation in aqueous $ZnBr_2$ solution.

Figure 5.5

Structure 4: ORTEP diagram of $[(C_5H_4CH_3)_2Mo_2(SC(CH_3)_2S)]$

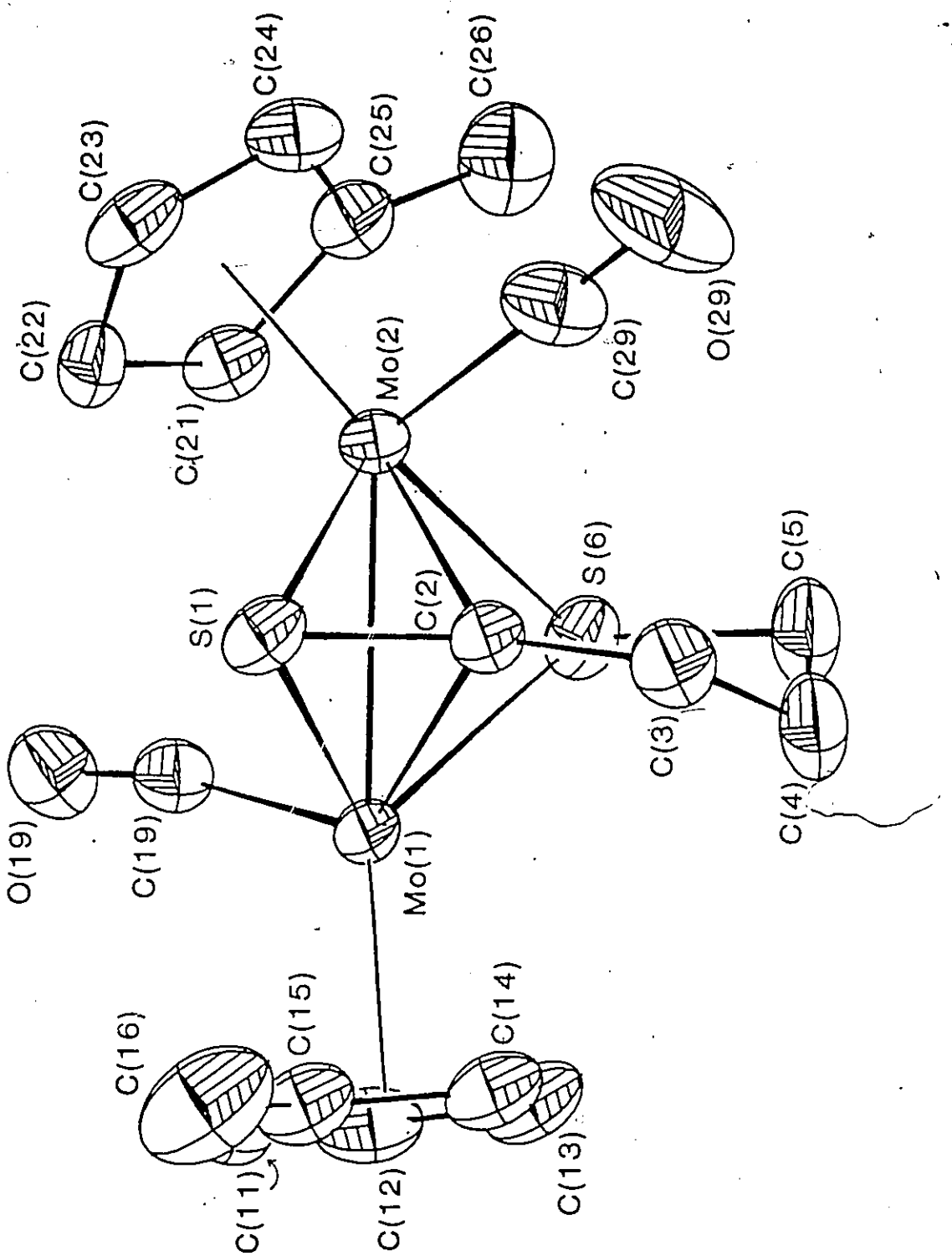


TABLE 5.8

Data Collection and Refinement for 4

diffractometer	Enraf-Nonius CAD4F
radiation	Mo Kα, graphite monochromator
λ of radiation, Å	0.70930 (α_1); 0.71359 (α_2)
scan mode	coupled ω-2θ
ω scan width, deg	0.55 plus α_1-α_2 dispersion
ω scan speed, deg min^{-1}	4-0.57
bkgd	scan extended by 25 % on each side
cryst size, mm	0.017 x 0.020 x 0.036
2θ range, deg	0-50
total no. of reflns	3258
obsd reflns	2984
no. of variables	298
final R_F	0.019
final R_{wF}	0.025
final GOF	1.81

TABLE 5.9

Fractional Atomic Coordinates for 4

atom	x	y	z	B_{eq}, A^2
Mo(1)	0.26019 (3)	0.162059 (7)	0.52659 (3)	1.98
Mo(2)	0.09020 (3)	0.111900 (7)	0.23592 (3)	2.08
S(1)	0.37089 (8)	0.14860 (2)	0.27388 (8)	2.70
C(2)	0.3389 (3)	0.10582 (8)	0.4079 (3)	2.36
C(3)	0.4461 (4)	0.06803 (10)	0.5059 (4)	3.43
C(4)	0.3753 (4)	0.05277 (11)	0.6556 (4)	4.04
C(5)	0.1810 (4)	0.04974 (11)	0.6169 (4)	3.98
S(6)	0.05625 (8)	0.10073 (2)	0.52907 (8)	2.75
C(11)	0.3717 (4)	0.22648 (11)	0.6722 (4)	4.24
C(12)	0.2829 (4)	0.20300 (11)	0.7739 (4)	4.11
C(13)	0.3725 (4)	0.16245 (11)	0.8260 (3)	3.54
C(14)	0.5154 (4)	0.16182 (11)	0.7580 (4)	3.43
C(15)	0.5172 (4)	0.20131 (10)	0.6636 (3)	3.65
C(16)	0.6538 (6)	0.21426 (23)	0.5772 (6)	6.47
C(19)	0.0669 (3)	0.20131 (8)	0.4200 (3)	2.69
O(19)	-0.0367 (3)	0.22923 (6)	0.3774 (3)	3.81
C(21)	-0.1869 (9)	0.14290 (9)	0.1541 (3)	2.81
C(22)	-0.0884 (4)	0.16486 (10)	0.0580 (4)	3.05
C(23)	-0.0444 (4)	0.13358 (11)	-0.0524 (3)	3.48
C(24)	-0.1151 (4)	0.09221 (10)	-0.0259 (4)	3.31
C(25)	-0.2044 (3)	0.09729 (9)	0.1019 (3)	2.85
C(26)	-0.3099 (5)	0.06249 (14)	0.1609 (5)	4.80
C(29)	0.1637 (4)	0.05203 (11)	0.1982 (4)	4.28
O(29)	0.2038 (4)	0.01603 (8)	0.1735 (4)	8.05

[a]Esd's refer to last digit printed. B_{eq} is the arithmetic mean of the principal axes of the thermal ellipsoid.

TABLE 5.10
Selected Interatomic Distances and Angles for 4

Bond Distances

Mo(1)-Mo(2)	2.790 (1)		
Mo(1)-S(1)	2.453 (1)	Mo(2)-S(1)	2.456 (1)
Mo(1)-C(2)	2.109 (2)	Mo(2)-C(2)	2.107 (3)
Mo(1)-S(6)	2.464 (1)	Mo(2)-S(6)	2.454 (1)
Mo(1)-C(11)	2.300 (3)	Mo(2)-C(21)	2.339 (3)
Mo(1)-C(12)	2.289 (3)	Mo(2)-C(22)	2.341 (3)
Mo(1)-C(13)	2.316 (3)	Mo(2)-C(23)	2.354 (3)
Mo(1)-C(14)	2.362 (3)	Mo(2)-C(24)	2.361 (3)
Mo(1)-C(15)	2.372 (3)	Mo(2)-C(25)	2.364 (3)
Mo(1)-C(19)	1.950 (3)	Mo(2)-C(29)	1.932 (3)
S(1)-C(2)	1.730 (3)	C(5)-S(6)	1.853 (3)
C(2)-C(3)	1.505 (4)	C(4)-C(5)	1.514 (5)
C(3)-C(4)	1.528 (5)	Mo(2)---C(19)	3.078 (2)
C(11)-C(12)	1.407 (5)	C(21)-C(22)	1.407 (4)
C(12)-C(13)	1.413 (5)	C(22)-C(23)	1.395 (4)
C(13)-C(14)	1.400 (5)	C(23)-C(24)	1.400 (4)
C(14)-C(15)	1.402 (4)	C(24)-C(25)	1.408 (4)
C(15)-C(11)	1.410 (5)	C(25)-C(21)	1.420 (4)
C(15)-C(16)	1.500 (5)	C(25)-C(26)	1.498 (4)
C(19)-O(19)	1.163 (3)	C(29)-O(29)	1.155 (4)

Bond Angles

Mo(2)-Mo(1)-S(1)	55.43 (2)	Mo(1)-Mo(2)-S(1)	55.31 (2)
Mo(2)-Mo(1)-C(2)	48.53 (7)	Mo(1)-Mo(2)-C(2)	48.61 (6)
Mo(2)-Mo(1)-S(6)	55.28 (2)	Mo(1)-Mo(2)-S(6)	55.61 (2)
Mo(2)-Mo(1)-C(19)	78.82 (7)	Mo(1)-Mo(2)-C(29)	121.6 (9)
Mo(2)-Mo(1)-Cp(1)	170.99	Mo(1)-Mo(2)-Cp(2)	129.60
S(1)-Mo(1)-C(2)	43.78 (7)	S(1)-Mo(2)-C(2)	43.74 (7)
S(1)-Mo(1)-S(6)	106.12 (3)	S(1)-Mo(2)-S(6)	106.31 (3)
S(1)-Mo(1)-C(19)	99.49 (8)	S(1)-Mo(2)-C(29)	96.95 (10)
S(1)-Mo(1)-Cp(1)	119.63	S(1)-Mo(2)-Cp(2)	125.50
C(2)-Mo(1)-S(6)	72.24 (7)	C(2)-Mo(2)-S(6)	72.48 (7)
C(2)-Mo(1)-C(19)	125.74 (10)	C(2)-Mo(2)-C(29)	75.20 (11)
C(2)-Mo(1)-Cp(1)	122.48	C(2)-Mo(2)-Cp(2)	169.21
S(6)-Mo(1)-C(19)	89.72 (8)	S(6)-Mo(2)-C(29)	98.14 (10)
S(6)-Mo(1)-Cp(1)	124.76	S(6)-Mo(2)-Cp(2)	116.15
C(19)-Mo(1)-Cp(1)	110.03	C(29)-Mo(2)-Cp(2)	108.59
Mo(1)-C(19)-O(19)	169.4 (2)	Mo(2)-C(29)-O(29)	178.4 (3)
Mo(1)-S(1)-Mo(2)	69.26 (2)	Mo(1)-S(6)-Mo(2)	69.11 (2)
Mo(1)-S(1)-C(2)	57.49 (8)	Mo(1)-S(6)-C(5)	108.63 (11)
Mo(2)-S(1)-C(2)	57.32 (8)	Mo(2)-S(6)-C(5)	106.46 (11)
Mo(1)-C(2)-Mo(2)	82.66 (9)		
Mo(1)-C(2)-S(1)	78.73 (10)	Mo(2)-C(2)-S(1)	78.94 (10)
Mo(1)-C(2)-C(3)	124.3 (2)	Mo(2)-C(2)-C(3)	135.5 (2)
C(2)-C(3)-C(4)	110.2 (2)	S(1)-C(2)-C(3)	135.6 (2)
C(3)-C(4)-C(5)	116.4 (3)	C(4)-C(5)-S(6)	116.9 (2)
C(15)-C(11)-C(12)	108.8 (3)	C(25)-C(21)-C(22)	108.2 (2)
C(11)-C(12)-C(13)	107.4 (3)	C(21)-C(22)-C(23)	108.1 (3)
C(12)-C(13)-C(14)	107.8 (3)	C(22)-C(23)-C(24)	108.1 (3)
C(13)-C(14)-C(15)	109.1 (3)	C(23)-C(24)-C(25)	108.9 (3)
C(14)-C(15)-C(11)	106.9 (3)	C(24)-C(25)-C(21)	106.7 (3)
C(14)-C(15)-C(16)	125.5 (4)	C(24)-C(25)-C(26)	126.8 (3)
C(11)-C(15)-C(16)	127.5 (4)	C(21)-C(25)-C(26)	126.3 (3)

Structure 4 consists of a $(C_5H_4CH_3)(CO)Mo\text{-}Mo(CO)(C_5H_4CH_3)$ skeleton with two sulfur atoms and one α-carbon bonded to each of the Mo atoms. In contrast to structure 2, the α-carbon is connected to the non-adjacent sulfur atom by an alkyl chain. Each Mo atom can be seen to be part of a six-membered ring. Mo(1), C(2), C(3), C(4), C(5) and S(6) exists in a boat conformation, and Mo(2), C(2), C(3), C(4), C(5) and S(6) exists in a chair conformation.

Comparison of the bond lengths in structure 2 and 4 indicates that the Mo-Mo bond of the latter was shorter (Mo-Mo in structure 2 : 2.8056(3), Mo-Mo in structure 4: 2.790(1)A). Moreover the Mo-α carbon distance of structure 4 (ave. 2.1098A) was shorter than that in structure 2 (ave. 2.129A). The Mo-S distances of 4 are also shorter than those of structure 2.

The S(1)-C(2) distance in structure 4 (1.730(3)A) is considerably shorter than those in structure 2 (1.769(6)A), the thiocamphor (1.807(6)A) and the thiolactone (1.790(11)A) derivatives (32,33). This suggests that there is an increased C=S character in structure 4 and therefore a larger ($\sigma+\pi$) contribution to the bonding of the thione to each of the Mo atoms.

The effect of the linking alkyl group was expected to be significant and this indeed is the case. Its effect can best be seen by examining the dihedral angles between planes of type Mo(1)-Mo(2)-L (L being a donor atom of the ligand). For example, the angles between planes Mo(1)-Mo(2)-C(2) and Mo(1)-Mo(2)-S(6) is 96.7(1)°. The corresponding dihedral angle in structure 2 is 111.1(1)°, indicating that C(2) and S(6) subtend a much smaller angle than when they exist in

separated ligands. An interesting result of this is that there is more room on the opposite side of the Mo-Mo bond for the carbonyl C(19)-O(19) to approach Mo(2) than in structure 2. The Mo(2)-C(19) distance of 3.078(2)A is significantly smaller than the corresponding distance in structure 2 (3.171(2)A). This results in the M-C-O angle being more bent in 4 (169.4(2)°) than in structure 2 (172.5(2)°).

The IR (KBr) spectrum of 4 displays two intense carbonyl stretching bands at 1881 and 1852 cm^{-1}. The molecular ion was observed in the mass spectrum (m/e 524), followed by the successive loss of carbonyl ligands as a major fragmentation pathway. The ^1H NMR spectrum and elemental analysis also supported the assigned structure.

Another example of structure 4 was prepared. Reaction of dithiobutyrolactone with $(C_5H_5)_2Mo_2(CO)_4$ in refluxing toluene gave red $[(C_5H_5)_2Mo_2(CO)_2(SC(CH_2)_3S)]$ in 44% yield. This product was characterized by spectral and analytical techniques (see experimental section). In terms of mechanism, the C-S bond cleavage can be explained satisfactorally by the mechanism in Figure 5.4, the only difference being that the dithioester is cyclic instead of acyclic.

To conclude, a cyclic dithioester was found to react with metal-metal triple bond dimers resulting in C-S bond cleavage in the dithiolactone and the formation of a novel structure which contains several unique features including a symmetrically bridged dithioligand and a very short metal-metal bond.

5.4 Reaction of Tetraalkylthiuram disulfides with $(C_5H_4R)_2Mo_2(CO)_4$ compounds.

Interesting S-S bond cleavage reactions were found to result from the interaction of tetraalkylthiuram disulfides with the metal-metal triple bond dimers $(C_5H_4R)_2Mo_2(CO)_4$ (R=H, CH_3), affording mononuclear dithiocarbamate complexes.

Treatment of commercially-obtained tetraisopropylthiuram disulfide with $(C_5H_5)_2Mo_2(CO)_4$ in toluene at room temperature afforded orange $[(C_5H_5)Mo(CO)_2(S_2CN(i\text{-}C_3H_7)_2]$ in 57 % yield. This compound was characterized by analytical, spectral and X-Ray analyses. The X-Ray crystal structure of this product, structure 5, is illustrated in Figure 5.6. Pertinent crystal data, data collection information, final atomic coordinates and selected bond lengths and bond angles are given in Tables 5.11-5.13.

The X-Ray analysis of structure 5 shows a mononuclear molybdenum complex containing two carbonyls and a cyclopentadienyl ligand plus a bidentate dithiocarbamate moiety. The Mo-S distances (averaging 2.497A) are typical of the Mo-S distances reported for other molybdenum-thiocarbamate complexes (41). The S(1), S(2), C(1), C(2) plane is tilted with respect to the cyclopentadienyl ligand at an angle of 6.9°. This appears to occur in order to maximize the separation of these atoms from the cyclopentadienyl ring. The analytical and spectral data obtained also supported the assigned structure. For example, the infrared (Nujol) displayed two carbonyl peaks at 1942 and 1852 cm^{-1}.

Figure 5.6

ORTEP diagram of Structure 5: $[(C_5H_5)Mo(CO)_2(S_2CN(i\text{-}C_3H_7)_2)]$

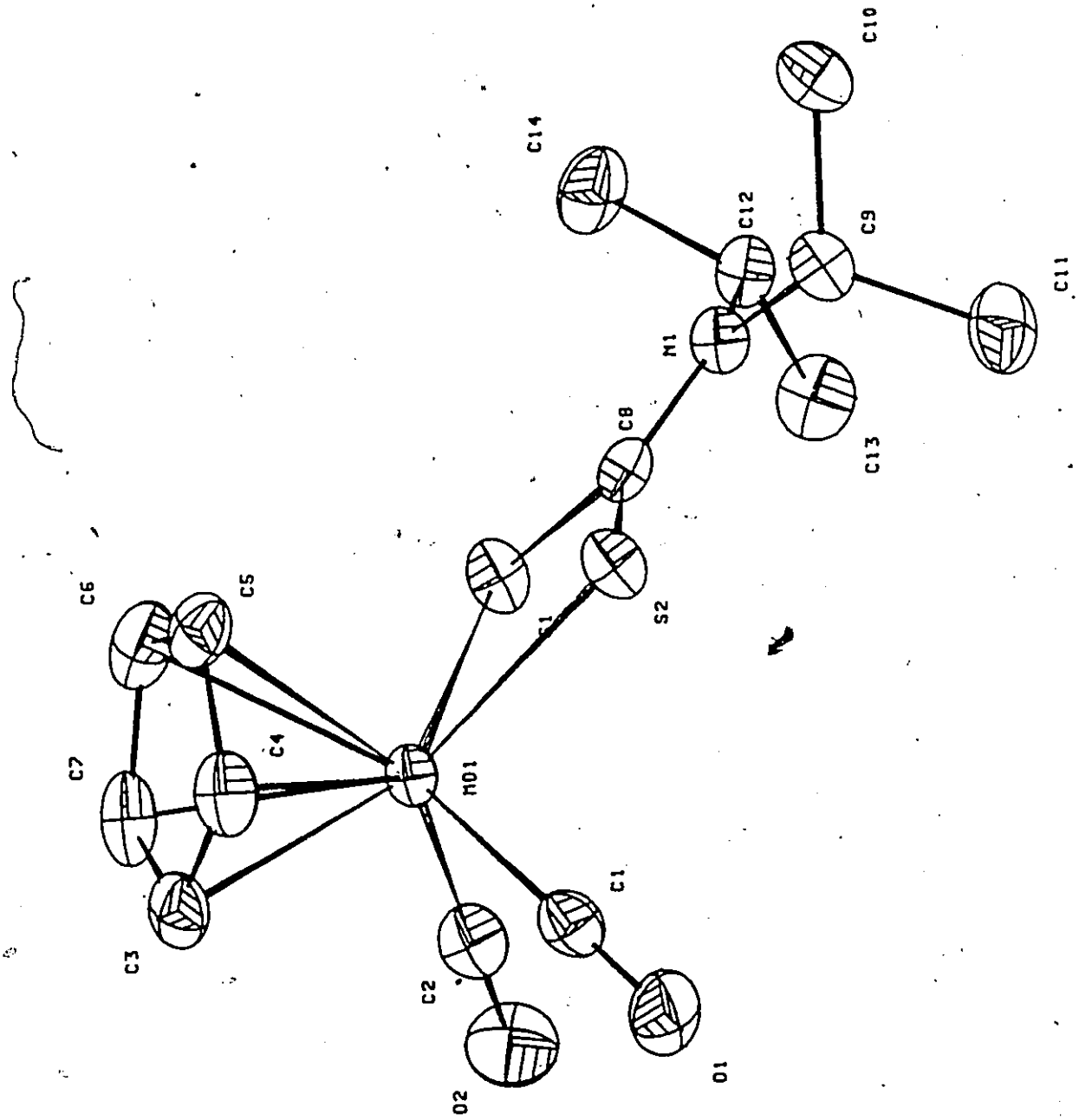


Table 5.11

Crystal Data and Data Collection Information for Structure 5 and Structure 6

	Structure 5	Structure 6
formula	$C_{10}H_{13}MoO_2PS$	$C_{14}H_{19}MoNO_2S_2$
molecular weight	324.18	393.37
space group	$P_{2_12_12_1}$	P1
a, Å	6.643(2)	7.800(1)
b, Å	13.643(5)	10.186(3)
c, Å	13.902(3)	10.250(3)
V, $Å^3$	1260.0	793.1
Z	4	2
d_c, g/ml	1.709	1.647
crystal dimension, mm	0.33 x 0.26 x 0.33	0.55 x 0.38 x 0.08
radiation	Mo-K_α	Mo-K_α
μ(Mo-K_α), cm^{-1}	12.80	10.60
transmission factors	0.670-0.844	0.782-0.913
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan width, deg in ω	1.20	1.10
scan speed, deg in ω	1.10-5.49	0.87-4.12
total no. of refl'ns	1683	2777
no. of obsd refl'ns	1355	2356
no. of variables	141	241
R_F	0.026	0.038
R_{wF}	0.030	0.051
GOF	1.13	1.03

Table 5.12

Atomic co-ordinates ($x10^4$) with e.s.d.'s in parentheses and U_{eq} ($x10^4$) for the non-hydrogen atoms of 5

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	1203.8(5)	2539.9(4)	2518.2(4)	201
S(1)	1376(2)	1524(1)	466(1)	255
S(2)	3449(2)	3490(1)	843(1)	244
O(1)	4335(5)	2140(5)	4288(4)	405
O(2)	1639(6)	-446(4)	3944(4)	433
N(1)	3810(5)	2501(4)	-1434(4)	225
C(1)	3181(7)	2298(5)	3633(5)	278
C(2)	1448(7)	647(5)	3383(5)	305
C(3)	-805(7)	3275(5)	4037(5)	302
C(4)	-45(7)	4415(5)	3322(5)	292
C(5)	-561(7)	4643(5)	1998(6)	312
C(6)	-1569(7)	3648(6)	1877(6)	361
C(7)	-1737(7)	2781(6)	3140(6)	342
C(8)	2984(6)	2501(4)	-253(5)	214
C(9)	5176(6)	3430(5)	-1881(5)	263
C(10)	5024(8)	4168(6)	-3309(6)	366
C(11)	6960(7)	2675(6)	-1658(7)	390
C(12)	3561(6)	1530(5)	-2319(5)	233
C(13)	3994(8)	66(5)	-1679(6)	333
C(14)	1772(7)	1772(6)	-2862(6)	367

Table 5.13

Selected Interatomic Distances (Å) and Angles (deg) for 5

Mo(1) — (S(1)	2.502(1)	S(2) — Mo(1) — S(1)	68.49(4)
Mo(1) — S(2)	2.491(1)	C(1) — Mo(1) — S(1)	120.7(1)
Mo(1) — C(1)	1.961(5)	C(1) — Mo(1) — S(2)	79.9(1)
Mo(1) — C(2)	1.959(5)	C(2) — Mo(1) — S(1)	82.1(1)
Mo(1) — C(3)	2.284(5)	C(2) — Mo(1) — S(2)	121.1(2)
Mo(1) — C(4)	2.308(5)	C(2) — Mo(1) — C(1)	73.1(2)
Mo(1) — C(5)	2.409(5)	C(8) — S(1) — Mo(1)	91.1(2)
Mo(1) — C(6)	2.408(5)	C(8) — S(2) — Mo(1)	91.2(2)
Mo(1) — C(7)	2.328(5)	C(9) — N(1) — C(8)	119.2(4)
S(1) — C(8)	1.719(5)	C(12) — N(1) — C(8)	123.7(4)
S(2) — C(8)	1.728(5)	C(12) — N(1) — C(9)	117.0(4)
N(1) — C(8)	1.324(6)	O(1) — C(1) — Mo(1)	179.1(5)
N(1) — C(9)	1.489(6)	O(2) — C(2) — Mo(1)	176.3(5)
N(1) — C(12)	1.500(6)	C(7) — C(3) — C(4)	107.6(5)
O(1) — C(1)	1.146(7)	C(5) — C(4) — C(3)	107.9(5)
O(2) — C(2)	1.152(7)	C(6) — C(5) — C(4)	108.5(5)
C(3) — C(4)	1.412(8)	C(7) — C(6) — C(5)	108.3(5)
C(3) — C(7)	1.411(8)	C(6) — C(7) — C(3)	107.6(5)
C(4) — C(5)	1.417(8)	S(2) — C(8) — S(1)	109.2(3)
C(5) — C(6)	1.379(8)	N(1) — C(8) — S(1)	127.3(4)
C(6) — C(7)	1.428(9)	N(1) — C(8) — S(2)	123.5(4)
C(9) — C(10)	1.521(7)	C(10) — C(9) — N(1)	112.9(4)
C(9) — C(11)	1.526(7)	C(11) — C(9) — N(1)	110.1(4)
C(12) — C(13)	1.524(7)	C(11) — C(9) — C(10)	112.2(4)
C(12) — C(14)	1.523(7)	C(13) — C(12) — N(1)	113.4(4)
		C(14) — C(12) — N(1)	112.0(4)
		C(14) — C(12) — C(13)	112.0(5)

The two terminal carbonyl ligands of the complex gave a single resonance at δ257.1 in the ^{13}CNMR spectrum, and the carbon of the dithiocarbamate moiety displayed a resonance at δ207.6 in line with that for other known dithiocarbamate complexes (42).

Several other examples of structure 5 were prepared. Reaction of tetraethylthiuram disulfide with $(C_5H_5)_2Mo_2(CO)_4$ in toluene at room temperature gave red $[(C_5H_5)Mo(CO)_2(S_2CN(C_2H_5)_2)]$ in 83 % yield. This compound was characterized by spectral techniques, (see experimental section).

Reaction of tetramethylthiuram disulfide with $(C_5H_5)_2Mo_2(CO)_4$ in toluene at room temperature afforded $[(C_5H_5)Mo(CO)_2(S_2CN(CH_3)_2)]$ in 37 % yield. It should be noted that while complexes of structural type 5 have been known for a number of years, no X-Ray analysis has apparently been reported for this class of complex.

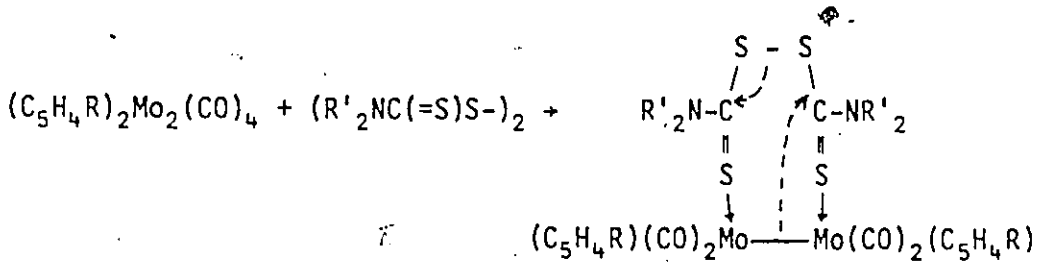
There exists a method in the literature for the preparation of compounds of type 5 which is similar to the method used in this thesis. In 1964, Cotton published a report (43) describing the generation of dithiocarbamate complexes by reaction of thiuram disulfides with the cyclopentadienylmolybdenum tricarbonyl dimer in refluxing methylcyclohexane (101°C). Since $Cp_2Mo_2(CO)_4$ is generated from a thermal decarbonylation of this dimer, it is likely that Cotton unwittingly generated the triple-bond dimer in situ which then reacted with the thiuram disulfides to afford the products. It is unlikely that Cotton realized that the active metal species in his reaction was the triple-bond dimer $(C_5H_4R)_2Mo_2(CO)_4$, since he did not rationalize the structure and bonding of multiply-bonded complexes until somewhat later

(1965) (2). Also, the existence of the molybdenum carbonyl multiply bonded dimer was not reported until 1967 (11).

In terms of mechanism, the sulfur-sulfur bond cleavage reaction may be initiated by a simple addition of the organic ligand to the triple bond dimer, followed by S-S and Mo-Mo bond cleavage:

Figure 5.7

Proposed Mechanism of S-S Bond Cleavage in 5



→ $2[(C_5H_4R)Mo(CO)_2(S_2CN(R')_2]$.

To conclude, this series of reactions has illustrated an interesting S-S bond cleavage reaction, induced under very mild (room temperature) conditions by the molybdenum carbonyl dimer, to afford mononuclear thiocarbamate complexes.

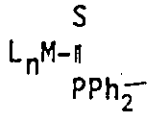
5.5 Reaction of Tetraalkylbiphospine disulfides with $(C_5H_4R)_2Mo_2(CO)_4$ dimers.

Interesting P-P bond cleavage reactions result from the interaction

of tetraalkylbiphosphine disulfides with $(C_5H_4R)_2Mo_2(CO)_4$(R=H, CH_3) affording complexes containing the novel η^2-(SP(R')$_2$) ligand. Reaction of tetramethylbiphosphine disulfide with $(C_5H_4CH_3)_2Mo_2(CO)_4$ in refluxing toluene afforded orange $[(C_5H_4CH_3)Mo(CO)_2(S\text{-}P(CH_3)_2)]$ in 26 % yield (structure 6). The structure of this compound was determined on the basis of spectral and X-Ray crystallographic analyses, and an ORTEP diagram is given in Figure 5.9. Pertinent crystal data, data collection information, final atomic coordinates and selected bond lengths and bond angles are given in Tables 5.11, 5.14 and 5.15.

Complex 6 is a mononuclear molybdenum complex containing two carbonyls, a $(C_5H_4CH_3)$ ligand an η^2-$(CH_3)_2PS$ moiety.

A few examples of η^2-R_2PS-containing complexes are known in the literature. Several rhodium and iridium complexes (44) contain η_2-Ph_2PS ligands and apparently have the following structure:



The only other complex containing an η^2-R_2PS ligand for which definitive X-Ray structural data is available is $[(\eta^2\text{-}Ph_2PS)_2Mo(CO)_2(PPh_3)]$ (45) (Figure 5.8).

Figure 5.8

Structure 7 : $[(\eta^2\text{-}Ph_2PS)_2Mo(CO)_2(PPh_3)]$

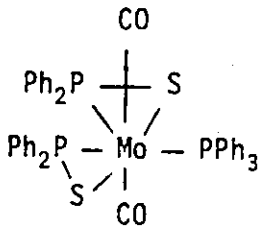


TABLE 5.14

Atomic co-ordinates ($x10^4$) with e.s.d.'s in parentheses and U_{eq} ($x10^4$) for the non-hydrogen atoms of 6.

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	1911.4(7)	659.8(3)	810.1(3)	237
P(1)	2976(2)	-990.1(9)	590.8(8)	254
S(1)	190(2)	-846(1)	57(1)	331
O(1)	6004(8)	1156(4)	-145(4)	540
O(2)	623(8)	1608(3)	-1130(3)	483
C(1)	4469(9)	974(4)	215(4)	354
C(2)	1057(9)	1253(4)	-418(4)	324
C(3)	-301(9)	605(5)	2184(4)	362
C(4)	-413(10)	1524(4)	1723(4)	366
C(5)	1496(10)	1989(5)	1787(4)	402
C(6)	2818(12)	1357(5)	2258(4)	429
C(7)	1714(10)	490(4)	2497(4)	379
C(8)	-2001(12)	-93(6)	2344(5)	529
C(9)	4803(9)	-1405(4)	-268(4)	378
C(10)	3171(13)	-1870(4)	1563(4)	387

TABLE 5.15

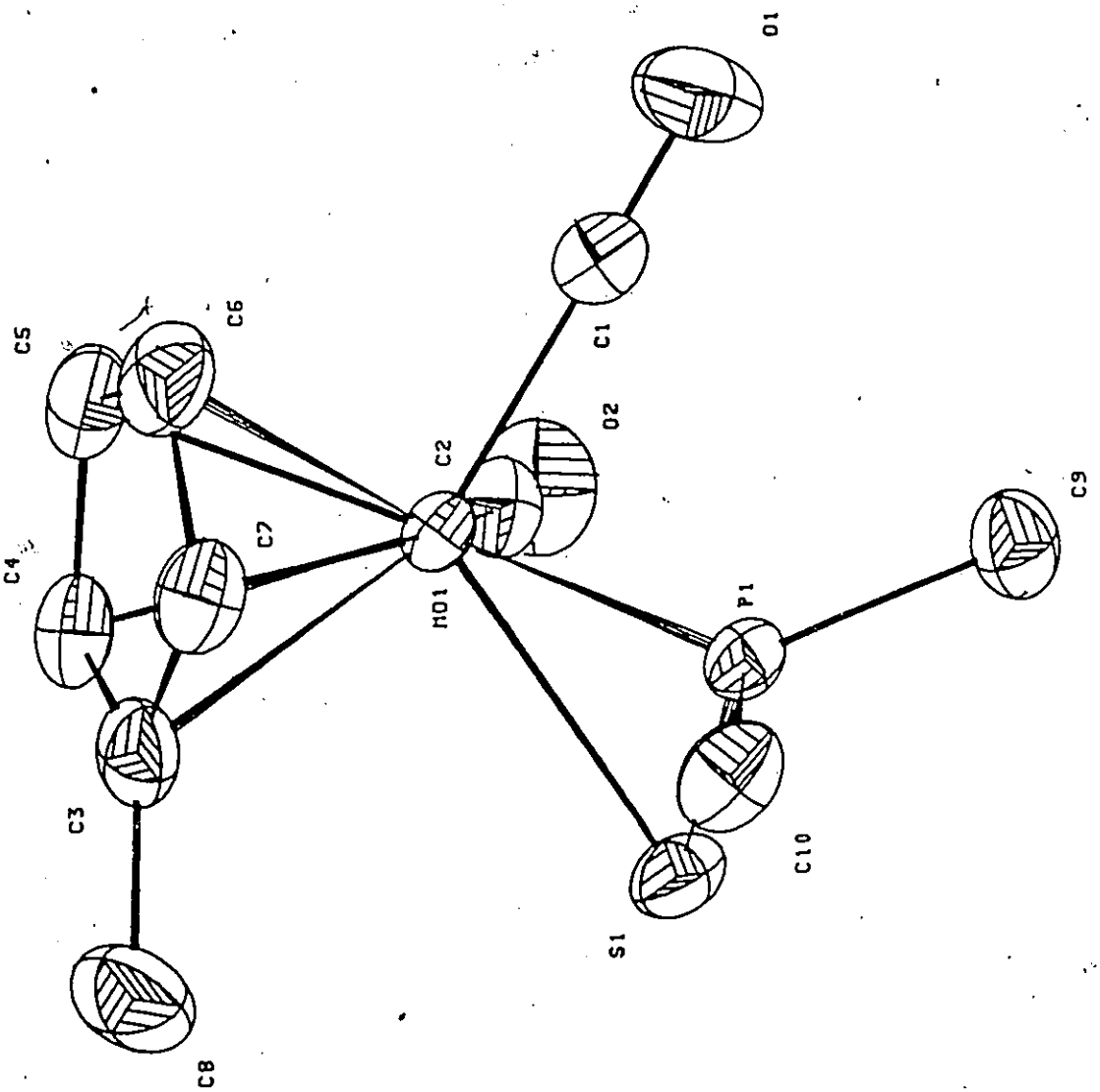
Selected Interatomic Distances (A) and Angles (deg) for 6

Mo(1) – P(1)	2.379(1)
Mo(1) – S(1)	2.574(1)
Mo(1) – C(1)	1.937(6)
Mo(1) – C(2)	1.973(6)
Mo(1) – C(3)	2.411(5)
Mo(1) – C(4)	2.321(6)
Mo(1) – C(5)	2.283(6)
Mo(1) – C(6)	2.306(6)
Mo(1) – C(7)	2.360(5)
P(1) – S(1)	2.003(2)
P(1) – C(9)	1.794(6)
P(1) – C(10)	1.812(5)
O(1) – C(1)	1.163(7)
O(2) – C(2)	1.139(7)
C(3) – C(4)	1.409(9)
C(3) – C(7)	1.416(9)
C(3) – C(8)	1.494(9)
C(4) – C(5)	1.421(9)
C(5) – C(6)	1.394(9)
C(6) – C(7)	1.431(9)

S(1) – Mo(1) – P(1)	47.5(1)
C(1) – Mo(1) – P(1)	83.9(2)
C(1) – Mo(1) – S(1)	113.1(2)
C(2) – Mo(1) – P(1)	111.3(2)
C(2) – Mo(1) – S(1)	81.3(2)
C(2) – Mo(1) – C(1)	78.0(3)
S(1) – P(1) – Mo(1)	71.4(1)
C(9) – P(1) – Mo(1)	125.8(2)
C(9) – P(1) – S(1)	114.2(2)
C(10) – P(1) – Mo(1)	123.5(2)
C(10) – P(1) – S(1)	114.0(3)
C(10) – P(1) – C(9)	103.8(3)
P(1) – S(1) – Mo(1)	61.1(1)
O(1) – C(1) – Mo(1)	179.5(5)
O(2) – C(2) – Mo(1)	177.9(6)
C(7) – C(3) – C(4)	106.7(6)
C(8) – C(3) – C(4)	126.5(6)
C(8) – C(3) – C(7)	126.7(6)
C(5) – C(4) – C(3)	108.8(6)
C(6) – C(5) – C(4)	108.4(6)
C(7) – C(6) – C(5)	107.3(6)
C(6) – C(7) – C(3)	108.8(6)

Figure 5.9

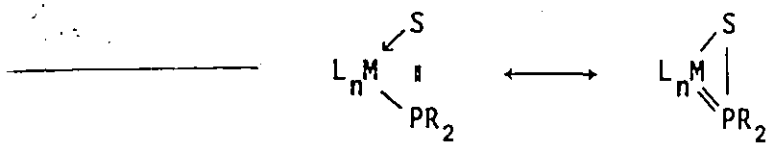
ORTEP diagram of Structure 6: $[(C_5H_4CH_3)Mo(CO)_2(\eta^2SP(CH_3)_2]$



The dimensions of the Mo-P-S ring in structure 6 are similar to those of 7 except that the Mo-S bond of structure 6 (2.574(1)Å) is shorter than the other Mo-S distances found in 7: (2.613(2) and 2.630(2)Å) (45). In accord with this, the P-S bond distance in 6 is intermediate in length between known P=S double bond distances (1.926-1.966Å) (46) and the P-S single bond distance of (2.122Å)(47).

The bond angles of the (η^2-R_2PS)Mo fragment in structure 6 are similar to those of one of the η^2-Ph_2PS moieties in 7. The steric bulk of the R groups on η^2-R_2PS moieties likely plays an important role in determining the bond lengths and bond angles of the (η^2-R_2PS)Mo fragment.

Irrespective of minor variations in dimensions of the Mo-S-P ring, the SPR_2 ligands probably act as a formal 3 electron donor to the metal, with either phosphorus or sulfur functioning as a one electron ligand. Thus, the η^2-bonding could perhaps be best described as a resonance hybrid:



This situation is similar to that of other known η^2 complexes such as η^2-acyl molybdenum species (48).

The infrared spectrum (Nujol) of structure 6 revealed two strong carbonyl bands at 1960 and 1875 cm^{-1}.

The two terminal carbonyl ligands give a single resonance at 267.9 in the ^{13}C NMR, suggesting the occurrence of a fluxional process in solution, due to rapid positional interchange of CO ligands.

A molecular ion peak was present in the mass spectrum at m/e 324, followed by the sucessive loss of carbonyl ligands as a major fragmentation pathway. The ^{1}H NMR spectrum was also in accord with the assigned structure.

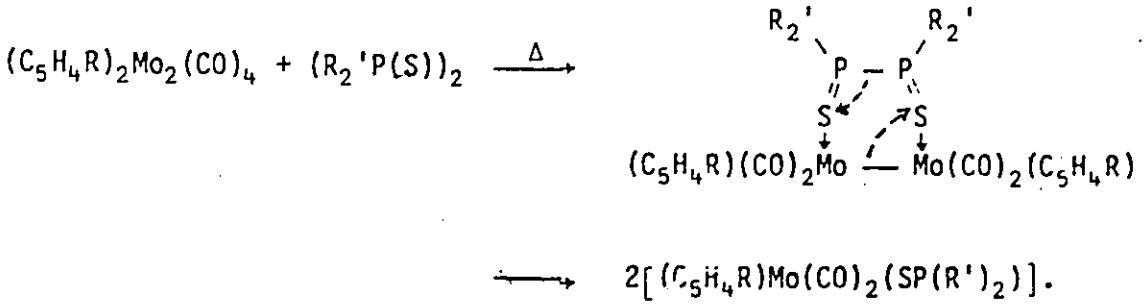
Another example of structure 6 was prepared by reaction of tetraethyldiphosphine disulfide with $(C_5H_5)_2Mo_2(CO)_4$ in refluxing toluene. The orange product $[(C_5H_5)Mo(CO)_2(SP(C_2H_5)_2)]$ was isolated in 6 % yield. This compound was characterized by infrared, ^{1}H NMR and mass spectral analyses (see experimental section).

It should be noted that a compound similar to structure 6 has been reported in the literature, although this compound was prepared by the reaction of diphenylphosphine sulfide ($Ph_2(H)PS$) with cyclopentadienylmolybdenum tricarbonyl chloride (46). (No X-Ray data was available for this compound. However its infrared carbonyl bands of 1958 and 1873 cm^{-1} agreed well with those found for structure 6).

In terms of mechanism, the P-P bond cleavage reaction may proceed by a mechanism (Figure 5.10) analagous to that proposed for the S-S cleavage of thiuram disulfides.

FIGURE 5.10

Proposed Mechanism for P-P Bond Cleavage in 6



To conclude, this series of reactions has illustrated an interesting P-P bond cleavage reaction, induced by the multiply-bonded molybdenum carbonyl dimer to afford an interesting class of η^2-R_2PS complexes.

Chapter 6

Experimental Data for Triple Bond Reactions

6.1 General Comments: Spectral determinations were carried out as described in Chapter 3, with the exception that some infrared spectra were obtained using a Nicolet MX-1 FT spectrometer.

Elemental analyses were obtained from MHW Laboratories, Phoenix, Arizona, and from Schwarzkopf Microanalytical Laboratories, Woodside, New York. Single crystal X-Ray analyses were carried out at Simon Fraser University, Burnaby, British Columbia, using a Nonius CAD4F diffractometer.

Dicyclopentadienyldimolybdenum hexacarbonyl was purchased from Strem Chemical Co., or Pressure Chemical Co., and was used as received. The tungsten analog and bis(methylcyclopentadienyl)dimolybdenum hexacarbonyl were prepared according to literature procedures (14). Literature procedures were also used to synthesize the dithioesters (35). The tetraalkylthiuram disulfide and tetraalkylbiphosphine-disulfide ligands were obtained from Aldrich Chemical Co., and were used as received. Solvents were dried and purified by standard procedures prior to use. All reactions and work-ups were carried out under a dry nitrogen atmosphere with the use of established vacuum line and Schlenk techniques.

6.2 Reactions of Acyclic Dithioesters with $L_2M_2(CO)_4$

6.2.1 Ethyl dithioacetate

A mixture of ethyl thioacetate (2.08 gm, 17.3 mmol) and Lawesson's reagent (4.86 gm, 12.0 mmol) was dissolved in toluene (80 ml) and refluxed vigorously for 2 days. The orange solution was concentrated and passed through a silica gel column using 9/1 hexane/ether as the eluent. Concentration gave a viscous orange oil (0.42 gm, 18%) with an extremely foul odor. ^1H NMR ($CDCL_3$) δ 0.88 (t; 3H, CH_3), 2.68(s; 3H; CH_3CS), 3.08 (q; 2H, SCH_2).

6.2.2 Structure 2:

$Cp_2Mo_2(CO)_2LL'$ ($L=SC_2H_5$, $L'=CH_3C(S)$)

Bis(cyclopentadienyl)dimolybdenum hexacarbonyl (1.00 gm, 2.0 mmol) was put into a Schlenk tube under nitrogen and refluxed vigorously in deoxygenated toluene (30 ml) overnight. Next day, the solution was checked by infrared spectroscopy which confirmed that the triple bond dimer $Cp_2Mo_2(CO)_4$ had been generated in situ. Ethyl dithioacetate (0.22 gm, 1.80 mmol) was added, the solution was refluxed vigorously overnight, and the crude product was subsequently evaporated to dryness. Column chromatography on silica gel with 49/1 hexane/ether afforded 0.19 gm (17%) of a red crystalline product. M.Pt. 85-90° (dec.). IR ν_{CO} (KBr) 1942 (s), 1884 (vs), 1842 (vs)cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25(t;3H,CH_3), 1.57(s;3H,$CH_3C(=S)$), 2.77(m;3H,SCH_2), 5.23(s;5H,Cp), 5.50(s;5H,Cp).

6.2.3 Structure 2:

$(CH_3C_5H_4)_2Mo_2(CO)_2LL'$ $(L=SC_2H_5, L'=CH_3C(S))$

This reaction was conducted in exactly the same manner as that described in (6.2.2), except that the metal dimer was $(CH_3C_5H_4)Mo_2(CO)_6$ and molar quantities were halved. Elution with 49/1 hexane/ether afforded a red crystalline product (0.07 gm, 14%), M.Pt. = 84-86°. IR ν_{CO} (KBr) 1891(s), 1882(vs) 1859 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t;3H,CH_3CH_2S), 1.94(S;3H,CH_3-CS), 2.00(S;3H,C_5H_4-CH_3), 2.08(S;3H, C_5H_4-CH_3), 2.87(m;2H,SCH_2), 4.73-5.27(m;8H,two C_5H_4); ^{13}C NMR ($CDCl_3$) δ 234.9, 286.3 (2 carbonyls); MS m/e 526 $[M]^+$; An X-Ray single crystal structure was obtained (R=0.019).

6.2.4 $(p\text{-}CH_3O\text{-}C_6H_4)CH_2S\text{-}C(=S)CH_2Ph$

This compound was prepared according to literature procedures (35,49). To prepare the thioester, 7.71 gm (50 mmol) of p-methoxybenzyl mercaptan was placed into an ice-cooled flask. Phenylacetyl chloride (7.83 gm, 57 mmol) was added dropwise, the reaction mixture allowed to cool to room temperature, and stirred for 3 hours to produce the thioester $(p\text{-}CH_3O\text{-}C_6H_4)CH_2S\text{-}C(O)CH_2Ph$ as off-white solid (11.5 gm, 84 %).

To (5.44 gm, 20.0 mmol) of the thioester in dry toluene (70 ml) was added 4.86 gm (12.1 mmol) of Lawesson's reagent. The yellow solution was heated for several hours and then stirred overnight at room temperature.

Next day, the viscous orange liquor was passed through a silica gel column with 9/1 hexane/ether. This solution was evaporated affording the orange dithioester, $[(p\text{-}CH_3O\text{-}C_6H_4)CH_2\text{-}S\text{-}C(=S)\text{-}CH_2Ph]$ as an oil. Yield: 4.44 gm (77 %). ^1H NMR ($CDCl_3$) δ 3.77(s,3H,OCH_3), 4.33(s,2H,CH_2), 4.37(s;2H,CH_2), 6.77(d;2H, protons ortho to methoxy substituent, J = 9Hz), 7.18(d;2H, protons meta to methoxy substituent, J = 9Hz), 7.28(s;5H,Ph); MS m/e 288 $[M]^+$.

6.2.5 Structure 2:

$Cp_2Mo_2(CO)_2LL'$ (L=S-CH_2-(C_6H_4)-p-OCH_3)
(L'=$PhCH_2$-C(S))

The procedure and molar quantities for this preparation are exactly the same as described in (6.2.2) except that the ligand was $[(p\text{-}CH_3O\text{-}(C_6H_4)\text{-}CH_2S\text{-}C(=S)CH_2Ph]$. The crude product was purified by chromatography on silica gel using 49/1 hexane/ether as the eluent, affording 0.06 gm (4 %) of a reddish product. M.Pt. = 180-185° (dec.) IR ν_{CO} (KBr) 1951(vs), 1923(s), 1887(vs) cm^{-1}.

6.2.6 Structure 3:

$Cp_2Mo_2(CO)_4L$ (L= Ethyl dithioacetate)

Into a Schlenk tube was dissolved 1.0 gm (2.0 mmol) of $[CpMo(CO)_3]_2$ in deoxygenated toluene (20 ml). The solution was refluxed vigorously

overnight in order to generate $[CpMo(CO)_2]_2$. The solution was cooled to room temperature, 0.24 gm (2.0 mmol) of ethyl dithioacetate was added, and the solution was stirred overnight at room temperature. The reaction mixture was concentrated by rotary evaporation, chromatographed on silica gel with 9/1 hexane/ether as eluent, affording 0.15 gm (13 %) of brown $[CpMo(CO)_2]_2(CH_3C(S)SC_2H_5)$. M.Pt. = 110-112°. IR ν_{CO} (KBr) 1960(vs), 1940(vs), 1918(vs), 1841(vs), 1806(ms)cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28(t;3H,CH_3), 1.54(s;3H,CH_3CS), 2.77(m;2H,SCH_2), 5.40(s;5H,Cp), 5.67(s;5H,Cp). Anal., calcd. for $C_{18}H_{18}Mo_2O_4S_2$: % C 39.17, % H 3.25; Found: % C 39.87, % H 3.67. An X-Ray single crystal structure was obtained (R=0.045).

6.2.7 Structure 3:

$(C_5H_4\text{-}CH_3)_2Mo_2(CO)_4L$ (L=Ethyl dithioacetate)

This reaction was carried out in a similar manner to that described in (6.2.6) except that the molar quantities were halved, and that the metal dimer used was $(C_5H_4\text{-}CH_3)_2Mo_2(CO)_6$. Work-up by silica gel chromatography (10/1 hexane/ethyl acetate) afforded 0.08 gm (14%) of brown $[(C_5H_4\text{-}CH_3)Mo(CO)_2]_2(CH_3C(S)\text{-}SC_2H_5)$. IR ν_{CO} (Nujol) 1956(vs), 1914(s), 1905(ms), 1869(ms); ^1H NMR ($CDCl_3$) δ 1.15(t;3H,CH_3), 1.46(S;3H,CH_3CS), 1.93(s;3H,$C_5H_4\text{-}CH_3$), 2.00 (s;3H,$C_5H_4\text{-}CH_3$), 2.43(m;2H,CH_2S), 4.90-5.15(m;8H, cyclopentadienyl protons).

6.2.8 Structure 3:

$Cp_2W_2(CO)_4L$ (L=Ethyl dithioacetate)

Into a Schlenk tube was placed 0.75 gm (1.1 mmol) of $Cp_2W_2(CO)_6$ and 20 ml of dry deoxygenated xylene. The triple bonded complex $[CpW(CO)_2]_2$ was generated by overnight refluxing of the solution. The mixture was cooled to room temperature, and 0.13 gm (1.1 mmol) of ethyl dithioacetate was added to the Schlenk tube. The reaction was then stirred overnight at room temperature, evaporated to dryness, and silica gel column chromatography (9/1 hexane/ether) afforded 0.06 gm (8 %) of brown $[CpW(CO)_2]_2(CH_3C(S)\text{-}CS_2H_5)$. M.Pt. = 113-115°. IR ν_{CO} (KBr) 1942(vs), 1902(vs), 1827(vs), 1791(ms); ^1H NMR ($CDCl_3$) δ 1.20(t;3H,CH_3), 1.63(S;3H,CH_3CS), 2.73(m;2H,CH_2S), 5.20(S;5H,Cp), 5.50(S;5H,Cp).

6.3 Reaction of a Cyclic Dithioester with $Cp_2Mo_2(CO)_4$

6.3.1 Dithiobutyrolactone

Dithiobutyrolactone was prepared by a modified version of Lawesson's procedure (50). A mixture of 2.04 gm (20.0 mmol) of thiobutyrolactone and 4.86 gm (12.0 mmol) of Lawesson's reagent was refluxed vigorously for 3 days in toluene (70 ml). The orange solution was concentrated and chromatographed on silica gel using 1/2 hexane/ether to give 1.70 gm (72 %) of orange dithiobutyrolactone. ^1H NMR ($CDCl_3$) δ 2.40(m,2H,CH_2), 2.95(t,2H,CH_2CS), 3.55(t,2H,CH_2S). MS m/e 118 $[M]^+$.

6.3.2 Structure 4:

$Cp_2Mo_2(CO)_2L$ (L=-$SC(CH_2)_3S$-)

Dithiobutyrolactone (0.23 gm, 1.9 mmol) was added to a toluene (30 ml) solution of the triple bond dimer $[CpMo(CO)_2]_2$ (obtained from 2 mmol of $[CpMo(CO)_3]_2$ and the mixture was refluxed for 18 hours. After cooling to room temperature, the solvent was evaporated and the residue was purified by silica gel chromatography using ethyl acetate as the eluent. A dark red crystalline product $[CpMo(CO)_2(SC(CH_2)_3S)$ (0.43 gm, 44 %) was isolated, M.Pt. = 63-65°.

IR ν_{CO} (KBr) 1889(s), 1849(s)cm^{-1}; ^{13}C NMR δ 27.07,31.23,31.56 (methylene carbons), 91.25(Cp), 94.16(Cp), 136.69(CS), 233.70(CO), 239.61(CO); MS m/e 496$[M]^+$, 468$[M-CO]^+$, 440$[M-2CO]^+$; Anal., calcd. for $C_{16}H_{16}Mo_2O_2S_2$: % C 38.72, % H 3.23. Found:% C 38.55, % H 3.37

Structure 4:

6.6.3 $(C_5H_4\text{-}CH_3)_2Mo_2(CO)_2L$ (L=-$SC(CH_2)_3S$-)

This reaction utilized the same procedure as that described in (6.3.2), except that the metal dimer used was $[(C_5H_4\text{-}CH_3)Mo(CO)_2]_2$. This reaction afforded (0.40 gm, 38 %) of a red crystalline product $[(C_5H_4\text{-}CH_3)Mo(CO)]_2(SC(CH_2)_3S)$. M.Pt. = 115-116°. IR ν_{CO} (KBr) 1881(s), 1852(s)cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00(s;3H,CH_3), 2.02(s;3H,CH_3), 2.0-3.3(m;5H, methylene protons), 5.03(m;4H,C_5H_4), 5.08(m;4H,C_5H_4).

MS m/e 524 $[M]^+$, 496$[M-CO]^+$, 468$[M-2CO]^+$. Anal., calcd. for $C_{18}H_{20}Mo_2O_2S_2$: % C 41.22, % H 3.84. Found: % C 40.75, % H 3.95. An X-Ray single crystal structure was obtained (R=0.019).

6.4 Reactions of Tetraalkylthiuram Disulfides with $Cp_2Mo_2(CO)_4$

6.4.1 Structure 5:

$CpMo(CO)_2L$ $(L=S_2CN(i\text{-}Pr)_2)$

Tetraisopropylthiuram disulfide (0.71 gm, 2.0 mmol) was added to a toluene (20 ml) solution of the triple bond dimer $[CpMo(CO)_2]_2$ obtained from 2 mmol of $[CpMo(CO)_3]_2$. This solution was stirred overnight at room temperature, concentrated by rotary evaporation and then purified by silica gel chromatography using methylene chloride as the eluent. The orange compound $[CpMo(CO)_2(S_2CN(i\text{-}Pr)_2)]$ was isolated in 57% yield (0.90 gm), M.Pt. = 200-203°. IR ν_{CO} (Nujol) 1942(s), 1852(s)cm^{-1}; ^1H NMR $CDCl_3$) δ 1.38(d;12H,$CH(CH_3)_2$), 4.20(m;2H,$CH(CH_3)_2$), 5.33(s;5H,Cp); ^{13}C NMR ($CDCl_3$) δ 19.9(CH_3 carbons), 49.3(CH), 94.3(Cp) 207.6($S_2CN[CH(CH_3)_2]_2$), 257.0(CO); Anal., calcd. for $C_{14}H_{19}MoNO_2S_2$: % C 42.39, % H 5.44, % N 4.00. Found: % C 42.36, % H 5.13, % N 3.51. An X-Ray single crystal structure was obtained (R=0.038).

6.4.2 Structure 5:

$CpMo(CO)_2L$ $(L=S_2CN(Et)_2)$

This reaction was conducted in the same manner as that described in (6.4.1) except that the organic reactant was tetraethylthiuram disulfide. Purification by silica gel column chromatography using methylene chloride as the eluent afforded (1.2 gm, 83%) of dark red $[CpMo(CO)_2(S_2CN(Et)_2)]$. M.Pt. = 123-125°. IR ν_{CO} (Nujol) 1958(ms), 1930(s), 1875(ms), 1860(s)cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t;6H, CH_3), 3.62 (q;4H,CH_2), 5.44(s,5H,Cp). MS m/e 365 $[M]^+$.

6.4.3 Structure 5:

$CpMo(CO)_2L$ $(L=S_2CN(Me)_2)$

This reaction was conducted in the same manner as that described in (6.4.1) except that the organic reactant used was tetramethylthiuram disulfide. Purification by column chromatography (silica gel) using 1/2 hexane/methylene chloride as the eluent afforded 0.50 gm (37 %) of bright red $[CpMo(CO)_2(S_2CN(Me)_2)]$. M. Pt. = 225-227°. IR ν_{CO} (Nujol) 1930(s), 1845(s)cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.02 (s,6H,CH_3), 5.35(s,5H,Cp); MS m/e 337 $[M]^+$.

6.5 Reaction of Tetraalkylbiphosphine disulfides with triple-bond complexes

Structure 6:

6.5.1 $(C_5H_4\text{-}CH_3)Mo(CO)_2L$ $(L=S\text{-}P(Me)_2)$

Tetramethylbiphosphine disulfide (0.372 gm, 2.0 mmol) was added to a toluene (20 ml) solution of the triple-bond dimer $[(C_5H_4\text{-}CH_3)Mo(CO)_2]_2$ obtained from 1.93 mmol of $[(C_5H_4\text{-}CH_3)Mo(CO)_3]_2$. The reaction mixture was refluxed for 15 hours, concentrated and purified by silica gel chromatography using 1/1 hexane/methylene chloride as the eluent, affording 0.13 gm (20 %) of orange-brown $[(C_5H_4\text{-}CH_3)Mo(CO)_2(S\text{-}P(Me)_2]$. M. Pt. = 56-58°. Ir ν_{CO} (Nujol) 1960(s), 1875(s)cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73, 1.87, 1.92 (s each; 9H, methyl protons), 5.17(m;4H,C_5H_4); ^{13}C NMR ($CDCl_3$) δ 267.9 (CO); MS m/e 324 $[M]^+$, 296$[M\text{-}CO]^+$, 268$[M\text{-}2CO]^+$. An X-Ray single crystal structure was obtained (R=0.026).

Structure 6:

6.5.2 $CpMo(CO)_2L$ $(L=S\text{-}P(Et)_2)$

This reaction was conducted in the same manner as that described in (6.5.1), except that the metal dimer was $[CpMo(CO)_2]_2$ and the organic reactant was tetraethylbiphosphine disulfide. Purification by column chromatography through silica gel using 1/2 hexane/methylene chloride as

the eluant afforded 0.08 gm (6 %) of orange-brown $[CpMo(CO)_2(S\text{-}P(Et)_2)]$. M. Pt. = 88-90°. IR ν_{CO} (Nujol) 1960(s),1940(s),1880(s),1835(s)cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.90(t;3H,CH_3), 1.25(t;3H,CH_3), 2.00(q;2H,CH_2), 2.10(q;2H,CH_2), 5.30(S;5H,Cp); MS M/e 338 $[M]^+$.

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CLAIMS TO ORIGINAL RESEARCH

1. Extremely mild carbonylation of primary and secondary amines to carbamates.

2. Extremely mild double carbonylation of secondary amines to oxamates.

3. Extremely mild carbonylation of allenes affording functionalized acrylates.

4. Mild carbonylation of alkynes to mono- and diacids.

5. Control of isomeric distribution of products of 1-decene hydroesterification by variation of CO/O_2 ratios.

6. Use of zeolites to suppress CO_2 co-production in amine and olefin carbonylation reactions.

7. CO_2 suppression by variation of CO/O_2 ratios in olefin hydroesterification reactions.

8. Use of acid-impregnated zeolites in acid promoted hydroesterification reactions.

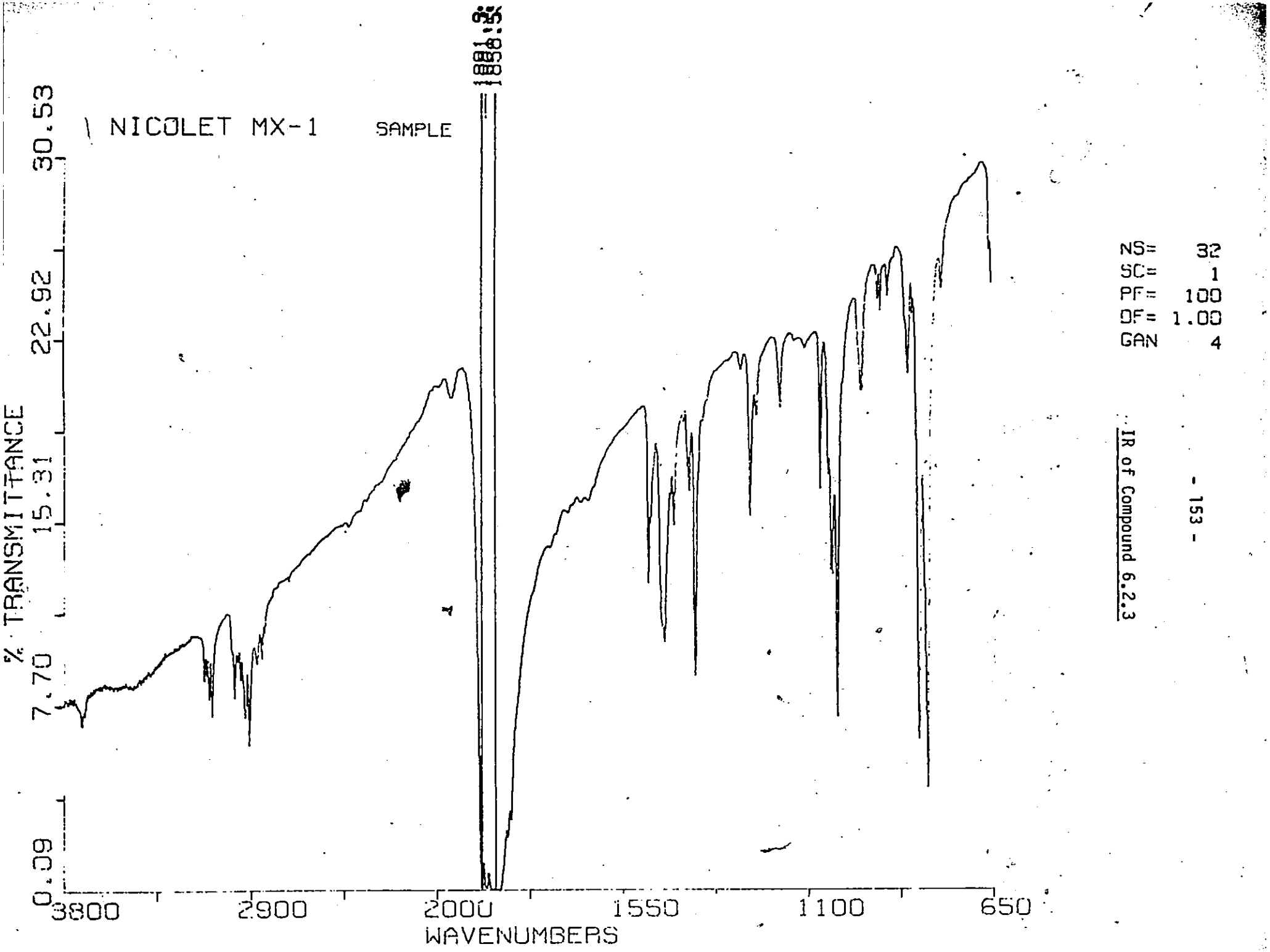
9. Use of di-t-butyl peroxide as a reoxidant instead of oxygen in the amine carbonylation reactions.

10. C-S bond cleavage in dithioesters promoted by molybdenum triple-bond dimers, and the formation of novel thioacyl/thioalkyl complexes.

11. S-S bond cleavage in tetraalkyl thiuram dissulfides induced by molybdenum triple-bond dimers.

12. P-P bond cleavage in tetraalkyl biphosphine disulfides induced by molybdenum triple-bond dimers. Formation of novel η^2-R_2PS molybdenum complexes.

IR of Compound 6.2.2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22.92
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0.09
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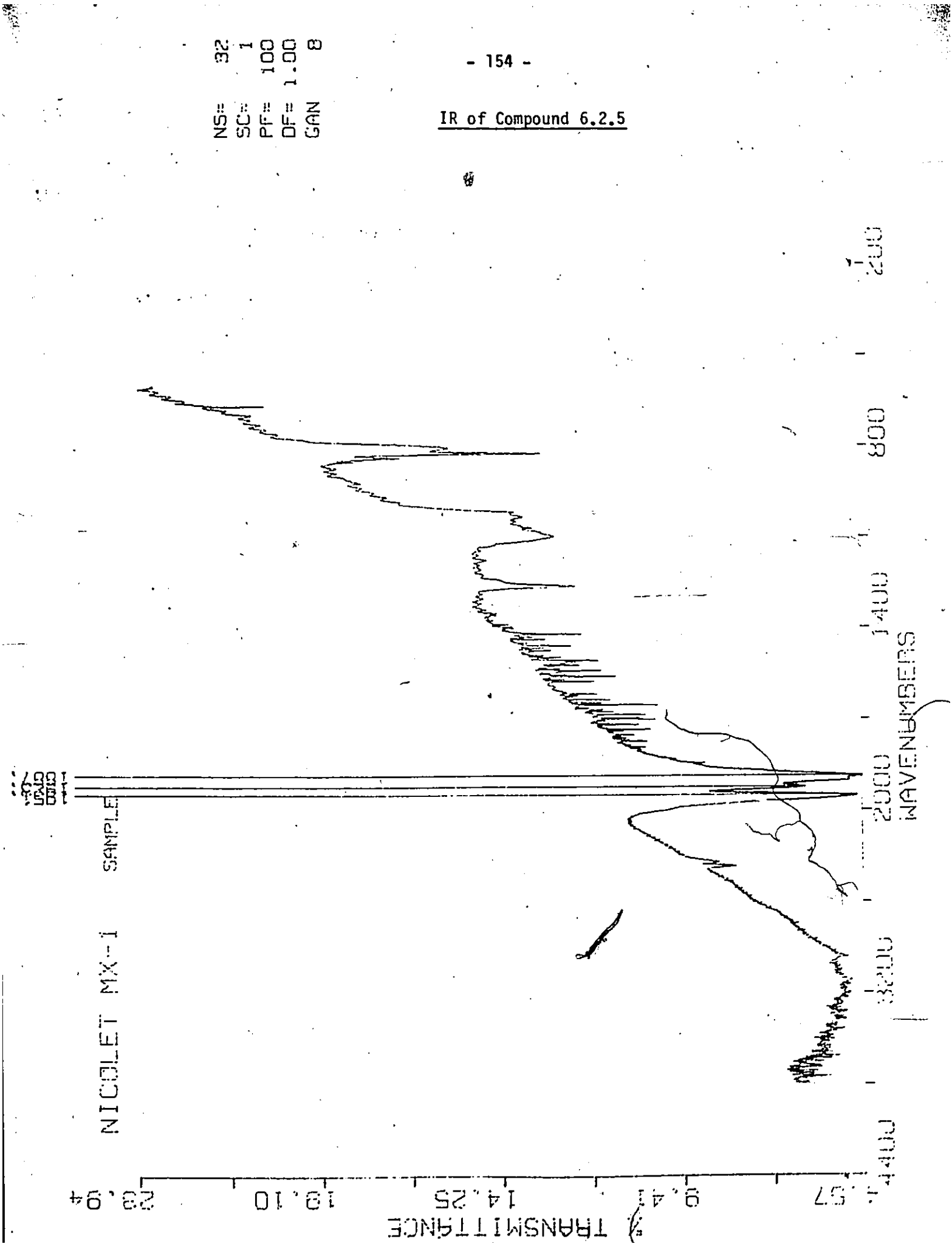
2900
2000
1550
1100
650
WAVENUMBERS
NS= 32
SC= 1
PF= 100
DF= 1.00
GAN 4
IR of Compound 6.2.3

IR of Compound 6.2.5



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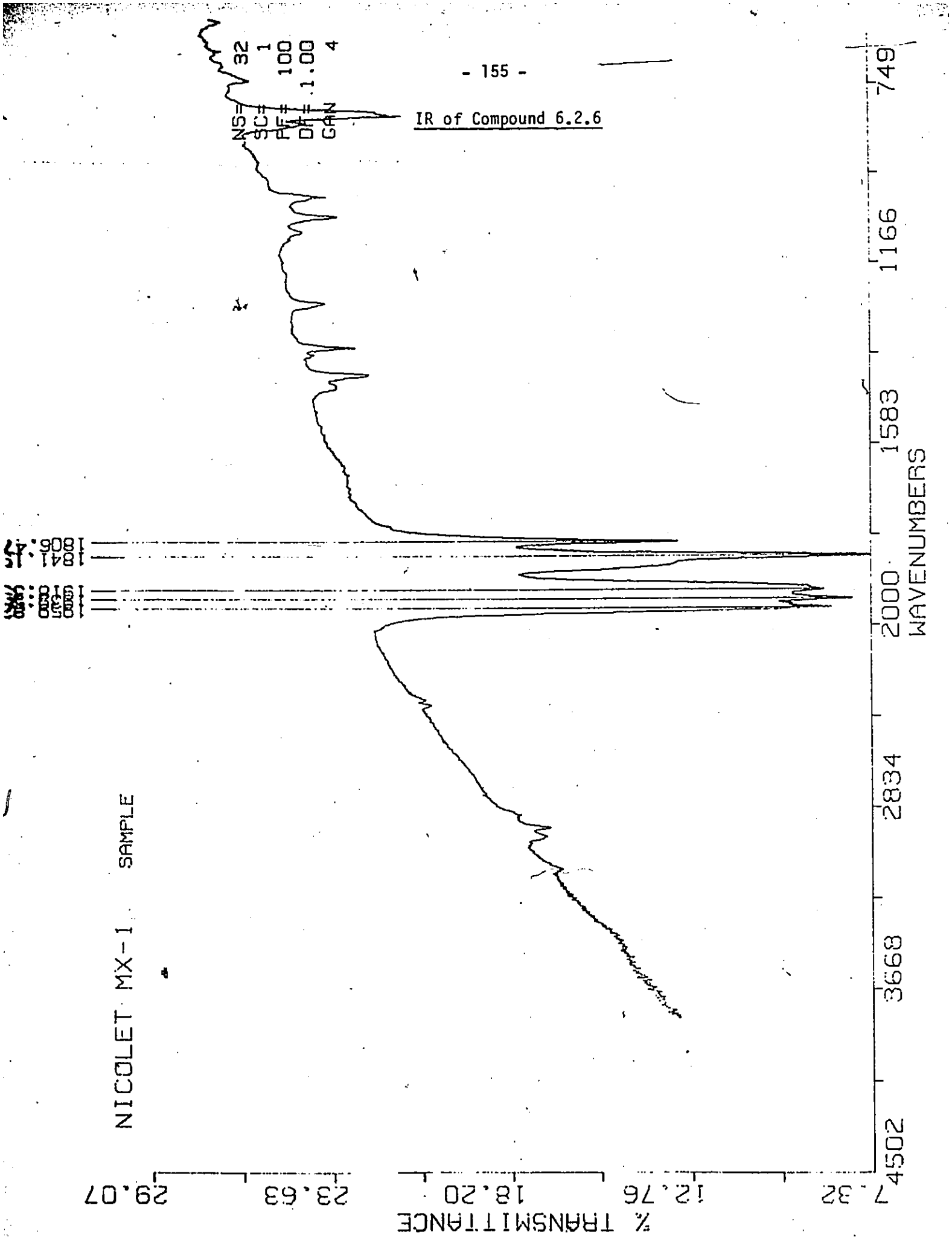
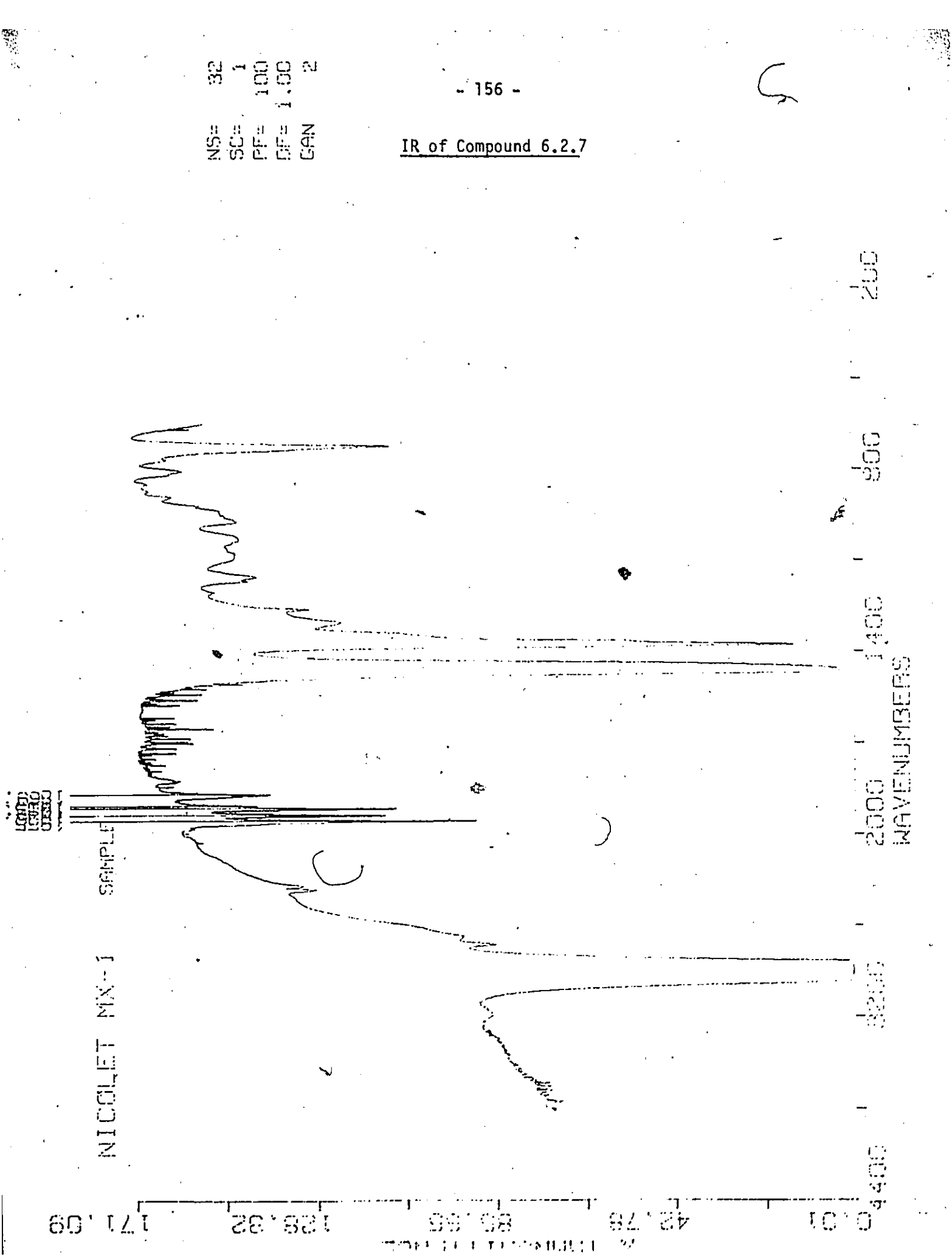
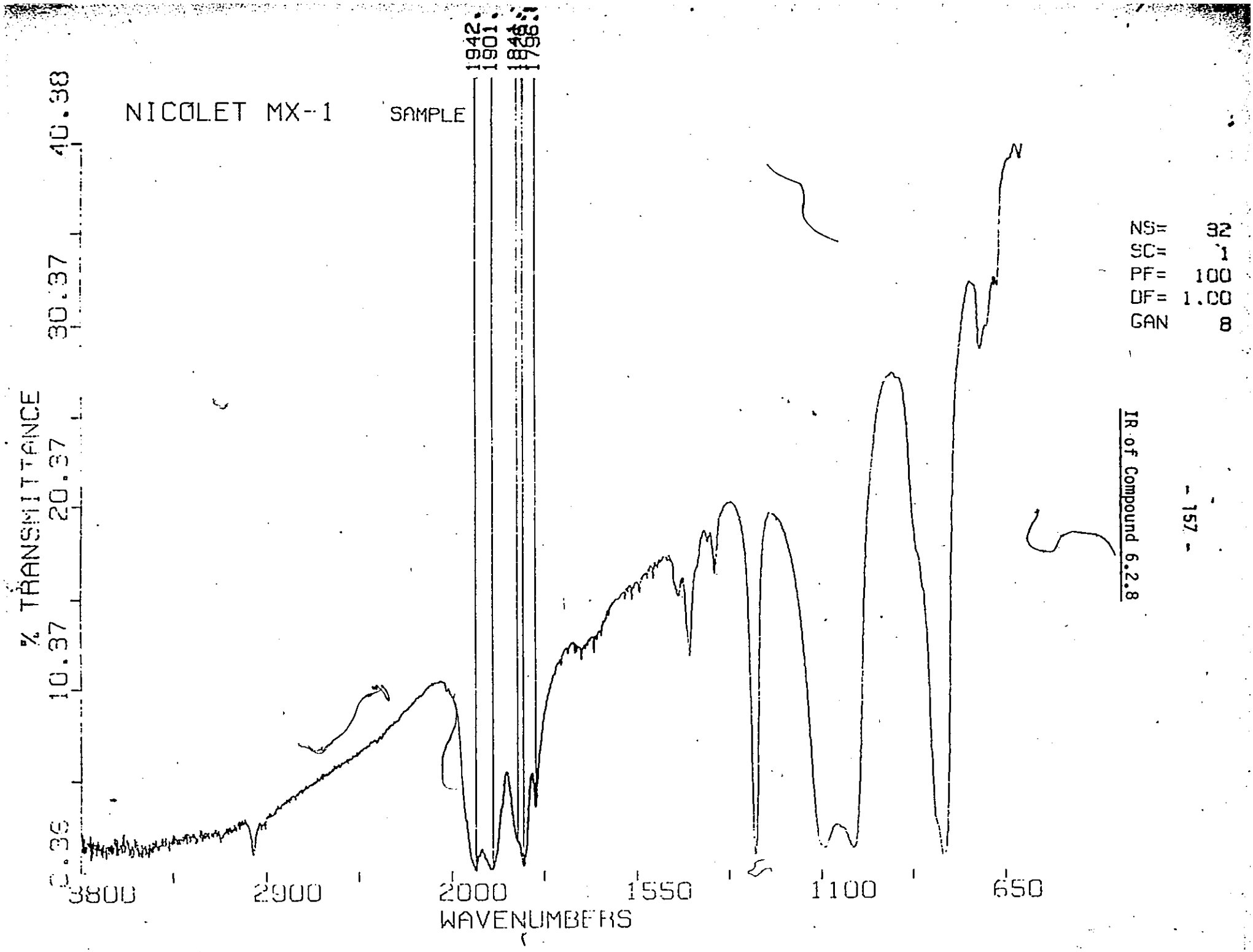


IR of Compound 6.2.7

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1796.
NS= 32
SC= 1
PF= 100
DF= 1.00
GAN 8
IR of Compound 6.2.8
- 157 -
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30.37
20.37
10.37
0.39
3800
2900
2000
1550
1100
650
WAVENUMBERS