SOME STUDIES ON ORGANOMOLYBDENUM CHEMISTRY

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To my family

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ABSTRACT

The first part of this thesis concerns an improved synthesis of π-allyl molybdenum complexes. Dicarbonyl-π-allylcyclopentadienyl molybdenum complexes were prepared in moderate to good yields from allyl halides and tricarbonylcyclopentadienyl molybdenum anion, followed by the treatment with trimethylamine-N-oxide. The reaction has been extended to tungsten analog. The nature of trimethylamine-N-oxide promoted σ to π rearrangement is discussed.

The second part of this thesis describes the molybdenum hexacarbonyl induced reductive cleavage of carbon-sulfur bonds. Aryl, benzylic, α-acyl mercaptans and thioethers were smoothly reduced. Functional groups such as chloro, bromo, methoxy, carboxylic acid, ketone and ether are stable under the reaction conditions. 9-Fluorenone thioketal afforded a mixture of fluorene and bifluorenylidene. The mechanism of these transformations is discussed.

CONTENTS

FORWARD

Molybdenum has played a unique role in organometallic chemistry[1] as well as in bioinorganic chemistry.[2] To illustrate, nitrogen fixation requires molybdenum compounds.[2] Molybdenum sulfide is employed as the catalyst for hydrodesulfurization process in petroleum refining industry.[3,4] It is noted that molybdenum can readily form metal-metal multiple bonds[5] and metal-carbon multiple bonds.[6] More recently, there are increasing number of papers concerning the use of organomolybdenum compounds in organic syntheses.[7-11]

In the first part of this thesis, a new synthesis of η^3-allyl molybdenum complexes will be described. These compounds have been proved to be useful in organic syntheses.[12-14]

Molybdenum hexacarbonyl has also been employed as a reducing agent for the reduction of carbon-halogen bonds.[15] In the second part of this work, the use of molybdenum hexacarbonyl to reductively cleave the carbon-sulfur bonds will be discussed.

1.1 INTRODUCTION

Unsaturated hydrocarbons, e.g. ethylene, butadiene, and benzene, do not normally undergo addition or substitution reactions with nucleophiles. However, when these molecules form complexes with transition metal cations, a wide range of nucleophiles such as H^-, R^-, CN^-, MeO^- and R_3N, can readily add to these moieties.[16,17] The greater reactivity of the coordinated unsaturated hydrocarbon can be attributed to metal-ligand bond which results in a net withdrawal of electron density from hydrocarbon ligand to the positively charged metal centre. To illustrate, organoiron olefin complex (1) reacted with liquid ammonia followed by several steps to afford β-lactam derivative (2) (eq. 1).[18]

Fp: $(\eta^5-C_5H_5)Fe(CO)_2$; Cp: $(\eta^5-C_5H_5)$

- 2 -
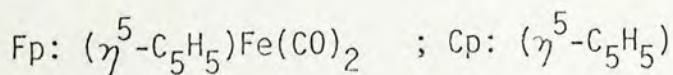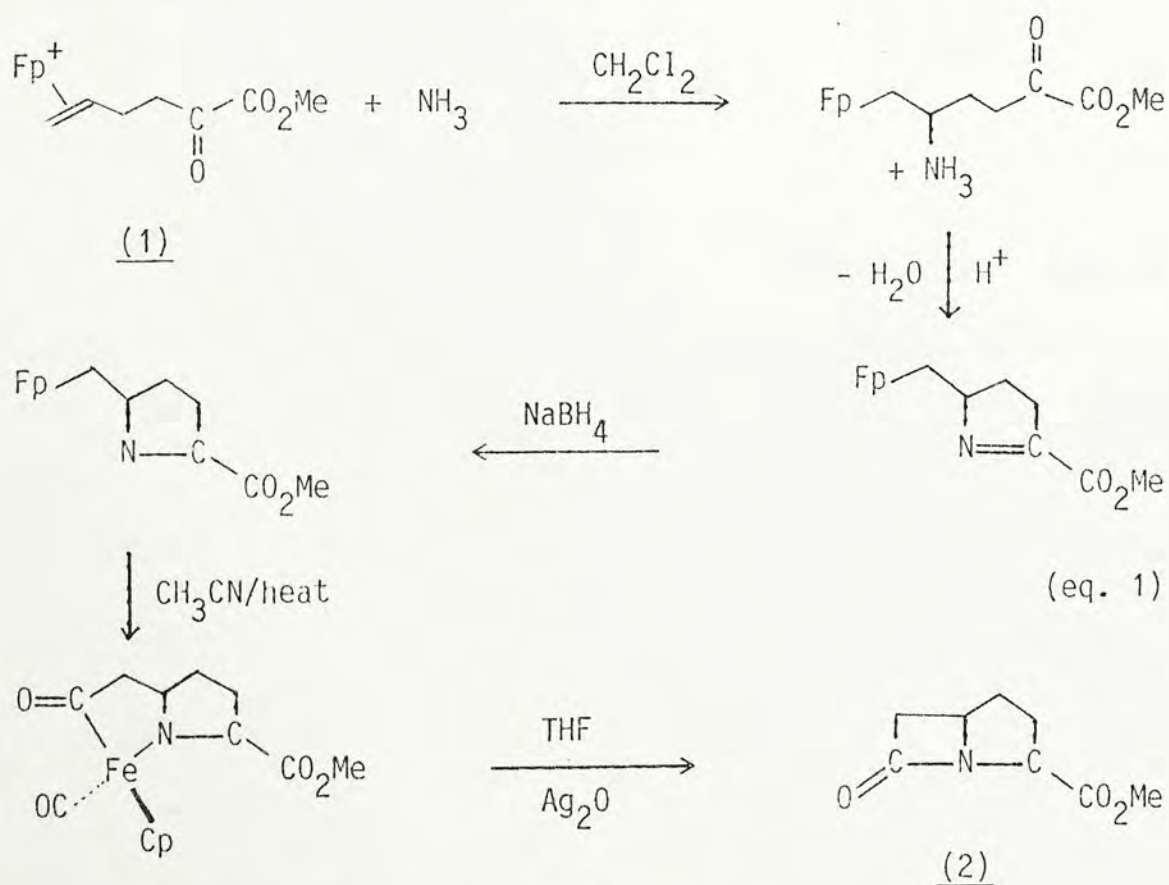
Faller and his coworkers[12] were the first to treat a molybdenum diene cation (3) with an enamine (eq. 2) to give, after hydrolysis, the corresponding allyl complex (4). More recently, Green and his coworkers[13] have extended these methods (eq. 3) to synthesize substituted butadienes such as pheromone (5).

(eq. 2)

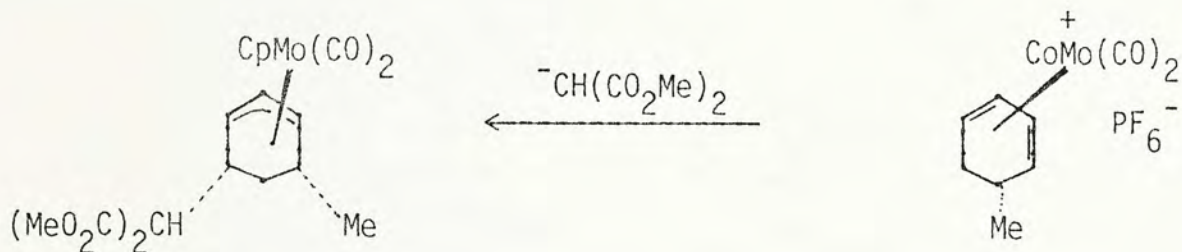$$\text{Li[Cu((E)-CH=CHC}_5\text{H}_{11})_2]$$

(eq. 3)

(5)
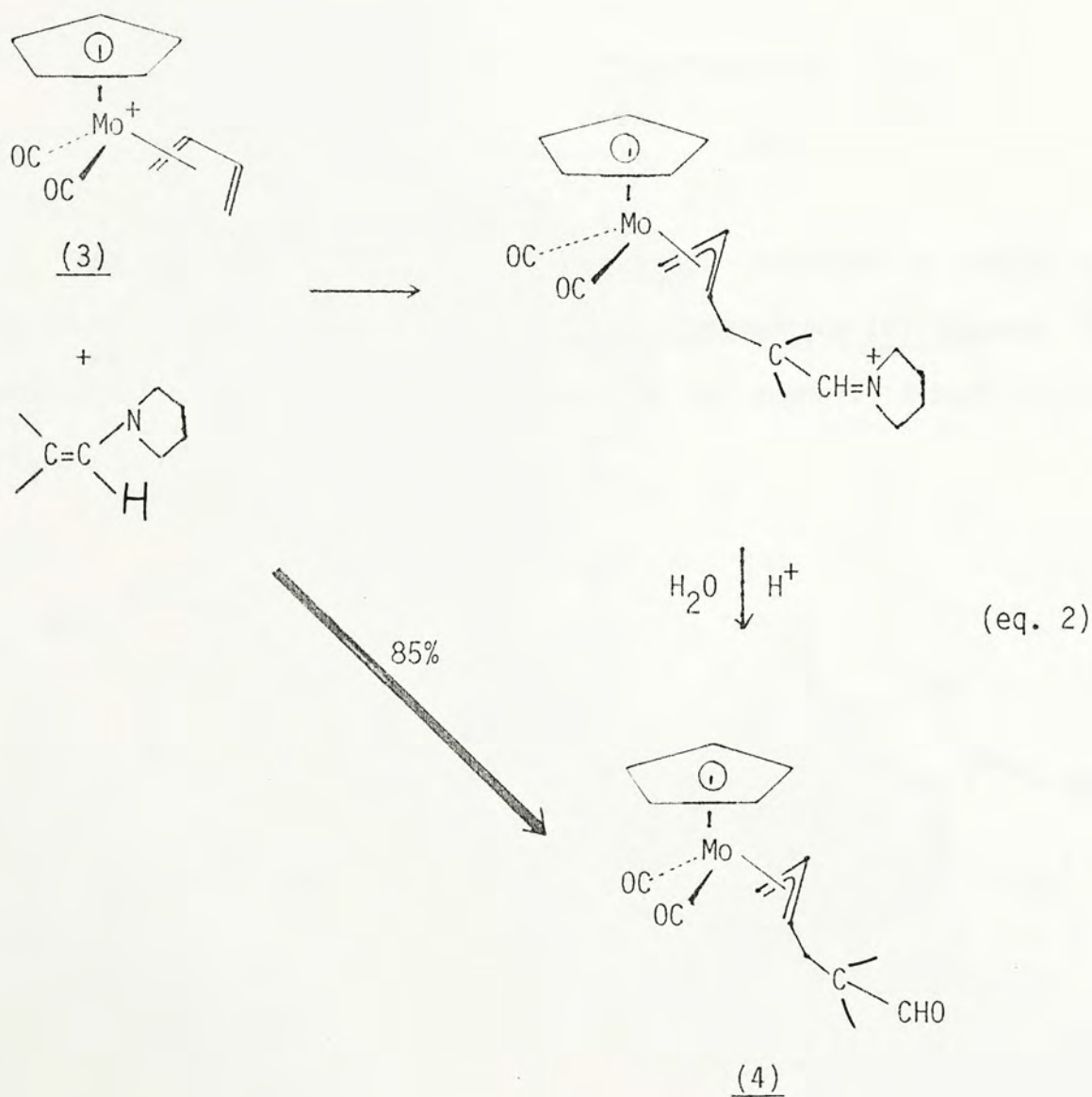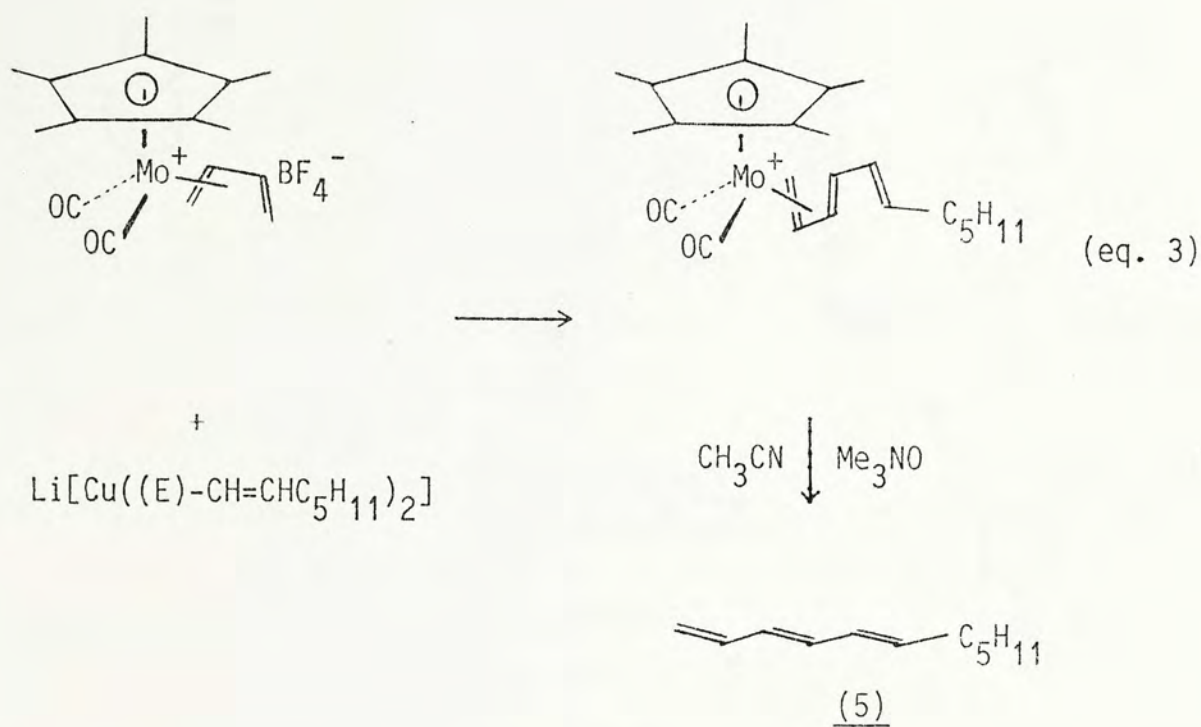
Pearson[14,19,20] and his students also reported a regio- and stereo-controlled synthesis of the key intermediate (6) towards the synthesis of magnamycin B (7) by means of nucleophilic attack on the molybdenum diene complexes (8) (eq. 4).

(6)

(7)
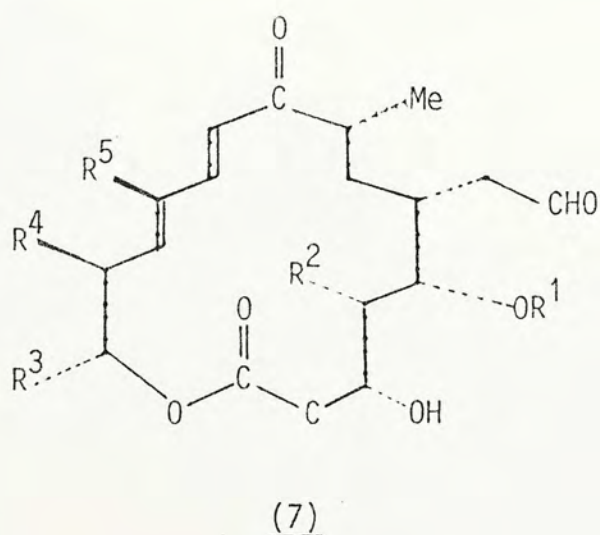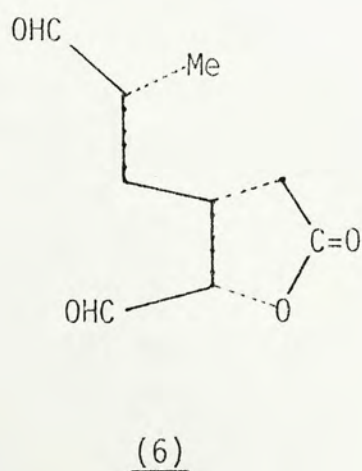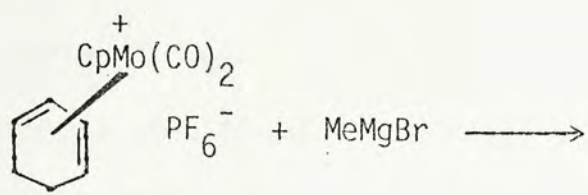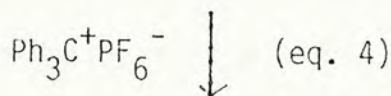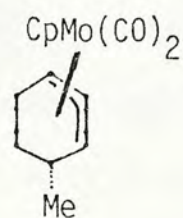
$$Cp: (\eta^5\text{-}C_5H_5)$$

The coordinated butadiene cation (3) can readily be prepared by hydride abstraction from the π-crotyl molybdenum complex (9) (eq. 5).[21] The first synthesis of π-allyl molybdenum complex $CpMo(CO)_2(\eta^3\text{-}CH_2\text{=}CH\text{=}CH_2)$ (10) was achieved in ca. 50% yield by the

$$Cp: (\eta^5\text{-}C_5H_5)$$

irradiation of the corresponding σ-allyl derivative $CpMo(CO)_3(\sigma$-CH_2-$CH=CH_2)$ (11) (eq. 6).[22] Alternatively, when the σ-allyl molybdenum complex (11) was refluxed in xylene, only 3% of the π-allyl molybdenum derivative (10) was obtaine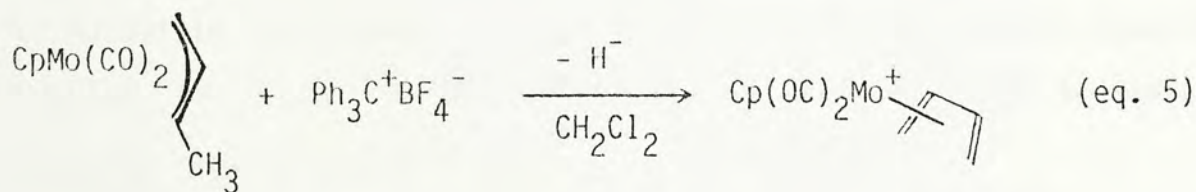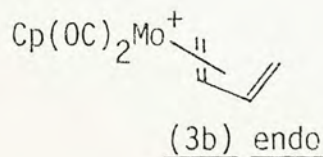d.[22] The reaction essentially involves a decarbonylation step followed by a σ to π rearrangement process.[23]

(eq. 6)

(11)   (10)
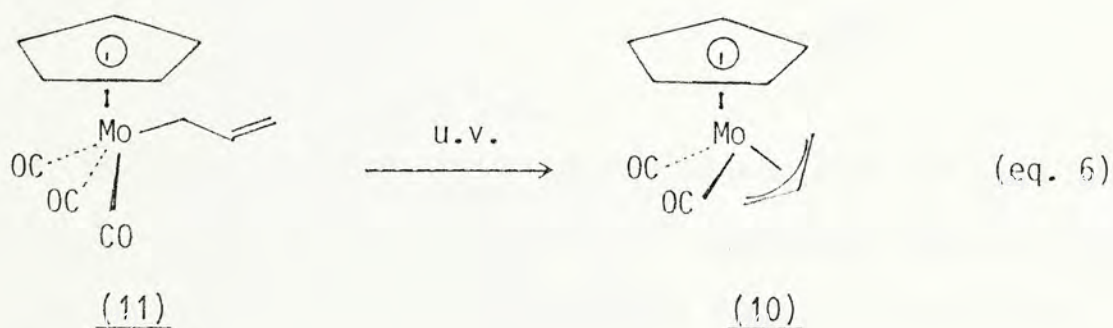
Furthermore, the yield for the preparation of the σ-allyl molybdenum complex (11) was 40%.[22] In other words, the overall yield of the complex (10) from $CpMo(CO)_3^-$ (12a) was about 20%.

In 1973, Abel and Moorhouse[24] claimed that cyclopentadienyl-trimethyltin (13) was treated with the π-allyl molybdenum chloride complex (14) (eq. 7) to give the corresponding π-allyl molybdenum compound (10) in excellent yield.

$ClMo(CO)_2(CH_3CN)_2$ ⟩⟩ + CpSnMe$_3$ ⟶ CpMo(CO)$_2$ ⟩⟩ (eq. 7)

(14)   (13)   (10)
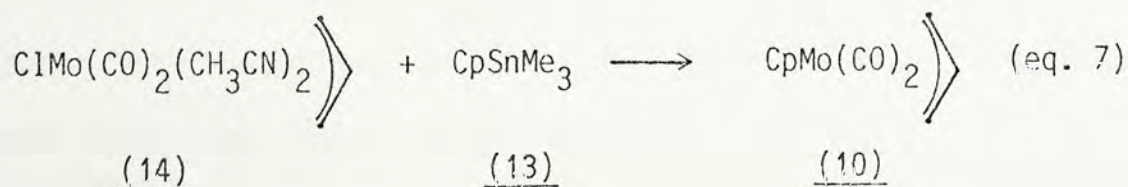
In the presence of a phase transfer catalyst, π-allyl molybdenum complex (10) was obtained in excellent yield from the $CpMo(CO)_3Cl$ (15) (eq. 8).[25]

$$CpMo(CO)_3Cl \ \underline{(15)}$$
$$+$$
$$CH_2=CH-CH_2-Br \qquad \xrightarrow[\text{C_6H_6, NaOH}]{\text{Cat., 8h, 45}^{\circ}\text{C}} \qquad CpMo(CO)_2 \hspace{-6pt}\left.\right\rangle\hspace{-6pt}\left.\right\rangle \qquad \text{(eq. 8)}$$
$$\underline{(10)}$$
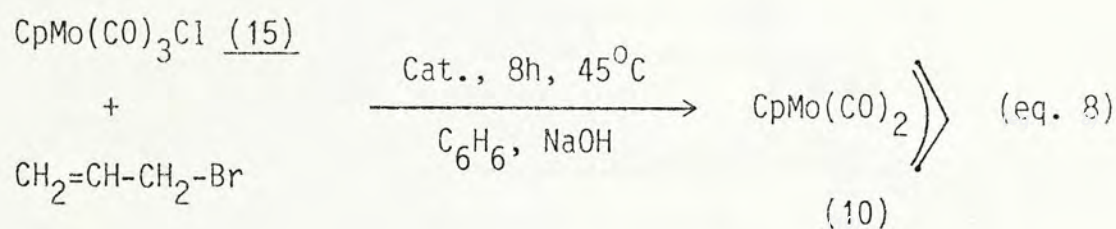
All these methods, however, may not be practical for the large scale preparation of the desired π-allyl molybdenum complex (16). Thus, we wish to develop a new synthetic method in the hope of permitting a more useful route for the synthesis of this important intermediate.

$$CpMo(CO)_2 \hspace{-4pt}\left.\right\rangle\hspace{-4pt}\left.\right\rangle \begin{array}{c} -R^1 \\ -R^2 \quad \underline{(16)} \\ -R^3 \end{array}$$

$Cp:(\eta^5-C_5H_5)$
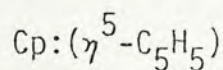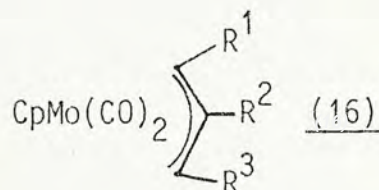
As mentioned above, the first step in the rearrangement of the complex $CpMo(CO)_3(\sigma-CH_2-CH=CH_2)$ (11) to $CpMo(CO)_2(\eta^3-CH_2\text{---}CH=CH_2)$ (10) involves decarbonylation. We felt that, in the presence of a suitable reagent other than photolysis or thermolysis, this step may smoothly proceed.[25,27]

In 1975, Shvo and Hazum[28] reported a facile synthesis of organic iron complexes by using trimethylamine-N-oxide (TMNO) to promote complexation of diene ligand with metal carbonyl. To illustrate this, cyclooctatetraenetricarbonyl iron (17) was prepared in excellent yield by this method (eq. 9).[28]

$$
\begin{array}{c}
\text{(cyclooctatetraene)} \\
+ \\
Fe(CO)_5 \ \underline{(18)} \\
+ \\
2Me_3N\text{-}O
\end{array}
\quad \longrightarrow \quad
\begin{array}{c}
\text{(cyclooctatetraene)}-Fe(CO)_3 \ \underline{(17)} \\
+ \\
Me_3N \\
+ \\
2CO_2
\end{array}
\qquad (eq. 9)
$$
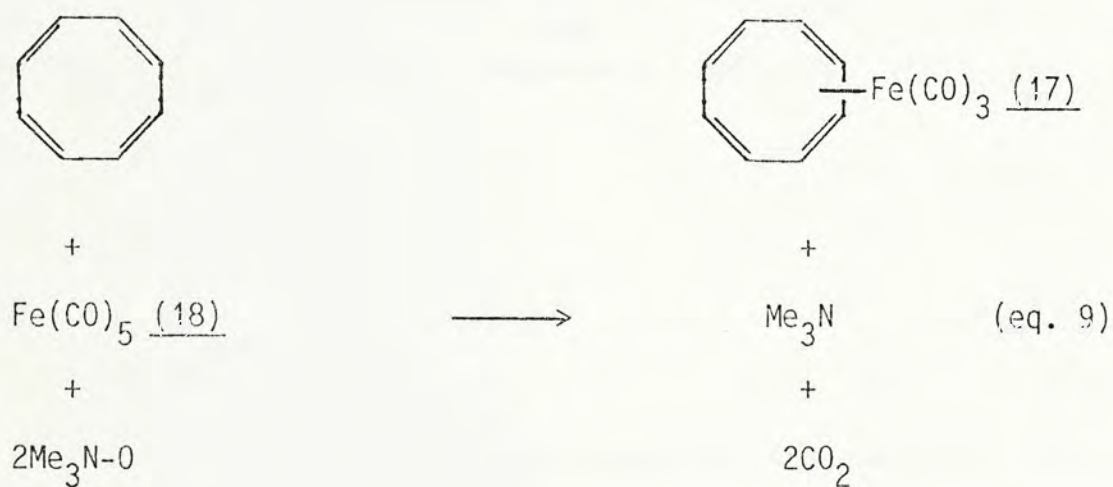
Since then, TMNO has demonstrated its extensive versatilities in organometallic chemistry.[26] Intermolecular ligand displacement reactions are well explored. Carbon monoxide ligand can selectively be replaced by other ligand.[29] Other types of reaction, such as oligomerization reactions[30,31] as well as deinsertion reactions[32] are also promoted by TMNO.

It is noted that TMNO also induces intramolecular ligand displacement reactions.[33] Thus, the second phosphine moiety of the bidentate ligand $Ph_2P(CH_2)_nP(Ph)_2$ (n = 1, 2, 3) was found to replace one CO ligand in compound (19) (eq. 10).[33]

$$CpFe(CO)_2^+ P(Ph)_2(CH_2)_nP(Ph)_2 \xrightarrow{\text{TMNO}} \text{[see structure]} \quad (eq. 10)$$

(19)

$$Cp: (\eta^5\text{-}C_5H_5) \quad ; n = 1, 2, 3$$
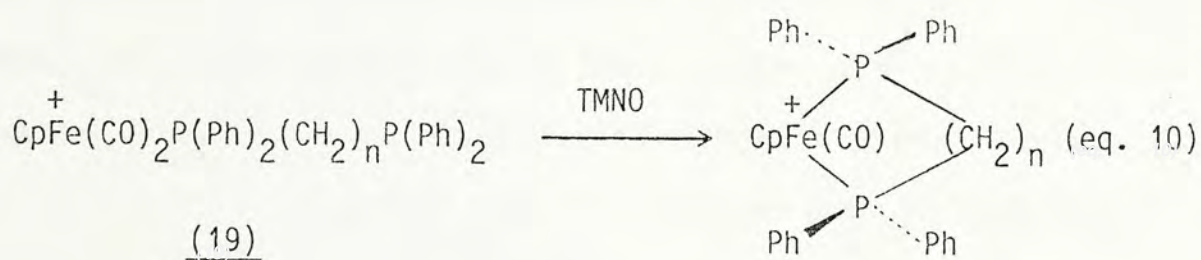
Having these ideas in mind, we deemed that TMNO may also catalyze the intramolecular rearrangement from the σ-complex (20) to the π-allyl derivative (16). In this work, this viewpoint has been tested and a convenient synthesis of $CpMo(CO)_2(\pi$-allyl) complexes (16) has hence been developed.*

CpMo(CO)$_2$ R^1, R^2, R^3 (16)   CpMo(CO)$_3$ R^1, R^2, R^3 (20)
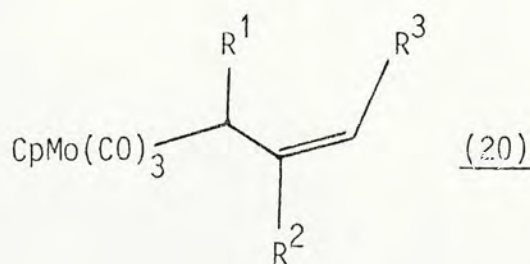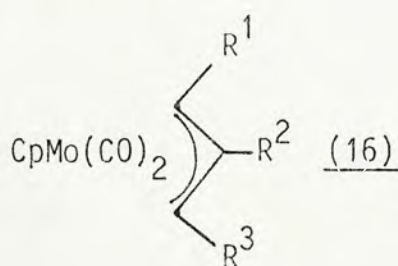
* Part of this work has been published.[34]

1.2 RESULTS AND DISCUSSIONS

The general synthesis of π-allyl molybdenum complexes is summarized in eq. 11. In a typical procedure, a THF solution of tricarbonylcyclopentadienyl molybdenum dimer (21a) was treated with sodium amalgam to give the corresponding anion $CpMo(CO)_3^-$ (12a), which was allowed to react with allyl halide to yield the σ-allyl complex $CpMo(CO)_3(\sigma$-allyl) (20). Without the isolation of σ-allyl molybdenum complex (20), the mixture was treated with TMNO at room temperature for 4 - 8 h. The desired π-allyl molybdenum complex $CpMo(CO)_2(\pi$-allyl) (16) was obtained. The allyl halides employed are shown in Scheme 1 and the results are summarized in Table 1.

$$[CpMo(CO)_3]_2 \xrightarrow{\text{Na-Hg}} CpMo(CO)_3^-$$

(21a)   (12a)

Cp: $(\eta^5-C_5H_5)$ $R\!-\!X \downarrow$ (eq. 11)

$$CpMo(CO)_2 \overset{R^1}{\underset{R^3}{\diagup}} R^2 \xleftarrow[-CO]{\text{TMNO}} CpMo(CO)_3 \overset{R^1 \quad R^3}{\underset{R^2}{\diagup}}$$

(16)   (20)

Scheme 1 Allyl halides

Br-CH$_2$CH=CH$_2$ _(22)_

Cl-CH$_2$CH=CHCH$_3$ _(23)_

Cl-CH$_2$C(CH$_3$)=CH$_2$ _(24)_

Cl-CH(CH$_3$)CH=CHPh _(25)_

Cl-CH(CH$_3$)C(CH$_3$)=CH$_2$ _(26)_

Cl-CH(CH$_3$)CH=CH(CH$_3$) _(27)_

Br-⬡ _(28)_

Br-CH$_2$CH$_2$CH=CH$_2$ _(29)_

Cl-CH$_2$Ph or Br-CH$_2$Ph _(30)_
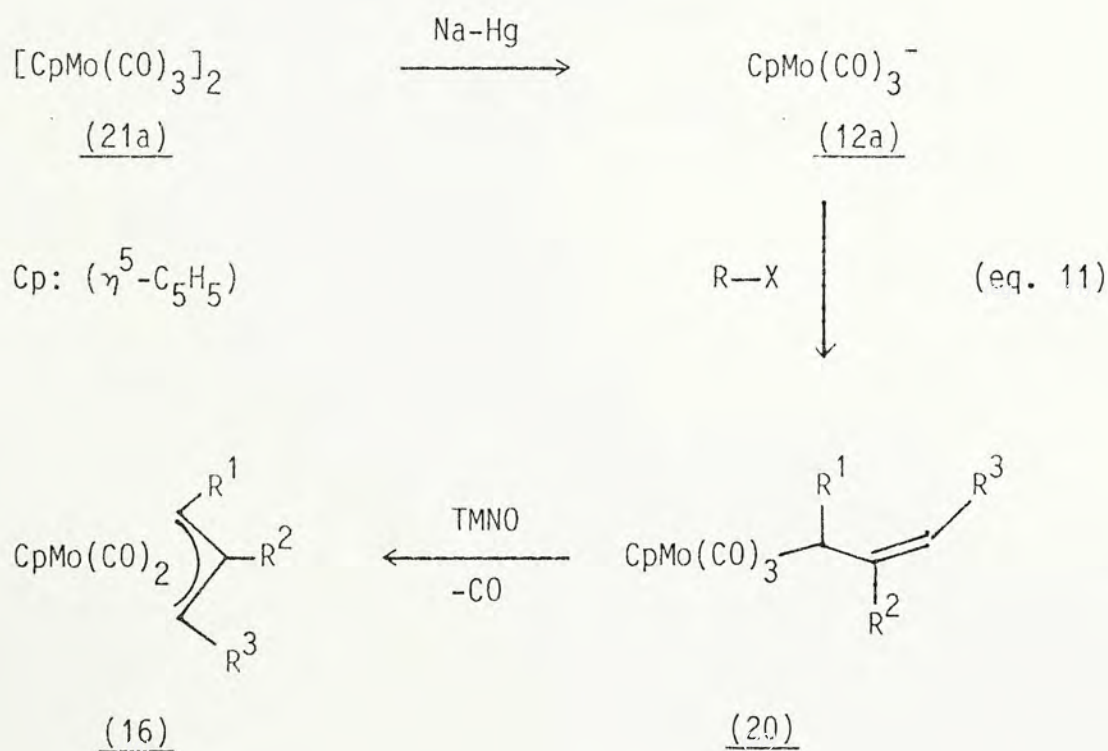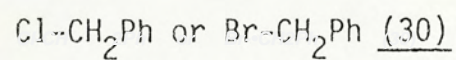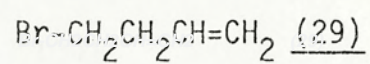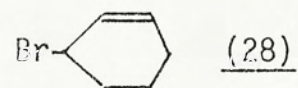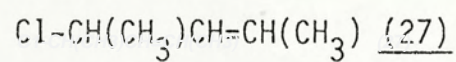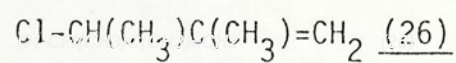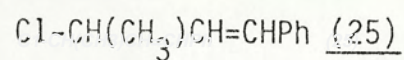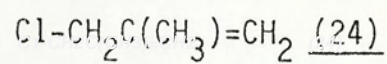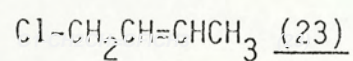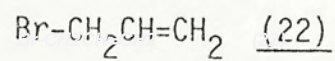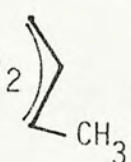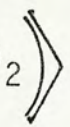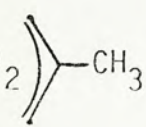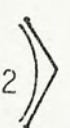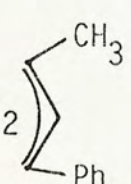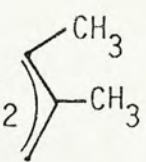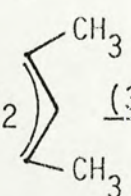
Table 1   TMNO promoted σ to π allyl rearrangement

Product	% yield[*]
$CpMo(CO)_2$ ⟩ $-CH_3$ (9)	82
$CpMo(CO)_2$ ⟩ (10)	75
$CpMo(CO)_2$ ⟩$-CH_3$ (31)	68
$CpW(CO)_2$ ⟩ (32)	42
$CpMo(CO)_2$ (33)	51
$CpMo(CO)_2$ ⟩ $-CH_3$, $-Ph$ (34)[a]	0
$CpMo(CO)_2$ ⟩ $-CH_3$, $-CH_3$ (35)[a]	0
$CpMo(CO)_2$ ⟩ $-CH_3$, $-CH_3$ (36)[a]	0

[*] Yield denotes the overall yield from $[CpMo(CO)_3]_2$ or $[CpW(CO)_3]_2$.

[a] Expected product.

These compounds are mainly characterized by infrared absorptions in the range from 1800 - 2100 cm^{-1}. They are listed in Table 2. A typical spectrum for a π-allyl molybdenum complex (9) is shown in Fig. 1. Other spectroscopic properties are described in the Experimental Section. Most of these compounds exhibit four CO absorptions, while there are only two CO ligands in each of these molecules. This is due to the presence of an equilibrium mixture of exo and endo isomers (eq. 12).[35]

(10a)   (10b)

exo isomer   endo isomer

(eq. 12)
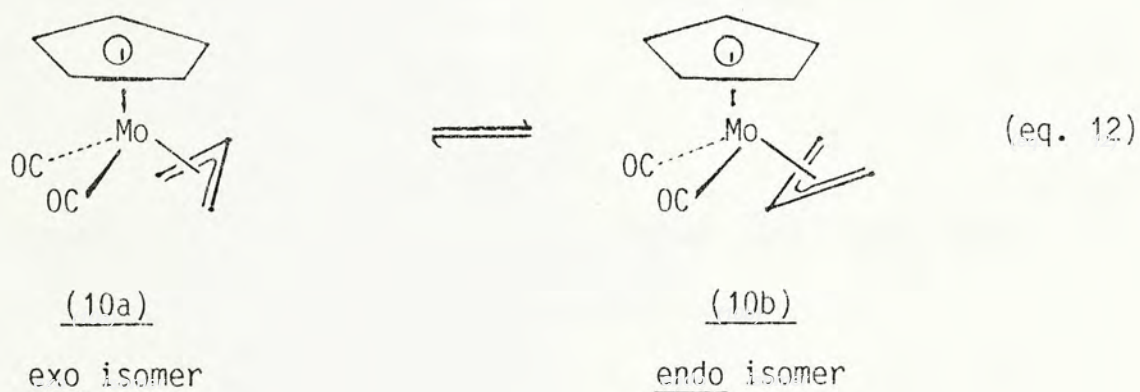
Table 2 The $\nu(CO)$ stretching absorptions of π-allyl molybdenum complexes

π-allyl complex	IR $\nu(CO)$ (C_6H_{12}) (cm^{-1})
CpMo(CO)$_2$ ... CH$_3$ (9)	1974, 1968, 1907, 1891
CpMo(CO)$_2$ (10)	1974, 1967, 1907, 1890
CpMo(CO)$_2$—CH$_3$ (31)	1969, 1900
CpW(CO)$_2$ (32)	1970, 1962, 1900, 1882

Fig. 1 The ν(CO) stretching absorptions of

π-allyl molybdenum (9)
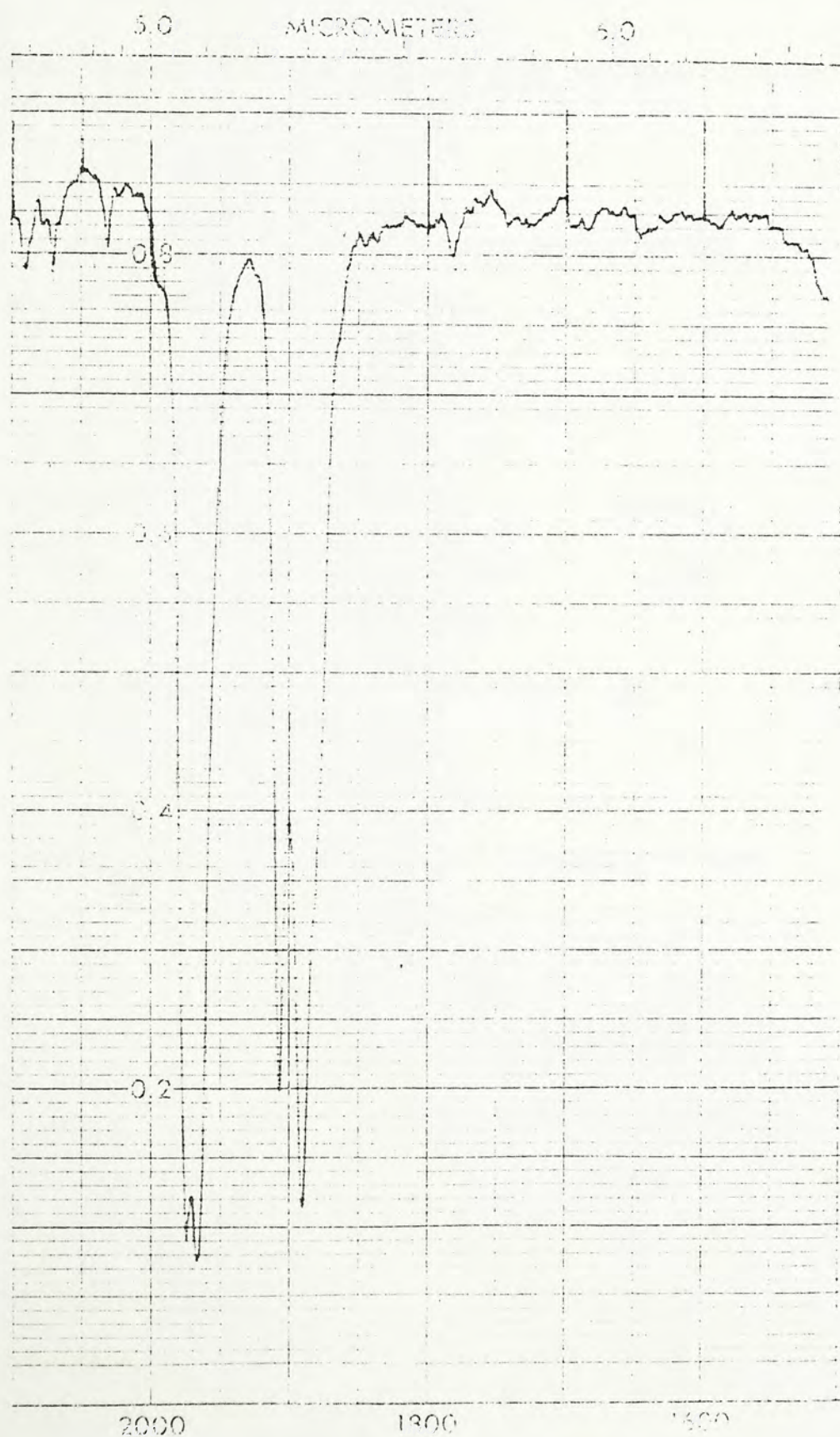
As shown in Table 1, simple allyl halides afforded the π-allyl complexes (9), (10) and (31) in good yields. It is noted that η^3-benzyl complex CpMo(CO)$_2$ ⌬ (33) was also prepared in 51% yield according to this method. Tungsten analog CpW(CO)$_2$(η^3-CH$_2$CH$\div$CH$_2$) (32) was in a similar manner (eq. 13).

[CpW(CO)$_3$]$_2$ $\xrightarrow{\text{Na-Hg}}$ CpW(CO)$_3^-$

(21b) (12b)

Cp: (η^5-C$_5$H$_5$) CH$_2$=CH-CH$_2$-Br (22) $\downarrow$ (eq. 13)

CpW(CO)$_2$ ⫽ $\xleftarrow[\text{-CO}]{\text{TMNO}}$ CpW(CO)$_3$⌒⌒

(32) (37)
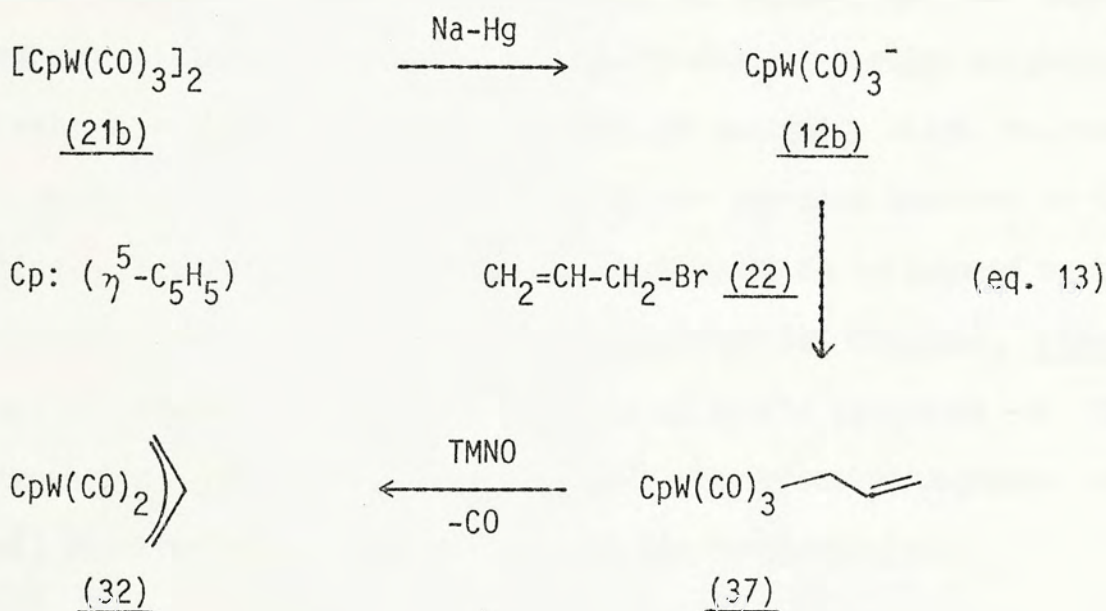
As mentioned earlier, the overall yield of π-allyl molybdenum complex from compound (12a) by photocatalyzed reaction was about 20%.[22] Our reaction with the simple allyl halides afforded the desired products in 68% - 82% yields. The reactions were carried out in one-pot from the anion $CpMo(CO)_3^-$ (12a) [or $CpW(CO)_3^-$ (12b)] without the isolation of the corresponding σ-allyl intermediate $CpMo(CO)_3(\sigma\text{-allyl})$ (20) [or $CpW(CO)_3(\sigma\text{-allyl})$ (37)] and the conditions are very mild. Consequently, our method demonstrates an improved procedure for the synthesis of the π-allyl molybdenum complexes.

The yield of the reaction seems to depend on the steric environment of the allyl halides. Thus, no desired σ-allyl molybdenum complexes were obtained from the reaction of secondary allyl halides. It is worth noting that the first step of our approach involves an S_N2 reaction. Accordingly, this step would greatly be influenced by the steric hindrance of the substrate. The nucleophile, $CpMo(CO)_3^-$ (12a), is quite crowded. Thus, any increase of steric hindrance at the electrophilic centre of allyl halide would greatly decrease the overall reaction rate. This may account for these results.

The key process for the σ to π-allyl rearrangement in this molybdenum complex $CpMo(CO)_3(\sigma\text{-allyl})$ (20) involves the oxidation of the CO ligand by TMNO so that a coordinatively unsaturated organometallic moiety can be generated. Some mechanistic studies on TMNO promoted decarbonylation reactions have been reported[36,37] and are summarized in eq. 14.

$$(OC)_4Fe=C=O + \overset{-}{O}-\overset{+}{N}Me_3 \longrightarrow (OC)_4\overset{-}{Fe}-C\diagup\diagup^{O}_{\diagdown O} \quad \overset{-CO_2}{\longrightarrow}$$

(18)

$Me_3\overset{+}{N}$

(eq. 14)

$$Me_3N \quad + \quad Fe(CO)_4 \rightleftharpoons (OC)_4Fe-NMe_3$$

$-CO_2$ / $-NMe_3$

As shown in eq. 14, the first step includes a nucleophilic attack of the oxygen end in TMNO to the carbon atom of a CO ligand. However, not all carbonyl ligands can be oxidized by TMNO. Empirical studies indicate that there is a reasonable correlation between reactivity of the metal carbonyl and TMNO, and the stretching force constants based on a simple energy-factor force field.[38,39] A parallel between $\nu(CO)$ and severity of conditions in metal carbonyl and amine oxide reactions has been suggested.[40] Koelle[41] and Brown[38] reported that the requirements that $K > 16.0$ and/or $\nu(CO) > 2000$ cm^{-1} are useful guidelines for predicting whether amine oxide reagent will react with a given substrate. To illustrate, $CpMo(CO)_3I$, $\nu(CO)$ 2064, 1989, 1968 cm^{-1}; $K_1=15.70$, $K_2=16.35$[42] reacts readily, while $CpMo(CO)_3CH_3$ (38) ($\nu(CO)$ 2018, 1950, 1964, cm^{-1}; $K_1=15.49$, $K_2=15.80$) is unreactive under the same conditions after several hours.

It is interesting to note that the absorptions in the carbonyl region for the $CpMo(CO)_3(\sigma-CH_2CH=CH_2)$ (11) are: $\nu(CO)$ 2021, 1949 cm^{-1} and are very similar to those for complex $CpMo(CO)_3CH_3$ (38). As mentioned earlier, the σ-allyl complex readily rearranged to the

π-allyl derivative upon treatment with TMNO. Such discrepancy is somewhat striking. The only difference between (11) and (38) is that the former contains an olefin moiety which may undergo intramolecular ligand displacement reaction, while the latter would involve an intermolecular ligand exchange process, if any. The role of the olefin moiety in this reaction, however, is not clear. The mechanism for the σ to π rearrangement is proposed as shown in eq. 15.

$$+ \quad TMNO \quad \xrightarrow{-CO_2} \qquad\qquad (eq.\ 15)$$

(11)

18e

16e

Cp: $(\eta^5\text{-}C_5H_5)$

$CpMo(CO)_2$ (10)
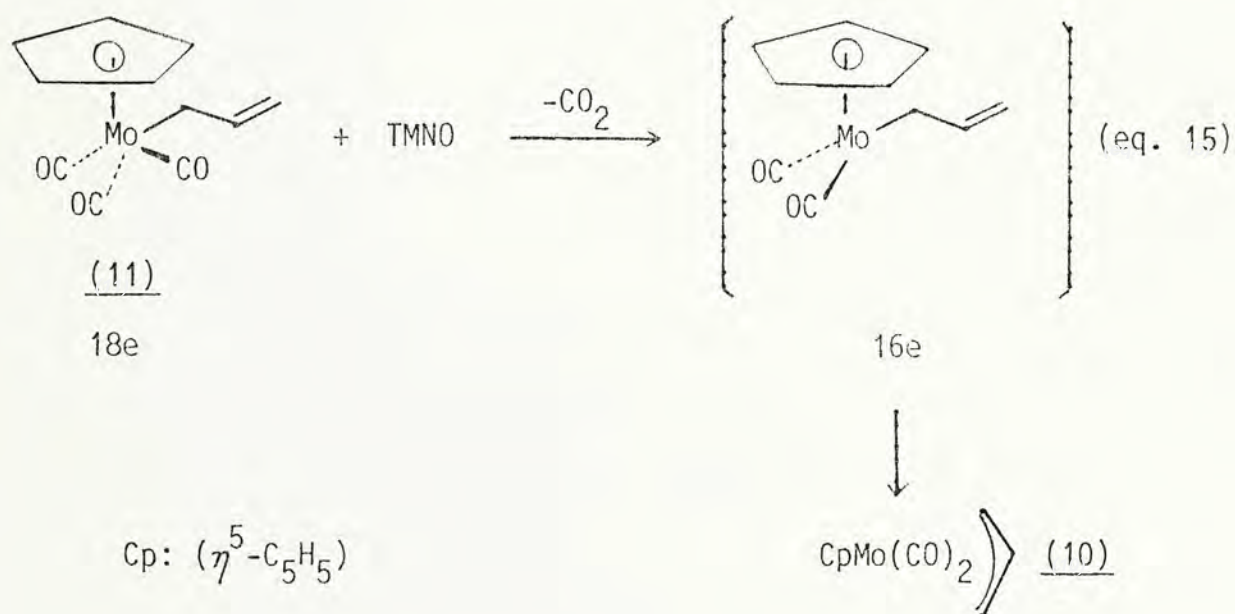
We have also attempted to study the possible intramolecular displacement of a CO ligand by an olefin moiety in the σ-butenyl complex (39). The complex (39) was synthesized by the usual manner from the reaction of the molybdenum anion (12a) and 4-bromo-1-butene (29) (eq. 16). Upon treatment with TMNO, complex (39) surprisingly afforded [CpMo(CO)₃]₂ (21a). Neither ligand exchange product (40) nor π-crotyl molybdenum complex $CpMo(CO)_2(\eta^3\text{-}CH_2CHCH\text{-}CH_3)$ (9) was detected. Presumably, TMNO in this case also serves as an oxidant to cleave the carbon-metal bond. The fate of the organic moiety, however, was not clear.

$\text{CpMo(CO)}_3^- \quad + \quad \text{Br}\diagup\diagdown\diagup\diagdown \quad \longrightarrow \quad \text{CpMo(CO)}_3\diagup\diagdown\diagup\diagdown \quad \text{(eq. 16)}$

(12a)   (29)   (39)

$\text{TMNO} \not\downarrow$

$\text{Cp:}(\eta^5\text{-C}_5\text{H}_5)$ $\text{Cp(OC)}_2\text{Mo}$
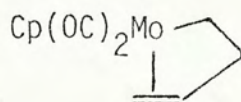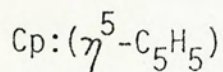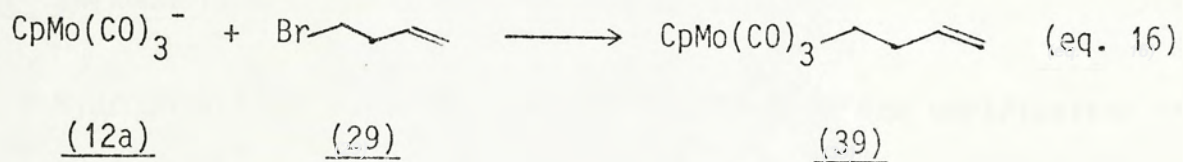
(40)

In summary, we have depicted the first example of trimethylamine-N-oxide promoted σ- to π-allyl rearrangement. The reaction serves as a convenient one-pot synthesis of complexes $\text{CpMo(CO)}_2(\pi\text{-allyl})$ (16) from $[\text{CpMo(CO)}_3]_2$ (21a).

CHAPTER 2 REDUCTIVE DESULFURIZATION REACTIONS

2.1 INTRODUCTION

Hydrodesulfurization process is important in the purification of fossil fuels.[43] The commonly used catalyst for this transformation consists of molybdenum sulfide with nickel or cobalt compounds as promoter (eq. 17).[44] However, the actual mode of this process is not

$$\diagdown C - S - \quad + \; H_2 \quad \xrightarrow{\text{Cat.}} \quad \diagdown C - H \qquad \text{(eq. 17)}$$
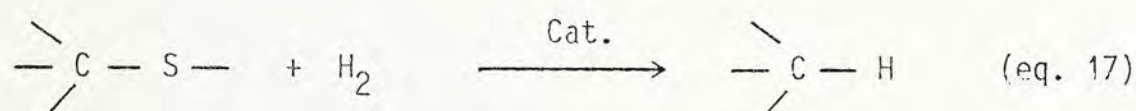
Catalyst: MoS_2

Promoter: Ni or Co compound

well understood. The reaction is essentially the reductive cleavage of carbon-sulfur bond. There are scattered examples using homogeneous organometallic reagent to promote reductive cleavage of carbon-sulfur bonds. Metal carbonyls are effective desulfurization reagents. Alper and his coworkers[45,46] used iron pentacarbonyl (18) in basic media to cleave carbon-sulfur double bond. The corresponding desulfurized product (41) was obtained (eq. 18).[45,46]

$$R_2C{=}S \quad + \quad Fe(CO)_5 \quad \xrightarrow{\text{KOH}} \quad R_2CH_2 \qquad \text{(eq. 18)}$$

$$(18) \qquad\qquad\qquad\qquad (41)$$
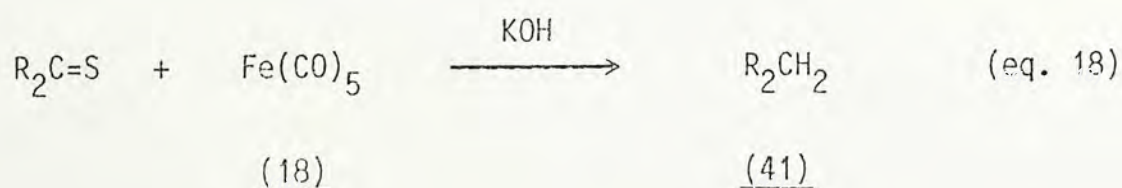
In the presence of phase transfer catalyst, $Fe_3(CO)_{12}$ was proved to be an active reagent to reductively cleave the carbon-sulfur bond (eq. 19).[47,48]

$$R^1R^2R^3C\text{-SH} + Fe_3(CO)_{12} \xrightarrow[\ (C_4H_9)_4N^+HSO_4^-\ ]{\text{NaOH, 60}^\circ\text{C, } C_6H_6} R^1R^2R^3C\text{-H} \quad (eq.\ 19)$$
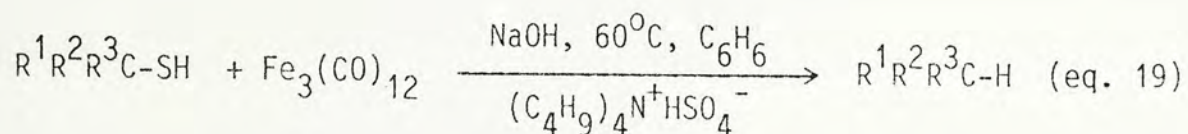
Other kinds of metal carbonyl can also catalyze the desulfurization reactions. To illustrate, Adams and his coworkers[49] achieved the reaction by using osmium carbonyl (43) to selectively break the aryl-sulfur bond in (42) to give (44) (eq. 20).[49]

$$RS\text{-Ph} + Os_3(CO)_{12} \xrightarrow[20\ h]{C_9H_{20}} \qquad (eq.\ 20)$$

(42)　　(43)

(44)

R = Me, ^{i}Pr
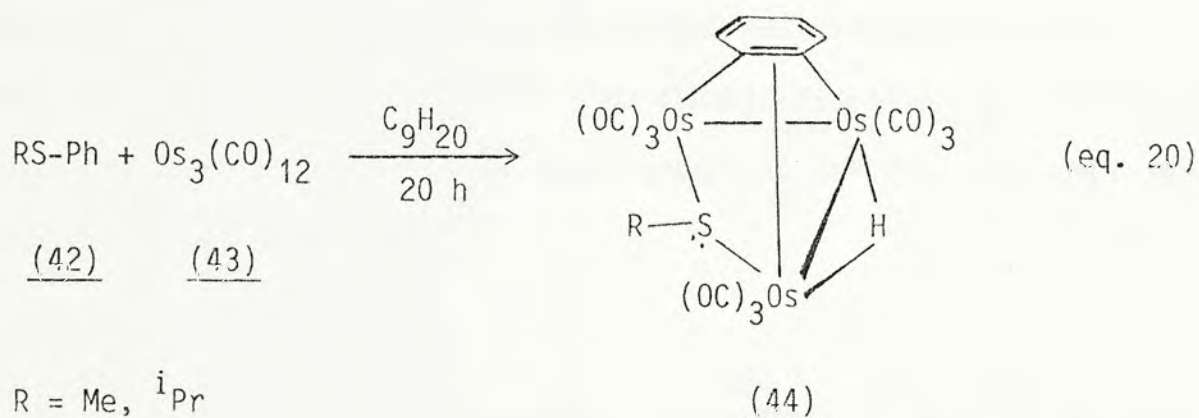
In 1974, Alper[50] claimed that manganese carbonyl (45) could also be used as an effective desulfurization reagent (eq. 21).[50]

$$(R\text{-}\langle\bigcirc\rangle\text{-})_2\text{-C=S} + Mn_2(CO)_{10} \longrightarrow \text{(46)} + [SMn(CO)_3]_n \quad (eq.\ 21)$$

(46)　　　(45)
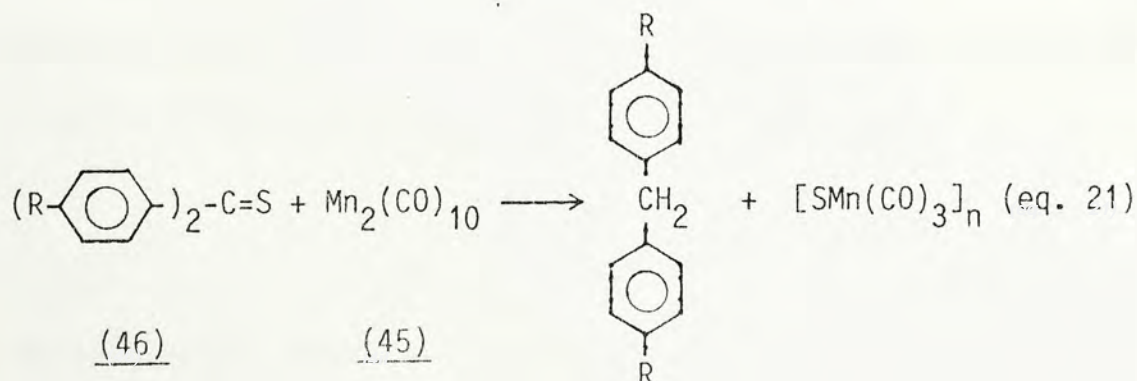
R = H, F, CH_3, OCH_3

Cobalt carbonyl was also employed as desulfurization agent (eq. 22).[51]

$$R\text{-}SH + CO + R'OH \xrightarrow[\text{H}_2\text{O } 190^\circ\text{C, 24 h}]{\text{Co}_2(\text{CO})_8} RCOOR' + H_2S \quad (eq. 22)$$
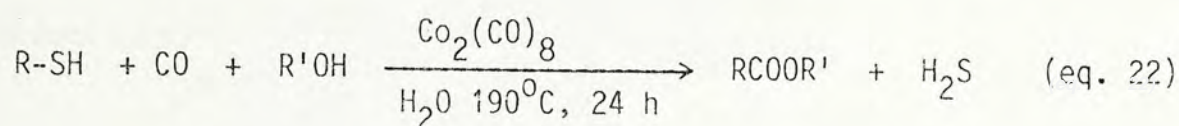
R: Aryl ; R': alkyl

Recently, Alper and Blais reported that molybdenum species generated by the absorption of molybdenum hexacarbonyl on silica gel was an active reagent to react with dibenzothiophene (47) affording biphenyl (48) (eq. 23).[52] No desulfurization occurred when (47) was exposed to $Mo(CO)_6$ in THF.[52]

(47)   (48)
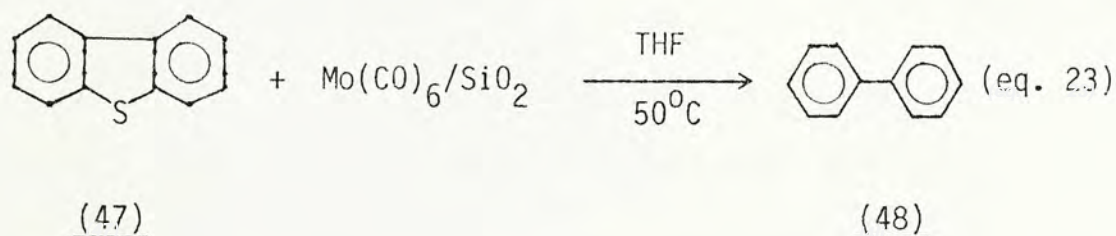
Similarly, the reaction was observed when thiol was treated with a preheated acetic acid solution of molybdenum carbonyl to give the hydrodesulfurization product and thioester (eq. 24).[53]

$$R\text{—}SH + Mo(CO)_6/HOAC \xrightarrow{115^\circ C} R\text{—}H + R\text{-}S\overset{\overset{\text{O}}{\|}}{\text{-}}C\text{-}CH_3 \quad (eq. 24)$$
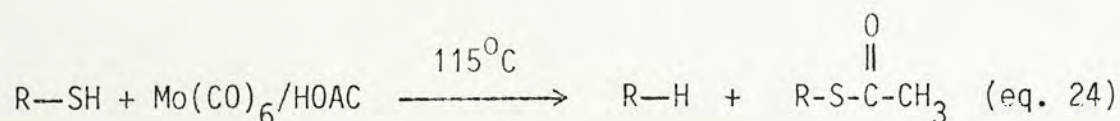
R: Substituted phenyl

In continuation of recent research on hydrodesulfurization reaction in this laboratory,[54,55] we decided to find out if other organometallic reagents would also be effective for the reduction of carbon-sulfur bond.

The Alper's work on activated molybdenum species promoted desulfurization reactions stimulates us to investigate if $Mo(CO)_6$ (56) itself may be able to selectively reduce other kinds of more reactive carbon-sulfur bond. This viewpoint by reacting various organosulfur compounds with $Mo(CO)_6$ has been tested in this study and the details will be described in the next section.

2.2 RESULTS AND DISCUSSIONS

In a typical run, a THF solution of organosulfur compound and $Mo(CO)_6$ was refluxed for 12 to 16 h to give the corresponding reduced products in moderate to good yields. The reaction is shown in eq. 25 and the sulfur compounds used in this study are outlined in Scheme 2. The results are summarized in Table 3.

$$R^1-S-R^2$$
$$+ \qquad \xrightarrow{\text{THF}} \qquad \text{Product(s)} \qquad\qquad \text{(eq. 25)}$$
$$Mo(CO)_6$$
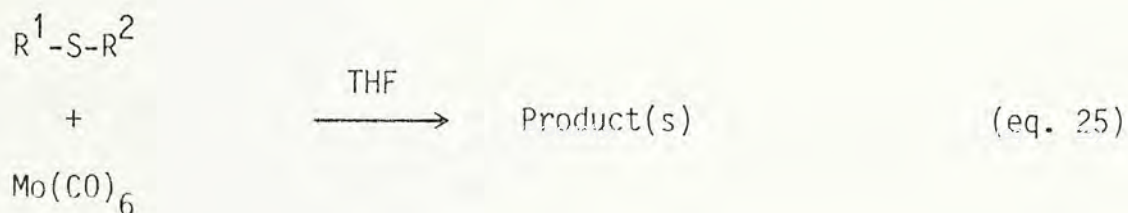
As shown in Table 3, benzylic mercaptans, thioethers were reduced smoothly. Functional groups such as chloro, bromo, methoxy and carboxylic acid as well as carbonyl groups remain intact under these reaction conditions. Thiomethoxy group α to carbonyl group can also undergo reductive cleavage under the reaction conditions. Thus, acetophenone (49) was obtained in 57% yield from its α-thiomethoxy precursor (50)[55].

Since the reaction was carried out in THF and no other possible hydrogen sources were included in the work-up procedure, it is likely that the hydrogen atom in the solvent molecules may be abstracted during the course of the reaction. It is known that the α-hydrogen atom in ethereal solvent molecules can be abstracted by radical species.[56,57] In this study, the α-hydrogen in THF should also be labile and consequently, the reaction may also proceed via a radical mechanism. The radical-like mechanism for the cleavage of carbon-sulfur bonds by means of $Co_2(CO)_8$ has recently been proposed (eq. 26).[51]

Scheme 2 Organosulfur compounds used in this study

(51)

(50)

(52)

(58)

Cl—◯—CH₂-S-H (53)

(59)

Br—◯—CH₂-S-H (54)

MeO—◯—CH₂-S-H (55)

(60)
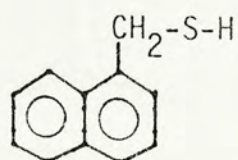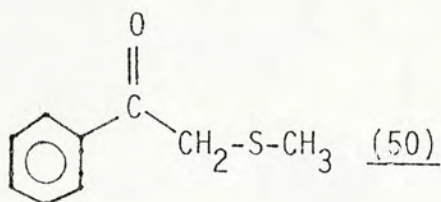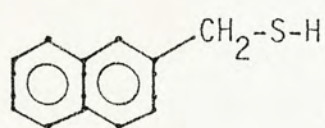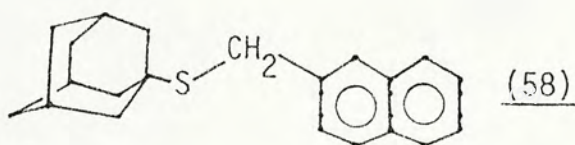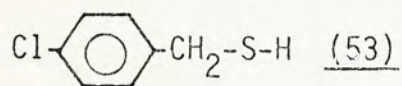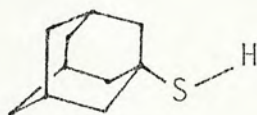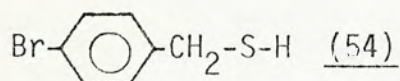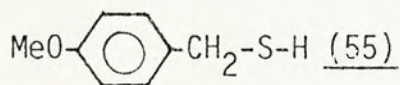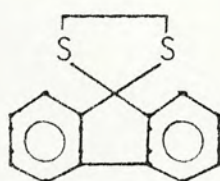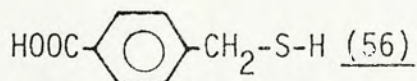
HOOC—◯—CH₂-S-H (56)
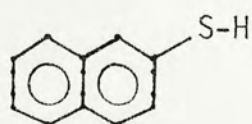
(57)
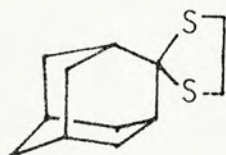
(61)
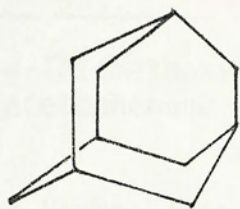
(62)
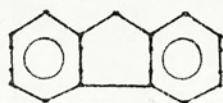
(63)
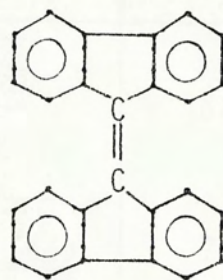
(64)

Table 3 Mo(CO)$_6$ induced hydrodesulfurization reactions

Substrate		Product(s)	% Yield
α-Thiomethoxy-acetophenone	(50)	Acetophenone (49)	57
1-Naphthalene-methanethiol	(51)	1-Methylnaphthalene (65)	79
2-Naphthalene-methanethiol	(52)	2-Methylnaphthalene (66)	67
4-Chlorobenzyl mercaptan	(53)	4-Chlorotoluene (67)	61
4-Bromobenzyl mercaptan	(54)	4-Bromotoluene (68)	63
4-Methoxybenzyl mercaptan	(55)	4-Methylanisole (69)	71
4-Carboxybenzyl mercaptan	(56)	4-Toluic acid (70)	67
2-Thionaphthol	(57)	Naphthalene (71)	43
1-Adamantyl-(2-aphthylmethyl) sulfide	(58)	2-Methylnaphthalene (66)	73
		1-Adamantanethiol (59)	49
1-Adamantanethiol	(59)	Adamantane (62)[a]	0
9-Fluorenone thioketal	(60)	Fluorene (63)[a]	42
		Bifluorenylidene (64)	34
Adamantanone thioketal	(61)	Adamantane (62)[a]	0

[a] Expected product.

- 28 -

$$Co_2(CO)_8 \xrightarrow{H_2O/C_2H_5OH} Co(CO)_4^-$$

$$R\text{-}SH + Co(CO)_4^- \longrightarrow R^\cdot + Co(CO)_4^\cdot + SH^-$$

$$\downarrow \qquad\qquad H_2O \downarrow -OH^-$$

$$\underset{\displaystyle R\text{-}\overset{\textstyle O}{\overset{\|}{C}}Co(CO)_4}{} \xleftarrow{CO} R\text{-}Co(CO)_4 \qquad H_2S$$

$$\downarrow C_2H_5OH/- HCo(CO)_4$$

$$R\overset{\textstyle O}{\overset{\|}{C}}OC_2H_5$$

$$HCo(CO)_4 + OH^- \longrightarrow Co(CO)_4^- + H_2O$$
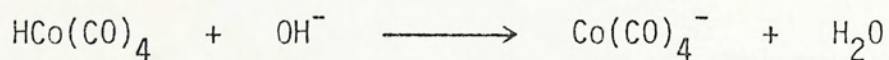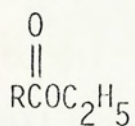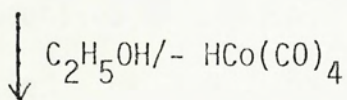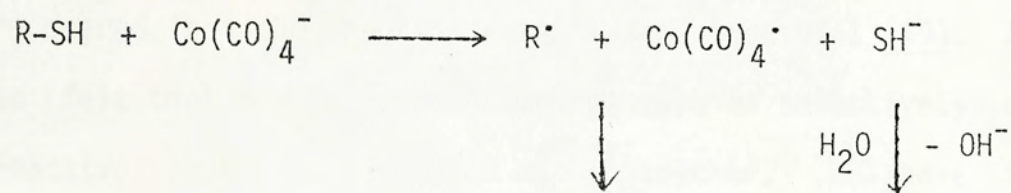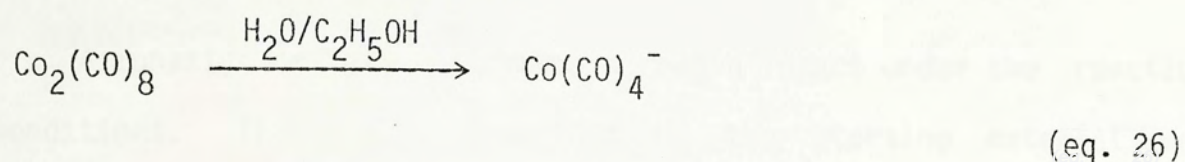
Aliphatic or alicyclic thiols remain intact under the reaction conditions. Thus, more than 80% of the starting material was recovered from the reaction with 1-adamantanethiol (59). Accordingly, we felt that Mo(CO)$_6$ reagent may be able to selectively cleave more reactive carbon-sulfur bond of a thioether. We have tested this viewpoint by studying the hydrodesulfurization reaction of 1-adamantyl-(2-naphthylmethyl) sulfide (58)[55]. 2-Methylnaphthalene (66) and 1-adamantanethiol (59) were obtained in 73% and 49% yields, respectively. Consequently, we believe that our reaction may be applied for removing the benzyl protective group for aliphatic or alicyclic thiols, which is normally deprotected under Birch reduction conditions.[58] The advantage of this reaction using Mo(CO)$_6$ is that all reactions are carried out under mild conditions and in neutral media.

From Table 3, it is noted that aryl-sulfur bond can also be reduced under the reaction conditions. Thus, 2-thionaphthol (57)[55] was transformed into naphthalene (71) in 43% yield. Similar to a previous report,[52] dibenzothiophene (47) did not undergo hydrodesulfurization under the reaction conditions. It is noted that aryl-sulfur bond seems to be more labile than the aliphatic analog in the metal catalyzed carbon-sulfur bond reductive cleavage reactions. Similar behaviour has also been observed in other examples.[49,54,55]

We have also carried out hydrodesulfurization reaction of 9-fluorenone thioketal (60) with Mo(CO)$_6$. A mixture of fluorene (63) and bifluorenylidene (64) was obtained in 42% and 34% yields,

respectively (eq. 27).

(eq. 27)

(60)   (63)

(64)
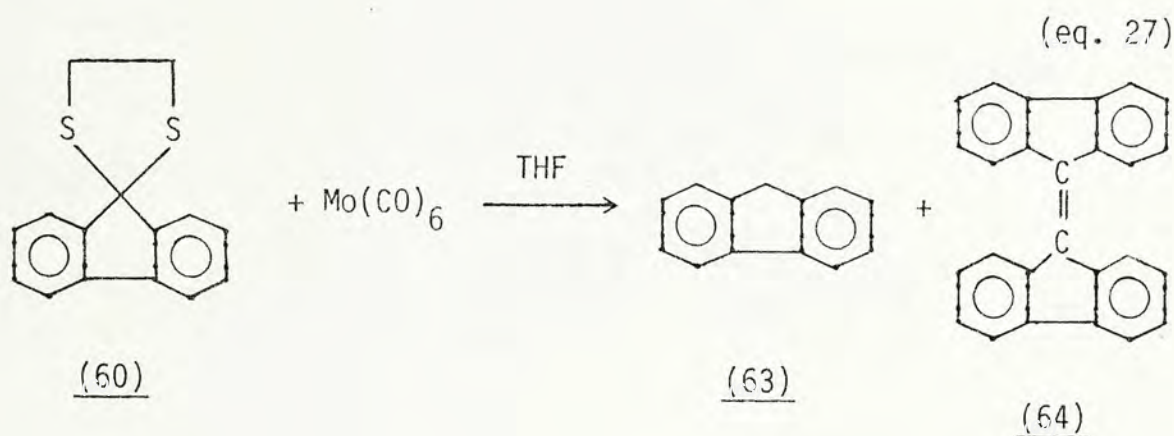
The isolation of the latter product (64) is somewhat interesting. This may be the first example of transforming a thioketal moiety into a dimer (64). Previous example has suggested that the thioketone (46) was treated with $Co_2(CO)_8$ [46,51] to give the dimerized olefin (72) (eq. 28). [46,51]

$$R'_2C=S + Co_2(CO)_8 \xrightarrow[C_6H_6]{} R'_2C=CR'_2$$ (eq. 28)

(46)   (72)

$$R' = (R-\langle\bigcirc\rangle)+$$
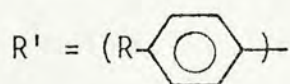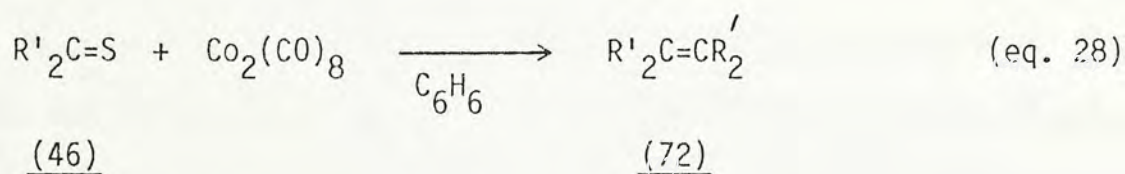
Presumably, this latter reaction may occur via a carbenoid intermediate. Indeed, when thiocarbonate (73) was treated with $Fe(CO)_5$ (18), an iron carbene complex (74) was obtained (eq. 29). [59] Several other related examples are also known. [60-63] Alper has reported that in the presence of manganese carbonyl (45), thioketone moiety (46) was transformed into dimerized product (75) (eq. 30). [50]

- 31 -

C=S (73)

+

Fe(CO)$_5$ (18)

heat $\longrightarrow$

C=Fe(CO)$_4$ (74)

+

$\overset{+}{\underset{+}{>}}$C=C$\overset{}{<}$

Fe$_3$S$_2$(CO)$_9$

(eq. 29)

(R$-\bigcirc-$)$_2$C=S (46)

+

Mn$_2$(CO)$_{10}$ (45)

$\xrightarrow{C_7H_{16}}$

(R$-\bigcirc-$)$_2$C=C$-(\bigcirc-$R)$_2$ (75)

+

[SMn(CO)$_3$]$_n$

(eq. 30)
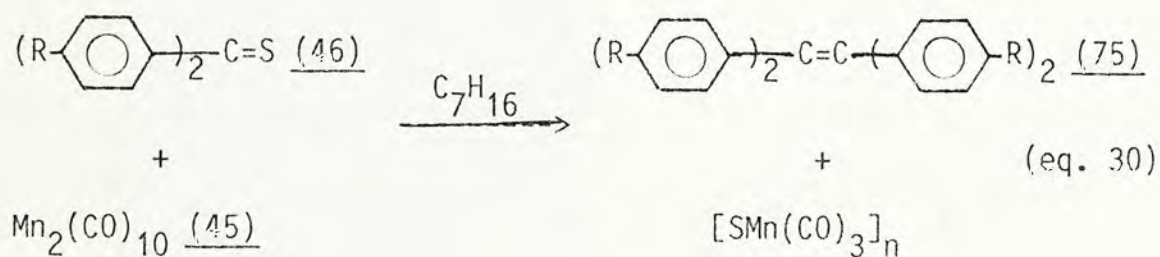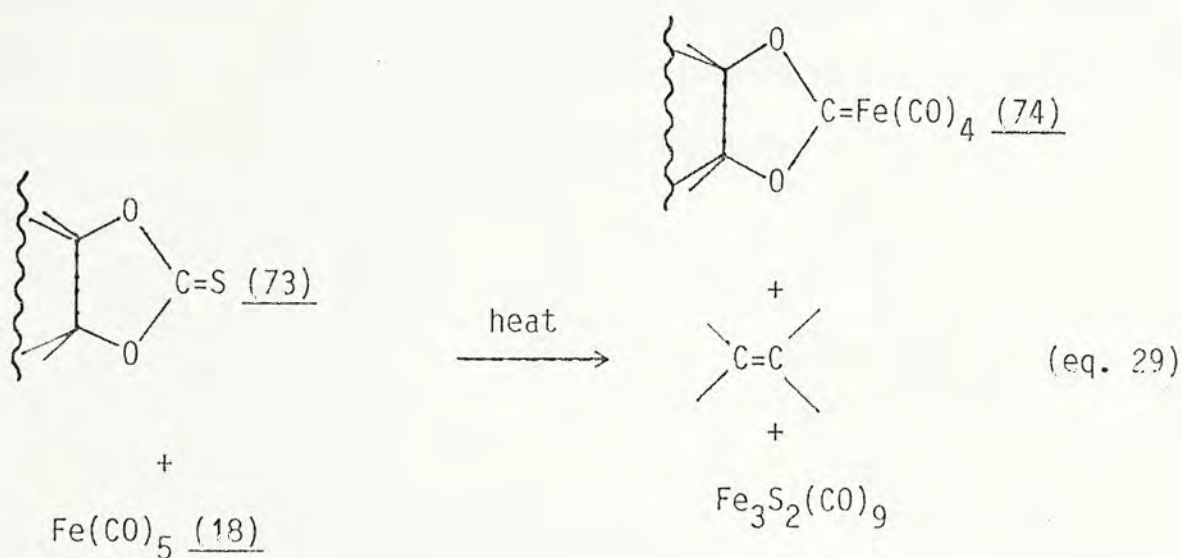
Consequently, it is likely that either fluorenylidene (76) or its molybdenum carbene complex (77) might be the intermediate which dimerizes to give (64) or abstracts hydrogen from the solvent to give (63). The two carbon-sulfur bonds may be stepwisely cleaved. Alternatively, the sulfur stabilized radical formed in the first step may abstract hydrogen from THF to give a thioether which may further react with the molybdenum species to reduce this second carbon-sulfur bond. The possible mechanism is proposed and summarized in eq. 31.

Attempts to desulfurize adamantanone thioketal (61) under these conditions were unsuccessful and only starting meterial was recovered.

In summary, we have depicted that benzylic, aryl and α-acyl activated carbon-sulfur bonds can be readily reduced by the treatment with Mo(CO)$_6$ in THF. The reaction may proceed via a radical-like mechanism. Nevertheless, further clarification is required.
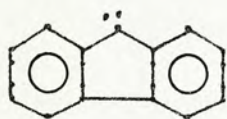
(76)
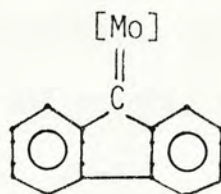
(77)
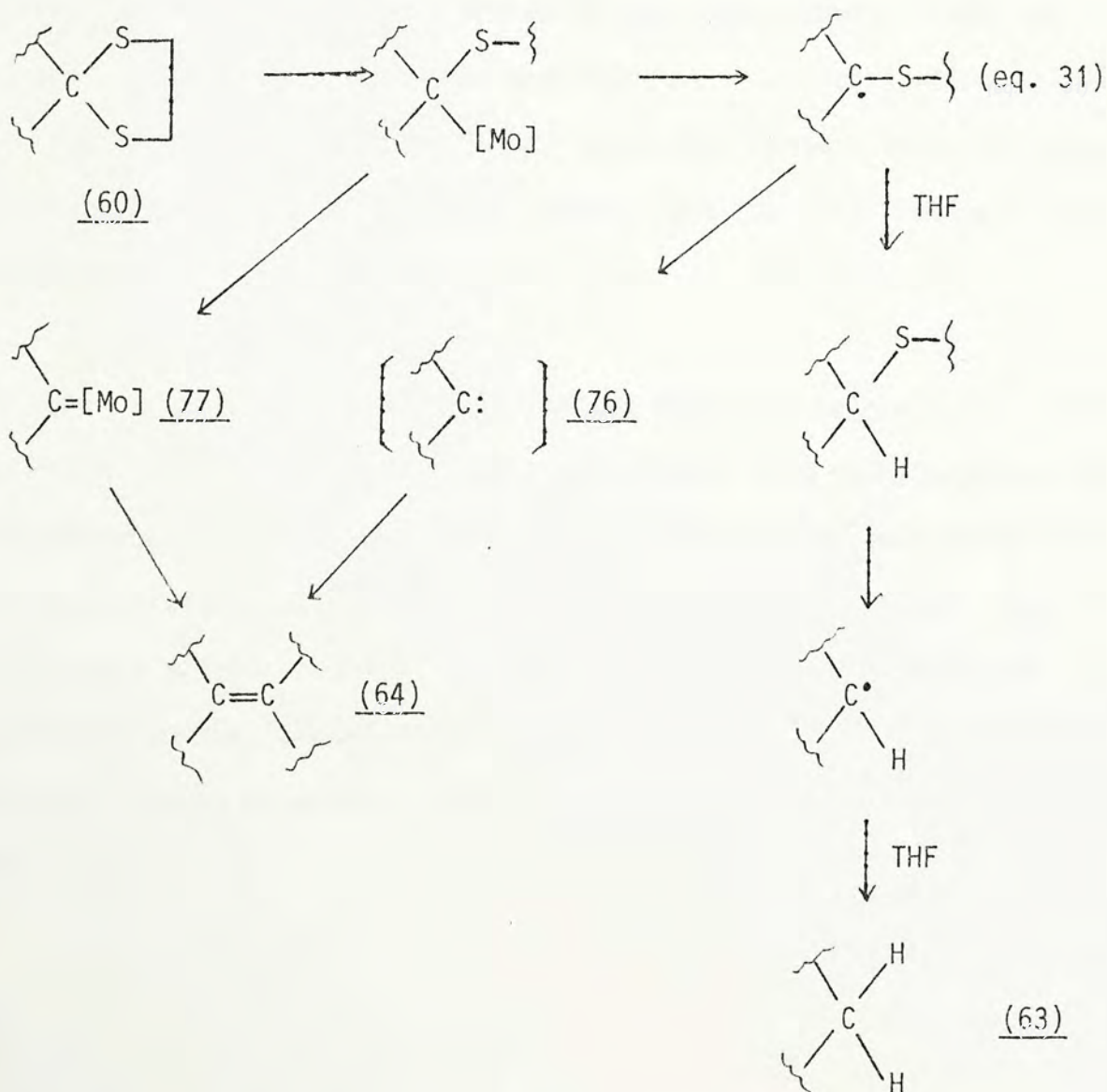
CHAPTER 3 EXPERIMENTAL

All reactions were carried out under nitrogen gas. Standard inert atmosphere techniques were applied for all reactions.[64]

All ^{1}H Nuclear Magnetic Resonance (NMR) spectra were recorded on a JOEL 60 HL (60 MHz) spectrometer and a Bruker WM 250 spectrometer using tetramethylsilane (TMS) as the internal standard. ^{13}C NMR spectra were measured on a Bruker WM 250 spectrometer (250 MHz). Infrared (IR) spectra were measured on a Perkin-Elmer 283 spectrophotometer. Melting points were determined with a Reichert microheating stage. Melting points and boiling points are uncorrected.

All organic solvents were dried and distilled before use. THF was first distilled from LiAlH$_4$ and then from sodium/potassium alloy/benzophenone.[65] Petroleum ether, 50°C - 70°C, was dried with sodium/potassium alloy and freshly distilled before use.[65] Tricarbonylcyclopentadienyl molybdenum dimer (21a) were prepared in accordance to the literature procedure.[66] Commercial available, allyl bromide, crotyl chloride, methallyl chloride were redistilled before use.

Dicarbonyl-π-crotylcyclopentadienyl molybdenum (9). The molybdenum dimer (21a) (2.1 g, 4.2 mmol) in THF (ca. 80 mL) was treated with sodium amalgam prepared from sodium (0.066 g, 2.6 mg - atom) and mercury (ca. 20 g) and the mixture was stirred for about 30 min. to give yellow color solution. After separation of excess mercury, crotyl chloride (23) (1.52 g, 7 mmol) in THF (ca. 15 mL) was added and the mixture was stirred for 4 h at room temperature (ca. 25°C). TMNO (1.3 g, 17 mmol) was then added and the mixture was stirred for another 4 h. After filtration, the filtrate was evaporated and the residue was again taken up into petroleum ether. The petroleum ether solution was chromatographed on alumina and eluted with petroleum ether. The bright yellow eluate was evaporated to give yellow solid (9) (1.68 g, 82%); IR ν(CO) (in C_6H_{12}) 1974, 1968, 1907, 1891 cm^{-1} (Lit.[21]: exo isomer: 1950, 1875, 1490 cm^{-1}; endo isomer: 1955, 1950, 1890, 1875 cm^{-1}); ^{1}H NMR exo isomer δ (CDCl$_3$): 5.15 (5 H, s), 3.5 - 4.0 (1 H, m), 2.46 (1 H, dd), 1.70 (4 H, m), 1.26 (1 H, m) (Lit.[21]: 5.20 (5 H), 3.83 - 4.0 (2 H), 2.8 (1 H), 1.32 (1 H), 0.95 (3 H)); endo isomer: δ (CDCl$_3$): 5.15 (5 H, s), 3.8 - 4.0 (2 H, m), 2.70 (1 H, dd), 1.25 (1 H, m), 0.87 (3 H, s) (Lit.[21]: 5.22 (5 H), 3.90 (1 H), 2.54 (1 H), 1.26 (1 H), 1.75 (4 H)).

Dicarbonyl-π-allylcyclopentadienyl molybdenum (10). The tricarbonyl-cyclopentadienyl molybdenum dimer (21a) (0.46 g, 0.95 mmol) in THF (ca. 80 mL) was treated with sodium amalgam prepared from sodium (0.066 g, 2.6 mg - atom) and mercury (ca. 20 g). The mixture was stirred for 15 - 30 min. Excess mercury was separated and the yellow THF solution of tricarbonylcyclopentadienyl molybdenum anion (12a) was

transferred to another flask to which allyl bromide (22) (0.87 g, 7 mmol) in THF (ca. 10 mL) was introduced. The mixture was stirred for 4 h at room temperature and then TMNO (0.4 g, 5 mmol) was transferred into the reaction mixture. The slurry was stirred for another 4 h and filtered. The filtrate was evaporated under reduced pressure and the residue was redissolved in petroleum ether. The solution was passed through alumina (Fluka 507C) and eluted with petroleum ether. The eluate was evaporated under reduced pressure to afford the desired product (10) (0.37 g, 75%); IR ν(CO) (in C_6H_{12}) 1974, 1967, 1907, 1890 cm^{-1} (Lit.[22]: 1961, 1886, 1871 cm^{-1}); ^{1}H NMR δ (CDCl$_3$): 5.15 (5 H, s), 4.00 (1 H, m), 2.90 (2 H, m), 1.0 (2 H, m) (Lit.[22]: 4.74 (5 H), 3.28 (1 H), 2.6 (2 H), 0.87 (2 H)); ^{13}C NMR δ (CDCl$_3$): 38.8, 66.2, 90.2, 236.2.

Dicarbonyl-π-methallylcyclopentadienyl molybdenum (31). Molybdenum dimer (21a) (0.5 g, 1 mmol) in THF (ca. 80 mL) was treated with sodium amalgam prepared with sodium (0.066 g, 2.6 mg - atom) and mercury (ca. 20 g) for about 20 min. to give the yellow molybdenum anion (12a). Excess amalgam was separated and the organic solution was allowed to react with methallyl chloride (24) (1.0 g, 10 mmol) in THF (ca. 15 mL). The mixture was stirred for 4 h and then TMNO (0.44 g, 6 mmol) was added. The yellow slurry was stirred for another 4 h and then filtered. The filtrate was evaporated to give yellow color residue which was trituated with petroleum ether and chromatographed on alumina eluted with petroleum ether afforded the yellow solid (31) (0.38 g, 68%); IR ν(CO) (in C_6H_{12}) 1969, 1900 cm^{-1}.[67]

Dicarbonyl-π-allylcyclopentadienyl tungsten (32). In a similar prodedure, tricarbonylcyclopentadienyl tungsten dimer (21b) (0.943 g, 1.42 mmol) in THF (ca. 80 mL) was treated with sodium amalgam prepared with sodium (0.066 g, 2.6 mg - atom) and mercury (ca. 20 g) for 30 min. Excess mercury was separated and the yellow tungsten anion (12b) was then treated with allyl bromide (22) (0.9584 g, 7.92 mmol) in THF (ca. 20 mL). After stirring for another 4 h, TMNO (0.86 g, 11.4 mmol) was introduced and the yellow slurry was stirred for another 12 h. After filtration, the filtrate was evaporated to afford yellowish brown residue which was then trituated with petroleum ether and chromatographed on alumina; eluted with petroleum ether. The yellow fraction was evaporated under reduced pressure to give yellow solid (32) (0.4113 g, 42%); IR ν(CO) (in C_6H_{12}) 1970, 1962, 1900, 1882 cm^{-1}.[69]

Dicarbonyl-π-benzylcyclopentadienyl molybdenum (33). Tricarbonyl-cyclopentadienyl molybdenum dimer (21a) (1.83 g, 3.73 mmol) in THF (ca. 80 mL) was treated with sodium amalgam prepared with sodium (0.066 g, 2.6 mg - atom) and mercury (ca. 20 g) for 30 min. to obtain yellow color molybdenum anion (12a). Excess amalgam was separated and the THF solution was mixed with benzyl chloride (30) (0.86 g, 6.6 mmol) in THF (ca. 15 mL) at room temperature for 4 h and then reacted with TMNO (1.1 g, 14.7 mmol). The above mixture was stirred for 4 h to afford orange color solution. The suspension was filtered and the filtrate was evaporated to give red color residue. The residue was trituated with petroleum ether, chromatographed on alumina and eluted with petroleum ether. The red color fraction was collected and

evaporated under reduced pressure to give red color solid (33) (1.17
g, 51%); ^{1}H NMR δ (CDCl$_3$): 7.03 (4 H, br. s), 6.40 (1 H, s), 5.15 (5
H, s), 2.85 (1 H, s), 1.90 (2 H, s). The π-benzyl molybdenum complex
(33) exhibited identical properties with the literature compound
(Lit.[68]: 7.03, 6.31, 5.04, 2.82, 1.81).

Attempted Preparation of Dicarbonyl-π-butenylcyclopentadienyl molyb-
denum (40). Molybdenum dimer (21a) (0.5 g, 1.02 mmol) in THF (ca. 80
mL) was treated with sodium amalgam prepared from sodium (0.066 g, 2.6
mg - atom) and mercury (ca. 20 g) for 30 min. After the above
solution turned to yellow color, excess mercury was separated. 4-
Bromo-1-butene (29) (0.53 g, 3.9 mmol) in THF (ca. 20 mL) was then
introduced to the anion (12a) solution and the mixture was stirred for
16 h to give the δ-complex (39) (IR ν (CO) in C$_6$H$_{12}$: 2021, 1948,
1886 cm^{-1}). To the THF solution of δ-complex (39), TMNO (0.21 g, 2.8
mmol) was then added and the slurry was stirred for 3 h to afford a
red color solution. The mixture was filtered and the filtrate was
evaporated to give red color residue which was then trituated with
petroleum ether and chromatographed on alumina. The red color eluate
was evaporated to give (21a); IR ν (CO) (in C$_6$H$_{12}$) 1996, 1970, 1926
cm^{-1}. No desired product (40) was obtained.

1-Naphthalenemethanethiol (51).[70,71] Commercial available thiourea
(8.85 g, 0.116 mol) in 95% ethanol (10 mL) was mixed with 1-chloro-
methylnaphthalene (17.7 g, 0.1 mol) in ethanol (30 mL). The mixture
was refluxed for 2 h, then cooled and filtered. The solid was air
dried and taken up into aqueous sodium hydroxide (10%, 100 mL). The
mixture was refluxed for 2.5 h. After neutralization with

hydrochloric acid (10%), the aqueous solution was extracted with diethyl ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to give a brown color liquid which was distilled to give the desired thiol (51) (5.2 g, 30%), bp. 86°C - 90°C/0.1 mm (Lit.[71]: 142°C - 143°C/0.5 mm); ^{1}H NMR δ(CDCl$_3$): 1.71 (1 H, t), 3.95 (2 H, d), 7.0 - 8.0 (7 H, m).

4-Chlorobenzyl bromide.[72,73] 4-Chlorotoluene (31.7 g, 0.25 mol) was mixed with NBS (44.5 g, 0.25 mol) in carbon tetrachloride (500 mL) and the mixture was refluxed for 2 h. After filtration, the filtrate was evaporated in vacuo and then recrystallized from ethanol to give the desired bromide (44.3 g, 86 %); mp. 51.5°C - 52°C (Lit.[74]: 51°C); ^{1}H NMR δ(CDCl$_3$): 4.37 (2 H, s), 7.23 (4 H, s).

4-Chlorobenzyl mercaptan (53).[70,75] A mixture of thiourea (9.0 g, 0.118 mol) and 4-chlorobenzyl bromide (24.3 g, 0.118 mol) in ethanol (40 mL) was refluxed for 2 h. The solution was cooled and the white solid which was filtered was taken up in sodium hydroxide (10%, 50 mL) and refluxed for 2.5 h. After cooling, the solution was neutralized and extracted with diethyl ether five times. The combined extracts were dried over anhydrous magnesium sulfate, filtered and evaporated to afford the crude product which was distilled to give pure 4-chlorobenzyl mercaptan (53) (12.8 g, 73%); bp. 64°C - 66°C/0.7 mm (Lit.[76]: 66°C - 67°C/0.4 mm); ^{1}H NMR δ(CDCl$_3$): 1.72 (1 H, t), 3.65 (2 H, d), 7.25 (4 H, s).

4-Bromomethylanisole.[72,73] 4-Methylanisole (30 g, 0.26 mol) was mixed with NBS (43.7 g, 0.26 mol) in carbon tetrachloride (500 mL). The mixture was refluxed for 2.5 h and the slurry was filtered and the filtrate was concentrated. Brown liquid was obtained and distilled to give 4-bromomethylanisole (45.5 g, 92%); bp. $80^{\circ}C$ - $84^{\circ}C/1$ mm (Lit.[74]: $105^{\circ}C$ - $110^{\circ}C/8$ mm); ^1H NMR δ (CDCl$_3$): 3.76 (3 H,s), 4.50 (2 H, s), 6.68 - 7.62 (4 H, m).

4-Methoxybenzyl mercaptan (55).[75,76] A mixture of thiourea (7.6 g, 0.1 mol) and 4-bromomethylanisole (21 g, 0.1 mol) in ethanol solution (60 mL) was refluxed for 2.5 h. The solution was cooled and the solid obtained was hydrolyzed with sodium hydroxide (10%, 50 mL) according to the procedure described above. The solution was acidified with hydrochloric acid to pH about 1 and extracted with diethyl ether. The organic solution was dried over anhydrous magnesium sulfate, filtered and evaporated in vacuo to give a brown liquid which was distilled to afford 4-methoxybenzyl mercaptan (55) (6.0 g, 39%); bp. $60^{\circ}C$ - $62^{\circ}C/0.1$ mm (Lit.[76]: $89^{\circ}C$ - $94^{\circ}C/2.5$ mm); ^1H NMR δ (CDCl$_3$): 1.7 (1 H, t), 3.53 (2 H, d), 3.57 (3 H, s), 6.64 - 7.20 (4 H, q).

Desulfurization of α-thiomethoxyacetophenone (50). α-Thiomethoxy-acetophenone (50)[55] (0.166 g, 1 mmol), Mo(CO)$_6$ (0.264 g, 1 mmol) in THF (ca. 40 mL) were converted into the reduced product (49) in a similar manner, (0.068 g, 57%) which is identical in every aspect with the authentic compound. The proton NMR δ (CDCl$_3$): 2.55 (3 H, s), 7.43 - 8.10 (5 H, m).

Desulfurization of 1-naphthalenemethanethiol (51). A mixture of 1-naphthalenemethanethiol (51) (0.348 g, 2 mmol) and $Mo(CO)_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) was refluxed under nitrogen atmosphere for 12 h. The solution turned brownish black with some precipitate. After cooling, the mixture was filtered and the filter cake was washed with three portions of diethyl ether. The filtrate was evaporated in vacuo and triturated with petroleum ether. The organic solution was evaporated in vacuo and the residue was chromatographed on silica gel and eluted with petroleum ether to give the reduced product, 1-methylnaphthalene (65) (0.224 g, 79%) which exhibited identical spectroscopic properties with the authentic sample. The proton NMR $\delta(CDCl_3)$: 2.57 (3 H, s), 7.03 - 8.0 (7 H, m).

Desulfurization of 2-naphthalenemethanethiol (52). 2-Naphthalene-methanethiol (52)[55] (0.174 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) in THF (ca. 40 mL) was refluxed under nitrogen atmosphere for 12 h. After cooling, the mixture was filtered and the filtrate was evaporated in vacuo to give brown residue which was chromatographed on silica gel and eluted with petroleum ether to give the desired product (66) (0.095 g, 67%), which was identical in every aspect with the authentic sample. The proton NMR $\delta(CDCl_3)$: 2.34 (3 H, s), 6.96 - 7.54 (7 H, m).

Desulfurization of 4-chlorobenzyl mercaptan (53). By the similar method described above, 4-chlorobenzyl mercaptan (53) (0.333 g, 2 mmol) was reduced to give 4-chlorotoluene (67) (0.163 g, 61%) which exhibited identical spectroscopic properties with the authentic sample. The proton NMR $\delta(CDCl_3)$: 2.17 (3 H, s), 7.10 (4 H, d).

Desulfurization of 4-bromobenzyl mercaptan (54). A THF solution of 4-bromobenzyl mercaptan (54)[55] (0.203 g, 1 mmol) and Mo(CO)$_6$ (0.264 g, 1 mmol) was refluxed with vigorously stirring for 16 h. The mixture was filtered and the residue was chromatographed on silica gel and eluted with petroleum ether to yield 4-bromotoluene (68) (0.108 g, 63%) which was characterized by comparing its spectroscopic properties with the standard sample. The proton NMR δ (CDCl$_3$): 2.27 (3 H, s), 6.93 - 7.42 (4 H, q).

Desulfurization of 4-methoxybenzyl mercaptan (55). 4-Methoxybenzyl mercaptan (55) (0.308 g, 2 mmol) and Mo(CO)$_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) was refluxed under nitrogen atmosphere for 12 h. After cooling, the mixture was filtered and the black solid was washed with diethyl ether three times. The combined extracts were evaporated in vacuo to give the residue which was chromatographed on silica gel and eluted with petroleum ether to give the desired product (69) (0.17 g, 71%) which showed identical physical properties as the authentic sample. The proton NMR δ (CDCl$_3$): 2.20 (3 H, s), 3.57 (3 H, s), 6.57 - 7.05 (4 H, q).

Desulfurization of 4-carboxybenzyl mercaptan (56). According to the similar procedure, a mixture of 4-carboxybenzyl mercaptan (56)[55] (0.157 g, 0.937 mmol) and Mo(CO)$_6$ (0.247 g, 0.937 mmol) in THF (ca. 40 mL) was transformed to 4-toluic acid (70) (0.078 g, 67%) which exhibited same physical properties with the authentic sample. The proton NMR δ (CDCl$_3$): 2.40 (3 H, s), 7.15 (2 H, d), 8.10 (2 H, d), 8.5 (1 H, m).

Desulfurization of 2-thionaphthol (57). 2-Thionaphthol (57)[55] (0.322 g, 2.01 mmol) and Mo(CO)$_6$ (0.528 g, 2 mmol) in THF (ca. 40 mL) were transformed according to the procedure described above to yield naphthalene (71) (0.112 g, 43%) which was identical to the authentic compound. The proton NMR δ (CDCl$_3$): 7.0 - 7.7.

Desulfurization of 1-adamantyl-(2-naphthylmethyl) sulfide (58). Compound (58)[55] (0.616 g, 2 mmol) was allowed to react with Mo(CO)$_6$ (1.056 g, 4 mmol) in THF (ca. 40 mL) at refluxing temperature for 16 h. After cooling, the mixture was filtered and the filter cake was washed with ether. The organic solution was evaporated in vacuo to give the brownish residue which was chromatographed on silica gel and eluted with petroleum ether. The first fraction afforded 2-methylnaphthalene (66) (0.1 g, 73% based on unrecovered starting material) which exhibited same spectroscopic data as the authentic sample. Further elution with petroleum ether yielded 1-adamantanethiol (59) (0.085 g, 49% based on unrecovered starting material), which showed identical properties as the authentic material, and recovered the starting material (0.3 g, 49%). The proton NMR for compound (66) δ (CDCl$_3$): 2.30 (3 H, s), 6.75 - 7.55 (7 H, m).

Desulfurization of 9-fluorenone thioketal (60). A mixture of 9-fluorenonethioketal (60)[55] (0.256 g, 1 mmol) and Mo(CO)$_6$ in THF (ca. 40 mL) was refluxed for 12 h to give an orange color suspension. After filtration, the filter cake was washed with diethyl ether several times. The combined ether solution was evaporated and the residue was chromatographed on silica gel and eluted with petroleum

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ether.   From the first fraction (<u>ca</u>. 100 mL), fluorene (63) (0.069 g,

42%)   was   obtained.   The   second   fraction   was   identified   as

bifluorenylidene (64) (0.055 g, 34%);   mp. 190°C - 191.5°C (Lit.[77]:

187°C); ^{1}H NMR for compound (64) δ (CDCl$_3$): 7.03 (8 H, m), 7.48 (4 H,

m), 8.13 (4 H, m); and the mass spectrum for compound (64) (m/e): 328,

164.

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