THIOKETONE-METAL CARBONYL REACTIONS

BY

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The undersigned hereby recommend to the Faculty of Graduate Studies acceptance of this report by Ned D. Silavwe in partial fulfillment of the requirements for the degree of Master of Science.

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CONTENTS

SECTION		PAGE
A.	Introduction	1
B.	Reactions of $\{(h^5C_5H_4R)_2M_2(CO)_n\}$(M=Mo,W; R=H, CH_3; n=4, 6) with Thiones, Allenes, Phosphines, etc.	16
C.	Results and Discussion	19
	1. Aromatic Thione Complexes (Synthesis)	22
	2. Non-Aromatic Thione Complexes (Synthesis)	26
	3. Reaction Mechanism	30
	4. Infrared Data	33
	5. Proton NMR Data	38
	6. Carbon-13 NMR Data	47
	7. Mass Spectroscopy	54
	8. Structure of Thione Complexes	54
	9. (a). Isomerisation of Monothione Complexes	65
	(b). Kinetic and Thermodynamic Data	75
	10. Population of Major and Minor Isomers of 58 as a Function of the Polarity of Solvents	77
	11. Infrared and Proton NMR Data obtained in DMSO.	79
D.	Experimental	115
	Determination of kinetic data	116
	Procedures for the synthesis of thione complexes	118
	X-ray analysis	147
	Appendix	150

CONTENTS (cont'd.)

TABLES

NO.	TITLE	PAGE
1.	Thione Complexes	87
2.	Analytical Data	89
3.	Infrared Data	90
4.	Proton NMR Data	92
5.	Carbon-13 NMR Data	94
6A.	Shielding of Cyclopentadienyl Protons by Different Solvents	95
6B.	Cyclopentadienyl Proton NMR Data: Mo Vs. W	96
7.	Concentration of Major and Minor Isomers (X and Y) of 54d as a Function of Time at 274.5K (in $CDCl_3$).	97
8.	Concentration of Major and Minor Isomers (X and Y) of 58 as a Function of Time at 293K (in $CDCl_3$).	98
9.	Kinetic Data	99
10.	Thermodynamic Data	99
11.	Population of Isomers of Diazocyanides in Relation to Their Dipole Moments.	100
12.	Population of the Trans and Gauche Isomers of $\{Cp_2Mo_2(CO)_6\}$ in Various Solvents (with Different Dielectric Constants).	101
13.	Population of the Major and Minor Isomers (X and Y) of 58 as a Function of Dielectric Constants of Different Solvents.	101
14.	Proton NMR and Infrared Data of Monothione Complexes in Different Solvents.	102
15.	Bondlengths and Bond Angles Data not included in Figures 6 and 7.	104

CONTENTS (cont'd.)

FIGURES

NO.	TITLE	PAGE
1.	Infrared Spectra of $\{Cp_2Mo_2(CO)_4L\}$, L=4,4'-Dimethoxythiobenzophenone, Thiobenzophenone, 4-methoxythiobenzophenone and Adamantanethione.	105
2.	Possible Interaction of Ring Currents of Phenyl Groups with Cyclopentadienyl Groups.	43
3.	Factors Leading to Formation of Semi-Bridging Groups.	56
4.	Proton NMR Spectra of Some Monothione Complexes.	106
5.	Proton NMR Spectra of 54d and 58 at Low Temperature.	107
6.	Bondlengths of 58.	108
7.	Bond Angles of 58.	109
8.	Ortep Diagram of the Crystal Structure of 58.	110
9.	Plot of $\ln\{[Y]_e - [Y]_t\}$ Vs Time: 54d.	111
10.	Plot of $\ln\{[Y]_e - [Y]_t\}$ Vs Time: 58.	112
11.	Proton NMR Spectra of Some Monothione Complexes in DMSO.	113
12.	Proton NMR Spectra of $\{Cp_2W_2(CO)_4$ (adamantanethione)$\}$ in DMSO:$CDCl_3$ Solvent Mixtures.	114
13.	Pattern of the Proton NMR Spectrum of $\{Cp_2Mo_2(CO)_4$ (thiocamphor)$\}$ in $CDCl_3$ at about -40^oC.	150
14.	Metal-metal Mo bonding sketch diagram.	21

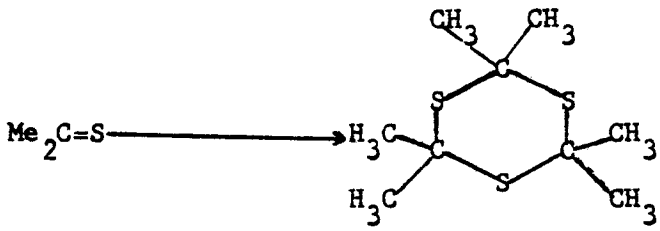
ABSTRACT

An account of the reaction of $\{(h^5\text{-}C_5H_5)_2M_2(CO)_6\}$ and $\{(h^5\text{-}C_5H_5)_2M_2(CO)_4\}$ (M=Mo,W) with aromatic and non-aromatic thiones to give mostly complexes of general molecular formula $\{(h^5\text{-}C_5H_5)_2M_2(CO)_4L\}$ (M=Mo, W; L=Thione) is given. $\{(h^5\text{-}C_5H_4CH_3)_2Mo(CO)_6\}$ and $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4\}$ react with thiones in a similar manner. Thiones used include thiofenchone, thiocamphor and 4,4'-dimethoxythiobenzophenone. Also complexes of general molecular formula $\{Cp_2Mo_2(CO)_nL_2\}$ (n=either 3 or 4; L=thione; Cp=π-C_5H_5) are isolated when $\{(h^5\text{-}C_5H_5)_2Mo_2(CO)_6\}$ is reacted with thiobenzophenone, 4,4'-dimethylthiobenzophenone, 4-methoxythiobenzophenone, 4,4'-difluorothiobenzophenone, thiocamphor and adamentanethione, and when $\{Cp_2Mo_2(CO)_4\}$ is reacted with 4,4'-difluorothiobenzophenone•Complexes of the type $\{(h^5\text{-}C_5H_4R)_2M_2(CO)_4L\}$ (M=Mo,W; R=CH_3,H; L=4-methoxythiobenzophenone, thiocamphor and adamantanethione) exist in at least two isomeric forms in non-polar and moderately polar solvents such as benzene, carbon tetrachloride and acetone. It is also noted that isomerisation depends on the polarity of solvent so that the population of one of the isomers increases with the polarity of solvent at the expense of the other. The proton NMR spectra of $\{(h^5\text{-}C_5H_4R)_2Mo_2(CO)_4L\}$ (L=thiocamphor, R=H,CH_3;R=H and L=4-methoxythiobenzophenone) at low temperature ($\sim$-40°C) show that one of the two isomers generally present in solution is overwhelmingly in larger proportion in solid state than the other one. The population of the major and minor isomers respectively decrease and increase as the temperature is raised or the mixture

is left to equilibrate. This property has made it possible to obtain both kinetic and thermodynamic data. Also the single crystal structure of $\{h^5\text{-}C_5H_5)Mo_2(CO)_4L\}$ (L=thiocamphor) has been obtained and the Mo-Mo and C-S bondlengths are found to be 3.145Å and 2.769Å respectively. In addition to the use of X-ray data characterisation of complexes has been done by utilisation of infrared spectroscopy and, proton and carbon-13 NMR spectroscopy as well as elemental analysis wherever and whenever possible and necessary.

A. INTRODUCTION

Unlike ketones thiones are generally unstable under ordinary conditons. They tend to form compounds in which the sulphur atom is not involved in multiple bond formation. For example thioacetone trimerizes[1] to 1 at room temperature. Such behaviour of thiones may be explained by the general tendency of main group elements



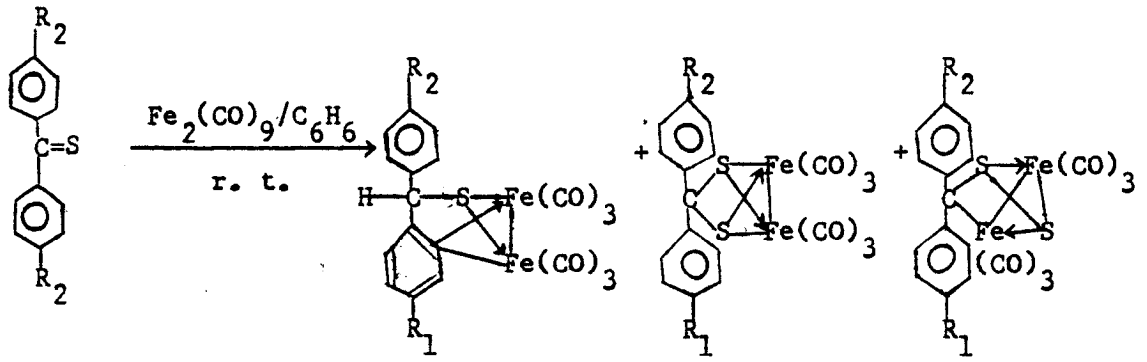
1

to form weaker multiple bonds as one goes down the groups[2]. Hence oxygen is expected to form stronger multiple bonds with carbon than sulphur.

However some thioketones are stable enough for their chemical as well as physical properties to be investigated. These include both aromatic[3] and non-aromatic[4] thiones. They have been reported to react with transition metals forming complexes in which the carbon - sulphur π-bond is either retained or ruptured depending on the nature of the complex. The rest of this section is devoted to the description of some of these complexes.

1. Iron and Ruthenium Complexes

Alper and Chan[5] have reported that $Fe_2(CO)_9$ reacts with 2(R_1,R_2=H, CH_3,OCH_3,NMe_2) to form complexes of general structure 3, 4, 5 and 6. The formation of 3 is possibly facilitated by resonance

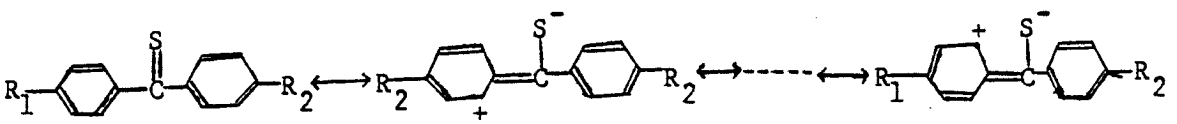


2 3 4 5

+ $S_2Fe_3(CO)_9$

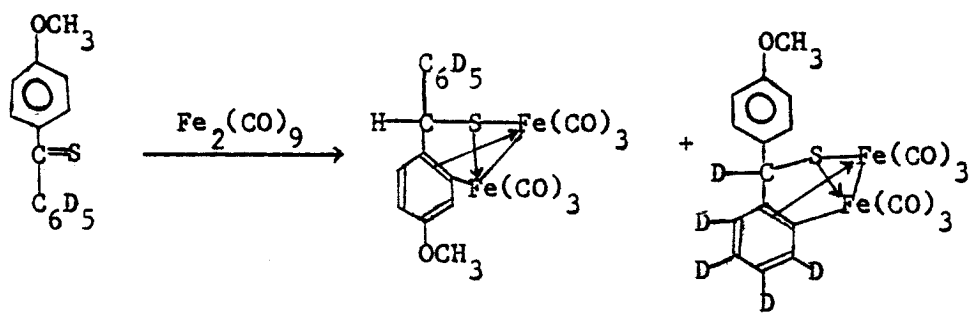
6

as illustrated by Scheme I. Such a representation is more favourable when R_1 and R_2 are fairly strong electron donating groups such as $N(CH_3)_2$ and OCH_3. This is supported by the fact that when 7 was reacted with



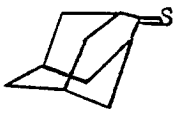
Scheme I

$Fe_2(CO)_9$ 8 was obtained as a major product[5]. Hence in para-substituted thiones the ortho-hydrogen is labilised by resonance. It must be also noted that 3 is only obtained when there is an ortho proton. Otherwise only analogues of 4, 5 and 6 may be obtained.



7 8 (major product) 9 (minor product)

However $Fe_2(CO)_9$ also reacts with non-aromatic thiones to give a variety of complexes, some of which are similar to those obtained with aromatic thiones[6]. Hence adamantanethione (10) reacts with $Fe_2(CO)_{10}$ at room temperature yielding 11, 12, 13 and 14.



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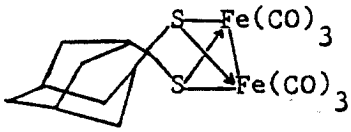

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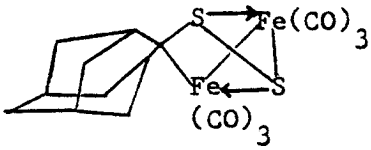

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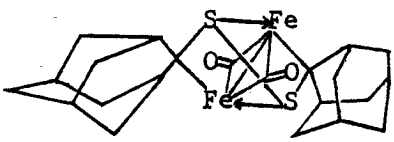

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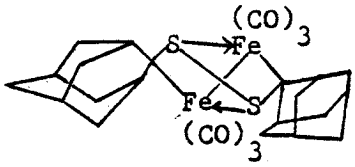

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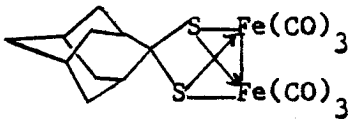
It is not clear why no dimer or bridging carbonyl complexes could not be formed in the reactions of aromatic thiones (2) with $Fe_2(CO)_9$. It may be due to steric and/or electronic factors. In fact steric crowding has been observed to affect the extent of reaction of a non-aromatic thione. Thiofenchone (16) has been found to react with $Fe_2(CO)_9$ resulting in the formation of $S_2Fe_2(CO)_6$ as the sole product[6].

Some non-aromatic thione complexes have been observed to isomerise when subjected to certain conditions. Treatment of

11 with $LiAlH_4$ results in 12. And when a petroleum solution of 11 is exposed to air in the dark and a carbon tetrachloride solution of 13 is left to stand complexes 15 and 14 are formed respectively.

The mechanism for the formation of these complexes is not definite, but it has been found that 17 reacts with $Fe_2(CO)_9$ to



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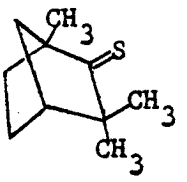

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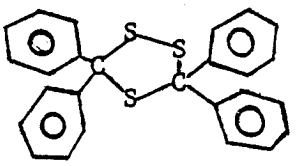

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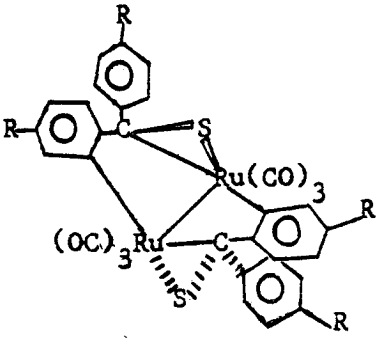
give 4, 5 and 6 accompanied with very little 3 (R_1=R_2=H)[5]. This suggests that in the presence of $Fe(CO)_9$ thiolanes are formed and these then further react with $Fe_2(CO)_9$ or some other species to form some of the observed products. Therefore to obtain some of the above products one does not have to start with thiones.

Also by reacting $Ru_3(CO)_{12}$ with 2(R_1=R_2=OCH_3, CH_3) orthometallated complexes with proposed general structure 18(R=OCH_3, CH_3) have been isolated[7].



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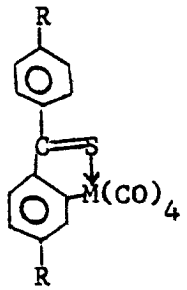
2. Manganese and Rhenium Complexes

It has been observed by Alper[8, 9] that refluxing a mixture of $M_2(CO)_{10}$(M=Mn, Re) and 2(R_1=R_2=NMe_2,NEt_2) in methylcyclohexane yields orthometallated complexes which have been suggested to have general structure 19 (M=Mn,Re;R=NMe_2,NEt_2). When $M_2(CO)_{10}$(M=Mn) and



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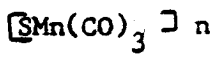
2(R_1=R_2=OCH_3,CH_3,H,H) are treated in the same way as above only 20(n is unknown) and 21(desulphurization product) are obtained[8]. While no reaction is observed when a mixture of $M_2(CO)_{10}$(M=Re)



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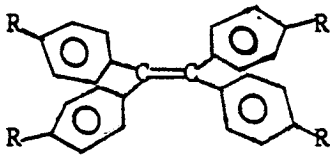

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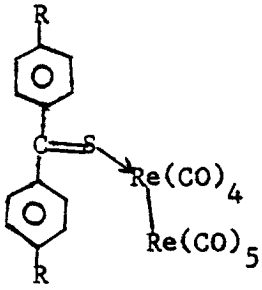
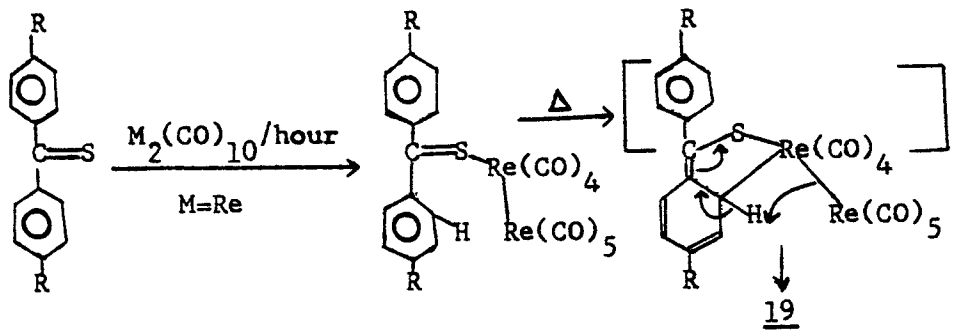
and 2(R_1=R_2=OCH_3) is refluxed in methylcyclohexane irradiation of the same mixture has been reported to afford a simple substitution complex 22(R=CH_3, OCH_3)[9].



22

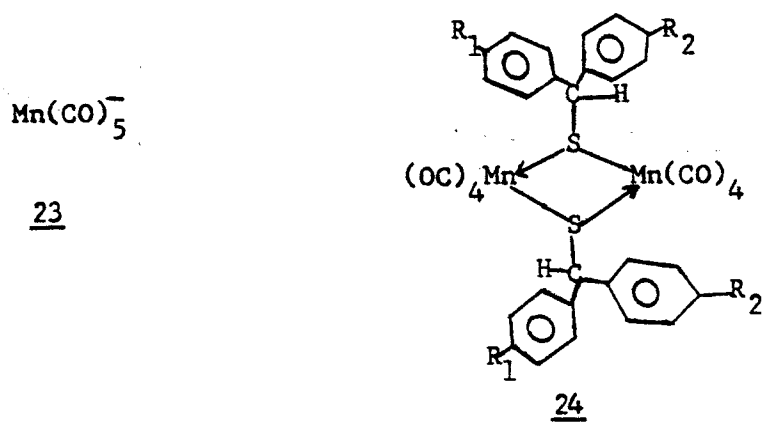
Nonetheless refluxing a methylcyclohexane solution of 22 affords 19(M=Re; R=CH_3,OCH_3)[9]. The formation of 22 and subsequent rearrangement to 19(M=Re) led Alper to propose the following mechanism for the formation of 19(M=Mn, Re)[9]:



Scheme II

A similar mechanism may be operative in the formation of certain complexes from reactions of $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$ with thiones.

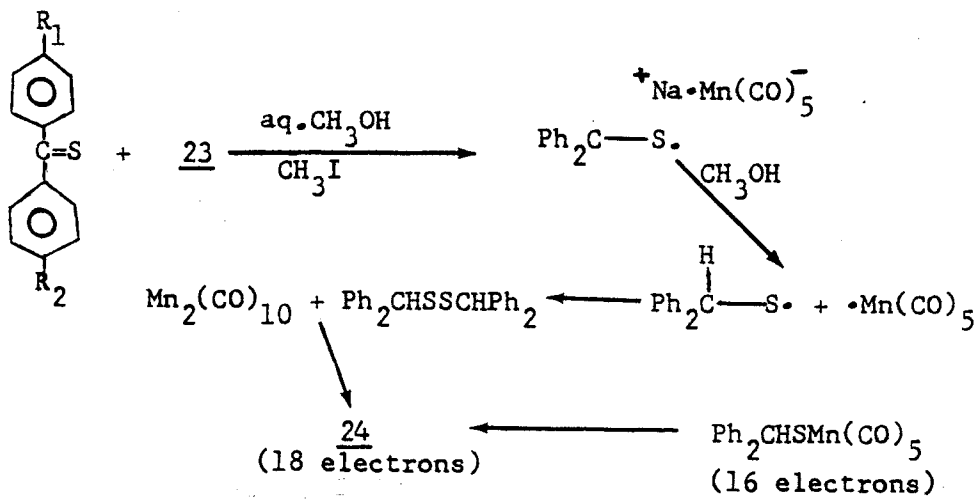
It has been also shown that the anion 23 reacts with 2(R_1,R_2=CH_3, OCH_3,NMe_2,H,F) to give 24 as the major product[10]. The interesting thing is that the same product may be obtained by reacting $Ph_2CHSSCHPh_2$ with



either 23 or $Mn_2(CO)_{10}$[10]. Yields, however, have been reported to be higher for cases where R_1 and R_2 are stronger electron donating groups. For example the yields increased in the order

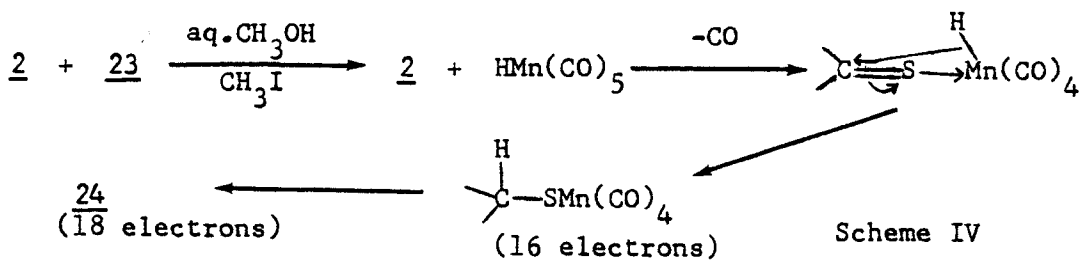
$$R_1{=}R_2{=}CH_3(32\%) > R_1{=}OCH_3, \quad R_2{=}H(21\%) > R_1{=}R_2{=}F(14\%).$$

The reaction mechanism has been proposed as follows[10]:



Scheme III

The following mechanism is also possible:



Scheme IV

In both schemes III and IV the rates of reaction and hence the yields would possibly be enhanced by electron donating groups (R_1 and R_2).

3. Group VIB Transition Metal Complexes

While $Fe_2(CO)_9$ and $M_2(CO)_{10}$(M=Mn,Re) react with thiones to give rise to a variety of complexes, group VIB transition metal carbonyls give exclusively simple substitution complexes.

Gladysz and Avakian[11] have irradiated benzene solutions of thiones and $M(CO)_6$(M=Cr, Mo,W) to obtain appropriate thione complexes of general formula 25(M=Cr,Mo,W; L= adamantanethione, thiobenzophenone, ethylenethiocarbonate).

$M(CO)_5L$

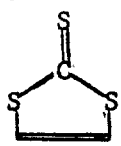
25

Tetrahydrofuran (THF) has been used as solvent in place of benzene. In such a case the initial product is possibly $M(CO)_5$(THF), which then reacts with thione to give 25. This method has been used to synthesise $Cr(CO)_5L$ (L=tetramethylethylenethiocarbonate)[12].

Another reaction that has been observed is that between 26(M=Cr,Mo; diolefin = bicyclo{2·2·1} heptadiene) and 27 to

(diolefin)$M(CO)_4$

26



27

afford 25[13]. It has been suggested that this reaction proceeds by transfer of carbonyl groups from (diolefin)$M(CO)_4$ to $M(CO)_4L$ (L=27) units to form 25. Supporting this suggestion is the observation that when the reaction was carried out under an atmosphere of carbon monoxide the yield was reported to be trebled.

Angelici and Gingenich[12] have synthesized 25(M=Cr, L=Me_2C=S; M=Mo, L=Me_2C=S; M=W, L=Me_2C=S, Ph_2C=S, MeEtc=S) by an indirect method. This has been done by first generating the acetone

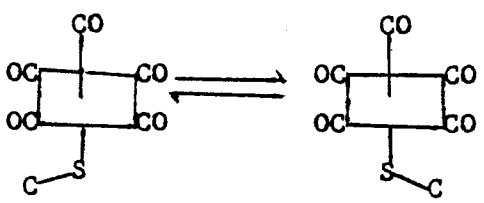
$$\{NEt_4\}\{M(CO)_5I\} \xrightarrow[\text{acetone}]{AgBF_4/\ -72^oC} AgI + \{NEt_4\}BF_4 + M(CO)_5(O{=}CMe_2) \quad \text{(i)}$$

Scheme V

$$M(CO)_5(O{=}CMe_2) + 3/2\ H_2S \xrightarrow[\text{acetone}]{AgBF_4/\ -72^oC} M(CO)_5(S \qquad H_2O + 1/2\ Ag_2S + HBF_4 \quad \text{(ii)}$$

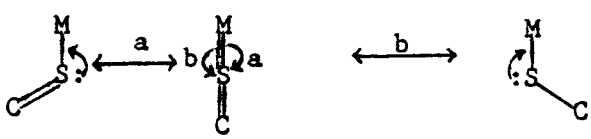
complex {Scheme V(i)} followed by bubbling hydrogen sulphide gas through the solution to obtain the appropriate thione complex 25. The advantage of this method is that the isolation of the thioketone is not necessary so that it may be used for the preparation of complexes of very unstable thiones such as thioacetone.

To determine the molecular structure of and nature of metal-ligand interactions in these complexes {$M(CO)_5L$, M=Cr,Mo,W; L=thione} a single crystal X-ray analysis has been procured for $Cr(CO)_5(S{=}CMe_2)$[12] and it has been found that the structure is virtually octahedral. The Cr-S-C angle has been determined to be 120°. It has been suggested that the molecule may be undergoing a kind of equilibration between two equivalent structures as illustrated by Scheme VI. Such a process has not been detected at low temperature (-100°C)[12].



Scheme VI

A change in the direction of the C-S bond may be effected by either rotation about the Cr-S bond or flipping of the C-S bond from one position to the other as shown by Scheme VII.

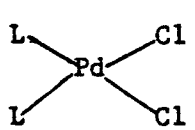


Scheme VII

The Cr-CS bond distance has been found to be 2.377Å, which is longer than the average Cr-CO distance of 1.898Å. However the Cr-CO bondlength trans to the tione group is shorter (1.835Å) than the average of the other Cr-CO bondlengths (1.898Å) possibly due to increased back bonding as a result of greater basicity of the thione ligand. The C-S bondlength was found to be 1.618A which is shorter than the one for ethylenethiourea[14] and thioacetamide[14](1.71Å) but longer than for hydrogen thiocyanate (1.561Å)[14]. Also the C-S bondlength in $Cr(CO)_5(S{=}CMe_2)$ is shorter than in $(OC)_5Ws{=}\underbrace{C\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}S}$ (thiazolidine-2-thionepentacabonyltungsten)(1.68Å), which has been reported by Marongiu and co-workers[15]. In the latter complex, like in the former, the W-CO bond distance trans to the thione ligand is shorter (1.97Å) than the average of the other W-CO didstances (2.03Å).

4. Palladium and Platinum Complexes

Reactions of thiones are not restricted to transition metal carbonyls. Palladium and platinum chlorides react with thiones to give both orthometallated and simple substitution complexes, just like metal carbonyls. Hence $PdCl_2(NCPh)_2$ has been reported to react with cyclohepta-triene thione yielding 28($L{=}\underbrace{CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}C}{=}S$)[16].

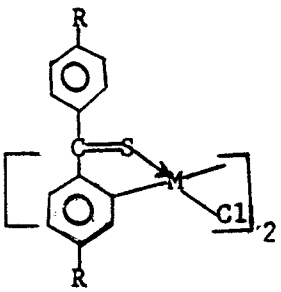


28

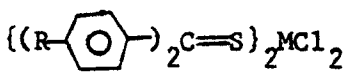
Judging from infrared data it has been proposed that 28 exists in cis form in the solid state. This is possibly because more

electronegative chloride groups trans to thione groups are able to "absorb" excess negative charge transferred to the metal by the more basic thione ligands. Also the cis form is expected to be more polar so that it would crystallise more easily in commonly used organic solvents, leaving most of the trans form in solution. The cis form should be sterically less favourable though.

However sodium tetrachloropalladate, Na_2PdCl_4, has been found to react with aromatic thiones giving dimeric orthometallated complexes of proposed general structure 29(M=Pd; R=CH_3,OCH_3)[17]. But potassium tetrachloroplatinate, K_2PtCl_4, reacts with aromatic



29



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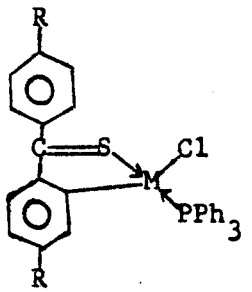


31

$(Ph_3P)_2MCl_2$

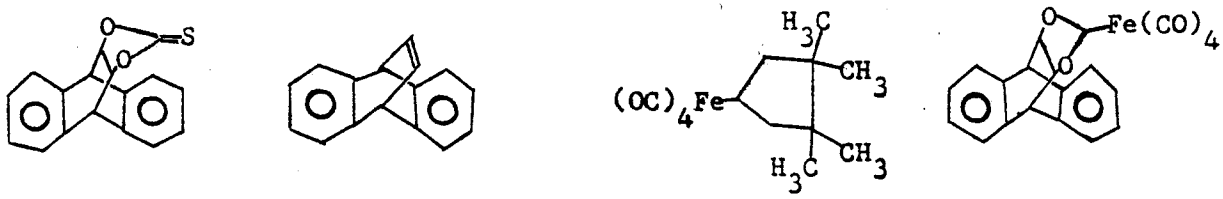
32

thiones yielding both the orthometallated complex 29(M=Pt; R=CH_3.OCH_3) and the simple substitution complexes 30(M=Pt; R=CH_3,OCH_3)[17]. 29 is cleaved by Lewis bases such as phosphines to afford monomeric orthometallated and simple substitution complexes. For example 29(M=Pd,Pt) reacts with triphenylphosphine to give 31(M=Pd,Pt; R=CH_3,OCH_3) and 32(M-Pd,Pt).

5. Desulphurization reactions.

It has been observed that when thiones are reacted with certain metal complexes desulphurization occurs. This has resulted

in the formation of either carbene complexes or olefins. For example Erhardt and co-workers[18] have isolated 34 by refluxing a xylene solution of 33 and $Fe(CO)_5$. Complex 35 has been isolated by irradiating a

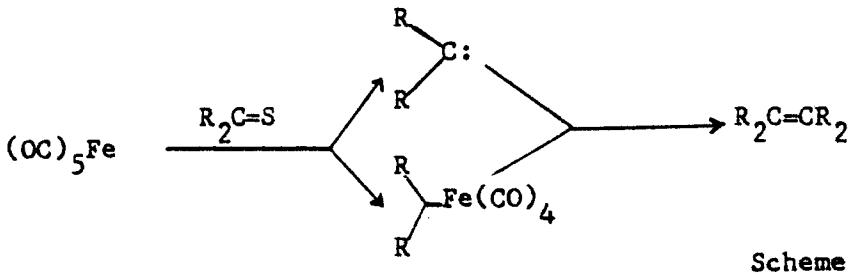


33 34 35 36

tetrahydrofuran solution of $M(CO)_5L$(M=Cr, Mo; L=tetramethylethylene-thiocarbonate) and $Fe(CO)_5$[19].

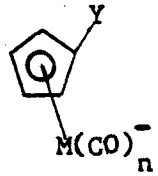
In other cases carbene complexes and olefins have been isolated from the same reaction. For instance Kappler and co-workers[20] have prepared 34 and 36 by heating a mixture of 33 and $Fe(CO)_5$ in toluene at 100°C. Reacting 33 with $Ni(COD)_2$ {COD= 1,5 - cyclooctadiene} also yields 34[21].

For all these cases it has been proposed that the formation of olefins is preceeded by the formation of carbene complexes (37) although such complexes have not been isolated from all the reactions. The overall proposed[20] mechanism is illustrated in scheme VIII. This mechanism would be especially confirmed if a carbene complex(e.g.36) was treated to yield an olefin (e.g.34).

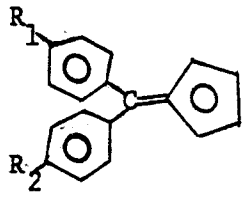


Scheme VIII

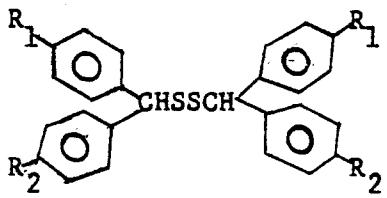
Alper and Paik[23] have obtained fulvenes of general structure 40 by reacting 2(R_1,R_2=CH_3,OCH_3,H) with metal carbonyl anions(38). These reactions have been effected in three different ways as illustrated by scheme IX.



38: M=Fe; n=2
M=Mo,W; n=3



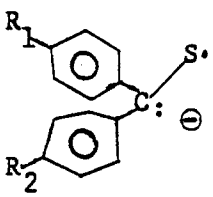
40



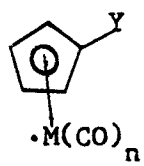
41

It has been found that molybdenum and tungsten anions are much less reactive than the iron anion so that reactions with the former have been conducted at higher temperature (110°- 120°C) in a carius tube. In addition to 40 disulphides (41) and dimers (39) have also been isolated. Phase transfer methods (B) and (C) have been found to give higher yields of 40 than method (A).

The mechanism for the formation of 40 is not definite. A number of mechanisms have been proposed all of which involve electron transfer from the metal carbonyl anion (38) to thione(2) to form 42 and 43. One of the mechanisms suggested by Alper and Paik is illustrated in scheme X.

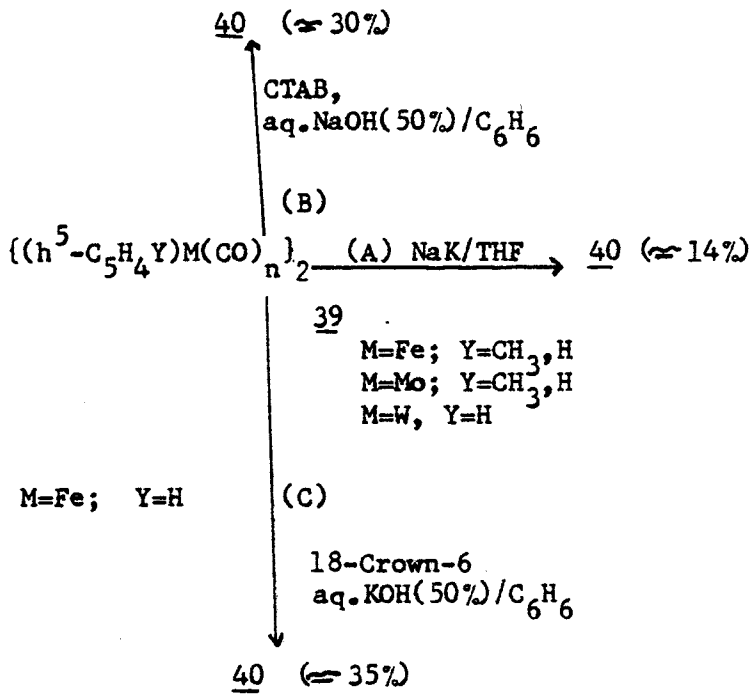


42

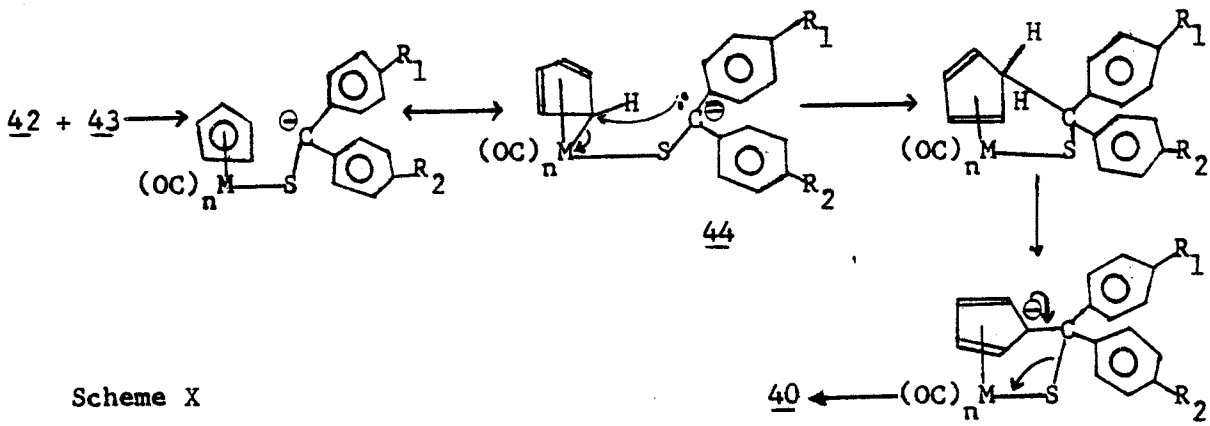


43

Another possible mechanism is the one involving nucleophilic attack of 38 on thioketone carbon as shown in scheme XI.



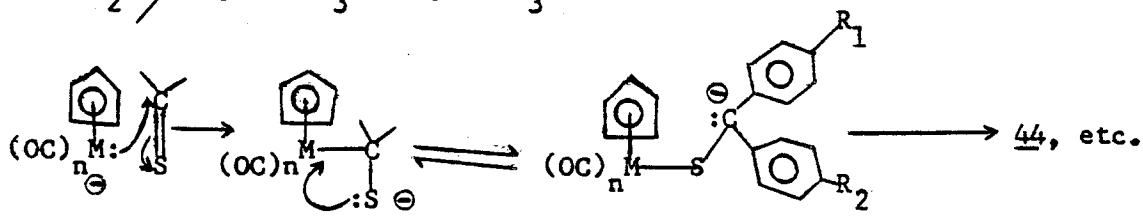
Scheme IX (M=Fe, n=2; M=Mo,W, n=3; CTAB=cetyltrimethylammonium bromide)



Scheme X

Both mechanisms (schemes X and XI) suggest that reactivity is expected in the order $\{(h^5\text{-}C_5H_5)Fe(CO)_2\}^- > \{(h^5\text{-}C_5H_5)Mo(CO)_3\}^- \gg \{(h^5\text{-}C_5H_5)W(CO)_3\}^-$, which compares favourably with the reported order[74]

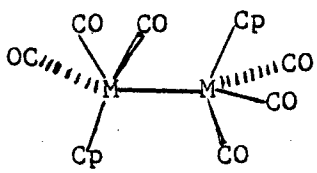
$CpFe(CO)_2^- > CpMo(CO)_3^- \simeq CpW(CO)_3^-$.



Scheme XI

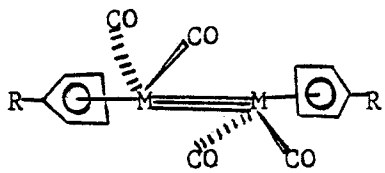
B. REACTION OF $\{(h^5\text{-}C_5H_5)M(CO)_3\}_2$ (M=Mo, W) AND $\{H^5\text{-}C_5H_5)M(CO)_2\}_2$ (M=Mo, W) WITH PHOSPHINES, ALLENE AND THIONES.

Having discussed reactions of thiones with some transition metals it would be interesting to see how other neutral Lewis bases compare with thiones in situations where they are quite capable of forming similar complexes.



45

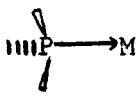
a: M=Mo
b: M=W



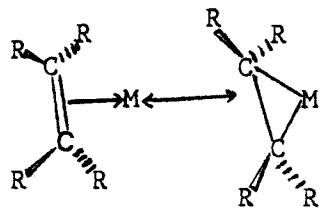
46

a: M=Mo; R=H
b: M=W; R=H
c: M=Mo; R=CH_3

Phosphines and olefins are among some of the commonest neutral Lewis bases encountered in coordination chemistry. While phosphines coordinate to a metal by donating a lone (non-bonding) pair of electrons to the empty orbital of a metal (47, M=metal) olefins do so by using π-electrons to form what is known as a π-complex (e.g. 48, M=metal; R=alkyl, H) which may be represented by two canonical forms {48(i) and 48(ii)}.



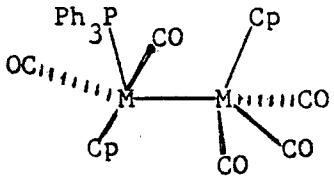
47



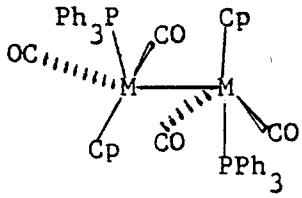
(i) (ii)

48

For example triphenyl phosphine has been reported to react with 45 (M=Mo) to give 49, 50 and 51[24] and with 46 (M=Mo) to give



49

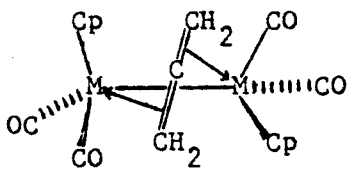


50

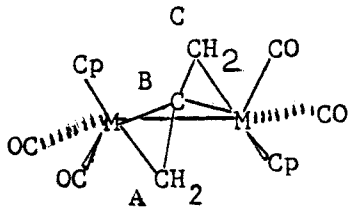
$\{CpM(CO)_3\}^+ \{CpM(CO)_2L_2\}^-$

51

exclusively 50[25]. An allene ($CH_2=C=CH_2$) has been shown to react with 46(M=Mo) to form 52[22]. From a single crystal x-ray structure of 52(M=Mo)[22] it has been found that the C_A-C_B-C_C angle of the allene group in 52(M=Mo) is 146° which implies that the contribution of 52(ii) is quite significant.



(i)

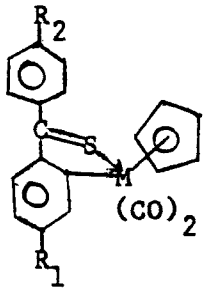


(ii)

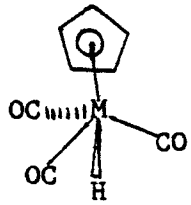
52

However no reactions between either 45(M=Cr, Mo, W) or 46(M=Cr, Mo, W) and thiones have been investigated so that it was the aim of this work to find out what kind of complexes could be obtained if such reactions were carried out. A careful look at thiones gives one the idea that they (thiones) are capable of behaving similar to phosphines (by using a lone pair of electrons) or olefins (by using π-electrons in the >C=S bond) when coordinated to a metal.

In fact it was hoped that 45 would be cleaved in the presence of aromatic thiones (2) resulting in the formation of orthometallated and hydride complexes 53 and 97 respectively. Also simple substitution



53



97

complexes similar to 49, 50 and 51 were expected from reactions with both aromatic and non-aromatic thiones. Although thiones are capable of forming both σ- and π- complexes thione complexes similar to 52 were not expected at all.

C. RESULTS AND DISCUSSION

Reaction of 45(M=Mo,W) and 46(M=Mo,W) with both aromatic and non-aromatic thiones gave complexes containing one or two thione ligands. As mentioned earlier these reactions may lead to either simple substitution products similar to 49 and 50(M=Mo,W) or products akin to 51 and 53(M=Mo,W) which would result from the cleavage of the metal-metal bond. From analytical and spectroscopic (e.g. IR and NMR) data (Tables 2, 3 and 4) the monothione complexes may have molecular

$\{Cp_2M_2(CO)_4L\}$ I (M=Mo,W; L=thione)

$\{Cp_2M_2(CO)_5L\}$ II (M=Mo,W; L=thione)

structure I or II. However a single crystal X-ray study has shown that there are only four carbonyl groups (Figure 8), so that I is the correct molecular formula of the monothione complexes. The exact structure of the dithione complexes is not known so that for the moment two possible structures will be assumed, namely III and IV.

The extent of reaction as well as the nature of products depend on the nature of thione and the reaction conditions. Both mono- and dithione complexes obtained from reactions under discussion are listed in Table 1.

The fact that complexes similar to 51 (i.e. ionic complexes) and 49 (resulting from the displacement of only one carbonyl group) were detected is quite a contrast to reactions between 45a and, phosphines and phosphites where such complexes have been obtained. This is possibly because thiones may be regarded as bidentate ligands (see above) rather than monodentate ligands (like tertiary phosphorus ligands).

One interesting observation that has been made is that the ease of formation of dithione complexes seems to be in the order $(p\text{-}FC_6H_4)_2CS > (C_6H_5)_2CS >$ adamantanethione $>$ thiocamphor $> (p\text{-}H_3CC_6H_4)_2CS > p\text{-}H_3COC_6H_4{\cdot}CS{\cdot}C_6H_5 > (p\text{-}H_3COC_6H_4)_2CS$. In fact not a trace of the dithione complex was detected in the case of 2(R_1=R=OCH_3). Considering aromatic thiones alone, the basicity is expected to be in the order $(p\text{-}H_3COC_6H_4)_2CS > (p\text{-}H_3CC_6H_4)_2CS \geqslant p\text{-}H_3COC_6H_4{\cdot}CS{\cdot}C_6H_5 > (C_6H_5)_2CS > (p\text{-}FC_6H_4)_2CS$. From the above arrangement it seems the ease of formation of dithione complexes decreases with the donor ability of the ligand. Another factor worth considering is the π-acidity of the ligands. Since, it seems, back-donation increases with electron deficiency on the ligand[73] (assuming that there are non-bonding electrons on the metal atom) the order of π-acidity of thione ligands will be expected to be the reverse of the above arrangement. This then seems to imply that the formation of dithione complexes is enhanced by the π-acidity of the ligand. This trend may be compared to the observations made by Haines and his co-workers[24,28] who have noted that when the groups attached to the phosphorus atom are more electronegative (for example in $P(OCH_3)$ and $P(OPh)_3$) there is less tendency to rupture the Mo-Mo bond when substitution of CO in 45a occurs. They have found that whereas phosphites (e.g. $P(OPh)_3$) react with 45a to form mainly complexes similar to 50 and 51, phosphines (e.g. PPh_3) do so to form complexes similar to 49 and 51. These observations have been explained by saying that more electronegative groups probably enhance the π-acidity of ligands, making them (ligands) behave more like CO.

That relatively poor π-acids may tend to destabilise metal-metal bonds may be explained in terms of the effect of the basicity of the ligand on the metal-metal bond. Figure 14 illustrates a simplified molecular orbital diagram of the metal-metal bond. The Mo-Mo bondlength in 45a has been reported to be about 3.235Å[38], which implies that it is rather weak, so that the antibonding orbital (σ^*) is not so high in energy. If this is the case excess charge (which may come from the ligands) from the metal atoms may flow to the antibonding orbital (σ^*) leading to a reduction in the metal-metal bond

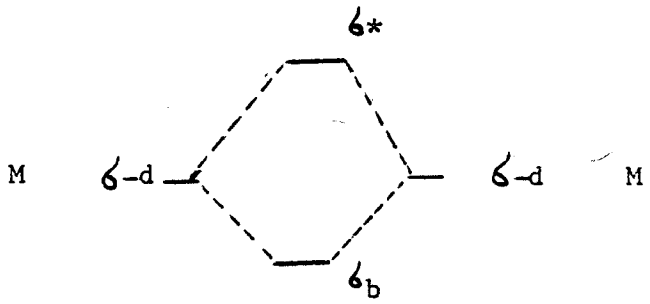


Figure 14: σ_b=bonding orbital; σ^*=antibonding orbital.

order. Wrighton and Ginley[69] have suggested that the rupture of the metal-metal bond in photolytic reactions of 45a possibly involves the excitation of an electron from the bonding orbital (σ_b) to the antibonding one (σ^*). It is conceivable that a good donor ligand which is a relatively poor π-acid may enhance such a process. Nonetheless there is not enough data from which to draw a definite conclusion about the effect of the basicity of a ligand on the metal-metal bond.

$\{Cp_2M_2(CO)_3L_2\}$ $\{Cp_2Mo_2(CO)_4L_2\}$

III IV

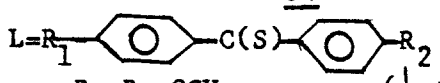
(L=thione) (L=thione)

Aromatic Thione Complexes

Reaction of 45a with most aromatic thiones in refluxing benzene gave mainly organic products none of which were fully characterised. Usually 54(M=Mo) and sometimes 55 were formed initially only to disappear towards the end of the reaction. This was possibly because thione complexes (e.g. 54a) were generally found to be unstable to heat. However 45a did react with 2(R_1=OCH_3,R_2=H) in refluxing

$$45a + 2 \xrightarrow{h\nu(3000\text{Å}) \text{ or } \Delta} \{Cp_2Mo_2(CO)_4L\} + \{Cp_2Mo_2(CO)_nL_2\}$$

54 55



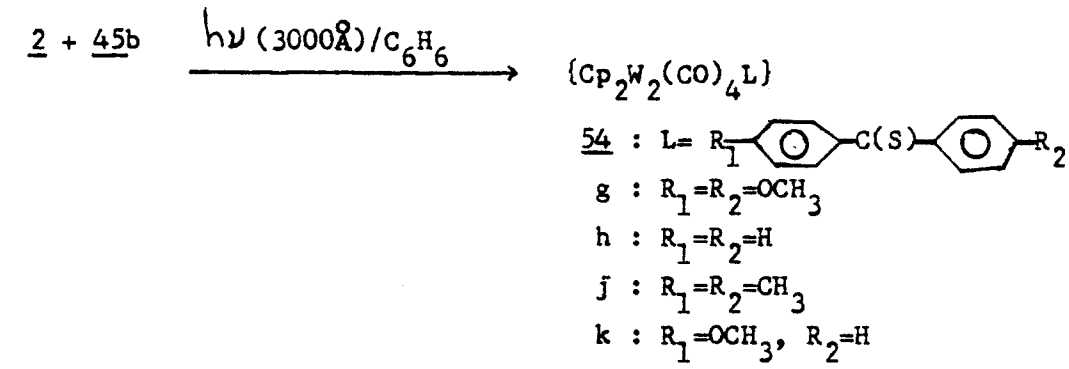
a : R_1=R_2=OCH_3 ($h\nu$)
b : R_1=R_2=H ($h\nu$)
c : R_1=R_2=CH_3 ($h\nu$)
d : R_1=OCH_3, R_2=H (Δ)
e : R_1=R_2=$N(CH_3)_2$ ($h\nu$)
f : R_1=R_2=F ($h\nu$)

benzene to give 54d in about 15% yield. A trace of 55d was obtained in only one of the four experiments that were carried out.

It is interesting to note that reactions which gave little or no metal carbonyl products in refluxing benzene did give much better

yields when they were effected by irradiation (with ultraviolet light). For example ultraviolet irradiation of a 1:1 mixture of 2(R_1=R_2=H) and 45a in benzene afforded 54b. Photolysis of a benzene solution of two parts of 2 (R_1=R_2=H) and 1 equivalent of 45a led to the initial formation of both 54band 55b. At the end of the reaction only the latter was present and hence isolated. Also irradiation of a 1:2 mixture of 45a and 2(R_1=R_2=OCH_3) in benzene yielded 54a in about 64% yield. This was the highest yield for reactions involving aromatic thiones effected either in refluxing benzene or by irradiation. Interestingly irradiation of a benzene solution of a mixture of 2 (R_1=OCH_3, R_2=H) and 45a resulted in the formation of mainly organic components none of which were identified. Only a trace of 54d was detected by infrared spectroscopy.

However reaction of 45b with aromatic thiones gave similar metal carbonyl products as those obtained from reactions of 45a except that no dithione complexes (55) were obtained. Another feature of reactions of 45b with aromatic thiones was that alot of unknown organic products were obtained so that it was more difficult to isolate metal carbonyl products than in the case of reactions involving 45a. Hence when a mixture of 45b and 2(R_1=R_2=OCH_3) in benzene was irradiated 54g was obtained in only 29% yield. Similar treatment of a mixture



of 45b and 2 (R_1=R_2=CH_3) resulted in the formation of 54j which could not be isolated and identified because of the presence of too many components with physical properties similar to those of the metal carbonyl complex (54j) both in solution and on the chromatographic column. Therefore the complex was identified simply by comparing its infrared data with those of the already characterised complexes such as 54a and 54c. Lower yields from reactions of 45b with thiones may have been either due to decomposition of thiones in the presence of the less reactive 45b or due to possible instability of the tungsten thione complexes compared to those of molybdenum, although the stability of the two types of complexes was found to be almost the same for the same thione ligand.

The triple bonded complex 46 (M=Mo,W) also reacted with thiones yielding mainly the monothioketone complexes (54). The advantage of this technique is that almost all the reactions were complete within afew minutes or seconds at room temperature so that they were much cleaner than the reactions of 45a and 45b. In fact by use of this technique, most of the monothione complexes which could not be isolated pure using the previous methods, were easily obtained and characterised even by elemental analysis.

The contrast between reactions of 46(M=Mo,W) and those of 45 (M=Mo,W) with thiones arises not only from the fact that the former

$$\underset{(M=Mo,W)}{46} + 2 \xrightarrow{r.t.} \underset{54(M=Mo,W;\ L=thione)}{\{Cp_2M_2(CO)_4L\}} + \underset{\substack{55\ (M=Mo;\ L=thione;\\ n=either\ 3\ or\ 4)\\ f:\ R_1=R_2=F}}{\{Cp_2M_2(CO)_nL_2\}}$$

gives higher yields of the monothione complexes (see experimental section) but also that the dithioketone complexes (55) are usually not obtained. In fact only in the case of 2(R_1=R_2=F) is the dithione complex obtained in addition to 54d. Hence reaction of thiobenzophenone (2, R_1=R_2=H) and 4,4'-dimethylthiobenzophenone (2, R_1=R_2=CH_3) with 46a yields 54b and 54c but not 55b and 55c respectively. This is possibly because to effect the formation of 55 heat is necessary. However the formation

$$46c + 2(R_1=OCH_3,\ R_2=H) \xrightarrow{r.t.} 66$$

of 55f may be explained by suggesting that 4,4'-difluorothiobenzophenone (2:R_1=R_2=F) is expected to be a better π-acid but a poorer donor than most, if not all of the thiones under consideration, so that it tends to labilise one of the carbonyl groups (most likely the one trans to the thione group in 54f). This would facilitate the formation of 55f especially if n=3. In addition 2(R_1=R_2=F) is expected to behave more like a carbonyl group making it easier for the formation of 55f from 54f if n=4. Also reaction of 46c with 2(R_2=OCH_3, R_2=H) gave 66.

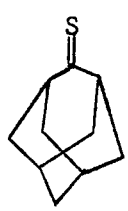
All the complexes prepared by both methods are listed in table 1. While it has been found that the stability of the molybdenum and tungsten monothione complexes is almost the same it is interesting but not very surprising that molybdenum monothione complexes are more stable than the corresponding dithione complexes. Hence while both the solutions and solids of monothione complexes may be handled in air without much difficulty those of dithione complexes should preferably be handled under an inert atmosphere. All the aromatic thione complexes are more soluble in moderately polar solvents such as chloroform

and methylene chloride. Their solubility decreases as the polarity of solvents is either decreased or increased. For example 54a is more soluble in chloroform and benzene than in methanol and n-hexane.

2. Non-Aromatic Thione Complexes

Non-aromatic thiones with either 45(M=Mo,W) or 46(M=Mo,W) under appropriate conditions to give complexes which were similar to those obtained from aromatic thiones. The main difference was that less sterically hindered non-aromatic thiones reacted with 45a in refluxing benzene to give much better yields of analogs of both 54 and 55.

In refluxing benzene 45a reacted with adamantanethione (10) to give 56 and 57 and with thiocamphor (V) to afford 58 and 59. It was interesting to note that 57 was also obtained by refluxing a



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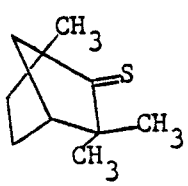

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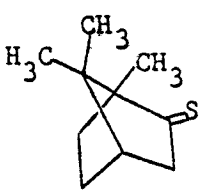
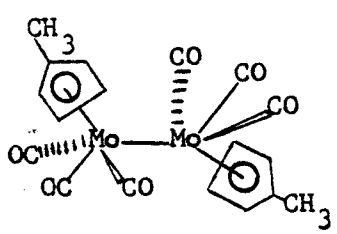


V



45c

benzene solution of a mixture of 56 and 10. Similarly $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6\}$ (45c) reacted with thiocamphor (V) to afford 65. No analogs of 57 and 59 were isolated. No reaction occurred, possibly for steric

$$\underset{(L=V,\ 10)}{45a + L} \xrightarrow{\Delta\,(\text{reflux})/C_6H_6} \{Cp_2Mo_2(CO)_4L\} + \{Cp_2Mo_2(CO)_nL_2\}$$

56 : L=10 (n=either 3 or 4)

58 : L=V 57 : L=10

59 : L=V

reasons, when a benzene solution of a mixture of 45a and thiofenchone (16) was refluxed for about 19 hours. When the same solution was

$$45c + V \xrightarrow{\Delta\ (\text{reflux}/C_6H_6} \{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4L\}$$

65 : L=thiocamphor

irradiated for about 94 hours 60 was obtained in about 9% yield.

$$45a + 16 \xrightarrow{h\nu(3000\text{Å})/C_6H_6} \{Cp_2Mo_2(CO)_4L\}$$

60 : L=thiofenchone

Thiocamphor (V) did not react with $\{Cp_2W_2(CO)_6\}$ (45b) in refluxing benzene but 69 was formed by photolysis. No tungsten analog of 59 was obtained.

Reaction of adamantanethione and thiocamphor with 46(M=Mo,W) gave exclusively monothione complexes identical to those obtained in reactions with 45(M=Mo,W) except that yields were considerably improved (see experimental section). Hence adamantanethione (10) reacted with 46a and 46b to afford 56(≃98% yield) and 68(≃ 73% yield) respectively. Also 10 reacted with $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4\}$ (46c) to give 67.

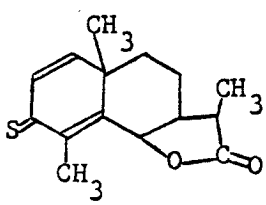
$$46 + 10 \xrightarrow{\text{r.t.}} \{Cp_2M_2(CO)_4L\}$$

56 : M=Mo, L=10
68 : M=W, L=10

$$46c + 10 \xrightarrow{\text{r.t.}} \{(h^5\text{-}C_5H_4CH_3)Mo_2(CO)_4L\}$$

67 : L=adamantanethione

Some of the above complexes were isolated in good enough purity to give satisfactory analytical data (Table 2). Although both the monothione and dithione complexes were found to decompose very little in solid state after being exposed to air for several hours (≃12 hours), the solutions of the latter decomposed slowly in non-polar solvents such as benzene and n-hexane and rapidly in polar solvents such as ether and acetone. Thiocamphor complexes were found to be more soluble than those of adamantanethione in the same solvent. For example 58 was found to be more soluble in chloroform than was 56. However like aromatic thione complexes they were found to dissolve better in moderately polar solvents such as chloroform and methylene chloride than in "very" polar and non-polar solvents such as acetone and n-hexane respectively.



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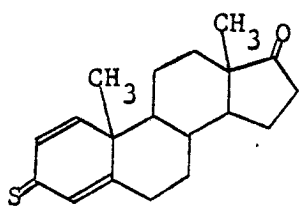
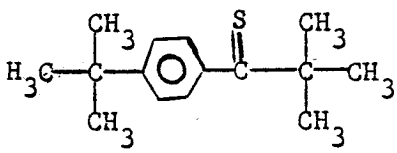


71

Thiosantonin and $\Delta^{1,4}$-androstadiene-3-thione-17-one (71) also react with 45a to afford appropriate monothione complexes 63 and 64 respectively. 64 is also obtained from the reaction of 71 with 46a. Infrared spectra of 63 and 64 look quite similar to those obtained for other monothione complexes (e.g. 54a) discussed above.

A detailed discussion about infrared and other data is given in appropriate sections below. Both 63 and 64 are fairly unstable both in an inert atmosphere and in air whether in solid state or solution.

As mentioned earlier on it was observed that reactions between 46(M=Mo,W) and thiones were extremely fast. It was found, however, that there are exceptions. Hence 72 and 73 reacted with



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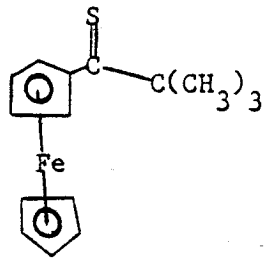


73

46a giving the corresponding monothione complexes 61 and 62 respectively but in much lower yields ($\leq$2%) than expected. In fact in the reaction between 46a and 72 some unreacted 46a and 72 were recovered after 12 hours of stirring the mixture in p-xylene. Similarly when 73 and 46a

$$\underline{46a} + L \xrightarrow{r.t.} \{Cp_2Mo_2(CO)_4L\}$$

(L=72, 73)

61 : L=72

62 : L=73

were reacted both reactants were present after stirring the mixture for about 2 hours. This is unlike the other reactions some of which were observed to be complete within one minute. The reason for the sluggishness of these reactions is probably due to the fact that in both cases the bulky tertiary butyl group is attached directly to the thiocarbonyl carbon giving rise to considerable steric interactions.

Both 63 and 64 could not be isolated pure so that no analytical and satisfactory infrared and proton NMR data could be obtained. Nonetheless the infrared data for 63 and 64 in the $\nu_{C\equiv O}$ region and proton NMR data for 64 in the cyclopentadienyl region resemble those of other monothione complexes (e.g. 54a) already identified (Table 3 and 4).

All the thione complexes prepared from this work are listed in Table 1.

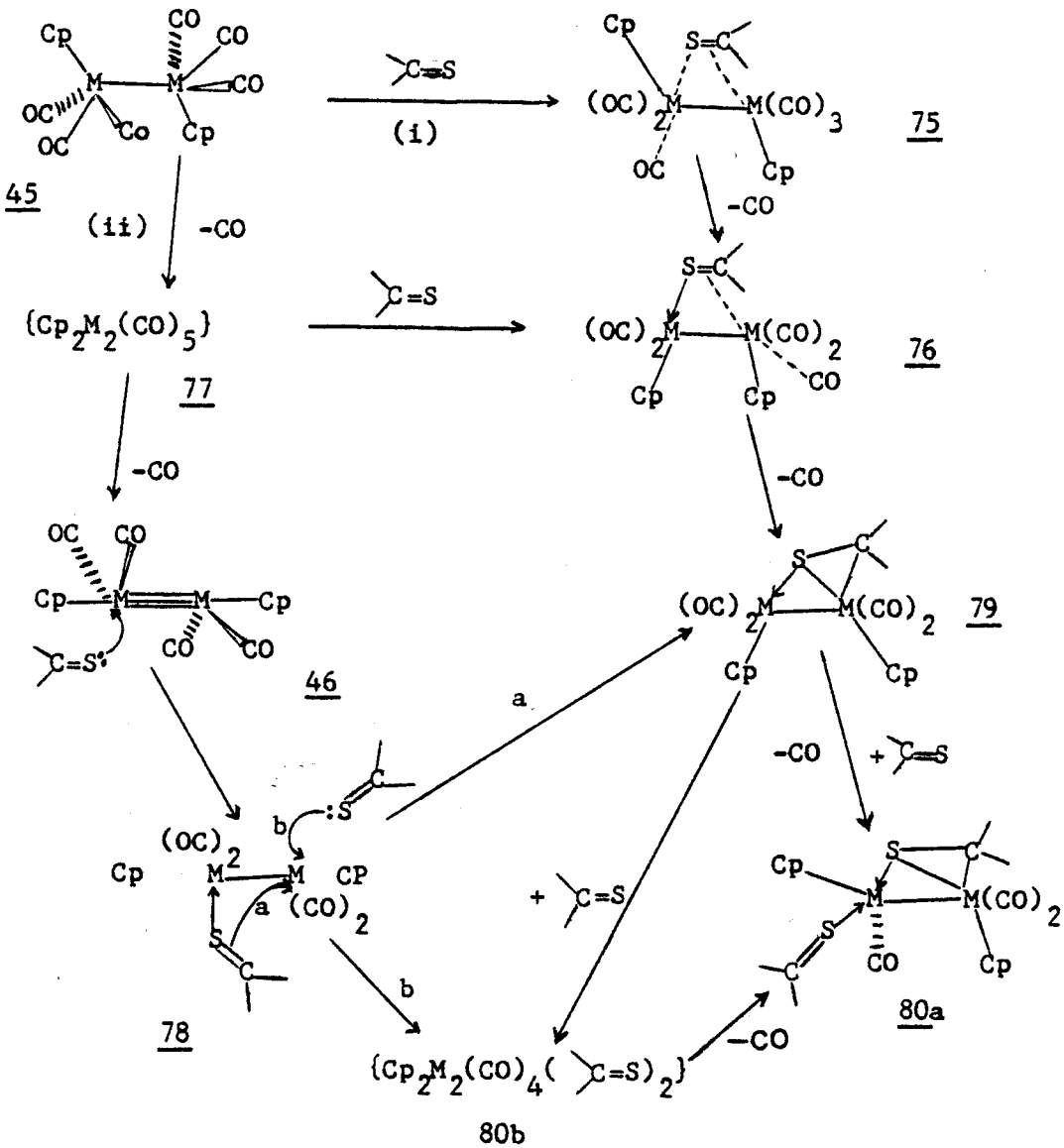
3. Mechanism of Reactions

Metal carbonyl substitution reactions have been reported[26] to proceed by three pathways. These processes are (i) associative, (ii) dissociative and (iii) a combination of (i) and (ii). The applicability of a mechanism to a particular reaction depends on the nature of reacting species. For example whereas the reaction of $(OC)_5W(CS)$ with triphenylphosphosphine (PPh_3) to form $W(CO)_4(CS)$ (PPh_3) has been found to occur by both the dissociative and associative mechanisms the reaction with the iodide species (I^-) to form $\{W(CO)_4(CS)I\}^-$ has been reported to obey an associative mechanism[27]. This is expected since the iodide ion is not only negatively charged but also smaller than the neutral triphenylphosphine ligand.

The exact mechanisms by which 45(M=Mo,W) and 46(M=Mo,W) react with thiones to form either the monothione or dithione complexes (e.g. 54a or 57) is not known. However the possible mechanisms are illustrated in scheme XII. Route (i) shows an associative process which involves the formation of an activated complex (75) by weak interaction between thione and 45(M=Mo,W). This may lead to the

labilisation of one of the carbonyl groups which is subsequently lost to form 76. Loss of an additional carbonyl group from 76 results in the formation of 79(M=Mo,W), Route (ii) depicts a dissociative mechanism. Loss of a carbonyl group from 45 is expected to lead to 77 which may then undergo two possible reactions. The first one would be the addition of a thione group to give 76 followed by loss of one more carbonyl group to form 79. The other reaction would involve the loss of another carbonyl group leading to the formation of 45(M=Mo,W). Addition of thione would afford 78, which would then give 79.

Dithioketone complexes may be formed either through 79 or 78. The formation of 80a may be as a result of loss of a carbonyl group from either 79 followed by addition of a thione ligand or 80b. However the addition of a thione to 78 may give 80b. Also the displacement of the bridging S→M bond by a second thione ligand would yield 80b. The formation of dithione complexes through 79 is supported by the fact that when a benzene solution of a mixture of 56 and adamantanethione (10) is refluxed 57 is obtained. Such a mechanism would be favoured by an electron withdrawing group. This is possibly the reason why 4,4'-difluorothiobenzophenone 2(R_1=R_2=F) reacts with 46(M=Mo) at room temperature to afford 55d, whereas other thiones such as 2(R_1=R_2=H) only give the appropriate monothione complexes under similar conditions.



Scheme XII (M=Mo,W; >C=S=thione)

In Scheme XII both routes(i) and (II) are possibly involved in the formation of already known complexes. For example the formation of $\{CP_2Mo_2(CO)_5(PPh_3)\}$(49)[24] from the reaction of 45a and PPh_3 may proceed by both routes (i) and (ii) but the formation of 46(M=Mo,W) by thermoclysis[25] of 45(M=Mo,W) most probably involves route(ii) of

Scheme XII. Different reactivities of thiones (see experimental section) towards a particular metal carbonyl seems to suggest that both routes (i) and (ii) are involved in the formation of thione complexes.

4. Infrared Data

Generally similar complexes have been observed to display a similar pattern of infrared spectra although a few variations are encountered on going from one thione ligand to another. In non-polar solvents such as n-hexane and carbon tetrachloride aromatic monothione complexes show four fairly sharp $\nu C\equiv O$ absorption bands. For example the infrared spectrum of 54a in carbon tetrachloride has $\nu C\equiv O$ absorption bands at 1958(Sh), 1936(VS), 1864(S) and 1815(VW) cm^{-1} (figure 1(a)). In polar solvents such as chloroform and methylene chloride all the infrared absorption bands are rather broad and shifted to lower frequency. Hence the spectrum of 54a shows $\nu C\equiv O$ absorption bands in chloroform at 1942(VW), 1927(VS), 1851(S) and 1792(VW) cm^{-1}. The absorption band at 1942 cm^{-1} appears as a shoulder on the absorption band at 1927 cm^{-1} and all the bands are broader than those obtained in carbon tetrachloride. Similarly 54d has $\nu C\equiv O$ absorption bands at 1960(VW), 1933(VS), 1858(S) and 1805(VW)cm^{-1} in chloroform and at 1961(Sh), 1938(VS), 1867(S) and 1818(W) in carbon tetrachloride. The lowest $\nu C\equiv O$ absorption band in the spectrum of each compound seems to be more affected by the change in the nature of solvent than other peaks. The infrared spectra of other aromatic monothione complexes have similar characteristics (Table 3).

The general pattern of infrared spectra of non-aromatic monothione complexes is similar to that of the corresponding aromatic complexes. This is especially the case when spectra are obtained in polar solvents such as chloroform and methylene chloride. Hence in chloroform 56 has $\nu C\equiv O$ absorption bands at 1958(S), 1910(VS), 1859(S) and 1800(VW)cm^{-1} and 58 has them at 1958(VS), 1920(VS), 1860(S) and 1795(VW) cm^{-1}. Similarly 60 has carbonyl stretching absorption bands at 1950(VW), 1918(VS), 1852(S) and 1810(VW) cm^{-1} in chloroform. It can be seen that infrared spectra of 56 and 58 each have a strong highest frequency $\nu C\equiv O$ absorption band compared to those of some non-aromatic and all the aromatic monothione complexes. Furthermore when infrared spectra of 56, 68 and 65 are run in non-polar solvents such as n-hexane and carbon tetrachloride the highest frequency $\nu C\equiv O$ absorption band of each one of them is split into two sharp peaks giving rise to a total of five absorption bands for each spectrum. For example 56 $\nu C\equiv O$ absorption bands at 1971(m, sh), 1961(W), 1929(VS), 1883(S) and 1823(m) cm^{-1} in hexane (Fig. 1(d)). This behaviour has been attributed to isomerism which is discussed in more detail in sections C.5, C.6, C.9 and C.10.

Another observation is that the lowest $\nu C\equiv O$ absorption bands of 63 and 64 are at relatively higher frequency than those of all the other monothione complexes (e.g. 54a and 58) when the spectra are obtained in the same solvent and on the same spectrophotometer. For example in chloroform the lowest frequency $\nu C\equiv O$ absorption bands for 63 and 64 are respectively at 1818 and 1814 cm^{-1} but those

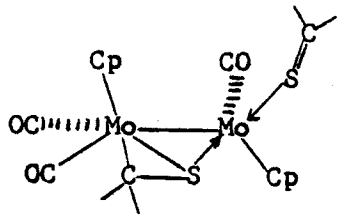
for 54 a and 58 are at 1792 and 1795 cm^{-1} respectively. This may be due to reduced basicity of thiosantonin (70) and $\Delta^{1,4}$-androstadiene-3-thione-17-one (71). This seems to be supported by the observation that the lowest $\nu C{=}O$ absorption band of 64(1814 cm^{-1}, $CHCl_3$) is at lower frequency than that of 63 (1818 cm^{-1},$CHCl_3$) in agreement with the expectation that 70 will induce stronger steric interactions when complexed than 71. Lower basicity of 2(R_1=R_2=F) seems to be the case in 54f where the lowest $\nu C{=}O$ absorption band is at higher frequency (1826 cm^{-1}, CCl_4) than all monothione complexes which have been investigated except 64 and possibly 63. However the importance of steric effects to explain infrared data of 63 and 64 in relation to those of the other monothione complexes is weakened by the fact that the lowest $\nu C{=}O$ bands for 61 and 62 occur at lower frequencies than those for 63 and 64. For example in carbon tetrachloride 62 and 64 have corresponding absorption bands at 1815 and 1829 cm^{-1} respectively despite the fact that 73 is expected to induce greater steric interactions because of the bulky tertiary butyl group which is attached directly to the thiocarbonyl carbon. It is conceivable that the tertiary butyl group enhances the basicity of 73 since the former is possibly a better electronic charge donor than the groups attached to the thiocarbonyl carbon in $\Delta^{1,4}$-androstadiene-e-thione-17-one (71).

Dithione complexes have characteristic spectra in the $\nu C{=}O$ region whose pattern varies with the polarity of solvent. For instance 59 has $\nu C{=}O$ absorptions bands at 1940(S) and 1806(m) cm^{-1} in n-hexane and at 1930(S),1840(W) and 1776(S) in chloroform. Also 57 has absorption bands at 1930(S), 1842(VW) and 1760(m) in chloroform.

The absorption bands at 1842 and 1840 cm^{-1} in 56 and 59 respectively vary in intensity from spectrum to spectrum possibly due to decomposition since all the dithione complexes have been found to be rather unstable. The infrared spectra of pure 55f show two strong absorption bands at 1986(VS) and 1879(S) cm^{-1} in carbon tetrachloride. Impure samples of the same compound give rise to an additional absorption band at 1900(VW) cm^{-1}.

The spectrum of 55b is rather interesting in that in chloroform it shows two rather broad $\nu C\equiv O$ absorption bands at 1973(m) and 1856(m) cm^{-1} but in n-hexane four relatively sharp $\nu C\equiv O$ absorption bands are observed at 1994(m), 1959(m), 1890(W) and 1812(m) cm^{-1}.

The two possible structures for dithione complexes are illustrated by 81 and 82. Structures 81 and 82 have C_1 and C_{2h} symmetry respectively so that the infrared spectra will be expected to show three and two $\nu C\equiv O$ absorption bands, respectively. Complexes similar to 82 have been reported to exhibit $\nu C\equiv O$ bands similar to those cited above[28]. For example, $\{CpMo(CO)_2P(OET)_3\}_2$ has been



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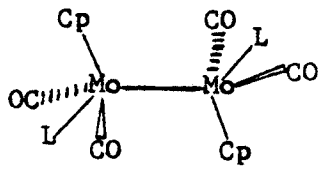


82(L=thione)

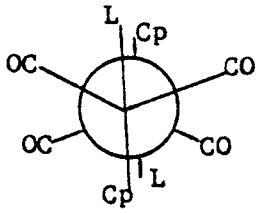
reported to show absorption bands at 1810 and 1846 cm^{-1}(nujol) and $\{CpMo(CO)_2P(OCH_3)_2\}$ displays absorptions at 1923(W), 1864(S) and 1848(S) cm^{-1} (CH_2Cl_2)[28]. Both of these complexes have been reported

to give five $\nu C\equiv O$ absorption bands when their infrared spectra are obtained in non-polar solvents such as cyclohexane. Hence $\{CpMo(CO)_2P(OC_2H_5)_3\}_2$ is reported to exhibit absorption bands at 1929, 1875, 1857, 1847 and 1827 cm^{-1} in cyclohexane. The most stable structure of both $\{CpMo(CO)_2P(OC_2H_5)_3\}_2$ and $\{CpMo(CO)_2P(OCH_3)_3\}_2$ has been postulated[28] to be 83, which happens to have C_{2h} symmetry and hence is expected to show two $\nu C\equiv O$ absorption bands. The additional bands have been attributed to possible presence of 84 as a result of isomerisation as shown by Scheme XIII.

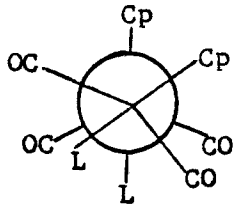
83 : trans 84 : cis

Scheme XIII: (L=$P(OCH_3)_3$, $P(OC_2H_5)_3$)

If the structure of dithione complexes corresponds to 82, isomerism is possibly present in 55b whose infrared spectrum shows four $\nu C\equiv O$ absorption bands in n-hexane. This may imply that there is either trans-cis(Scheme XIII) or trans-gauche (Scheme XIV) isomerisation in certain sclutions of some of the dithione complexes such as 55b and 59. The trans-gauche isomerism has been reported by Cotton and Adams[29] who have tried to explain the infrared spectra of 45a in different solvents. If this is the case then the polarity of solvents has a different effect on 55b and 59 since the latter shows three peaks in chloroform and two in n-hexane.



105 (a) : trans



105 (b) : gauche

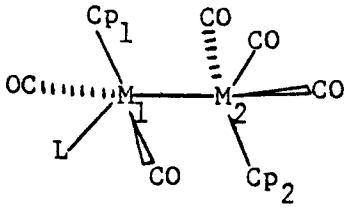
Scheme XIV (L=CO)

However if the structure of dithione complexes is depicted by 81 the agreement is good with infrared spectra of 57 and 59 but not 55b, 55f, 55c and 55d in chloroform.

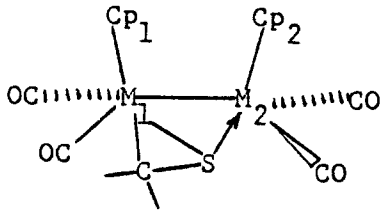
Furthermore it is seen that the $\nu C{\equiv}O$ absorption bands of aromatic dithione complexes are at higher frequencies than those of the non-aromatic ones. This is especially so when the lowest frequency bands are considered. For instance the $\nu C{\equiv}O$ absorption bands of 55b, 55c, 55d and 55f are at 1856($CHCl_3$), 1892($CHCl_3$), 1892($CHCl_3$) and 1881(CCl_4)cm^{-1} and those of 57 and 59 are at 1760($CHCl_3$) and 1776($CHCl_3$)cm^{-1}, respectively. The same trend applies to the rest of the bands. They may be due to the expected difference in basicity of thione ligands. If this is the case then it would seem that non-aromatic thiones are more basic than aromatic ones.

5. ^{1}H NMR Data

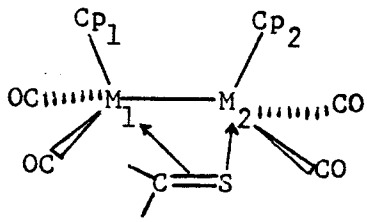
Both monothione and dithione complexes show proton nuclear magnetic resonance signals in the cyclopentodienyl region in the range δ4.00 to δ5.80ppm in deuterochloroform. Whenever possible cyclopentadienyl resonance signals were used to either explain the solution behaviour of or identify some of these complexes.



89 (L=thione)



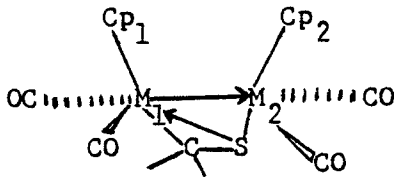
90(i)



90(ii)

Monothione complexes may be divided into two categories. The first group consists of those complexes that exhibit two equally intense cyclopentadienyl resonance signals (Figure 4(a)) which are indicative of the presence of at least two different cyclopentadienyl groups. These include 54a, 54b, 54c and 60 (Table 4). Hence 54a has cyclopentadienyl signals at δ 4.68 and 5.30 ppm and 60 has the same at δ 5.31 and 5.43 ppm. If the structure of monothione complexes is 89 then the resonance signal at higher field is assigned to Cp_1 and the one at lower field to Cp_2. While these assignments have been made by assuming that M_1 is more negative than M_2 they are also in agreement with the observations made by Haines and his co-workers[24], who found that the cyclopentadienyl chemical shift at higher field belonged to the moiety $CpMo(CO)_2(PPh_3)$ of the complex $Cp_2Mo_2(CO)_5(PPh_3)$, 49, which has been proposed to have a structure similar to 89. They made this assignment because it was found that of the two cyclopentadienyl chemical shifts of 49, only the one at higher field appeared as a doublet as a result of coupling

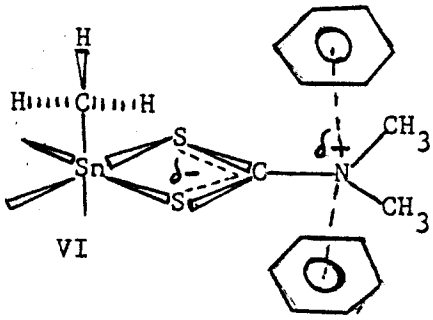
between protons of the cyclopentadienyl group (Cp_1) and phosphorus-31 of the phosphine ligand. Another possible structure of monothione complexes is the one corresponding to I (Page 19). This may be represented by three canonical forms, namely 90(i), 90(ii) and 91. Charge distribution between the two molybdenum



91

atoms will depend on the importance of each of the canonical forms. The resonance structure 90(i) suggests that M_1 is more negative than M_2 whereas the reverse is suggested by 90(ii) and 91. Therefore the assignment of cyclopentadienyl chemical shifts of I (Page 19) will depend on how much each of the resonance forms contributes to the "overall structure". It seems that

cyclopentadienyl groups bonded to the more positive metal center (i.e. M_1 or M_2) are at lower fields than those bonded to the more negative ones and this is supported by the fact that the cyclopentadienyl chemical shifts at lower field vary more significantly with solvent change than those at higher field (Table 6A). This may be explained by suggesting that the more positive center is more solvated than the more negative one[34]. A similar observation has been reported[63] for bis(N,N-dimethyldithiocarbomato) dimethyltin where it has been found that the chemical shift changes for N-CH_3 and Sn-CH_3 in moving from $CDCl_3$ to C_6D_6 are +0.93 and -0.32 ppm respectively. The nature of the interaction of the above tin complex with benzene solvent molecules has been proposed to be as shown by VI.



VI

The second group of monothione complexes incorporates all those that show more than two cyclopentadienyl chemical shifts (Figures 4(b) and (c)) suggesting that there are at least three different cyclopentadienyl groups. These include such complexes as 54d, 56, 68 and 69 (Table 4). For example the cyclopentadienyl

chemical shifts of 54d are at δ4.61, 4.67, 5.25 and 5.28ppm in the ratio 2:3:3:2 and those of 58 are at δ5.32, 5.27, 5.49 and 5.46 ppm in the ratio 43:41:43:41 in chloroform. This is explained by suggesting that there are at least two isomers in certain solutions of each of these complexes so that a pair of the cyclopentadienyl chemical shifts may be assigned to each of the two isomers. Hence for 54d the resonance signals at δ4.67 and 5.25 ppm are assigned to one (major) isomer and those at δ4.61 and 5.28 ppm to the other (minor) isomer. Similar assignments may be made for other complexes with similar spectra. Complexes 56 and 69 show only three cyclopentadienyl resonance signals each. Complex 56 has signals at δ5.26, 5.34 and 5.37 ppm in the ratio 3:5:2 and 69 has them at δ5.34, 5.40 and 5.55 ppm in the ratio 9:5:14 in chloroform. It is easy to see that each of the chemical shifts at δ5.34 and 5.55 ppm for 56 and 69 respectively belongs to two cyclopentadienyl groups each of which belongs to a different isomer. That is to say that for 56 the assignment of chemical shifts is as follows: δ5.26(Cp'), 5.34(Cp+Cp') and 5.37 ppm (Cp) where Cp and Cp' are cyclopentadienyl groups due to the major and minor isomoers respectively.

In addition it is noteworthy that each of the spectra of 54a and 54c show two resonance signals due to methoxy and methyl groups, respectively. This should not be confused with isomerism. For example 54c has sharp methyl resonance signals at δ2.29 and 2.26 ppm. This is attributed to the orientation of the thione ligand (Figure 2) so that the two aromatic rings together with

their substituents (e.g. in the case of the 4,4'-dimethylthiobenzophenone complex, 54c) are in different environments from each other. A similar observation has been made with 54a except that the two resonance signals are so close together that at a sweep width of 500 Hz (VARIAN T-60 spectrometer) a singlet is observed. However when the sweep width is expanded by about twenty times a doublet results.

One other thing that is striking is that the difference (ΔCp) in chemical shifts between Cp_1 and Cp_2 is much larger in monothione complexes containing aromatic ligands than in those with non-aromatic thiones. For example ΔCp's in 54a, 54b and 54f are about 37, 39 and 36 HZ respectively whereas those in 56, 58, 60, 63 and 64 are respectively about 3, 10, 7, 3 and 2.4 Hz. Suppose that the structure of monothione complexes is represented by either 90 or 91. The thione ligand will interact with Cp_1 more than with Cp_2 (Figure 2). Two effects may be considered here. The first one will be steric interaction which will tend to deshield[41] Cp_1 more than Cp_2. The second effect will be due to ring currents.[69] Aromatic rings have stronger ring currents than non-aromatic groups because of electron

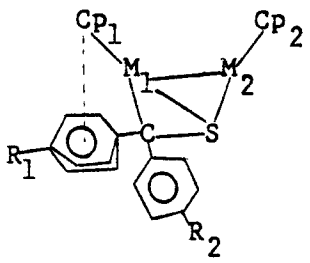


Figure 2.

delocalisation in the former. An aromatic ring may be considered as having a dish-like shape so that when the plane of its ring is perpendicular to the applied magnetic field a proton at the edge and the one situated over the ring will resonate at lower and higher fields respectively[30]. Therefore it is possible that the protons of Cp_1 are posibioned "face-to-face" with at least one aromatic ring in complexes such as 54a and 54b. This may imply that the effect of ring current dominates over that of steric interactions. However the competition between steric and ring current effects may be considerable in 61 which has one benzene ring and two tertiany butyl groups one of which is attached directly to the thiocarbonyl carbon. This possibly accounts for the fact that 61 has cyclopentadienyl chemical shifts at δ4.99 and δ 5.80 ppm resulting in the value of ΔCp of about 49 HZ. These results may be correlated with the effect that when proton NMR spectra are obtained in benzene cyclopentadienyl chemical shifts are at higher field than when the same spectra are obtained in chloroform or acetone (Table14). For example 54d has chemical shifts in chloroform at δ 4.61, 4.67, 5.25 and 5.28 ppm and in benzene at δ 4.46, 4.50, 4.86 and 4.90 ppm. Similarly 58 has cyclopentadienyl chemical shifts in chloroform at δ 5.23, 5.27, 5.41 and 5.43 ppm and in benzene at δ 4.75, 4.81,

4.97 ppm. This is in agreement with the observations that aromatic solvents shield [31, 34] as compared to other solvents such as chloroform and acetone.

Surely a third factor may arise as a result of the difference in basicity between M_1 and M_2, due to lack of symmetry (Figure 2), such that in aromatic thione complexes the difference in electronic charge density between the two metal centers is greater than in non-aromatic ones. But this does not clearly explain why the difference in cyclopentadienyl resonance signals is much larger in aromatic complexes (Figure 4(a)) than in non-aromatic one (Figure 4(b) and (c)). From reasonance considerations (see Scheme I, Page 2) it appears that aromatic thiones are more basic than non-aromatic ones. Increasing the basicity of thiones, however, will tend to favour resonance forms 90(i) and 91 (see Pages 39,45). The canonical form 90(i) is expected to decrease the difference in charge density between M_1 and M_2 more than 91. It is not clear whether in aromatic thione complexes 91 is more important than in non-aromatic ones.

It has been found that cyclopentadienyl chemical shifts of molybdenum monothione complexes are at a higher field than those

of tungsten analogs(Table 6B). This is possibly related to the extent to which molybdenum and tungsten orbitals interact with those of the ligands. Gansow and his co-workers[32] have suggested that the reason why carbon-13 carbonyl chemical shifts of the group VI transition metal hexacarbonyls are in the order $Cr(CO)_6$(δ212.5)> $Mo(CO)_6$(δ 202.0) >$W(CO)_6$(δ 192.1 ppm) is that heavier metals are less efficient at transporting electron density to the π^*(antibonding π)carbonyl orbitals due to the larger size of d orbitals. The same argument may apply to thione complexes.

The proton nuclear magnetic resonance spectra of dithione complexes show two cyclopentadienyl resonance signals of equal intensity in the same range as that for monothione complexes (Table 4). This implies that there are at least two different cyclopentadienyl groups. Like in the case of monothione complexes aromatic dithione complexes have a higher value of ΔCp than non-aromatic ones. The same explanation as that given for monothione complexes possibly applies here. The proton cyclopentadienyl chemical shifts of 55b and 55f are respectively at δ4.37, 5.08 and 4.47, 5.14 ppm. Those of 57 and 59 are at δ5.22, 5.29 and 5.01, 5.11 ppm respectively (Table 4).

In discussing infrared data (Section C.4) it was suggested that there are two possible structures of dithione complexes, namely 81 and 82. While 81 has two different cyclopentadienyl groups, 82 has two identical ones so that the former would be expected to exhibit two cyclopentadienyl signals compared to only one expected

for the latter. In 81 the chemical shift at higher field would be assigned to Cp_2 and the one at lower field to Cp_1 since it is assumed that M_2 is more negative than M_1. However if 82 underwent isomerisation(Schemes XIII and XIV) then more cyclopentadienyl signals would be expected. In contrast, although isomerisation has been proposed to explain infrared data of $\{CpMo(CO)_2P(OC_2H_5)_3\}_2$ only one doublet (due to coupling between phosphorous-31 and cyclopentadienyl protons) in the cyclopentadienyl region has been observed by Haines and his co-workers[28]. The presence of two cyclopentadienyl resonance signals of equal intensity and which are fairly different from each other seems to favour structure 81 more than 82 although the latter may not be ruled out completely.

All the chemical shifts of thione complexes are recorded in Table 4.

6. Carbon-13 Nuclear Magnetic Resonance Data

To gain more information about the structure of monothione complexes Carbon-13 spectra have been obtained. The carbon-13 cyclopentadienyl resonance signals correspond fairly well to those obtained from proton NMR spectra except that in certain cases (e.g. 56 and 58)the order of the chemical shifts of the major isomer relative to those of the minor isomer is reversed.

As in the case of proton NMR data monothione complexes may be divided into two groups, namely those that show two cyclopentadienyl resonance signals and the ones that exhibit either three or four of them. Hence 54a shows cyclopentadienyl signals at δ 93.60 and 95.83 ppm,

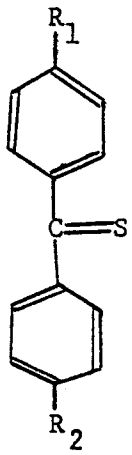
carbonyl chemical shifts at δ 244.45, 236.93, 234.65 and 233.41 ppm and two methoxy carbon signals at δ 55.17 and 55.33 ppm indicative of two different methoxy groups. The reason for the existence of two methoxy carbon signals is the same as that given for the observation of two methoxy proton signals (see Section C.5.). The monoadamantanethione complex (56) shows four cyclopentadienyl chemical shifts at δ 93.23 (Cp), 93.58 (Cp'), δ 94.10(Cp) and 94.82(Cp') ppm, where Cp and Cp' are cyclopentadienyl groups of the major and minor isomers respectively. Complex 56 also shows carbonyl signals at δ245.30, 239.90, 237.50, 236.40, 236.00 and 235.90 ppm. Similarly 58 has cyclopentadienyl resonance peaks at δ 93.99 (Cp'), 93.02(Cp'), 93.36(Cp) and 92.38(Cp) ppm and carbonyl resonances at δ 244.64, 239.30, 238.13, 236.32, 235.57 and 235.43 ppm. The carbon-13 NMR spectrum of 68 shows cyclopentadienyl signals at δ 93.91, 92.46 and 91.75 ppm. Possibly one of the chemical shifts corresponds to two cyclopentadienyl groups since four peaks are expected so that there is agreement with the presence of two isomers as in proton NMR data.

Thiocarbonyl resonance signals have been observed in the carbon-13 spectra of 58 and 54a. Consistent with the suggestion that there are two isomers in chloroform solutions of 58, two thiocarbonyl resonances (δCS) are observed at δ 114.94 and 104.84 ppm. The fairly large difference between the two chemical shifts suggests that the C-S bond of one of the isomers has more π character than the other. The spectrum of 54a exhibits two resonance signals at δ 106.93 136.41 ppm. Only one isomer or species is expected to be present

so that only one δCS is expected in chloroform solution of 54a. It is likely that δ 106.93 ppm corresponds to δCS because of its vicinity to the two resonance signals of 58. The thiocarbonyl carbon chemical shifts for both 54a and 58 are at a much higher field than expected for a normal >C=S→M(M=metal) group. For example Alper[33] has reported that the chemical shift of the >C=S group in $(OC)_5MoL$(L=thiocamphor) occurs at δ 272.8 ppm which is not very different from the value of the unbound thiocamphor (δ 271.5 ppm). Similarly the complex $(OC)_5MoL$ (L=tetramethylthiocarbonate) has been found [19] to have the >C=S chemical shift at 193.16 ppm only about 0.2 ppm down field from the free ligand. This then may imply that the bonding in monothione complexes (e.g. 58) may be quite different from that in $(OC)_5MoL$ (L= thiocamphor, tetramethylthiocarbonate).

Again the assignment of the cyclopentadienyl resonance signals will depend on the distribution of charge between M_1 and M_2. The distribution of charge will depend on how much each of the canonical forms (90(i), 90(ii) and 91) contributes to the overall structure. If the canonical structure 90 (ii) is considered M_2 will be expected to be more negative than M_1. However, whatever the case the cyclopentadienyl chemical shift at lower field is assigned to the cyclopentadienyl group attached to the more negative center and the one at higher field to the cyclopentadienyl group attached to the less negative center.

However Gansow and his co-workers[35] have studied carbon-13 NMR data of $CpFe(CO)_2X$ (X =Cl, Br, etc.) by varying the electronegativity of X. They have found that both cyclopentadienyl and the carbonyl chemical shifts move to higher field with increasing electron withdrawing capability of X. This has been justified by suggesting that the reduction in π-back donation by electron withdrawing groups increases the paramagnetic shielding parameter (σ_p)



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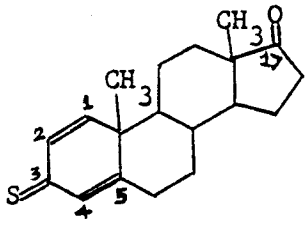
leading to a shift to higher field. Consideration of carbon-13 NMR data obtained by Gansow and his co-workers[35] and Bodner[36] indicates that a slight change in electronic charge on the metal center does not lead to significant changes in cyclopentadienyl chemical shifts to enable one to make a reliable correlation.

Cyclopentadienyl resonance signals of all the monothione complexes for which carbon-13 NMR data has been obtained fall in the region normally reported for similar compounds such as $\{Cp_2Mo_2(CO)_4(H_2C{=}C{=}CH_2)\}$(52) whose spectrum has been reported [22] to have a cyclopentadienyl chemical shift at δ 93.09 ppm. The latter (52) has also been reported [22] to show carbonyl resonance signals at δ 233.48 and 237.16 ppm which are in the same range as those for 54a, 58 and 56 (Table 5), but not the androstadiene complex, 64, which, surprisingly, exhibits carbonyl signals at a higher field (δ 220.64, 220.48 and 216.57 ppm) than all the rest although the explanation for this is rather obscure. It is possible that the basicity of the thione ligand is somewhat reduced in 64 resulting in a shift of carbonyl signals to higher field. This may result from possible interaction of one of the olefinic groups with one of the molybdenum atoms (see structure 92 and 94).

It is difficult to make an unambiguous assignment of chemical shifts to olefinic, thioketonic and ketonic groups of 64 because of the complexity of the carbon-13 spectrum. In the unsaturated carbon region there are peaks at δ 144.17, 142.00, 140.76, 135.91, 132.95, 121.75, 130.20, 129.03 and 123.99 ppm. The partly decoupled spectrum gives doublets at δ135.91, 132.94 and 123.99 ppm. Free $\Delta^{1,4}$-

androstadiene-3-thione-17-one has chemical shifts of unsaturated carbons at δ219.59(C3), 161.11(C17), 147.53(C1), 142.43(C5), 135.44(C4) and 133.34 ppm(C2). The free ligand assignments were made with the aid of a partly decoupled spectrum of the same compound. The chemical shifts of the complex due to the ligand olefinic carbons fall in the



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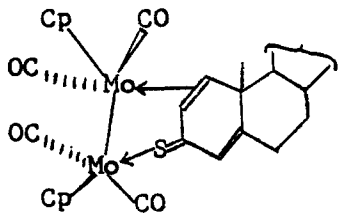
same range as those of the free ligand. The complexity of the spectrum in this region is possibly due to the presence of impurities since 64 is fairly unstable in polar solvents such as chloroform where the spectrum was obtained.

From the partly decoupled carbon-13 NMR spectrum of 64 the chemical shifts at δ135.90, 132.90 and 123.99 ppm may be assigned to any of the unsaturated carbons C1, C2 and C4. Whichever of the chemical shifts is assigned to C1 will result in an upfield shift of at least 232 Hz. Suppose that δ135.90 ppm is assigned to C1 and that C2 experiences an upfield shift comparable to that of C1. Then δ132.94 and 123.99 ppm may be assigned to C4 and C2 respectively. The postulated upfield shift of C1 and C2 may be due to interaction between the C1-C2 double bond and the orbitals of the metal atoms. Such an observation has been made in the case of $\{(h^5\text{-}C_5H_5)Mo_2(CO)_4(H_2C{=}C{=}CH_2)\}$ (52)[22] where on complexation the chemical shift of the

terminal carbons of the allenic group shifts from δ74 ppm to δ36 ppm possibly due to a reduction in the multiple bond character of the C-C bonds. Possible structures of 64 include 92, 93, 94 and 95. Structures 92 and 93 are more likely to correspond to the right configuration since they are expected to experience less steric interactions. Also the choice of 92 and 93 makes it possible to explain why there is a greater shift of C1 and C2 than C4 (and possibly C5) to higher field. If either 92 or 94 is present then one of the resonance signals at δ220.64, 220.48 and 216.57 ppm which have been assigned to the carbonyl groups may be due to the >C=S group which exhibits a chemical shift at δ219.59 ppm in the free ligand. Nonetheless chemical shifts due to >C=O and CS (if either 93 or 95 is present) may be among the unassigned resonance signals (see Table 5).



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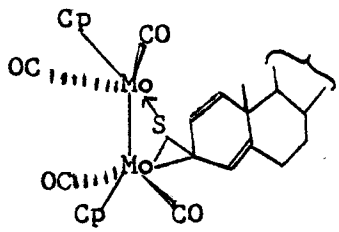

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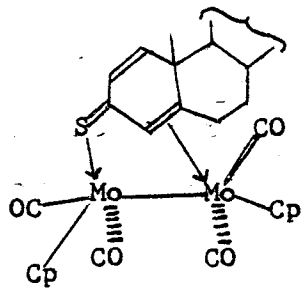

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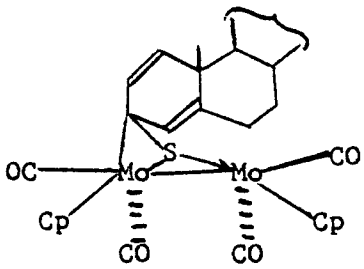

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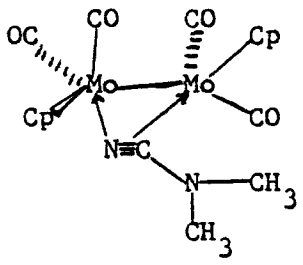
7. Mass Spectroscopy Data

Several attempts were made to obtain mass spectra for a number of complexes among which were 54a, 56 and 57, but none of them gave a satisfactory spectrum. However, 57 showed a broad band around m/e 385 which was assigned to the fragment $\{CpMo(CO)_2C_{10}H_{14}S\}^{+\cdot}$. Such a fragment was probably as a result of heterolytic cleavage of the metal-metal bond. The failure to obtain good mass spectroscopic data is possibly due to instability of thione complexes when subjected to heat.

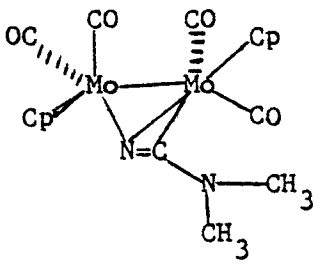
8. Structure of Thione Complexes

Using analytical, infrared and nuclear magnetic resonance data it was not possible to determine the exact molecular formula and structure of thione complexes. However this was made possible by obtaining a single crystal X-ray picture of 58 (Figure 8). Bond distances and angles are listed in Figures 6 and 7, and Table 15.

The presence of only four carbonyl groups in 58 was not expected. This finding eliminated the earlier belief that monothione complexes had structure 89. Although no thione complex with a structure similar to that of 58 has been reported a similar complex, namely $\{Cp_2Mo_2(CO)_4(NCNMe_2)\}$ (99) has been isolated[37] and characterised by X-ray crystallography. While for 99 bonding may be depicted as in



(a)



(b)

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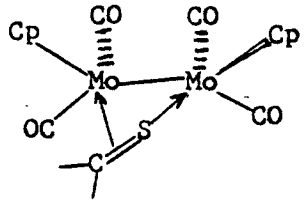
99(a) or 99(b) for 58 it may be depicted as in 90, 91 or 90(b). Both 58 and 99 may be thought of as using a multiple bond to co-ordinate with one molybdenum atom and a lone pair of electrons to bond to the other.



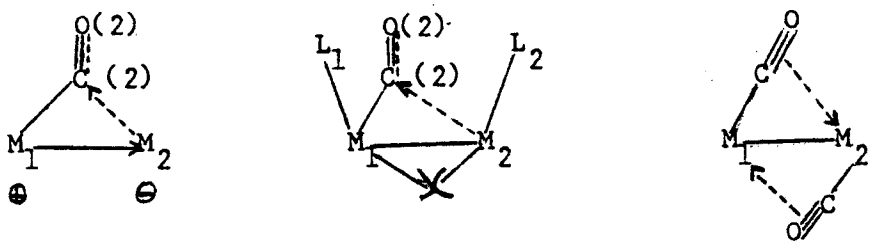
90 (b)

The Mo(1)-Mo(2) bondlength is 3.145Å which is shorter than that in 45a (3.235Å)[38] but, much longer than that in the triple bonded 46a(2.448Å)[39]. The Mo-Mo bond distance is also longer than those found in $\{Cp_2Mo_2(CO)_4(H_2C{=}C{=}CH_2)\}$ (3.117Å)[22] and $\{Cp_2Mo_2(CO)_4(HC{\equiv}CH)\}$ (2.98Å)[40]. The explanation for the variation of the Mo-Mo bondlengths in moving from one ligand to the other is said [40,22,50] to be possibly due to the closer approach that is required between certain ligands and the metal atoms in order to have an effective overlap of orbitals. Hence the two metal atoms in $\{Cp_2Mo_2(CO)_4(HC{\equiv}CH)\}$ need to come closer together in order to effect a good bond formation with the π orbitals of the acetylenic group than in the case of $\{Cp_2Mo_2(CO)_4(H_2C{=}C{=}CH_2)\}$ where the two π bonds in the allenic group are more far apart. Steric factors may also contribute to the extent of metal-metal variations.

The average Mo-CO bond-length 58(1.943Å) is slightly shorter than that in 45a (1.973Å)[42]. While the C(2)-O(2) bond distance (1.182Å) is fairly long the other three carbonyl groups have C-O bond-lengths which average to about 1.148Å which is about the same as those

found in 45a[42]. The carbonyl group with the longest C-O distance forms a semi-bridging bond of the type Mo(1)-C(2).....Mo(2) where the dotted line indicates the semi-bridging bond. The Mo(2)...C(2) bond distance is about 2.666Å which lies between the semi-bridging bond of 46a (2.56Å)[39] and that of $\{CP_2Mo_2(CO)_4(HC{\equiv}CH)\}$ (2.826Å)[47]. The Mo(2)-Mo(1)-C(2) angle of 57° in 58 is smaller than that of 67.6° in 46a[39]. Also in 58 the M(1)-C(2)-O(2) angle of 162° is much smaller than the average of the other three (177.1°). It is surprising that in 46a the Mo-C-O groups are almost linear (176°)[39] despite the fact that they are involved in semi-bridging bond formation. However the extent of bonding of the M-C-O group may depend on the nature as well as the extent of semi-bridging interaction.

Semi-bridging carbonyl groups[46] may be a result of three main factors. The first factor may arise when there is unequal distribution of charge such that of the two metal atoms bonded to each other one (M_1) is more negative than the other(M_2). To offset



(a) Unequal charge distribution between M_1 and M_2.

(b) Equal distribution of charge. SBCO arises from crowding.

(c) Equal or unequal distribution of charge. SBCO arises from unsaturation or electron deficiency at either M_1 or M_2 or both.

Figure 3: (SBCO=semi-bridging carbonyl group).

the violation of Pauling's principle of electroneutrality the carbonyl group bonded to M_1 bends over to M_2 and uses its empty antibonding π orbitals (π^*) to accept electronic charge from M_2 giving rise to a weak bond (semi-bridging bond) (Figure 3(a)). This kind of interaction has been proposed to be operative in $\{Cp(OC)_3V \longrightarrow V(CO)_2Cp\}$[44] and $CpMn_2(CO)_6(AsMe_2)$[45]. The metal-metal bond is such that there is a co-ordinate bond from the more positive side to the more negative side.

A second factor may arise from steric crowding. Consider Figure 3(b). Supposing that $\mathcal{X}$ is so bulky that L_1, L_2 and CO(2) are pushed to one side and all of them are almost opposite the $\mathcal{X}$ group. CO(2) will be expected to bend towards M_2 and in so doing two things may happen. The first one is that its empty antibonding π orbitals (π^*) may interact with a filled d orbital of M_2 resulting in a semi-bridging bond as illustrated by Figure 3(b). The second thing is that there may be repulsive interaction between CO(2) and L_2. Both of these effects may lead to the distortion of the linearity of the M_1-C2-O2 group[22]. Steric crowding has been proposed to be responsible for semi-bridging bonds in $\{Cp_2Mo_2(CO)_4(HC{\equiv}CH)\}$ and $\{Cp_2Mo_2(CO)_4(EtC{\equiv}CEt)\}$[47]. This proposal is supported by the absence of semi-bridging carbonyl groups in 52 where[22] it is expected that there is less crowding.

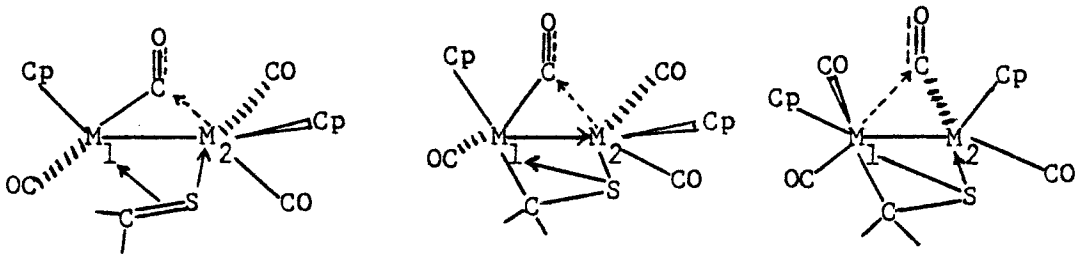
The third factor that may bring about semi-bridging carbonyl groups is unsaturation or electron deficiency on the two metal atoms bonded to each other. The nature of interaction is

illustrated by Figure 3(c). Such an interaction is expected to lead to less distortion of the linearity of the M_1-C_2-O_2 group than in the other cases. Hence this third factor is possibly present in 46a where the semi-bridging carbonyl groups maintain linearity of the Mo-C-O groups (176°).

It is worth mentioning at this point the possibility that situations may arise where a combination of the above factors may come into play. All the these factors are expected to lead to a reduction in C-O bond order and hence the presence of an absorption band in the bridging νC≡O region. For example {$Cp_2Mo_2(CO)_4$ (EtCCEt)}[47] has an absorption band at 1830 cm^{-1} which has been assigned to the semi-bridging carbonyl group. The presence of semi-bridging carbonyl groups in monothione complexes seems to be supported by the fact that all monothione complexes have a weak ν C≡O absorption band around 1800 cm^{-1}(Table 3). Also the carbon-13 NMR spectra of 54a, 56 and 58 have respectively got carbonyl chemical shifts at δ 244.45, 245.30 and 244.64 ppm which have been assigned to the semi-bridging carbonyl groups.

From X-ray data it is likely that the presence of a semi-bridging carbonyl group in 58 is a result of both steric effects and unequal distribution of charge. The possible structures that may describe monothione complexes with a semi-bridging carbonyl group include 96(i), 96(ii) and 98. It can be seen that these structures are derived from canonical forms 90(ii), 92(ii) and 90(i) (Page 37). The nature of semi-bridging will depend on how much each of

these canonical forms contributes to the overall structure. Canonical forms 96(i) and 96(ii) contribute to the same structure where 98 is different. In 96(i) and 96(ii) M_2 is assumed to be more negative than M_1; and in 98 the reverse is assumed to be true. A more detailed discussion on how these structures are interrelated is given in section D.9 (below).



96(i) (M_1=M_2=Mo,W) 96(ii) (M_1=M_2=Mo,W) 98 (M_1=M_2=Mo,W)

Furthermore the C-S bond distance is about 1.769Å which is longer than the one in $(OC)_5CrS{=}CMe_2$ (1.618Å)[48] and only slightly shorter than the C-S bondlength of ethylene sulphide (1.819Å)[49]. The structure of 58 is interesting in that one molybdenum atom (M_1) is bonded to both the carbon (C16) and sulphur of the thione. At the same time the other molybdenum atom (M_2) is bonded to the same sulphur as the first one. Judging from the C-S bond distance the π-character of the C-S bond should be quite small, which is in agreement with

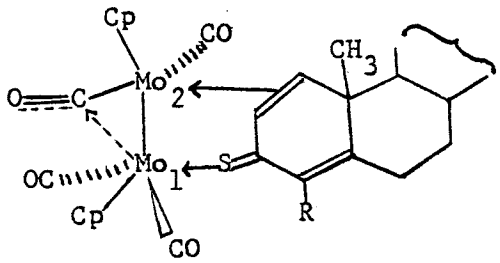
carbon-13 data of 54a and 58(Table 5). The sulphur atom is involved in the formation of two three-membered rings one consisting of C16, Mo_1 and S, and the other comprising Mo_1, Mo_2 and S. The latter is almost trans to the Mo_1-C_2-Mo_2 ring which results from the semi-bridging bond formation. The Mo_1-S and Mo_2-S bondlengths are 2.371 and 2.397Å respectively so that they are considerably shorter than the sum of the covalent radii (2.65Å) of sulphur and molybdenum stoms. This is possibly because of backbonding from filled d orbitals of the metal atoms to the empty d orbitals of sulphur. All the Mo-CO bond-lengths are almost the same. No carbonyl group is "really trans" to the sulphur group. The Mo_1-C_{16} bondlength (2.363Å) is about the same as some of those between molybdenum and cyclopentadienyl carbons (e.g. Mo_1-C_6=2.368Å). What is fascinating is the fact that the two Mo-S bondlengths are almost the same as the Mo-C16 and Mo-C6 bond distances. However the Mo-S bond distances in 58 (Figure 6) are about the same as the Cr-S bondlength (2.377Å) in $(OC)_5Cr(S{=}CMe_2)$ reported by Karcher and Jacobson[48]. The lengthening of the Mo-C_{16} bond distance, for example, may probably be due to steric interactions.

The proton and carbon-13 nuclear magnetic resonance as well as infrared data are in agreement with the structure of monothione complexes as depicted by Figure 8 except for cases where the observed data have been explained in terms of isomerisation (see Section C.5. and C.6.). Hence due to the similarity of spectroscopic data of 58 to those of other monothione complexes it is reasonable to conclude that all the other monothione complexes have structures similar to that of 58. In the solid state the structure of 58 has C_1 symmetry so

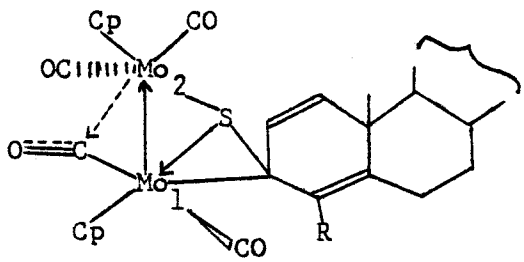
that four ν C≡O absorptions bands will be expected, which is in agreement with infrared data (Table 3) of all the aromatic monothione complexes and some of the non-aromatic ones. For certain complexes such as 58, 56, 65, 67, 68 and 69 although four absorption bands are observed in polar solvents (such as chloroform and acetone) (Tables 3 and 4) five of them are observed in non-polar solvents such as n-hexane. It is proposed that the fifth νC≡O absorption band is due to a second isomer, which has also been detected by both proton and carbon-13 NMR spectroscopy for 56, 58 and 69 (see Section C.5 and C.6. and Tables 3 and 5). Despite the fact that $\{Cp_2M_2(CO)_4(p\text{-}CH_3O\ C_6H_4C(S)\Phi)\}$ (54d:M=Mo; 54k:M=W) have proton NMR data (Table 4) that indicate the presence of two isomers their infrared data are somewhat different from those of other complexes (e.g. 58 and 68) which show similar proton NMR properties. Hence 68 has νC≡O absorption bands at 1960(W), 1947(W), 1916(VS), 1859(S) and 1808(W) cm^{-1} and 54d has them at 1961(W), 1938(VS), 1867(S) and 1818(M) cm^{-1} in carbon tetrachloride. This may be due to the difference in symmetry.

The presence of a semi-bridging carbonyl group in the X-ray picture of 58 has given rise to another possible explanation for the observed contrast between the νC≡O absorption bands of 63 and 64 and those of the other monothione complexes under investigation. One may wonder whether structures 92, 93, 94 and 95 may not have any semi-bridging carbonyl groups. This does not

seem to be the case since if structure 92 is considered the bonding is such that one molybdenum is bonded to the sulphur and the other to the olefinic π-bond so that the need for the formation of a semi-bridging bond may still arise because of even greater inequality of distribution of electronic charge between the two molybdenum atoms. Also there will be even greater steric interactions which would lead to even larger distortions of the ligands similar to the type shown in Figure 3(b). These effects may then lead to the formation of a semi-bridging bond similar to the one in 92(b) if it is assumed that Mo_1 is more negative than Mo_2. However if 93 is considered the semi-bridging bond may be formed as shown in 93(b). Also suppose that 63 and 64 have structure 92 or 94. The Mo-Mo



92b (R=CH_3, H)

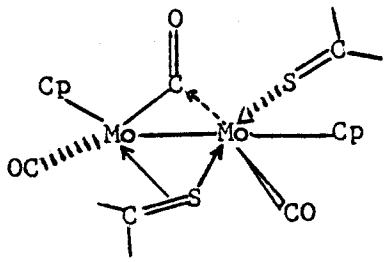


93b (R=CH_3, H)

bond in both cases would be expected to be longer than in such complexes as 54a and 58 so that the semi-bridging bond is expected to be weaker, if not entirely absent, in 63 and 64. A similar reasoning has been

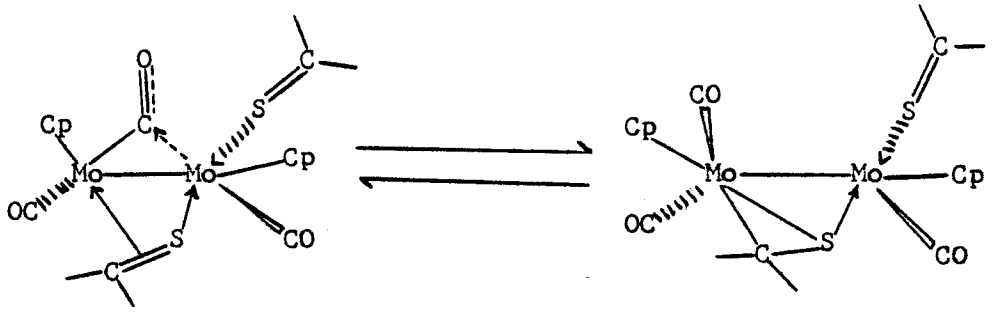
proposed[50] to explain why there is a semi-bridging carbonyl group in $\{Cp_2Mo_2(CO)_4\text{-}(HC{=}CH)\}$ (Mo-Mo= 2.984Å)[43] and none in $\{Cp_2Mo_2(CO)_4(H_2C{=}C{=}CH_2)\}$ (Mo-Mo=3.117Å)[22].

It is possible that if dithione complexes have structure 81 they may have semi-bridging carbonyl groups as illustrated by 100. This may especially be the case for non-aromatic dithione complexes where the lowest $\nu C{\equiv}O$ absorption bands are at quite low frequencies. For example 57 and 59 have lowest $\nu C{\equiv}O$ peaks at 1760 and 1776 cm^{-1} respectively. For aromatic dithione complexes this does not seem



100

to be the case since all their $\nu C{\equiv}O$ absorption bands are at fairly high frequencies (Table 3). It was previously mentioned that 55b shows two and four $\nu C{\equiv}O$ absorption bands in chloroform and n-hexane at 1973, 1856 and 1994, 1959, 1890, 1812cm^{-1} respectively. It is possible that in hexane there is isomerisation similar to the



100 81

type shown in Scheme XV so that there is an equilibrium between 81 and 100. In chloroform 55b possibly exists entirely in a form which corresponds to 81. As in the case of monothione complexes no fluxional behaviour has been observed.

9(a). Isomerisation of Monothione Complexes

Proton and carbon-13 NMR data show the presence of at least two isomers in chloroform solutions of 54d, 54k, 56, 65, 66, 67, 68 and 69(Tables 4 and 5). Low temperature studies have been conducted for 56, 58, 68, 54d and 65. From these studies it is found that 65, 54d and 58 crystallise mainly in one isomeric form. All attempts to isolate the crystals of the other (minor) isomer of 58 have failed. Complexes 56 and 68 show cyclopentadienyl chemical shifts at δ5.26(Cp'), 5.34(Cp+Cp'), 5.37(Cp) and 5.39(Cp), 5.43(Cp'), 5.47(Cp), 5.50(Cp')ppm in the ratio of about 4:11:7 and 9:8:9:8 respectively indicative of the presence of two isomers in the solution of each complex even when the solid of the appropriate complex is dissolved in chloroform at a temperature as low as -40°C. Almost the same ratios are obtained when the same solutions are left to equilibrate at room temperature (~20°C). Note that Cp and Cp' correspond to the cyclopentadienyl groups of the major and minor isomers respectively.

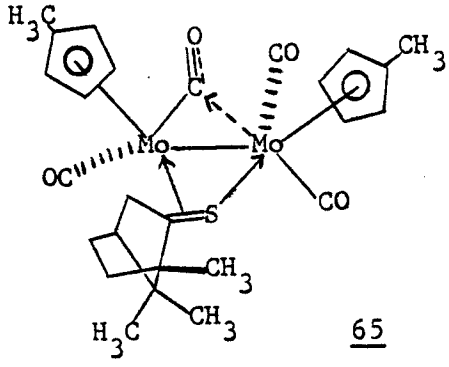
Immediately after dissolving the solid in chloroform at low temperature (≃10°C) the proton NMR spectrum (Fig. 5(a)) of 58 gives four resonance signals (in the cyclopentadienyl region) at about 5.23(Cp'), 5.27(Cp), 5.41(Cp') and 5.43(Cp) ppm in the ratio of about 1:5:1:5. All the resonance signals are sharp. When the solution is left to equilibrate and temperature increased the population of the minor isomer (δ 5.23, 5.41 ppm) increases and that of the major isomer (δ 5.27, 5.43 ppm) decreases. This is reflected in the increase of the intensity of the resonance signals

of the former and decrease of those of the latter. It is also observed that the rate of equilibration increases with temperature (Table 9).

Also, 54d shows cyclopentadienyl signals at δ 4.61 and 5.28 ppm due to the major isomer and at δ 4.67 and 5.25 ppm due to the minor isomer (at about -40°C) in about the same ratio as in the case of 58). The ratio of isomers of 54d shows the same temperature dependence as that of 58. One major difference is that unlike 58 the major isomer of 54d in solution is the major isomer in the solid state. It is possible that the minor component in solution is more stable in the solid state of 54d. Also the order of cyclopentadienyl resonance signals of the two isomers of 54d at lower field are reversed when compared with those of 58.

However 65 shows two methyl resonance signals at δ 2.25 and 2.08 ppm in 1:1 ratio when the solid is dissolved in cold chloroform ($\simeq$ -30°C). As time passes (at constant temperature) and temperature increased the signal at δ 2.25 ppm decreases and the one at δ 2.08 ppm increases in intensity until at room temperature ($\simeq$ 20°C) the two resonance signals are in the ratio of about 2:1. It is proposed that the resonance signal at δ 2.25 be assigned to the methyl group (Cp-CH_3) attached to one of the cyclopentadienyl groups of the major isomer so that the resonance signal at δ 2.08 ppm is assigned to the methyl groups (2 Cp-CH_3') attached to the cyclopentatienyl groups of the minor isomer plus the remaining methyl group (Cp-CH_3) attached to the cyclopentadienyl group of the major isomer.

This implies that in the solid state of 65 only one isomer is present. Like in the case of 54d and 58 no fluxional behaviour is observed.



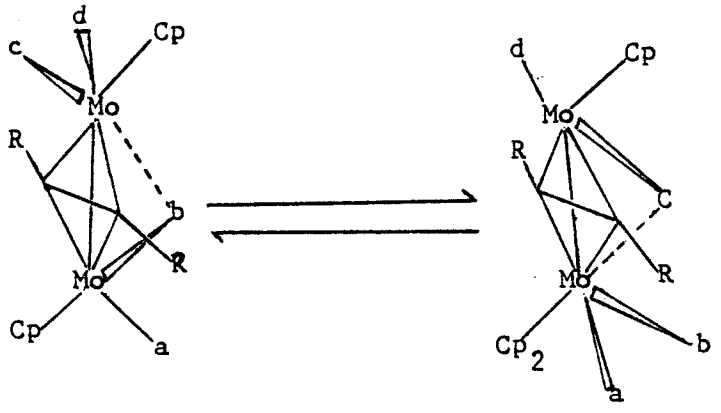
65

A dimethylsulphoxide solution of 58 was heated up to 90°C but no change in the pattern of the proton NMR spectrum was observed. Also when the chloroform solution of 54a was cooled to as low as -65°C no change was detected in the nature of the proton NMR spectrum.

It is noteworthy that when equilibration has taken place at a particular temperature lowering the temperature does not give rise to any observable change in the intensity of resonance signals. This is possibly because the equilibrium constants do not vary much with temperature (Table 9).

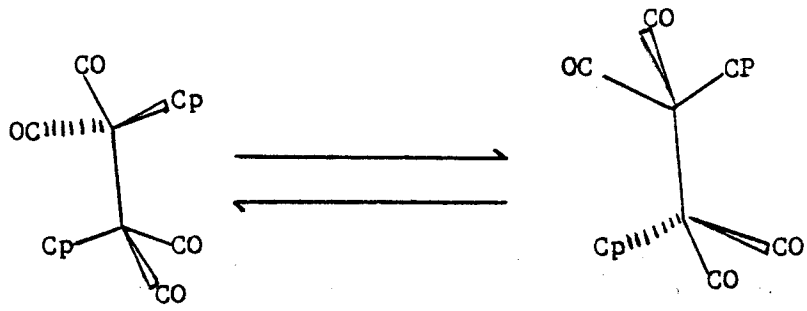
Although carbon-13 NMR data do support the presence of isomerisation in chloroform solutions of 56, 58 and 68 no variable temperature studies have been conducted. In view of this it is difficult to state conclusively the role of carbonyl groups in isomerisation of thione complexes. However Cotton and his co-workers[50] have investigated the isomerisation of $\{(h^5\text{-}C_5H_5)_2Mo_2(CO)_4\text{-}(RC{\equiv}CR)\}$ (R=H, Et, Ph) by using both carbon-13 and proton NMR specroscopy at different temperatures. They have found that all the complexes are

fluxional so that at room temperature carbonyl (^{13}C) and cyclopentadienyl (^{13}C and ^{1}H) signals appear as singlets. On lowering the temperature these singlets have been found to broaden and eventually split into two cyclopentadienyl and carbonyl signals. Lowering the temperature even further the two carbonyl resonance signals have been reported to finally split into four resonance signals. They have also reported that no rapid scrambling of carbonyl groups has been observed (up to 90°C). From these results Cotton and his co-workers have suggested that there are two energy processes, namely the low and high energy processes. The former has been proposed to involve the interchange of semi-bridging carbonyl groups such that, in Scheme XVI, b in interchanges with c and a interchanges with d.



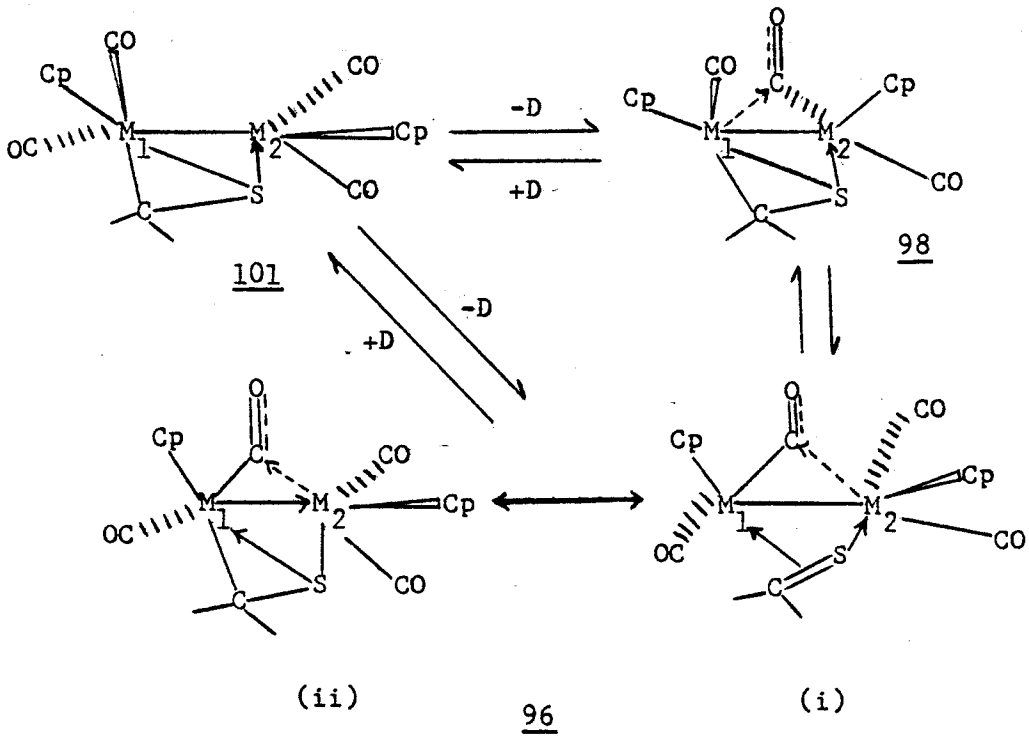
Scheme XVI: b $\rightleftharpoons$ c (R=H, Et, Ph; a=b=c=d=CO)

The high energy process has been suggested to involve partial rotation about the Mo-Mo bond as illustrated by Scheme XVII, where the change in orientation of groups from (i) to (ii) has been somewhat exaggerated.



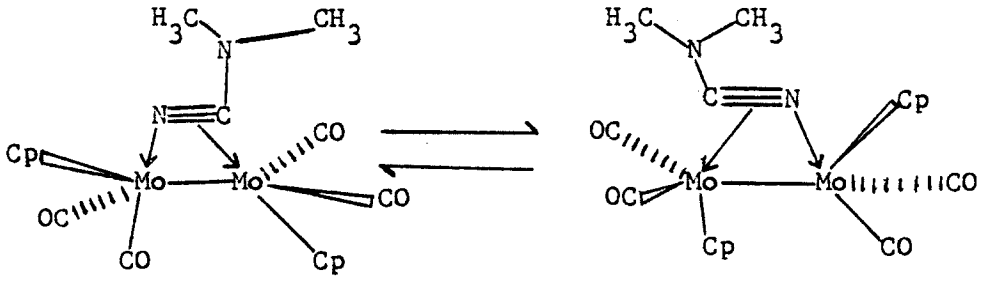
Scheme XVII

The nature of isomerisation of monothione complexes is not clear. Despite the apparent non-reversibility of isomerisation with temperature in solution it has been found that the two isomers of 58 do interconvert on a thin layer chromatographic plate. Therefore it may be assumed that equilibration of monothione complexes does exist in solution also. A possible mechanism is shown in



Scheme XVIII (M_1=M_2=Mo,W; D=Solvent Molecule).

Scheme XVIII. From Figure 8 the structure of monothione complexes may be represented by two canonical forms, 96(i) and 96(ii), which may isomerise to either 98 or 101. The formation of 101 from 96 may be aided by a donor solvent such as acetone and tetrahydrofuran which would help cleave the semi-bridging bond. Isomer 98 might be formed through an intermediate similar to 102. The equilibrations between 98 and 101, 96 and 98, and 96 and 101 are expected to be energetically similar to those proposed by Cotton and his co-workers for $\{(Cp_2Mo_2)CO)_4(RC{\equiv}CR)\}$ (R=H, Et, Ph). Also 99, which may be considered to have isomerisation properties similar to those of monothione complexes has been reported by Cotton et al [37] to exhibit fluxional behaviour. It has been proposed that 99 possibly isomerises by a mechanism similar to the one illustrated by Scheme XXIII. The fact that no fluxional behaviour is observed in the case of monothione complexes suggests that the complexes reported by cotton and his co-workers differ in either energies of activation or mechanism of isomerisation, from monothione complexes.



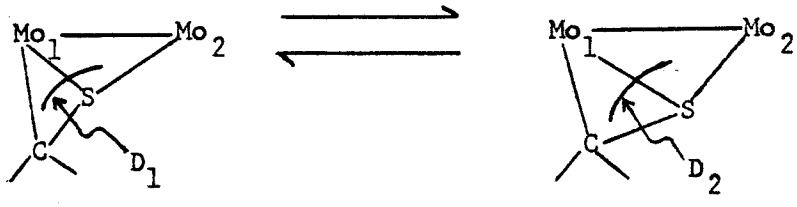
Scheme XXIII: Isomerisation of 99

The stability of 101 relative to 96 and 98 may depend on the distribution of charge between M_1 and M_2. If M_2 is more negative than M_1 then 96 will be favoured, otherwise 98 will be favoured. Nonetheless if M_1 and M_2 are of about the same basicity the formation of 101 will be preferable. It is conceivable that the distribution of charge may be influenced by the hybridisation of the CS carbon. For example structures 96(i) and 98 may be favoured depending on whether the hybridisation of the CS carbon is sp^2 or sp^3.

From the above considerations the most likely structure of the major isomer of 58 (Figure 8) is 96, and that of the minor isomer is either 98 or 101. While the choice of 98 (as a minor isomer) is inconsistent with both infrared (in the ν C≡O region) and carbon-13 NMR data (in the carbonyl region) the choice of 101 (as a minor isomer) is only inconsistent with infrared data (in the νC≡O region). The discrepancy with the choice of both 98 and 101 may be rationalised as follows. The failure to observe two carbonyl resonance signals in the carbon-13 spectra of both 58 and 56 (if 98 is present together with 96) may be justified by suggesting that the two signals coincide (at 244.64 for 58 and 245.30 ppm for 56). That this is the case for both 56 and 58 is doubtful. However, the intensity of the resonance signals assigned to the semi-bridging carbonyl groups is large enough to be assigned to two carbonyl groups. A similar explanation may be given for the fact that only four or five νC≡O absorption bands are

observed instead of a maximum of eight expected for the two isomers. That is to say that it is possible that there is accidental degeneracy of vibration modes of 96 and those of either 98 or 101.

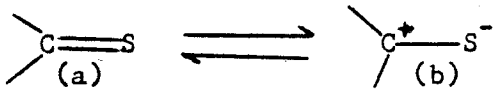
It has been noted (Table 15) that the plane of the Mo_1-C16-S three-membered ring forms an angle of 115° with Mo_1-Mo_2-S ring and 171° with the Mo_1-Mo_2-C_2 ring. One wonders whether isomerisation also involves a change in the angles that the three rings form with each other, especially the angle (D) between the Mo_1-C16-S and Mo_1-Mo_2-S planes as illustrated by Scheme XIX where D_1 is the angle in the major isomer and D_2 that in the minor isomer such that D_1 is less than D_2. Such a process, however, is not very possible. The driving force behind it would be the



Scheme XIX ($D_1 \angle D_2$)

reduction of steric interactions as a result of either opening up of the ring to give 101 or exchange of semi-bridging carbonyl groups (Scheme XVIII), both of which mechanisms would result in M_1 being more crowded than M_2.

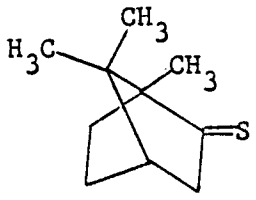
While an attempt has been made to explain why semi-briging bonds may be formed it is not clear why isomerisation has not been observed with certain monothione complexes. The same factors that lead to the formation of semi-bridging bonds may be instrumental in preventing isomerisation in certain complexes. These factors may include electronic and steric effects. In Scheme XX a less basic thione will favour the formation of (a) more than (b) and vice versa. Thiones which favour the formation of (a) would be expected to be



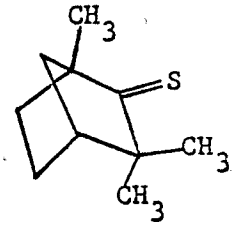
Scheme XX

more inclined to form isomers 96(i), and those that preferably exist in form (b) would be expected to favour the formation of 96(ii), 98 and 101. As has already been mentioned the nature of the complex or isomer present may depend on both the electronic environment and steric interactions. Whichever are the determining factors behind isomerisation it implies that those thiones which lie on the two extremes of the above effects may predominantly favour one form of the isomers or another and those that are moderate may exist in two or more isomeric forms. In certain cases it is more clear cut why only one isomer is observed. For example 58 (which contains the thiocamphor group) shows isomerisation and 60 (which contains the thiofenchone group) does not. Due to steric effects it is likely

that 60 prefers structure 96(i) which requires less interaction between the thiocarbonyl carbon and the metal atom (Mo or W) to reduce steric interactions.



Thiocamphor (V)



Thiofenchone (16)

What is difficult to explain is the fact that 54a, 54b and 54c do not seem to isomerise whereas 54d does. Steric properties of these complexes are expected to be similar. In fact while 54b is expected to be less crowded than both 54a and 54c the steric properties of 54d are expected to lie somewhere between the two sets. This is also possibly true in terms of basicity so that the order is $(p\text{-}H_3COC_6H_4)_2CS > (p\text{-}H_3CC_6H_4)_2CS \geqslant p\text{-}H_3COC_6H_4{\cdot}CS{\cdot}C_6H_5 > (C_6H_5)_2CS$. If this is the case one wonders whether the structure of 54b is somewhat different from that of 54a and 54c. From steric and electronic consideration this may imply that 54b has structure 96(i) and 54a and 54c have structure either 98 or 101. Such speculation then leads to the expectation that 54d would have intermediate properties so that isomerisation would involve an interconversion of 96(i) with either 98 or 101. Nonetheless in the absence of X-ray data of all these complexes these suggestions are highly hypothetical!

9 (b). Kinetic and Thermodynamic Data

For the interconversion between the major (X) and minor (Y) isomers equilibrium conditions were assumed (Scheme XXII). Kinetic and thermodynamic data of 58 and 54d (Table 9 and 10) were obtained by measuring the rate of decrease and increase of the intensities of the resonance signals of the minor and major isomers respectively as a function of time and temperature.

$$X \underset{k_y}{\overset{k_x}{\rightleftharpoons}} Y$$

Scheme XXII

The rates of reaction (Table 9) were generally found to increase with temperature. The equilibrium constants (k_x/k_y) for each complex were found not to vary very much with temperature (-9 to 9°C for 54d and 10 to 25°C for 58). Although activation energies are apparently the same for 54d and 58 the rates of interconversion of 54d are slightly larger than those of 58. This is possibly because 58 contains the bulkier ligand (thiocamphor) than 54d (which contains 4-methoxythiobenzophenone). It is probably for the same reason that the Gibb's free energy of activation for 54d is smaller than that of 58. Also while the kinetic data for 54d were obtained between -9 and 8°C those of the 58 were obtained between +10 and +25°C. Below +5°C the rate of interconversion of 58 was found to be extremely slow. Another contrast between 58 and 54d

was that for the former the rate constants for the forward process were larger than for the reverse process whereas the reverse was true for the latter. This seems to correlate with the observation that 54d has the major isomer in solution as the minor isomer in solid state.

In support of lack of fluxional behaviour for monothione complexes the activation parameters for 54d and 58 are larger than those reported by Cotton and his co-workers[50] for $Cp_2Mo_2(CO)_4(RCCR)$ (R=H, Et, Ph), which have been proposed to undergo semi-bridging carbonyl exchange (Scheme XVI). For example the Gibb's free energy of activation, activation energy and enthalpy of activation for 54d for the forward process are 19.31 ± 0.20, 21.13 ± 4.49 and 20.59 ± 4.49 kcal mol^{-1} respectively whereas the corresponding values for the high energy process of interconversion of $\{Cp_2Mo_2(CO)_4(PhCCPh)\}$[50] are 10.3 ± 0.2 , 9.9 ± 0.2 and 2.1 ± 0.4 kcal mol^{-1}. Thermodynamic parameters for 58 (Table 10) are closer to those that have been reported for $\{Cp_2Fe_2(CO)_3P(OPh)_3\}$[57] for the carbonyl group scrambling process, for which the activation energy has been estimated to be 19.8 ± 0.2. However there is no evidence of fast scrambling in solutions of 54d and 58.

From both kinetic and thermodynamic data it is obvious that the energy barrier of isomerisation of monothione complexes is higher than that of $Cp_2Mo_2(CO)_4(RCCR)$ (R=H, Et, Ph), although it is not exactly clear by which mechanism the isomers of the two types of complexes interconvert.

For error analysis see appendix II (page 153)

10. Solvent dependence of isomerisation of monothione Complexes

It is found that when proton NMR spectra of 58 are obtained in different solvents the ratio of the two isomers X (major isomer) and Y (minor isomer) varies with the polarity of solvent. The results show that while the concentration of X increases that of Y decreases with the dielectric constant of solvent. The concentration of each isomer has been measured by integrating the appropriate cyclopentadienyl resonance signals. The values of the quantity ([X]/[Y]) are recorded in Table 13.

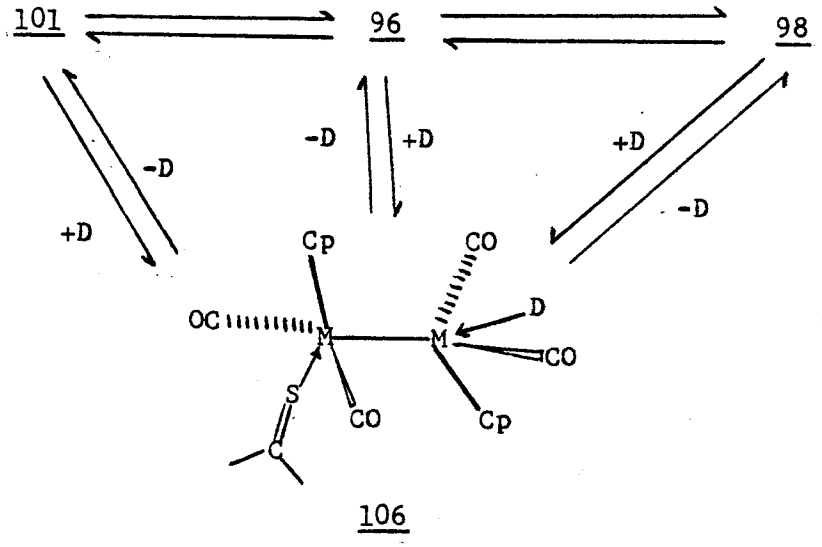
Some workers[51] have observed that the major of the two isomers of diazocyanides has a larger dipole moment than the minor (Table 11). Similarly Cotton and Adams[29] have carried out a study of the infrared spectrum of $\{Cp_2Mo_2(CO)_6\}$ (45a) (in the carbonyl stretching region) as a function of the polarity of solvents (Table 12). An X-ray study[38] has shown that 45(a) has a trans structure {105(a)} in the solid state. Cotton and Adams[29] have reported that in addition to 105(a) there is a minor component which has been assigned a gauche structure (105(b)). It has been found that the concentration of 105(b) increases with solvent polarity (Table 12). This has been justified[29] by saying that 105(b) is more polar than 105(a) so that by increasing the polarity of solvent, solvation of the more polar isomer is enhanced resulting in slower conversion of 105(b) to 105(a).

Assume that the structures present in solutions of monothione complexes are 96 and either 98 or 101. For the three structures the population of each one of them in a solution will possibly depend on its dipole moment. The order of the dipole moments is expected to be 101 < 98 < 96 so that as the polarity of solvent is increased the concentration of 96 is expected to increase at the expense of either 98 or 101. Another factor which may determine the fate of each of the isomers is the ease with which a solvent may cleave the semi-bridging bond. However, if isomerisation involves cleaving the semi-bridging bond, 96 and 98 are expected to be destabilized in relation to 101 with an increase in the polarity of solvent. Hence the concentration of isomer 101 is expected to increase with the polarity of solvent. At the same time 96 will possibly be more stable than 98 since the latter is expected to form a weaker semi-bridging bond because of possible steric interactions.

Since it is likely that 96 is the major isomer it is probable that either 98 or 101 is the minor isomer. If 101 is the minor isomer the fact that its concentration decreases with the polarity of solvent is surprising. This seems doubtful.

11. Proton NMR and Infrared Data in Dimethylsulphoxide Solution

It was mentioned earlier on that 58 undergoes isomerisation to different extents in different solvents of varying polarity. One wonders whether or not the same process is present in dimethylsulphoxide solutions of monothione complexes. This is because when proton NMR spectra are obtained in DMSO all monothione complexes

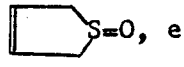
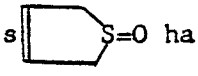


Scheme XXI (D=dimethylsulphoxide molecule; M=Mo,W; structures of 96, 98 and 101 are as shown on page 69)

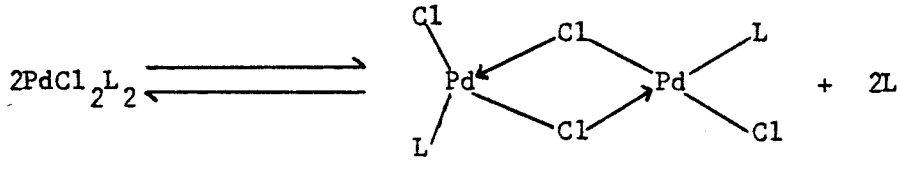
except 68, 69 and 56 exhibit in the cyclopentadienyl region two additional sharp resonance signals which do not seem to belong to any of the original species. It seems then that two types of species exist when monothione complexes are dissolved in DMSO. The first kind of these is most probably the original species since some proton NMR spectra display a pattern of cyclopentadienyl resonance signals which is quite similar to that of spectra obtained in other solvents (e.g. chloroform). For example the proton NMR spectrum of 54d in deuterochloroform has sharp resonance signals in the cyclopentadienyl region of 4.61, 4.67, 5.25 and 5.28 ppm in the ratio 2:3:3:2. For the same complex in DMSO resonance signals are obtained at δ4.67, 4.73, 5.30, 5.35, 5.40 and 5.44 ppm in the ratio 2:3:1:3:2:1. Those at δ4.67, 4.73, 5.35 and 5.40 ppm are assigned to the original species and the ones at δ5.30 and 5.44 ppm are assigned to the second species. For all the aromatic monothione complexes investigated the second set of proton NMR signals consists of a peak on either side of the signal(s) at lower field of the original species (Figure 11). Let the first and second species be denoted by I and II respectively. In the case where no or normal isomarisation is observed species I incorporates all such isomers as exist in such solvents as chloroform. Because the concentration of II does not seem to change with time despite the presence of an excess of solvent an equilibrium between I and II

may be assumed. It has been found that among all the aromatic monothione complexes 54f gives the highest yield of species II so that the quantity II/I equals 0.8. No attempt has been made to isolate II from the DMSO solutions. Although a reaction between DMSO and 46a has been tried no characterisable products have been isolated. Some of the proton NMR and infrared data of different monothione complexes in various solvents are recorded in Table 14.

A possible mechanism through which DMSO interacts with I to form species II is illustrated by Scheme XXI. Any of 96, 98 and 101 may constitute species I and 106 represents species II.

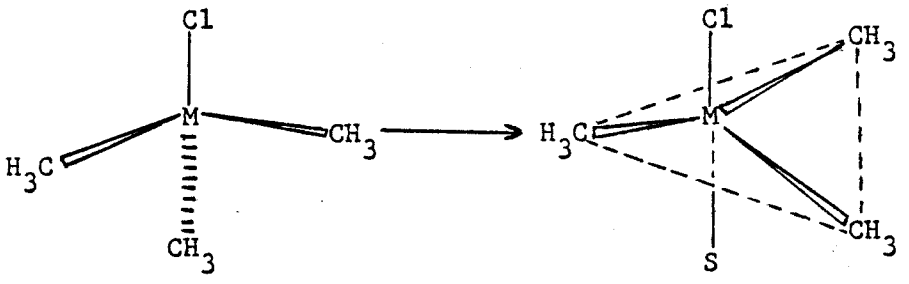
The bonding in 106 is possibly through sulphur. Kellog and his co-workers[66] have prepared and characterised complexes of general formula $(OC)_5CrL$ (L=Me_2S=O,  =O, etc.). The complex for L equals  =O has been characterised by X-ray and it has been found that the bonding is through sulphur, with the Cr-S bondlength of 2.331Å.

Kitching and his co-workers[58] have reported the isolation of complexes of the general structure $PdCl_2L_2$(L=DMSO, Et_2SO, Ph_2SO, PhCN). From infrared data they have suggested that the



Scheme XXIII

complex ($PdCl_2L_2$) with L equals Et_2SO very likely experiences a kind of equilibration (in chloroform solution) similar to the one depicted by Scheme XXIII. The complex $\{Co(DMSO)_6\}I$ has also been reported[62]. Furthermore it has been reported [64] that $M(CH_3)_3Cl$ (M=Sn, Pb) is solvated according to Scheme XXIV. It has been suggested that the extent to which 103(b) approaches a trigonal bipyramidal structure will depend on the donor ability of solvent (S). From proton NMR data it has been proposed[64] that when S equals pyridine (Py) 103(b) attains a trigonal bipyramidal structure.

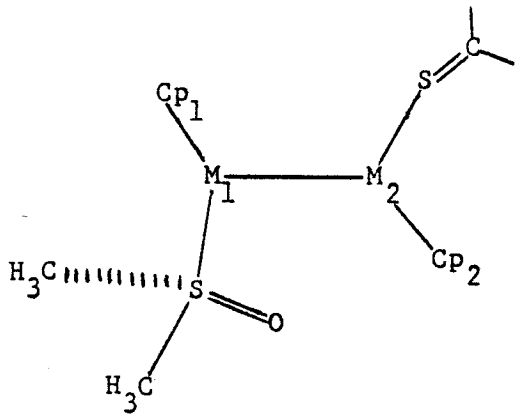


103 (a) 103 (b)

Scheme XXIV (M=Sn, Pb; S=C_6D_6, DMSO, Py, etc.)

From the proton NMR data in Table 14 it can be seen that cyclopentadienyl resonance signals are at lower field in DMSO than when other solvents (such as chloroform and benzene) are used. For example 54d does show cyclopentadienyl proton NMR signals at δ 4.46, 4.50, 4.86 and 4.90 ppm in benzene and at δ 4.67, 4.73, 5.35 and 5.40 ppm in DMSO (Table 14). The variation of the chemical shifts with

the nature of solvent is, as has already been mentioned above (Page 38), due to the interaction between molecules of the solvent and those of the solute[56]. If the DMSO molecule was coordinated, to say 58, in a manner shown by 107, the following might happen. Since



107

DMSO is expected to be a worse donor ligand than a thioketone M_2 will be more negative than M_1 so that the resonance signal due to Cp_1 will appear at lower field than that of Cp_2. However, the $>S=O$ group of the DMSO molecule will be expected to interact with Cp_2 more than with Cp_1 resulting in greater deshielding of Cp_2. This possibly accounts for the fact that the cyclopentadienyl signals of 106 are closer and at lower field (Figure 11) than those of say 54b (Figure 4(a)).

While all the aromatic monothione complexes give proton NMR spectra in DMSO that show one sharp resonance signal on either side of the cyclopentadienyl resonance signal(s) at lower field

(Figure 11(a)) non-aromatic ones are different. For example the spectrum of 58 (Figure 11(c)) has resonance signals at δ 5.36, 5.45, 5.53 and 5.67 ppm in the ratio 1:9:1:9. This pattern is just the reverse of the case with aromatic monothione complexes such as 54d. It is not conceivable that species I will experience a greater shift to lower field than species II. One explanation may be that species II is the major component in the DMSO solution of 58. Also, in contrast to 54d where the two isomers are present in the same ratio as in the other solvents, only one isomer is apparently present when 58 is dissolved in DMSO.

Complexes 56 and 68 each show a single sharp resonance signal in the cyclopentadienyl region at δ 5.50 and 5.69 ppm respectively although the former shows two barely visible peaks at 5.35 and 5.46 ppm. If species I are present in DMSO solutions of 58 and 68, the presence of a single cyclopentadienyl signal may be a result of the cyclopentadienyl groups becoming identical. Also there is a possibility of fast ligand - DMSO exchange.

An attempt was made to investigate by proton NMR spectroscopy the behaviour of 56 and 68 in a mixture of solvents. The proton NMR spectra of 68 as a function of DMSO:$CDCl_3$ ratio in the cyclopentadienyl region are shown in Figure 12. Note that δ_A , δ_B and δ_C are all cyclopentadienyl resonance signals in the range δ 5.30 to δ 5.90 ppm. As the concentration of DMSO was increased the intensity of the resonance signal δ_A increased, and δ_B and δ_C decreased. It looks like on addition of a little DMSO to a $CDCl_3$ solution of 68

three species are present. As the concentration of DMSO increases one species increases whereas the other two decrease in concentration. In a DMSO solution of 68 (and possibly 56) it is likely that only species II is present. On addition of chloroform it seems that two more species are formed giving rise to the two resonance signals, δ_B and δ_C.

When one starts with a chloroform solution of 68 the decreasing resonance at δ_B and δ_C possibly correspond to species I which are composed of 96 and either 98 or 101 and the chemical shift at δ_A to species II (106). The fact that only one cyclopentadienyl signal is observed for each component which is supposed to contain two cyclopentadienyl groups is not clearly understood but it is possible that the cyclopentadienyl groups happen to be identical by chance. Another possibility, which has already been mentioned, is that some of the complexes may be undergoing fast ligand - DMSO exchange. However, a more thorough study is required in order to understand more fully the effect of different solvent mixtures on the behaviour of monothione complexes such as 56 and 68.

The infrared data obtained for both aromatic and non-aromatic monothione complexes in dimethylsulphoxide (Table 14) indicate that at least two types of species are present in DMSO solution. Again these may be denoted species I and II since the pattern and position of $\nu C{\equiv}O$ absorption bands assigned to I are very similar to those obtained for monothione complexes in other

solvents where normal or no isomerisation has been observed. Hence two types of ν C≡O absorption bands may be separated out. The first type is assigned to species I and the second to species II. Just to illustrate consider the following cases. The infrared spectrum of 54a in chloroform has ν C≡O absorption bands at 1963(vw), 1938(vs), 1862(s) and 1810(vw) cm^{-1}. In DMSO the same complex has absorption bands at 1955(w), 1928(s), 1854(m) and 1811(vw) cm^{-1} all of which may be assigned to species I and at 2121(vvw) and 2011(w,b) which are assigned to species II. The same feature has been observed for all the other IR spectra of monothione complexes in DMSO (Table 14). The ν C≡O absorption band that has been assigned to the semi-bridging carbonyl group is not lowered on changing from chloroform (54a: 1810 cm^{-1}) to DMSO (54a: 1811 cm^{-1}) as compared to changing from say carbon tetrachloride (54a: 1815 cm^{-1}).

It is interesting that when the infrared spectrum of 54d was obtained in acetone only three ν C≡O absorption bands were observed (at 1959(w), 1934(vs) and 1865(m) cm^{-1}) as compared to four ν C=O absorption bands observed (at 1960(w), 1933(vs), 1858(m) and 1805(w) cm^{-1} in chloroform. However the infrared spectrum of 54a in the same solvent (acetone) has four ν C≡O absorption bands including the one at 1812 cm^{-1}. Again no lowering of the semi-bridging ν C≡O absorption band is observed, on changing from chloroform to acetone. It is not clear whether there is a limit to which an absorption band may be lowered or there is a weakening of the semi-bridging bond as a result of solvation.

Table 1 : Thione Complexes

Complex	Molecular Formula	L (= thione)	Method of Preparation*
54a	$[(h^5\text{-}C_5H_5)_2Mo_2(Co)_4L]$	$(4\text{-}CH_3OC_6H_4)_2CS$	II, III
54b	"	$(C_6H_5)_2CS$	II, III
54c	"	$(4\text{-}CH_3C_6H_4)_2CS$	II, III
54d	"	$4\text{-}CH_3OC_6H_4 \cdot CS \cdot C_6H_5$	I, III
54e	"	$(4\text{-}Me_2NC_6H_4)_2CS$	II
54f	"	$(4\text{-}FC_6H_4)_2CS$	II. III
54g	$[(h^5\text{-}C_5H_5)_2W_2(CO)_4L]$	$(4\text{-}Ch_3OC_6H_4)_2CS$	II, III
54h	"	$(C_6H_5)_2CS$	III
54j	"	$(4\text{-}CH_3C_6H_4)_2CS$	II, III
54k	"	$4\text{-}CH_3OC_6H_4C\ (S)\phi$	III
55b	$[(h^5\text{-}C_5H_5)_2Mo_2(CO)_nL_2]$	$(C_6H_5)_2CS$	II
55c	"	$(4\text{-}CH_3C_6H_4)_2CS$	II
55d	"	$4\text{-}CH_3OC_6H_4C(S)C_6H_5$	I, II
55f	"	$(4\text{-}FC_6H_4)_2CS$	II, III
56	$[(h^5\text{-}C_5H_5)_2Mo_2(CO)_4L]$	$C_{10}H_{14}S$ (adamantanethione)	I, II, III
57	$[(h^5\text{-}C_5H_5)_2Mo_2(CO)_nL_2]$	$C_{10}H_{14}S$ (adamantanethione)	I

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Table 1 : Thione Complexes (cont'd.)

Complex	Molecular Formula	L (= thione)	Method of Preparation*
58	$[(h^5\text{-}C_5H_5)\ Mo_2(CO)_4L]$	$C_{10}H_{16}S$ (thiocamphor)	I, II, III
59	$[(h^5\text{-}C_5H_5)\ Mo_2(CO)_nL_2]$	$C_{10}H_{16}$ (thiocamphor)	I
60	$[(h^5\text{-}C_5H_5)_2Mo_2(CO)_4L]$	$C_{10}H_{16}S$ (thiofenchone)	II
61	$[(h^5C\text{-}C_5H_5)_2Mo_2(CO)_4L]$	$(H_3C)_3C$-⟨O⟩-$C(S)$-$C(CH_3)_3$	III
62	"	⟨O⟩-Fe-⟨O⟩-$C(S)$-$C(CH_3)_3$	III
63	"	Thiosantonin (70)	I, III
64	"	$\Delta^{1,4}$-androstadiene-3-thione-17-one	I, III
65	$[(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4L]$	$C_{10}H_{16}S$ (thiocamphor)	I
66	"	$4\text{-}CH_3OC_6H_4C(S)C_6H_5$	III
67	"	$C_{10}H_{14}S$ (adamantanethione)	III
68	$[(h^5\text{-}C_5H_5)_2W_2(CO)_4L]$	$C_{10}H_{14}S$ (adamantanethione)	III
69	$[(h^5\text{-}C_5H_5)_2W_2(CO)_4L]$	$C_{10}H_{16}S$ (thiocamphor)	III

* These complexes were obtained:

I : by thermolysis,

II : by photolysis,

III : through $cp_2M_2(CO)_4$

COMPOUND	C	H	N			C	H	N		
54a	50.55	3.62	4.75	26.45	691	50.29	3.49	4.63	27.70	692.
54b	50.56	3.16	4.93	nd	nd	51.27	3.17	5.06		
54c	52.76	3.92	4.86	nd	nd	52.73	3.64	4.85		
54d	50.20	3.82	4.56	nd	nd	51.69	3.39	4.92		
54f	48.17	2.75	4.62	nd	nd	48.50	2.69	4.79		
54g	40.21	3.16	nd	nd	nd	40.10	2.77	-		
54h	40.10	2.57	3.61	nd	nd	40.10	2.49	3.97		
54j	41.37	3.16	nd	nd	nd	41.67	2.89	-		
54k	40.30	2.55	4.61	nd	nd	40.13	2.65	3.83		
55*	59.41	4.15	10.45	nd	nd	57.84	3.64	7.72		
55f*	52.65	3.00	7.19	nd	nd	53.22	2.90	7.10		
57*	53.03	5.08	7.68	nd	nd	53.26	4.96	8.36		
59*	53.00	6.00	8.78	nd	nd	52.99	5.47	8.33		
60	47.68	4.72	5.18	nd	nd	47.84	4.32	5.32		
63	50.15	3.43	nd	nd	nd	49.92	4.16	-		
64	53.31	4.24	nd	nd	nd	53.95	4.63	-		
68	37.47	2.91	4.34	nd	nd	37.13	3.09	4.13		
69	37.54	3.65	nd	nd	nd	37.03	3.34	-		
58	47.97	4.90	5.32	nd	nd	47.84	4.32	5.32		
56	48.13	3.95	5.45	30.24	610	48.00	4.00	5.33	31.96	60

1. nd = not done

* For $[cp_2Mo_2(CO)_nL_2]$ (L = thione), n has been assumed to be equal to 4, which is not very different from when n equals 3.

Table 3 : Infrared Data

Compound	$\nu_{C\equiv O}$ (cm^{-1})	Other Absorption Bands (cm^{-1})
54a	1958(w), 1936(vs), 1864(s), 1815(w)[2]	3074(w), 2993(vw), 2968(vvw), 1473-1633(w,b), 906(w), 767(w,b), 674(m,sh), 1237-1327(w,b), 1178(w), 1035(w).
54b	1959(w), 1938(vs), 1864(s), 1816(w)[2]	1598(vw), 1501(vw,b)1026(vw), 1007(vw), 841(w), 501(w)574(w), 557(w), 22974(vw,6).
54c	1962(w), 1938(vs), 1867(s), 1823(w,b)	1582(w), 1259(vvw), 1044(vw), 834(vw,b), 584(vw,b).
54d	1961(w), 1938(vs), 1867(s), 1818(m)[2]	2970(vw), 2858(w), 1604(w), 1510(w), 1413)vvw), 1440(vv), 1297(w), 1255(e), 1176(vw), 1035(vw), 927(vvw), 800(vw), 697(vw), 552(vw)
54e	1950(w), 1927(vs), 1849(s), 1805[1]	
54f	1962(w), 1941(vs), 1872(s), 1826(w)[2]	1549 (m,b), 1154(w), 834 (m,b).
54g	1946(w), 1924(vs), 1847(s), 1804(w)[2]	3140(vw), 3035(vvw), 2975(vw), 2925(vvw), 2853(vw), 1603(w), 1504(w), 1454(vw), 1432(vvw), 1283(w), 1253(w), 1160(w), 1020(w), 895(m,sh), 622(vw), 585(vw).
54h	1954(w), 1926(vs), 1851(s), 1811(w)[2]	3121 (w,b), 1441(vw,b), 700-900(m,b).
54j	1955(w), 1929(vs), 1853(s), 1813(w)[2]	3155(vvw), 3058(vw), 2990(vw), 2958(vw), 2903(vvw), 835(w,b), 585(w,b).
54k	1952(w), 1926(vs), 1849(s), 809(w)[2]	1176(w,sh), 1037(w), 839(m,b).
55b	1994(m,sh), 1959(m,sh), 1890(w,sh), 1812(m,sh)[3]	1598(vw), 1115(w), 1015(m,b), 672(m,b).
55c	1973(m), 1856(m)[1]	
55d	1969(s), 1892(m)[1]	
55f	1986(vs,sh), 1879(m)[2]	1504(s,b), 1235(w), 1154(s), 1105(m,sh), 800(m,sh).
56	1964(s,sh), 1954(w), 1922(vs,sh), 1817(w), 1875(s)[2]	790(m,b), 2990(w,b).

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Table 3 : Infrared Data (cont'd.)

Compound	$\nu_{C\equiv O}$ (cm^{-1})	Other Absorption Bands (cm^{-1})
57	1930(s,b), 1812(vw), 1760(m,b)[1]	2903(m), 2850(w), 1600(w), 1096(w), 968(w), 903(w), 825(w,b).
58	1961(s), 1925(vs), 1870(m), 1814(w)[2]	2968(w,b), 2888(vw), 805(w,b), 587(m,b).
59	1930(s,b); 1840(w), 1776(s,b)[1]	2930(m), 2870(w), 1600(w), 1430(w), 1385(w), 1370(w), 1103(w), 1002(w), 892(w), 815(w).
60	1950(w), 1918(vs), 1852(s), 1810(w)[1]	2870(vw), 2920(w,b), 1440(vw), 1380(vw), 1355(vw), 990-1140(w,b), 600-850(w,b).
61	1965(w), 1942(vs), 1870(m), 1808(w)[2]	
62	1957(w), 1934(vs), 1864(m), 1815(w)[2]	
63	1957(w), 1937(vs), 1864(s), 1818(vvw)	1780(w, $\nu_{C=O}$), 3090(vvw), 2998(vvw), 2954(vvw), 2914(vvw), 2884(vvw), 1141(vw), 1122(w), 1015(vw), 922(vw), 899(w,sh), 834(m,b).
64	1948(w), 1938(vs), 1873(s), 1829(w)[2]	3051(vvw), 2966(w), 2921(vvw), 2881(vvw), 1745($\nu_{C=O}$), 836(m,b), 581(w,b).
65	1954(vs,sh), 1916(vs), 1859(m,b), 1801(w)[2]	1582(vw), 1461(vw), 1071(w,b), 794(vw,v), 581(vw,b).
66	1952(w), 1934(vs,b), 1859(vs,b), 1808(w)[1]	3109(vw), 2956(vw), 2860(vw), 1603(w), 1511(w,b), 1304(vw), 1109(vvw), 1032(w), 877(vvw), 834(w), 598(vw), 589(vw), 553(w).
67	1969(s), 1957(w), 1925(vs), 1878(m), 1820(w)[2]	790(m,b).
68	1960(w), 1947(w), 1916(vs), 1859(s), 1808(w)[2]	2917(w), 2878(w,b), 813(w,b), 578(m,b).
69	1950(m), 1917(vs), 1849(s), 1788(s)[1]	2985(w,b), 855(m,b)[1].

Infrared spectra were obtained in: 1 : $CHCl_3$, 2 : CCl_4, 3 : n-hexane, 4 : DMSO, 5 : Acetone, 6 : CH_2Cl_2, 7 : C_6H_6.

COMPOUND	cyclopentadienyl chemical shifts (δppm)	Other chemical shifts (δppm)
54a	5.26(S,5H,cp), 4.61(S,5H,cp)[1]	3.77(d,6H,-OCH_3)7.11(pheny-H),6.74(pheny-H),6.59(pher H)
54b	5.25(S,5H,cp), 4.58(S,5H,cp)[1]	6.94-7.41 (complex, broad, 10H, pheny-H)
54c	5.24(S,5H,cp), 4.61(S,5H,cp)[1]	2.29(S,3H,CH_3),2.26(S,3H.CH_3),6.76-7.28(complex,8H, phenyl H)
54d	4.46(s,cp′), 4.50(s,cp), 4.86(s,cp),4.90(s,cp′)[7]	3.32(s,-OCH_3),3.27(s,-OCH_3),6.36-7.56(complex, 9H, phenyl H)
54f	4.66(s,5H,cp), 5.26(s,5H,cp)[1]	0.68-7.38(complex, 8H, phenyl H)
54g	4.75(s,5H,cp),5.38(s,5H,cp)[1]	3.75(s,6H,OCH_3),6.54(phenyl H),6.63(phenyl H), 6.76 phenyl H), 7.03(phenyl 4) 7.15(phenyl H)
54h	4.72(s,5H,cp),5.38(s,5H,cp)[1]	7.13(multiplet, broad, 10H, pheny H)
54j	4.74(s.5H,cp),5.38(s,5H,cp)[1]	2.28(s,3H,-CH_3),2.31(S,3H,-CH_3),6.86-7.35(multiplet,8H phenyl H)
54k	4.73(s,cp)4.77(s,cp) 5.36(s,cp),5.41(s,cp)[1]	3.78(s,3H,-OCH_3),6.65-7.32(complex,9H, phenyl H)
55b	4.37(s,5H,cp),5.08(s,5H,cp)[1]	6.6-7.93(complex, 20H, phenyl H)
55f	4.47(s,5H,cp),5.14(s,5H,cp)[1]	5.57-8.10(complex, 16H, phenyl H)
56	5.26(s,cp′), 5.34(s,cp+cp′) 5.37(s,cp)[1]	1.5-2.8 (complex, 14H)
57	5.29(s,5H),5.22(s,5H)[1]	1.54-2.18(complex, 28H, methylene H)
58	5.27(s,cp′),5.32(s,cp), 5.46(s,cp′), 5.49(s,cp)[1]	0.69-2.00(complex),0.68(-CH_3),0.72(-CH_3),0.97(-CH_3), 1.04(-CH_3)
59	5.01(s,5H),5.11(s,5H)[1]	0.72-1.25(complex,32H)
60	5.31(s,5H),5.43(s,5H)[1]	0.73-2.7 (broad, 16H)

	shifts (δppm)	
61	4.99(s,cp), 5.80(s,cp)[1]	1.34(s,$-CH_3$), 7.00-8.00(complex, phenyl H).
63	5.39(s,cp), 5.36(s,cp)[1]	5.23(s,H_{21}),5.07(s,H_{21}),4.16(s,H_{12}),3.99(s,H_{12}), 4.87(broad,-c-o-c-H),0.66-2.66(complex)
65	4.96-5.53(complex,8H)[1]	2.25(s,cp-CH_3^*),2.08(s,cp-CH_3^*+Cp-CH_3^*+cp-CH_3^*),0.69-1 (complex)
66	5 .53-4.53(multiplet), 4.43-4.00(complex)	3.74(s,3H,-OCH_3),1.68(s,cp-CH_3^*),1.76(s,cp-CH_3^*),1.9 cp-CH_3^*+ cp-CH_3^*), 6.57 - 7.57 (complex, 9H, phenyl
67	4,86-5.63(complex,8H)[1] 5.39(s,cp),5.43(s,cp′)	2.04(s,cp-CH_3^*);2.10(s,cp-CH_3^*),2.13(s,cp-CH_3^*),2.21(cp-CH_3),1.29-2.79(complex,14H)
68	5.47(s,cp),5.50(s,cp′)[1]	1.50-3.00(complex, 14H)
69	5.34(s,cp),5.40(s,cp′), 5.55(s,cp+cp′)[1]	1.72(broad, 1.28(broad),0.97(C_3 broad,-CH_3),0.93(b CH_3),0.91 (broad, - CH_3),0.71(s,-CH_3), 9.68(s,-CH
45a	5.33	
45b	5.38	

KEY

1 : Deuterochloroform

7 : Benzene - d_6

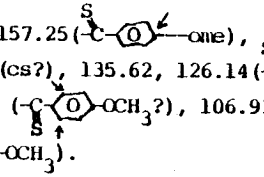
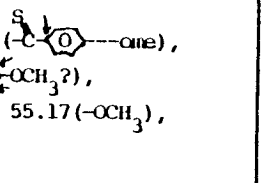
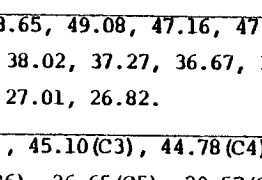
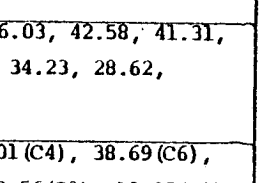
cp : cyclopentadienyl group of the major isomer

cp′ : cyclopentadienyl group of the minor isomer

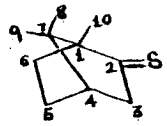
s : singlet

* : proton(s) responsible for the chemical shift

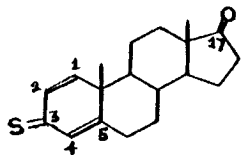
Table 5 : ^{13}C NMR Data[1] of some Monothione Complexes

Compound	Cyclopentadienyl (CP) & Olefinic (OFN) Chemical Shifts (δppm)	Metal Carbonyl (C≡O)[2] Chemical Shifts (δppm)	Other Chemical Shifts (δppm)
54a	93.60(cp), 95.83(cp).	244.45(SBCO), 236.93, 234.65, 233.41.	158.85, 157.25(), 147.05(), 136.41(cs?), 135.62, 126.14(), 112.66 (), 106.93(CS), 55.17(-OCH_3), 55.33(-OCH_3).
56	93.23(cp), 93.58(cp'), 94.10(cp), 94.82(cp').	245.30(SBCO), 239.90, 238.9, 237.50, 236.40, 236.00, 235.90.	54.40, 53.65, 49.08, 47.16, 47.03, 46.03, 42.58, 41.31, 38.56, 38.02, 37.27, 36.67, 35.69, 34.23, 28.62, 28.46, 27.01, 26.82.
58	93.99(cp'), 93.36(cp), 93.02(cp'), 92.38(cp).	244.64(SBCO), 239.30, 238.13, 236.32, 235.57, 235.43.	45.56(C3), 45.10(C3), 44.78(C4), 44.01(C4), 38.69(C6), 37.94(C6), 26.65(C5), 20.57(C8), 19.56(C9), 19.05(C9), 14.21(C10), 61.28(C1), 114.94(C5), 104.84(C5), 49.32(C7), 49.17(C7)[3].
64	94.41(cp), 93.19(cp), 135.90(C1), 123.99(C2), 132.95(C4), 131.75(OFN) 130.20(OFN), 129.03(OFN), 144.17(OFN?), 142.00(OFN?), 140.76(OFN?), 135.91(OFN).	220.64, 220.48, 216.57(CO?).	53.20, 50.94, 47.72, 39.86, 35.69, 32.65, 32.48, 32.14, 31.95, 31.51, 31.40, 22.61, 21.75, 20.82, 20.61, 20.49, 14.09, 13.82, 216.57(CS?).
68	93.91(cp), 92.46(cp), 91.75(cp).	Not observed.	55.12, 48.94, 46.34, 45.50, 42.51, 42.25, 41.53, 38.46, 38.34, 37.92, 37.64, 36.94, 35.93, 34.25, 28.15, 27.15, 26.86.

1. All spectra were obtained in $CDCl_3$.
2. SBCO = semi-bridging carbonyl carbon.
3. Some of these assignments were made with the help of carbon-13 data for free thiocamphor (V) and work done by Paul V. Demarco et al in reference 65.



V (in 58)



71 (in 64)

Table 6B : ^1H NMR data of $[cp_2M_2(CO)_4L]$ (L=thione; M=Mo,W) in the cyclopentadienyl region: Mo Vs. W

L	cyclopentadienyl chemical shifts (δppm)		
	M=Mo	M=W	$\Delta\bar{\nu}(H_B)$[1]
$(4\text{-}CH_3OC_6H_4)_2C{=}S$	5.26,4.61	5.38,4.75	7.8
$(C_6H_5)_2C5$	5.25,4.58	5.38,4.72	8.1
$(4\text{-}CH_3C_6H_4)_2CS$	5.24,4.61	5.38,4.74	8.1
$C_{10}H_{14}S$ (adamantanethione)	5.26,5.34,5.37	5.39,5.43,5.47,5.50	7.2
$C_{10}H_{16}S$ (thiocamphor)	5.27,5.32,5.46,5.49	5.34,5.40,5.55	4.5
2CO (carbon monoxide)	5.33	5.38	3.0

1. $\Delta\nu$ is the average of the differences between corresponding cyclopentadienyl chemical shifts for M=Mo and M=W. For example for $L=\Phi_2CS$ (refer to figure 2)

$$\Delta\nu_1 = cp_1(W) - cp_1(Mo)$$
$$\Delta\nu_2 = cp_2(w) - cp_2(Mo)$$
$$\Delta\nu = \frac{\Delta\nu_1+\Delta\nu_2}{2}$$

Table 7 : Values of [X] and [Y] (in intensity units) of 54d as a function of time at 274.5K

Time (sec)	RAW DATA		AVERAGED DATA	
	[X]	[Y]	[X]	[Y]
0	27.00	20.00	30.19	22.36
103	25.00	23.00	27.37	25.18
269	25.00	24.00	26.81	25.74
375	25.00	27.00	25.27	27.29
497	25.00	27.00	25.27	27.29
837	27.00	30.00	24.89	27.66
1031	23.00	27.00	24.18	28.38
1188	22.00	28.00	23.12	29.43
∞	29.00	39.00	22.41	30.14

Table 8 : Values of [X] and [Y] (in intensity units) of 58 as a function of time at 29

Time (sec)	RAW DATA		AVERAGED DATA	
	[X]	[Y]	[X]	[Y]
0	39.00	14.00	40.98	14.71
62	39.50	16.00	39.64	16.06
147	38.50	16.00	39.34	16.35
234	39.00	18.50	37.77	17.92
332	38.00	20.50	36.18	19.52
431	35.00	20.00	35.44	20.25
508	34.50	20.50	34.93	20.76
642	34.00	22.00	33.81	21.88
803	34.00	22.50	33.51	22.18
986	33.50	22.50	33.32	22.38
1218	32.50	23.50	32.32	23.37
1450	32.00	23.00	32.40	23.29
1548	32.00	23.50	32.11	23.58

Table 9 : Kinetic Data (rate constants) at Temperature Tn (K).

Compound	SET I			SET II			SET III			SET IV		
	T_1 (K)	Rate constants $x10^3$ (s^{-1}) Forward Process	Rate constants $x10^3$ (s^{-1}) Reverse Process	T_2 (K)	Rate constants $x10^3$ (s^{-1}) Forward Process	Rate constants $x10^3$ (s^{-1}) Reverse Process	T_3 (K)	Rate constants $x10^3$ (s^{-1}) Forward Process	Rate constants $x10^3$ (s^{-1}) Reverse Process	T_4 (K)	Rate constants $x10^3$ (s^{-1}) Forward Process	Rate constants $x10^3$ (s^{-1}) Reverse Process
54d	264.0	0.39± 0.05	0.33± 0.05	269.5	1.22± 0.33	0.91± 0.24	274.5	2.51± 1.06	1.70± 0.70	278.5	2.79± 0.94	1.92± 0.63
58	283.0	0.18± 0.05	0.32± 0.09	286.0	0.42± 0.14	0.65± 0.20	293.0	0.98± 0.19	1.34± 0.25	298.0	1.84± 0.34	2.58± 0.46

Table 10 : Thermodynamic Data.

Compound	Energy of Activation, Ea (kcal/mol)		$\Delta G^{\ddagger}$ (kcal/mol)		$\Delta H^{\ddagger}$ (kcal/mol)		$\Delta S^{\ddagger}$ ($cal mol^{-1} K^{-1}$)		$\log_{10} A$ (A = Arrhenius constant)	
	Forward Process	Reverse Process	Forward Process	Reverse Process	Forward Process	Reverse Process	Forward Process	Reverse Process	Forward Process	Reverse Process
54d	21.13± 4.49	18.63± 4.20	19.31± 0.20	19.73± 0.20	20.59± 4.49	18.09± 4.20	4.28± 16.66	-5.48± 15.61	14.12± 3.64	11.99± 3.41
58	24.61± 4.72	22.06± 4.41	21.14± 0.19	20.97± 0.18	24.03± 4.72	21.49± 4.41	9.70± 16.16	1.74± 15.13	15.33± 3.54	13.59± 3.31

Table II

Comparison between population and dipole moments of isomers (taken from reference 51).

Compound	Dipole moment (D)	
	Minor Isomer	Major Isomer
Benzene diazocyanide		5.00
P-toluene diazocyanide		4.40
p-chlorobenzene diazocyanide	2.93	3.73
p-bromobenzene diazocyanide	2.91	3.78
o-bromobenzene diazocyanide	3.79	5.32
p-nitrobenzene diazocyanide	2.04	1.47
2:4:6-tribromobenzene diazocyanide	2.50	4.00
α-naphthalene diazocyanide	3.20	5.60
β-naphthalene diazocynanide	4.00	6.90
Diphenyl-4-diazocyanide	4.50	5.50

Table 12 : Concentration of the Gauche Isomer of $[cp_2Mo_2(CO)_6]$ in different solvents

(taken from reference 29)

	Intensity of Peak Assigned to Gauche Isomer (> 2000cm-1)	Dielectric Constant of Solvent
Cyclohexane	0.00	2.02
Benzene	0.30	2.27
Carbon disulphide	0.20	2.64
Chloroform	0.44	4.70
THF	1.00	7.36
Methylene chloride	0.50	8.90
Acetone	1.50	20.70
Nitrobenzene	1.10	34.60
Acetonitrite	1.64	36.20
DMSO	1.98	47.60

Table 13 : Isomerisation of 58 in Different Solvents

Solvent	Dipole moment of Solvent (D)	Dielectric constant of solvent	$\frac{1}{K_r} = {}^{[X]}/_{[Y]}$ (K_r = equilibrium constant)
CCl_4	0.00	2.24	1.12
Benzene-d_6	0.0	2.28	1.26
$CDCl_3$	1.15	4.80	1.40
THF-d_8	1.75	7.58	2.38
Acetone-d_6	2.69	20.70	3.90
Nitromethand-d_3	3.56	35.87	8.60
DMSO-d_6	3.90	46.68	possibly a reaction took place

* average mean deviation for $1/Kr \simeq \pm 0.26$

Table 14 : Infrared and ^1H NMR Data of $cp_2M_2(CO)_4L$ (M=Mo, W; L=thione) in Different Solvents

Compound	Solvent*	Cyclopentadienyl chemical shifts (δ) assigned to $cp_2M_2(CO)_4L$ (L=thione, M=Mo, W) : I	Other chemical shifts (δ) present in the cyclopentadienyl region : II	II/I	ν C≡O (cm^{-1})
54a	DMSO	4.78 (s,sh), 5.42 (s,sh).	5.36 (s,sh), 5.46 (s,sh).	0.39	2121 (vvw), 2011 (w,b), 1955 (w). 1928 (s), 1854 (m), 1811 (vw).
	Acetone	4.73 (s,sh), 5.39) s,sh).	–	0.00	1948 (w), 192 (vs), 1850 (s), 1812 (w).
	Chloroform	4.68 (s,sh), 5.30 (s,sh).	–	0.00	1963 (cw), 1938 (vs), 1862 (s), 1810 (vw).
54c	DMSO	4.71 (s,sh), 5.40 (s,sh).	5.34 (s.sh), 5.47 (s.sh).	0.27	–
	Chloroform	4.63 (s,sh), 5.23 (s.sh).	–	0.00	1960 (vw), 1934 (vs), 1858 (s), 1808 (w).
54d	DMSO	4.67 (s,sh), 4.73 (s.sh), 5.35 (s,sh), 5.40 (s,sh).	5.30 (s.sh), 5.44 (s.sh).	0.40	–
	Acetone	–	–	–	1959 (w), 1934 (cw), 1865 (m).
	Benzene	4.46 (s,sh), 4.50 (s,sh), 4.86 (s,sh), 4.90 (s,sh).	–	0.00	–
	Chloroform	4.61 (s,sh), 4.67 (s,sh), 5.25 (s,sh), 5.28 (s,sh).	–	0.00	1960 (vw), 1933 (vs).
56	DMSO	5.50 (s,sh).	5.35 (s,sh), 5.46 (s,sh).	0.08	2121 (w), 2016 (s,b), 1954 (s,b), 1856 (s) 1851 (m), 1809 (w).
	Chloroform	5.26 (s,sh), 5.34 (s,sh), 5.37 (s,sh).	–	0.00	1960 (cw), 1933 (vw), 1858 (s), 1805 (vw).
58	DMSO	5.45 (s,sh), 5.67 (s,sh).	5.36 (s,sh), 5.53 (s,sh).	0.09	2127 (vvw), 2007 (m,b), 1949 (vs), 1909 (vs), 1852 (s), 1805 (w).
	Benzene	4.75 (s,sh), 4.81 (s,sh), 4.97 (s,sh).	–	0.00	–
	Chloroform	5.23 (s,sh), 5.27 (s,sh), 5.41 (s,sh), 5.43 (s,sh).	–	0.00	1958 (s), 1920 (s), 1869 (m), 1795 (w).

.../cont. on next page

Table 14 : Infrared and ^1H NMR Data of $cp_2M_2(CO)_4L$ (M=Mo, W; L=thione) in Different Solvents (cont'd.)

Compound	Solvent*	Cyclopentadienyl chemical shifts (δ) assigned to $cp_2M_2(CO)_4L$ (L=thione, M=Mo, W) :I	Other chemical shifts (δ) present in the cyclopentadienyl region :II	II/I	ν C≡O (cm^{-1})
54f	DMSO	4.71(s,sh), 5.33(s,sh).	5.32(s,sh), 5.42(s,sh).	0.77	-
54h	DMSO	4.78(s,sh), 5.49(s,sh).	5.40(s,sh), 5.57(s,sh).	0.14	2113(vw), 2013(m,b), 1959(w), 1915(vs), 1838(s), 1800(vw).
54k	DMSO	4.78(s,sh), 4.83(s,sh).	5.44(s,sh), 5.61(s,sh).	0.33	2103(vw), 2003(w,b), 1948(w), 1901(vs), 1841(s), 1803(vw).
68	DMSO	5.69(s,sh).	-	0.00	2117(w,b), 2017(vs,b), 1950(vs,b), 1892(s), 1836(s), 1800(w).
	Chloroform	5.39(s,sh), 5.43(s,sh), 5.47(s,sh), 5.50(s,sh).	-	-	-
	Carbon Tetra-Chloride	-	-	-	1960(w), 1947(w), 1916(vs), 1859(s), 1808(w).

*Deuterated solvents were used for all ^1H NMR spectra. Normal solvents were used for all infrared spectra.

Mo(1)...C(5)	2.317(10)	S-Mo(1)-C(2)	106.4(2
Mo(1)...C(6)	2.373(9)	C(2)-Mo(1)-C(16)	113.9(3
Mo(1)...C(7)	2.375(8)	Mo(1)-Mo(2)-C(3)	90.2(2
Mo(1)...C(8)	2.328(9)	Mo(1)-Mo(2)-C(4)	123.0(2
Mo(1)...C(9)	2.291(13)	S-Mo(2)-C(2)	85.8(2
Mo(2)...C(10)	2.322(7)	S-Mo(2)-C(3)	111.8(2
Mo(2)...C(11)	2.364(9)	C(2)-Mo(2)-C(4)	139.3(3
Mo(2)...C(12)	2.374(10)	C(16)-C(15)-C(20)	105.5(6
Mo(2)...C(13)	2.315(9)	C(21)-C(15)-C(22)	115.8(7
Mo(2)...C(14)	2.302(8)	Mo(1)-C(16)-C(15)	122.7(4
Mo(2)-Mo(1)-C(1)	108.9(2)	S-C(16)-C(17)	120.3(4
Mo(2)-Mo(1)-C(16)	75.6(1)	C(15)-C(21)-C(23)	115.2(7
S-Mo(1)-C(1)	115.4(2)	C(18)-C(21)-C(24)	113.8(8
		Plane(1)-Plane(2)	115.0*

* Plane(1) and Plane(2) correspond to three-membered rings Mo1-C16-S and Mo1-Mo2-S respectively. The angle indicated is the one that the two rings form with each other.

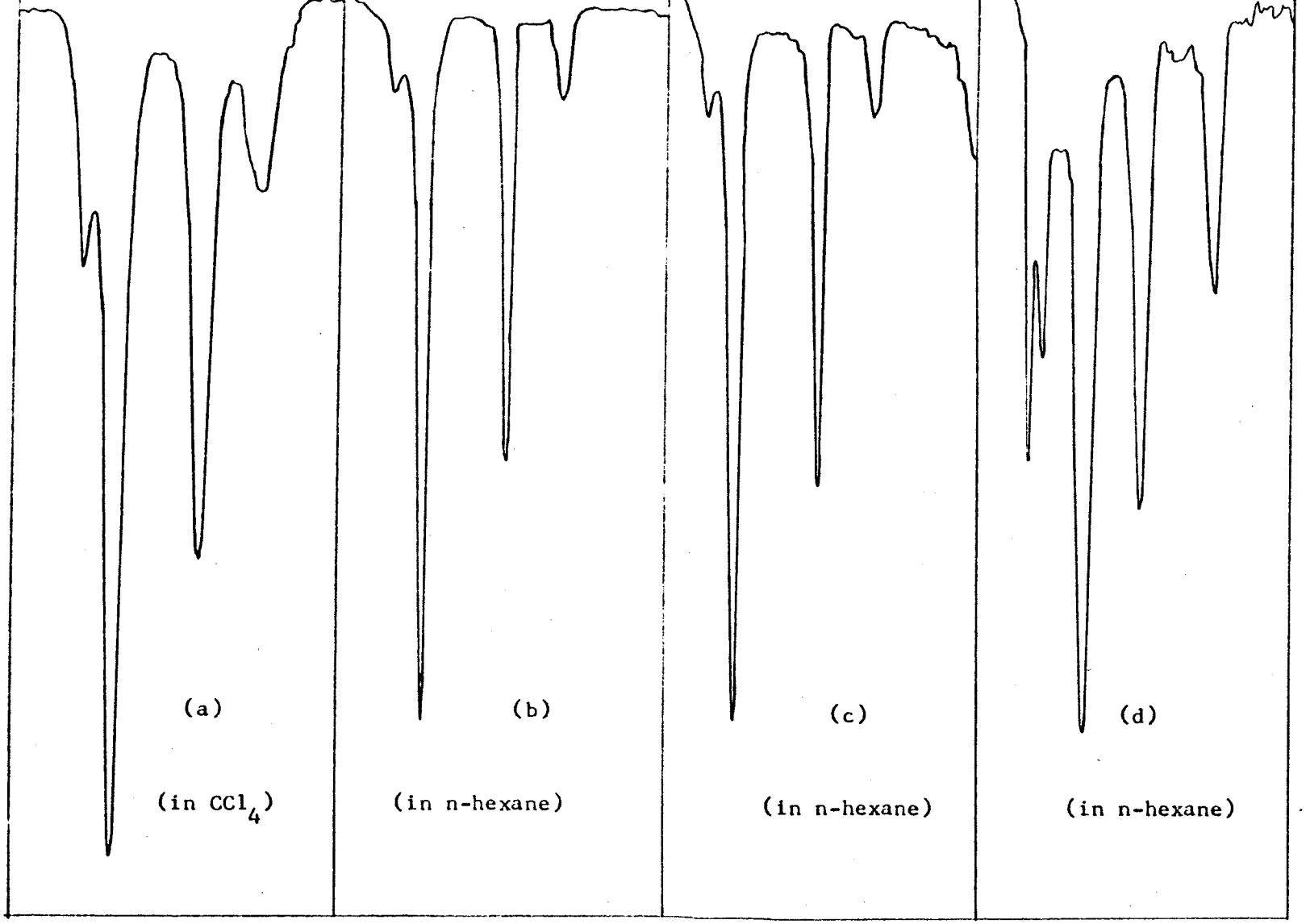


Figure 1: Infrared spectra (ν C≡O) of $\{Cp_2Mo_2(CO)_4L\}$: L equals (a) $(4\text{-}H_3COC_6H_4)_2CS$, (b) $(C_6H_5)_2CS$, (c) $4\text{-}H_3COC_6H_4\cdot C(S)\cdot C_6H_5$ and (d) adamantanethione.

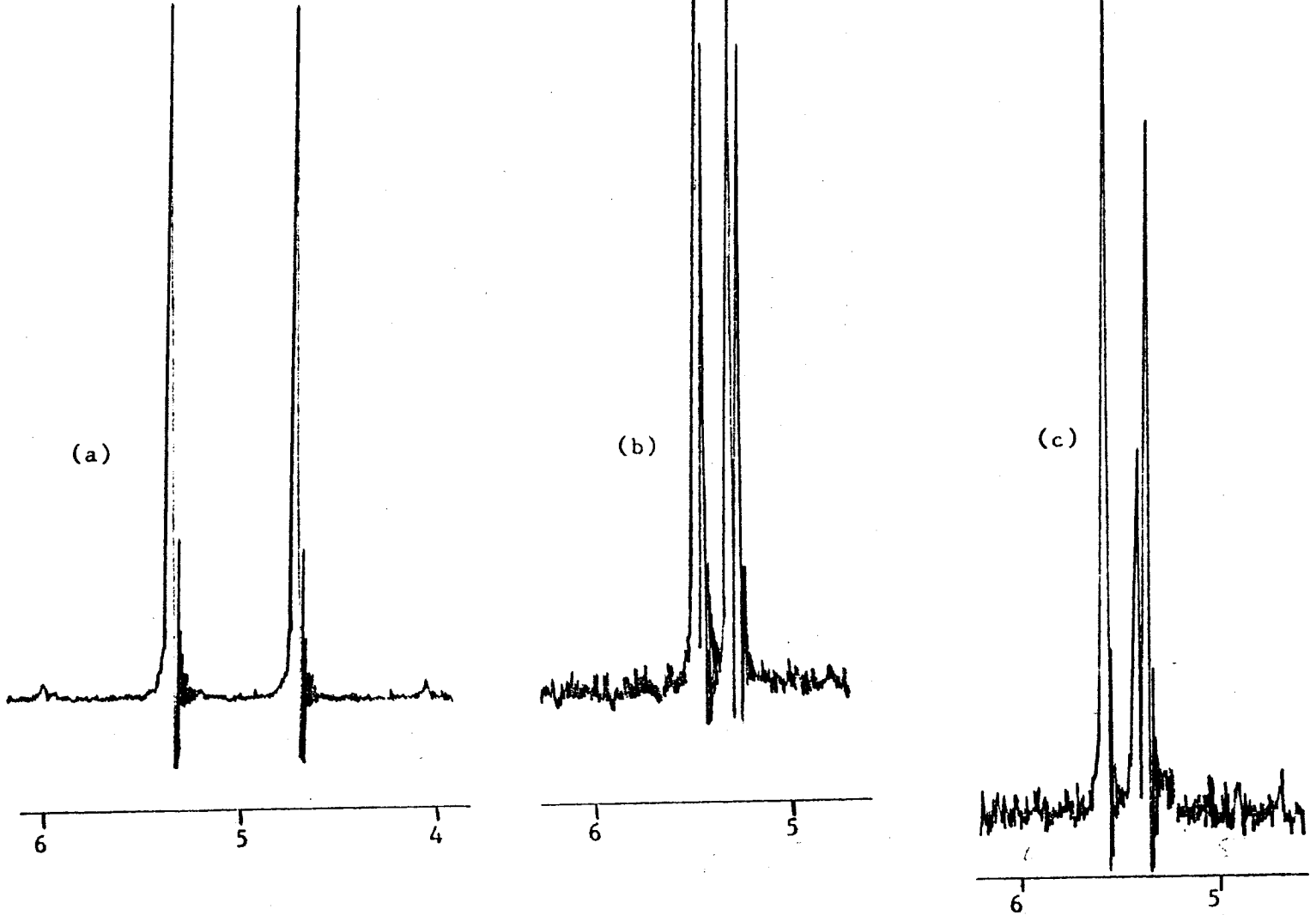


Figure 4: Proton cyclopentadienyl chemical shifts (δ ppm) of $\{Cp_2M_2(CO)_4L\}$ (in $CDCl_3$):
(a) M=Mo, L=$(C_6H_5)_2CS$, (b) M=Mo, L=thiocamphor and (c) M=W, L=thiocamphor.

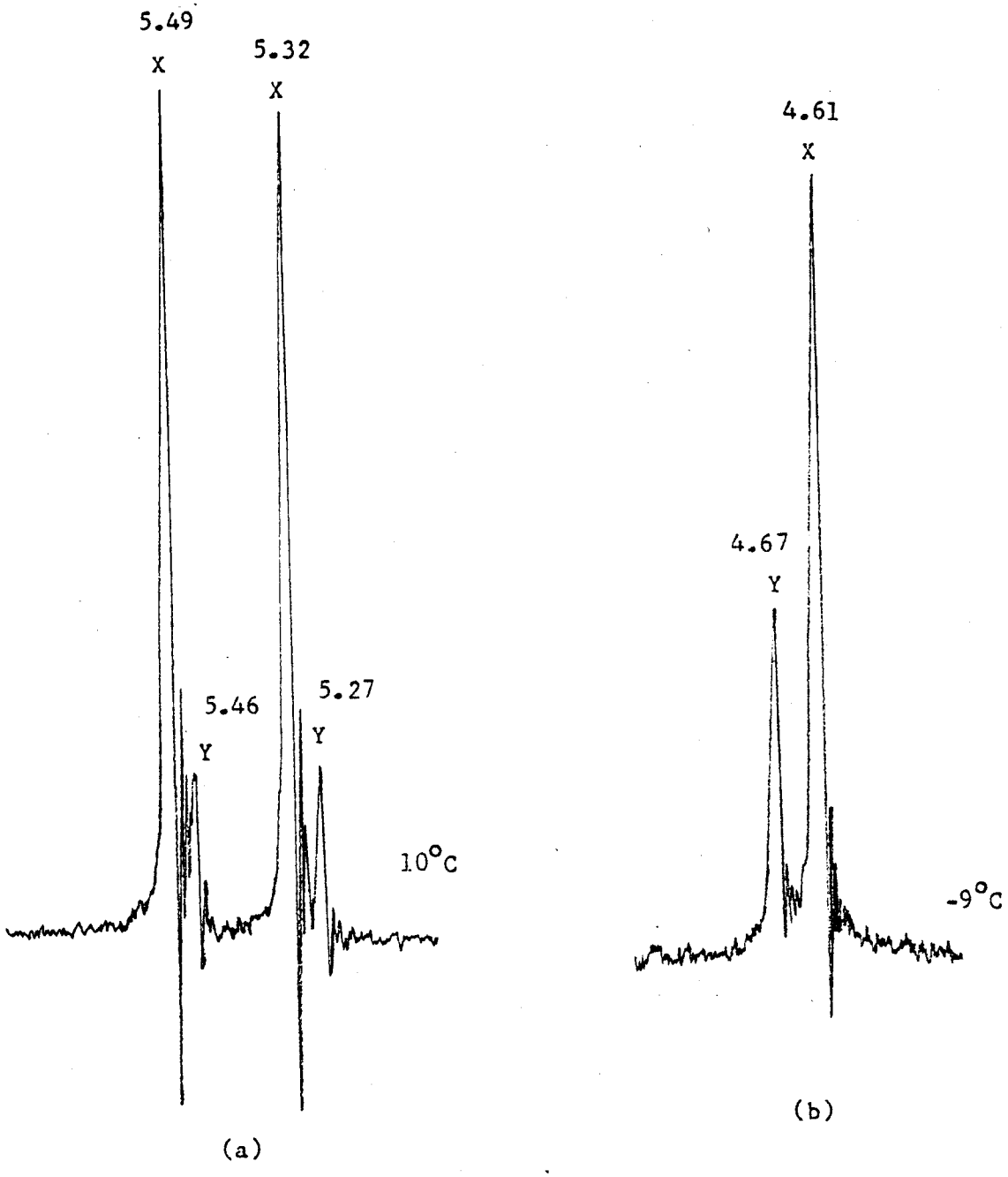


Figure 5: Cyclopentadienyl proton chemical shifts (δ ppm) of $\{Cp_2Mo_2(CO)_4L\}$ in $CDCl_3$ at low temperature: (a) L=thiocamphor and (b) L=p-$H_3COC_6H_4 \cdot C(S) \cdot C_6H_5$ (only the pair at higher field is shown).

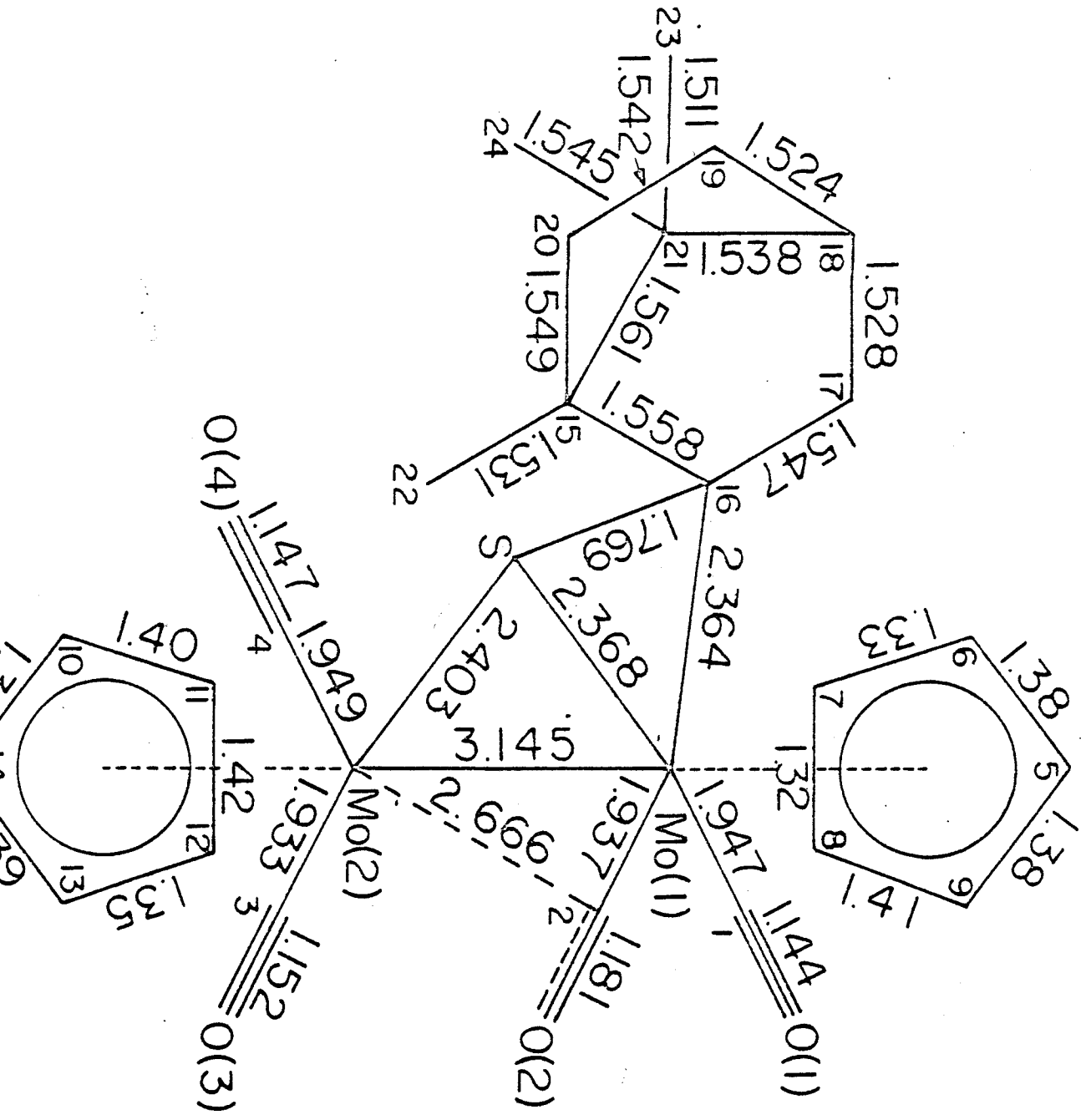


Figure 6:- X-ray picture of 58: bondlengths.

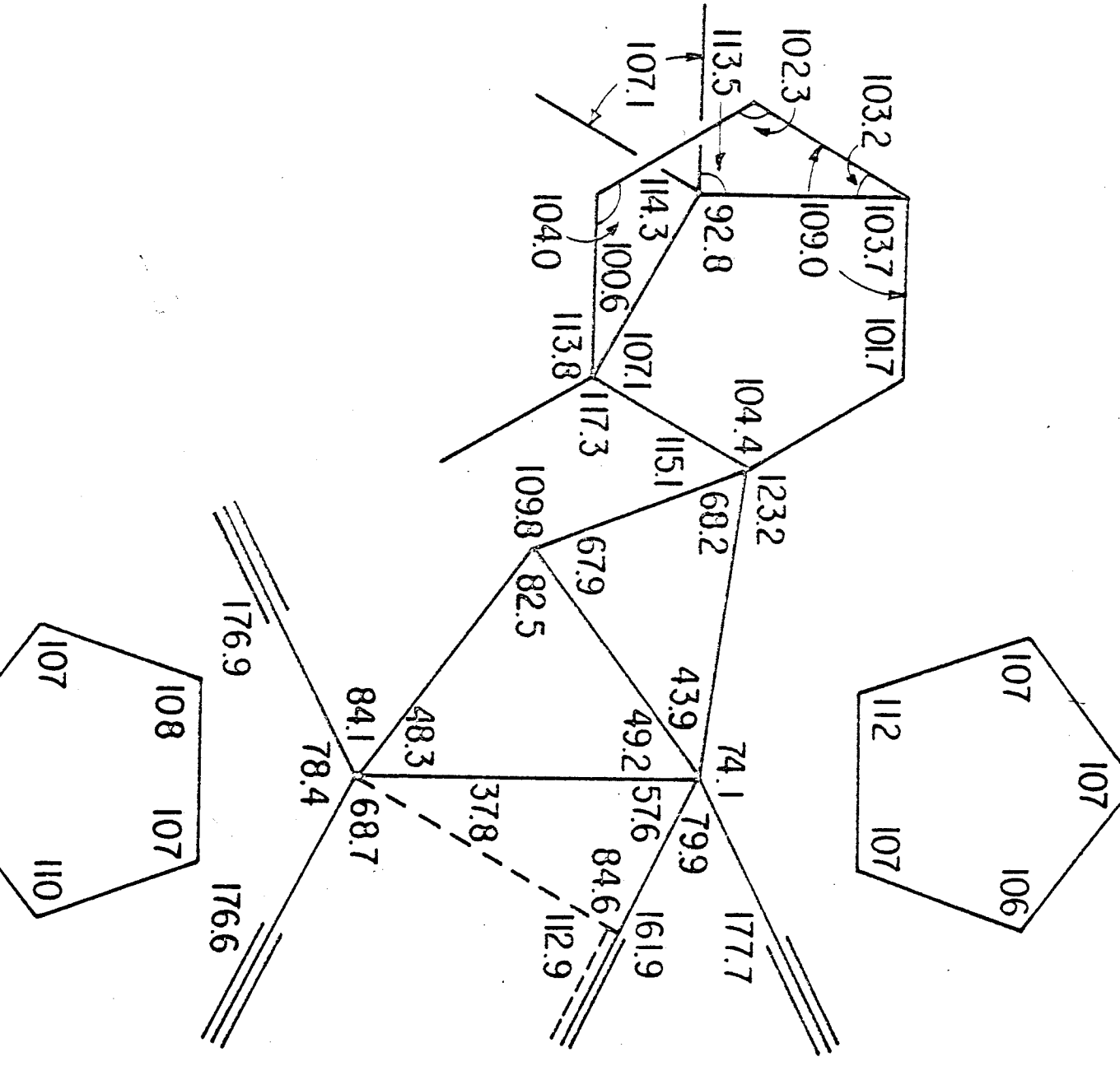


Figure 7:- X-ray picture of 58: bondangles

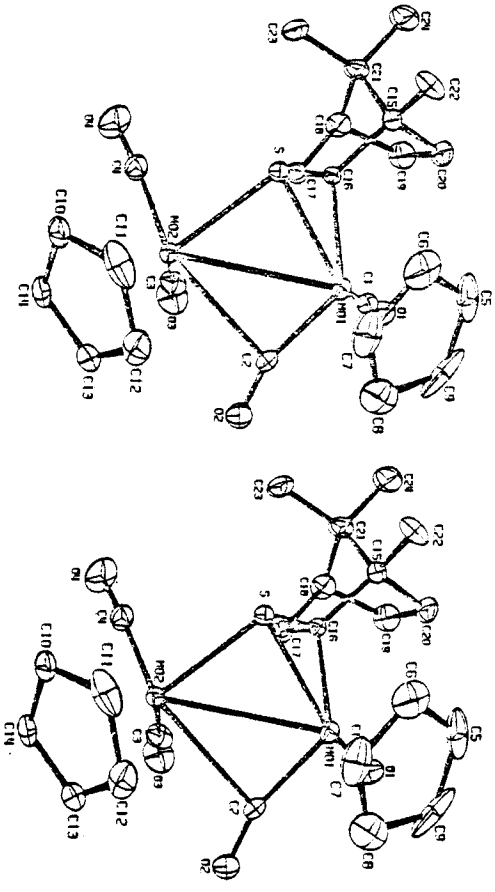


Figure 8:- An ORTEP diagram of 58: orientation of atoms.

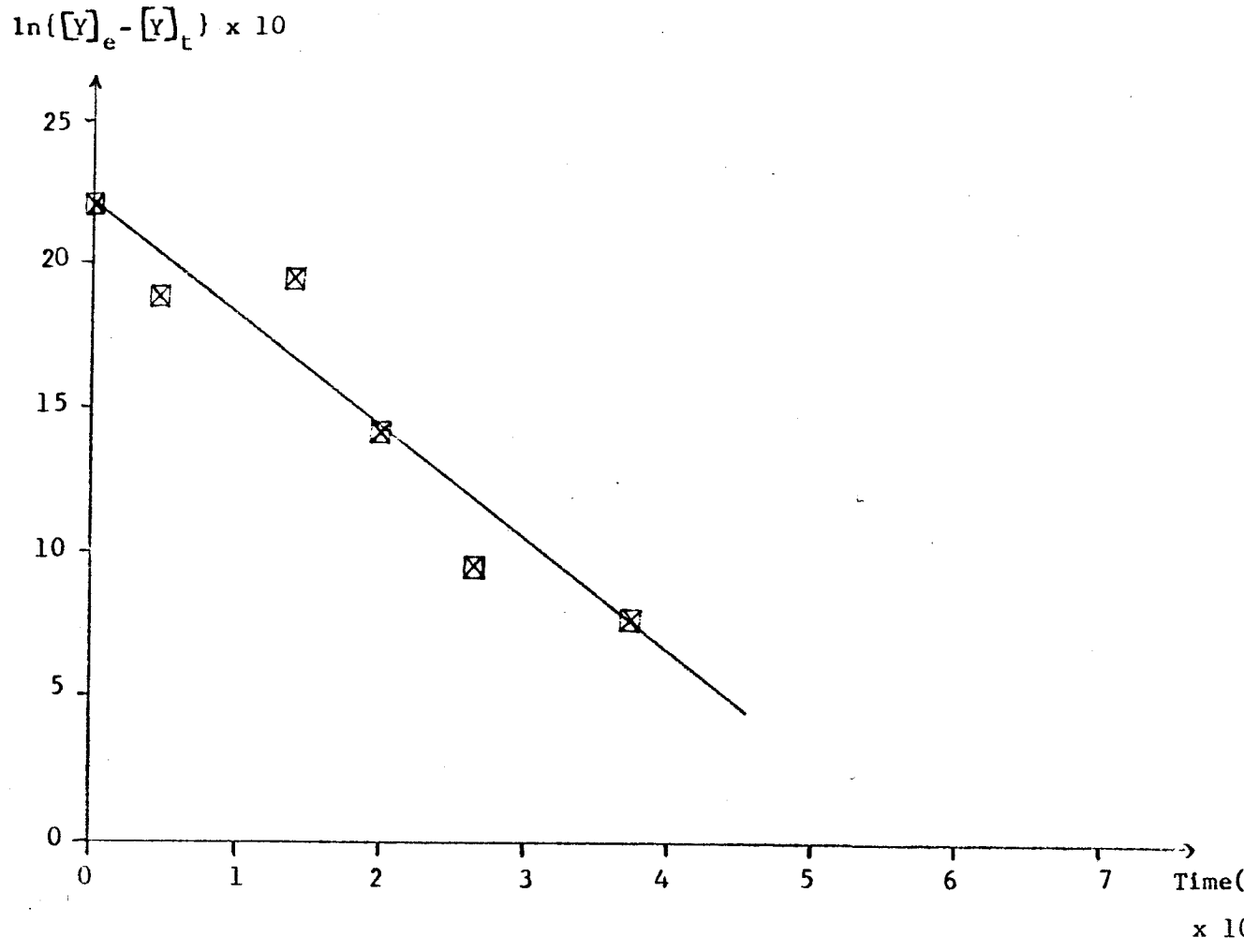


Figure 9: A plot of $\ln\{[Y]_e-[Y]_t\}$ against time for 54d at 274.5K.

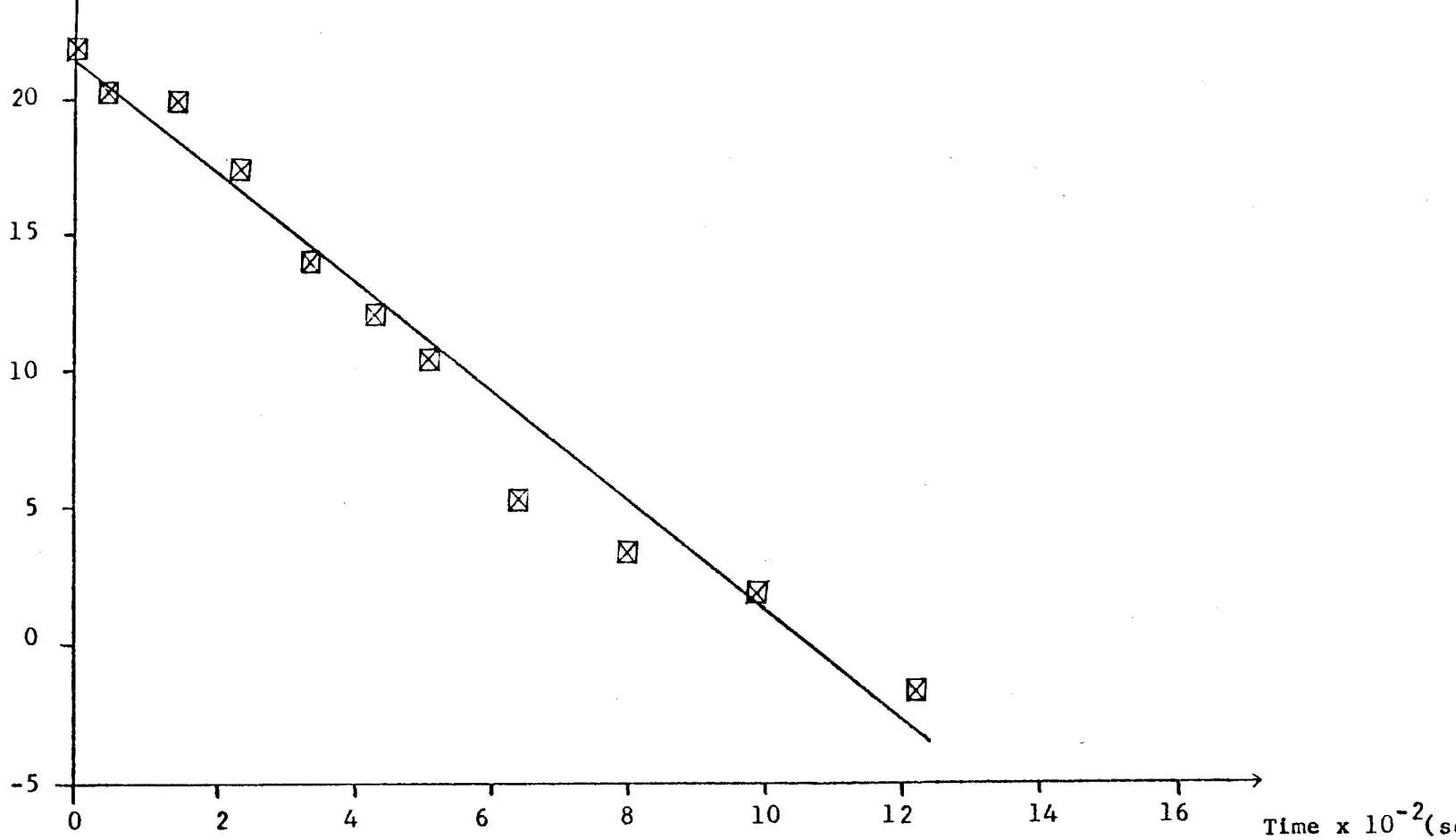


Figure 10: A plot of $\ln([Y]_e-[Y]_t)$ against time for 58 at 293K.

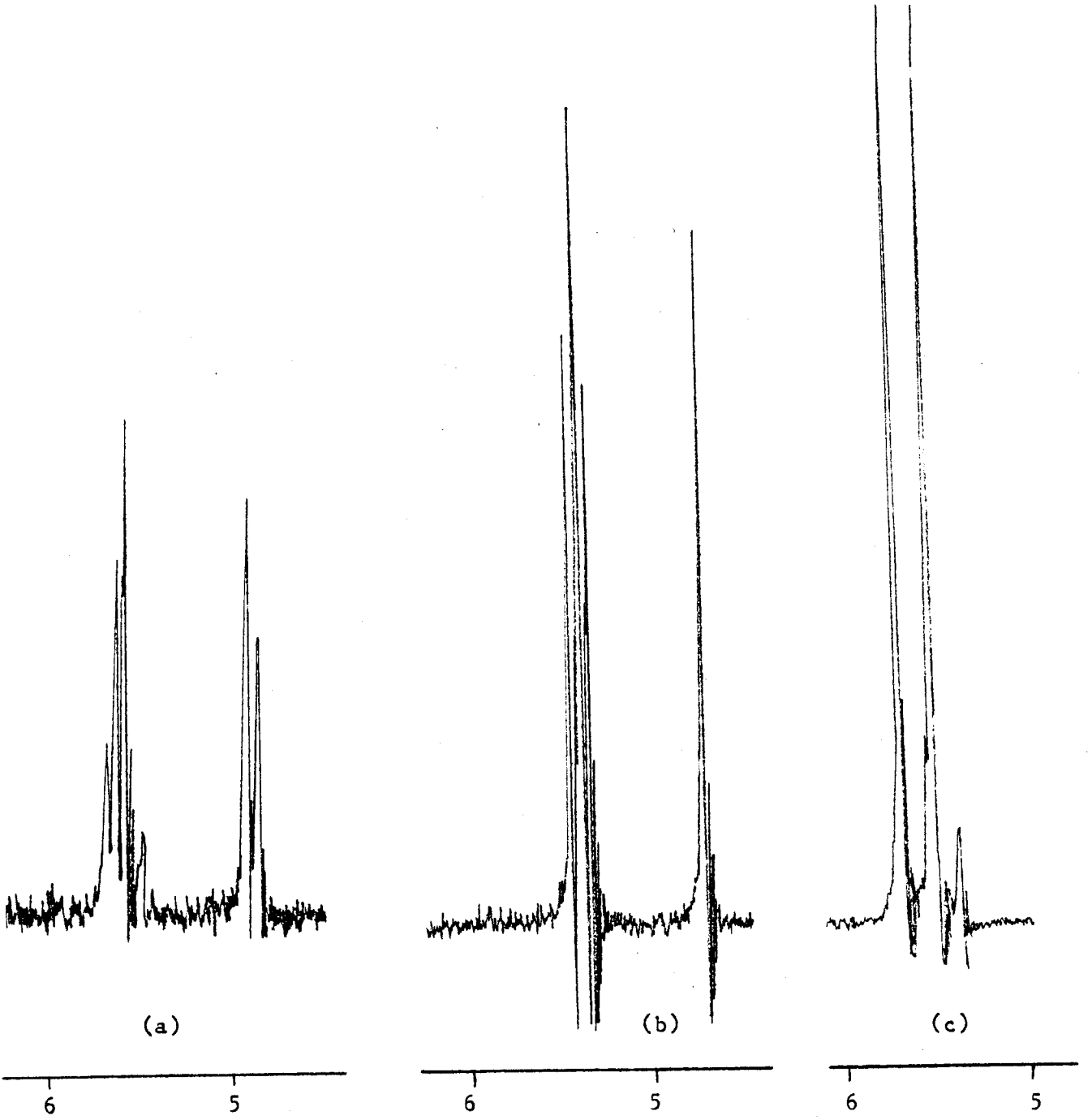


Figure 11: Cyclopentadienyl proton chemical shifts (δ ppm) of $\{Cp_2Mo_2(CO)_4L\}$ in DMSO: (a) L=4-$H_3COC_6H_4 \cdot C(S) \cdot C_6H_5$ (b) L=(4-FC_6H_4)CS and (c) L=thiocamphor.

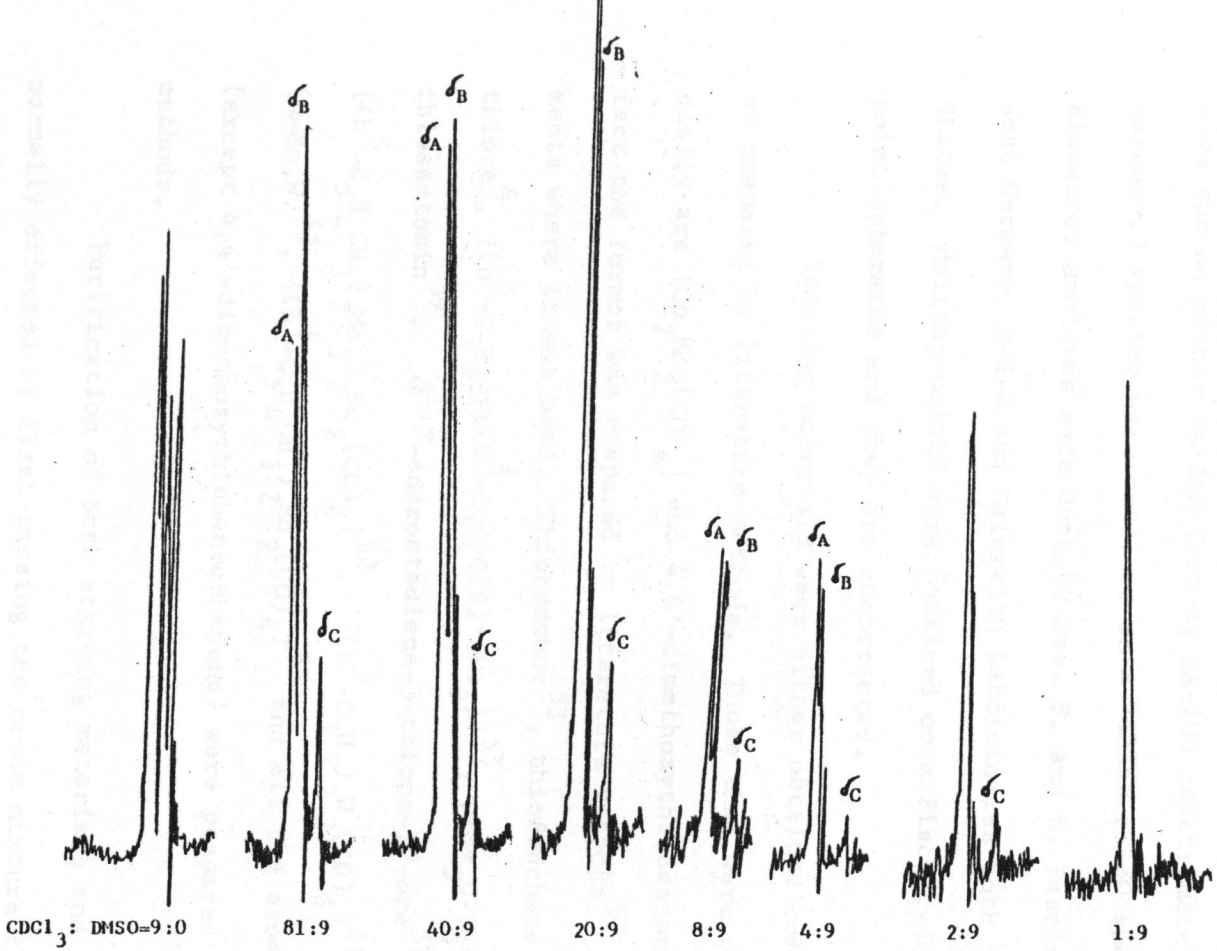


Figure 12: Cyclopentadienyl proton chemical shifts (δ ppm) of $\{Cp_2W_2(CO)_4$(adamantanethione)$\}$ as a function of the $CDCl_3$:DMSO ratio.

D. EXPERIMENTAL.

Infrared spectra were obtained on either BECKMANN IR-20 or UNICAM SP1100 infrared spectrophotometers. Proton NMR spectra were run on either VARIAN T-60 or HA-100 spectrometers, whereas carbon-13 spectra were obtained on a VARIAN FT-80 spectrometer. Elemental analyses were done by Drs. F. and E. Pascher, Bonn, West Germany; M-H-W and Galbraith Laboratories both of the United States. Melting points were obtained on a Fischer-Johns melting point apparatus and they are uncorrected.

Starting materials were either obtained commercially or prepared by literature methods. Those that were obtained commercially are $\{Cp_2Mo_2(CO)_6\}$ and 4,4'-dimethoxythiobenzophenone. In fact the former was prepared by literature methods[52] for most experiments where it was used. Thiocamphor[53], thiofenchone[54], adamantanethione[4], $\{(h^5\text{-}C_5H_5)Fe(h^5\text{-}C_5H_4{\cdot}C(S){\cdot}CMe_3)\}$[55], $p\text{-}Me_3C{\cdot}C_6H_4{\cdot}C(S){\cdot}CMe_3$[53], thiosantonin[59], $\Delta^{1,4}$-androstadiene-3-thione-17-one[59], $\{(h^5\text{-}C_5H_4CH_3)_2Mo_3)_2Mo_2(CO)_6\}$[52], $\{(h^5\text{-}C_5H_5)_2W_2(CO)_6\}$[52], $\{(h^5\text{-}C_5H_5)_2M_2(CO)_4\}$ (M=Mo,W)[52], $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4\}$[52] and all the aromatic thiones[53] (except 4,4'-dimethoxythiobenzophenone) were prepared by literature methods.

Purification of both starting materials and products was normally effected by first passing the crude mixture through a chromatographic column followed by either recrystallisation from a suitable solvent or distillation depending on whether the compound

exists as a solid or an oil at room temperature. All the choromatographic materials such as alumina, silica gel and florisil were obtained commercially.

All solvents were dried either by distillation from $LiAlH_4$ under a nitrogen atmosphere or over an appropriate molecular sieve before use. All reactions as well as separation of products were conducted under a dry nitrogen atmosphere.

Photolytic reactions were effected by exposing appropriate benzene solutions to UV radiation (3000Å) from a Rayonet Photochemical reactor.

Determination of Kinetic and Thermodynamic Data

The proton NMR spectra of both 54d and 58 showed four resonance signals in the cyclopentadienyl region two of which were assigned to each isomer. Let X and Y be the major and minor isomers respectively (Figure 13). When the solid of each of 54d and 58 was dissolved in cold deuterochloroform (between -40°C and 25°C) the concentration of X and Y decreased and increased respectively with time, at constant temperature until an equilibrium was reached. For each complex (i.e. 54d and 58) the concentration of each isomer was determined by integrating the appropriate resonance signals as a function of time. For each of the two complexes this was done at four different temperatures (Table 9). Some of the raw data for 54d and 58 are shown in tables 7 and 8 respectively. Due to some irregularities raw data were averaged according to appendix I. Some of the averaged data are shown in Tables 7 and 8 for 54d and 58 respectively.

Assuming that X and Y are in equilibrium and that the mechanism of interconversion is first order equations (1) and (2) may be derived[61]. The assumption that X and Y interconvert by a first order mechanism is supported by the fact that when

$$X \underset{k_y}{\overset{k_x}{\rightleftharpoons}} Y$$

Scheme XXII

$\ln\{[Y]_e - [Y]_t\}$ was plotted against time an almost straight line curve[60] was obtained for both 54d (Figure 9) and 58(Figure 10). In Scheme XXII, k_x and k_y are forward and backward rate constants respectively. In equations (1) and (2) $[X]_o$ is the initial concentration of X, $[X]_t$ is the concentration of X at time t, $[X]_e$ is the equilibrium concentration of X, $[Y]_o$ is the initial concentration of Y, $[Y]_t$ is the concentration of Y at time t, $[Y]_e$ is the concentration of Y at equilibrium and Keq is the equilibrium constant.

$$\ln\left(\frac{[Y]_e - [Y]_o}{[Y]_e - [Y]_t}\right) = \left\{\frac{[X]_o + [Y]_o}{[Y]_e}\right\} kt \qquad (1)$$

$$K\ eq = \frac{k_x}{k_y} = \frac{[Y]_e}{[X]_e} \qquad (2)$$

Using equation (1) values of k_x (Table 9) for both 54d and 58 at the four temperatures (Table 9) were calculated by the least squares method.[71] Using the known values of $[Y]_e$, $[X]_e$ and k_x values k_y (Table 9) were determined from equation (2).

Activation energies (Ea) (Table 10) were obtained from equation (3) by the least squares method.[71] In equation (3) Ea, k', R, T and A are the activation energy, rate constant, gas constant, absolute temperature and the pre-exponential constant respectively.

$$\ln k' = -\frac{Ea}{RT} + \ln A \qquad (3)$$

Furthermore using equations (4)[60] and (5)[60] values of Gibb's free energy of activation ($\Delta G^{\neq}$), entropy of activation ($\Delta S^{\neq}$) and enthalpy of activation ($\Delta H^{\neq}$) were determined. In equation (4) k and h are Boltzmann and Planck's constants respectively.

$$\ln k' = \left(\frac{kT}{h}\right)\exp\left(-\frac{\Delta G^{\neq}}{RT}\right) = \left(\frac{kT}{h}\right)\exp\left(\frac{\Delta S^{\neq}}{R}\right)\cdot\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \qquad (4)$$

$$Ea = \Delta H^{\neq} + RT \qquad (5)$$

Thermodynamic and kinetic data are recorded in Tables 10 and 9 respectively.

<u>Preparation of $\{(h^5\text{-}C_5H_5)_2Mo_2(CO)_4((p\text{-}CH_{30}C_6H_4)_2CS)\}$</u>

A solution of 0.258 g (1 mmol) of $(p\text{-}CH_{30}C_6H_4)_2CS$ and 0.246 g (0.5 mmol) of $\{Cp_2Mo_2(CO)_6\}$ in benzene (70 ml) was irradiated under a nitrogen atmosphere for 39 hours. At the end of the reaction all the molybdenum carbonyl had been used up leaving some unreacted thioketone and the colour of the solution had changed from a purple-blue to a brownish colour.

The solvent was then rotary-evaporated until there was just enough solvent to keep the product in solution. The solution was then chromatographed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company). Elution with 1:5 benzene/hexane gave a blue solution which on evaporation yielded 0.11 g of unreacted thioketone. Elution with benzene gave a brown viscous solid. This was then crystallised from 1:4 diethyl either/hexane in an acetone-dry ice bath to give 0.22 g (64%) of brownish green shiny crystals of product (54a). Analytical, infrared, and proton and carbon-13 NMR data are listed in Tables 2, 3, 4 and 5 respectively.

Preparation of $\{Cp_2Mo_2(CO)_4(\Phi_2CS)\}$

A solution of 0.32g (1.6 mmol) of Φ_2CS and 0.393g (0.8 mmol) of $\{Cp_2Mo_2(CO)_6\}$ in benzene (100 ml) was irradiated for 44 hours. The colour of the solution changed from a purplish red to brown. The solvent was then evaporated to leave a brown semi-solid, which was dissolved in a minimum amount of benzene and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Some unknown colourless components were eluted with hexane. Elution with 1:1 hexane/benzene gave 0.13 g brown (major) and colourless (minor) components. All attempts to separate the two components failed. By comparing the ^1H NMR and IR data to that of 54a the brown component was assigned the molecular formula $\{Cp_2Mo_2(CO)_4(\Phi_2CS)\}$, 54b. ^1H NMR and IR data are listed in Tables 4 and 3 respectively. The colourless component was identified as benzophenone.

Preparation of $\{Cp_2Mo_2(CO)_4(\Phi_2CS)_2\}$, 55b

A solution of 0.792g (4 mmol) of Φ_2CS and 0.98g (2 mmol) of $\{Cp_2Mo_2(CO)_6\}$ in benzene (90 ml) was irradiated for 41 hours. A very small brownish-purple spot and a large brown spot were seen on the TLC plate. While $\{Cp_2Mo_2(CO)_6\}$ was still present no thiobenzophenone was seen on the TLC plate.

Then 0.79 g (4 mmol) of thiobenzophenone was added to the reaction mixture and irradiation was continued for another 54 hours. Now there was no $\{Cp_2Mo_2(CO)_6\}$ but a very small amount of the brown component and a considerable amount of unreacted thiobenzophenone was present. In addition there was a brown purple component.

The solvent was reduced (under vacuum) to about 10 ml and the resulting solution was then placed on a column of alumina (80-200 mesh, A-540). Elution with hexane gave unreacted impure thione.

Elution with 1:1 hexane/benzene afforded a minute amount of a brown semi-solid consisting of one brown and several other colourless components. From the infrared data the mixture was found to contain 54b, which could not be isolated so that no analytical data could be obtained.

Elution of a red-purple band with benzene gave a red-purple solution. As the red-purple band moved down the column it left a trail of green material probably due to decomposition. Evaporation of the solvent gave a purple viscous solid which was then chromatographed on a preparative TLC plate to give about 0.61 g ($\simeq$46%) of slightly impure red purple solid of 55b,

m.p.150°C (dec). Due to continuous decomposition in both solution and solid state satisfactory analytical data (Table 2) could not be obtained. ^1H NMR and infrared data are listed in Tables 4 and 3 respectively.

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with $(p\text{-}CH_3C_6H_4)_2CS$

A solution of 0.226 g (1 mmol) of $(p\text{-}CH_3C_6H_4)_2CS$ and 0.245 g (0.5 mmol) of $Cp_2Mo_2(CO)_6$ was irradiated in benzene (50 ml) for 35 hours. At the end of the reaction the colour of the solution had changed from purplish red to brown. The solvent was reduced (under vacuum) to about 10 ml. The crude product was then placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 1:1 benzene/hexane afforded 0.092 g of the unreacted thione. Elution was continued with the same solvent mixture to remove all the organic components. Elution with benzene gave a brown viscous solid which was then crystallised from hexane at -78°C to give 0.185 g (56%) of $\{Cp_2Mo_2(CO)_4(p\text{-}CH_3C_6H_4C(S)C_6H_4CH_{3\text{-}p})\}$, 54c, as dark-green crystals; m.p. 125°C(dec). Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Elution with benzene gave a mixture of red and colourless crystals. All attempts to isolate the two components failed. From infrared data (Table 3) the red component was assigned the molecular formula $\{Cp_2Mo_2(CO)_4((p\text{-}CH_3C_6H_4)_2CS)_2\}$, 55c.

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with $p\text{-}CH_3OC_6H_4\overset{S}{\overset{\|}{C}}\phi$

A solution of 0.735 g (1.5 mmol) of $\{Cp_2Mo_2(CO)_6\}$ and 0.342 g (1.5 mmol) of thione was refluxed until all the thione was consumed. The solution was cooled to room temperature, concentrated to a small volume and then chromatographed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Co.).

Elution with 1:10 benzene/pet. ether (60-80°C) yielded 0.2243 g of unreacted $\{Cp_2Mo_2(CO)_6\}$. A brown band was eluted with 1:3 benzene/pet. ether (60-80°C) to give a brown viscous solid. The solid was then dissolved in a minimum of diethyl ether. To the resulting solution was added twice the volume of hexane. Concentration of the solution by evaporation resulted in the appearance of a brown solid. This was left to stand in the refrigerator for about an hour. The solid was then washed with cold hexane and dried to yield 0.103 g (15%) of a brown powdery solid of $\{Cp_2Mo_2(CO)_4(p\text{-}CH_3OC_6H_4C(S)\phi)\}$, 54d, m.p. 105°C (dec).

In one of the three attempts made to prepare 54d an impure orange semi-solid was obtained. From infrared data (Table 3) it was assigned the molecular formular $\{Cp_2Mo_2(CO)_n(p\text{-}CH_3OC_6H_4C(S)\phi)_2\}$, 55d (n=either 3 or 4).

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with Adamantanethione

A solution of 0.332 g (2 mmol) of thioketone and 0.98 g (2 mmol) of metal carbonyl was refluxed in benzene (40 ml) until there was no thioketone present (36 hours). Evaporation of

solvent (under vacuum) gave a purple-brown solid. This was then dissolved in a minimum of benzene and placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Half the red band of $\{Cp_2Mo_2(CO)_6\}$ was eluted with hexane. With the same solvent the rest was eluted together with a purple component to give a purple solution. Evaporation of solvent resulted in a purple viscous solid (A). Elution with benzene gave a dark purple viscous solid (B). With 4:1 hexane/diethyl ether was eluted a purple and a purplish violet band (C).

Portions A, B and C were combined and passed through a column of silica gel (60-200 mesh, Baker analysed reagent). Elution with 1:1 hexane/benzene removed all the $\{Cp_2Mo_2(CO)_6\}$. A mixture of green, purple and purplish violet compounds was eluted with additional 1:1 hexane/benzene.

The top of the column was found to contain an undissolved purple solid, which was then transferred to a medium sized pore sintered glass funnel and eluted with chloroform. Evaporation from a mixture of hexane and chloroform ($\simeq$1:1) gave 6.2 mg. of purple crystals.

The mixture was then placed on a preparative TLC plate of silica gel (HF -254, EM reagents) which was dipped into a bath containing 1:4 diethyl ether/hexane. One broad poorly resolved band developed. After about 8 hours the front part of the band was scraped off the plate and eluted with chloroform to give 83.3 mg of a purple crystalline solid. The remaining mixture was then eluted

and passed through a column of silica gel (60-200 mesh, Baker analysed reagent). Elution with hexane gave a purple solution, evaporation of which yielded 9.5 mg of a purple crystalline solid.

The three portions of the purple solid were all found to correspond to the compound of molecular formula $\{Cp_2Mo_2(CO)_n$ (adamantanethione)$_2\}$, 57 (n=either 3 or 4), m.p. 150°C(dec.). The total yield for 57 was found to be 0.102 g (14%, n=4). Analytical, infrared and ^1H NMR data is listed in Tables 2, 3 and 4 respectively.

A green viscous solid obtained on elution with 1:1 hexane/benzene was then recrystallised from hexane to give 56.6 mg (5%) of a green crystalline solid of $\{Cp_2Mo_2(CO)_4$(adamantanethione)$\}$, 56, m.p. 122°C. The yield of 56 could be improved to as high as 50% by using an excess of thione (say about 4 times the amount used in this procedure). Analytical data, infrared and proton and carbon-13 NMR data are listed in Tables 2, 3, 4 and 5 respectively.

Elution with 1:4 diethyl ether/hexane yielded a rather impure purple-red solid (8.2 mg). ν C≡O($CHCl_3$): 1949(vw), 1896(vs), 1829(w) cm^{-1}. ^1H NMR($CDcl_3$): 5.20 (s,cp), 1.50-2.53 (complex, broad, saturated C-H). This compound was never obtained in a pure enough form for elemental analysis.

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with thiofenchone

A solution of 0.305 g (1.8 mmol) of thiofenchone and 0.49 g (1 mmol) of $\{Cp_2Mo_2(CO)_6\}$ was refluxed in benzene (40 ml) for 19 hours. No reaction was observed. The reaction mixture was then transferred to a quartz irradiation vessel and irradiated for

94 hours. Thin layer chromatography indicated the presence of violet grey product as well as both starting materials.

The solvent was evaporated (under vacuum) to leave a dark brown solid. This was dissolved in a minimum amount of benzene and chromatographed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Thiofenchone together with other components was eluted with 1:1 hexane/benzene. Further elution with 1:1 hexane/benzene gave 0.20 g of unreacted $\{Cp_2Mo_2(CO)_6\}$. Elution with benzene gave a dark violet purple viscous solid. Crystallisation from hexane yielded 54.3 mg (15%) of $\{Cp_2Mo_2(CO)_4(\text{thiofenchone})\}$, 60, which was obtained as a violet purple shiny crystalline solid, m.p. 143°C.

Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Reaction of $\{CpMo(CO)_3\}_2$ with thiocamphor

A solution of 0.246 g (0.5 mmol) of $\{Cp_2Mo_2(CO)_6\}$ and 0.337 g (2 mmol) of thiocamphor in benzene (50 ml) was refluxed for 56 hours.

The solvent was evaporated leaving a purplish violet solid. The solid was then dissolved in a minimum of benzene and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Elution with 1:1 benzene/hexane gave a red solid. This was found to be mostly a mixture of colourless components with no $\nu C{\equiv}O$ absorption bands in the infrared spectrum. Further elution

with 1:1 benzene/hexane yielded a purple viscous solid. This was then crystallised from hexane to give 66 mg (17%) of purple crystalline $\{Cp_2Mo_2(CO)_n(thiocamphor)_2\}$, 59 (n=either 3 or 4), m.p. 248°C(dec.). Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Elution with benzene gave a green-brown solid which was then crystallised from hexane affording 96 mg (32%) of $\{Cp_2Mo_2(CO)_4(thiocamphor)\}$, 58, m.p. 190°C. This complex was also prepared by irradiating a benzene solution of the same starting materials as used in the above procedure. A much higher yield of about 74% was obtained. Analytical, infrared and ^1H NMR data are recorded in Tables 2, 3 and 4; carbon-13 NMR data are recorded in Table 5.

Reaction of $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_3\}_2$ with Thiocamphor

A solution of 0.541 g (3 mmol) of thiocamphor and 0.777 g (1.50 mmol) of the metal carbonyl in benzene (50 ml) was refluxed until no $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6\}$ was seen on the TLC plate. Evaporation of solvent left a green semi-solid, which was dissolved in a minimum of benzene and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

A mixture of yellow and purple components was eluted with hexane. Evaporation of solvent left a purplish-red semi-solid which was found to be mainly composed of unreacted thione. The yellow component could not be isolated and hence characterised.

Elution with benzene gave a green viscous solid. The solid was then dissolved in a minimum amount of 1:1 diethyl

ether/hexane mixture. Ether was then slowly evaporated resulting in the formation of shiny green crystals. Filtration of the solid and vacuum drying afforded 0.71 g (75%) of $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4$ (thiocamphor)}, 65, m.p. 189°C(dec.). Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Reaction of $\{CpMo(CO)_3\}_2$ with $(p\text{-}FC_6H_4)_2CS$

A solution of 0.735 g (1.5 mmol) of the metal carbonyl and 1.17 g (5 mmol) of $(p\text{-}FC_6H_4)_2CS$ was irradiated for about 32 hours. At the end of the reaction the colour of the solution had changed from a purple-blue to brown. The solvent was evaporated to leave a brown blue semi-solid. This was then dissolved in a minimum of benzene and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Elution with hexane yielded 0.354g of unreacted thione. Elution with 1:1 benzene/hexane afforded a small amount of a mixture of uncharacterised products.

Elution with benzene gave a purple compound which was found to contain some colourless compounds. The solvent was then reduced to about 10 ml and placed on a column of silica gel(60-200 mesh, Baker Analysed reagent).

A purple band was eluted with benzene to give 60 mg (≈6%) of not very pure brown-purple powdery solid of $\{Cp_2Mo_2(CO)_4$ $(p\text{-}FC_6H_4C(S)C_6H_4F\text{-}p)_2\}$, 55f (n=either 3 or 4) m.p. 160°C. An attempt to purify 55f further failed so that no analytical data was obtained. It was assigned the above structure by comparing its infrared and ^1H NMR data (Tables 3 and 4) with that of 59 and 57.

Reaction of $\{CpMo(CO)_3\}_2$ with $(p\text{-}Me_2NC_6H_4)_2CS$

A solution of 0.2284 g (1 mmol) of thioketone and 0.50 g (1 mmol) of the molybdenum carbonyl in benzene (80 ml) was irradiated until most of the molybdenum dimer was consumed.

The solvent was then evaporated to give a fluffy green solid. This was redissolved in a minimum amount of benzene and placed on a column of silica gel (60-200 mesh, Baker Analysed reagent).

Elution with benzene gave a green-yellow solution which on evaporation yielded a very small amount of green mixture of components, none of which was isolated or characterised.

Further elution with benzene gave a viscous yellow-brown solid which when examined on the TLC plate was found to contain four poorly separated components in almost equal amount. Attempts to isolate them failed. The mixture always left a green trail on both alumina and silica gel columns possibly due to decomposition.

In the $\nu C{\equiv}O$ region the infrared spectrum (in $CHCl_3$) of the mixture showed four absorption bands at 1950(vw), 1927(vs), 1849(ms) and 1805 cm^{-1}(vw). Due to the similarity between these infrared data and those of 54a (Table 3) the four absorption bands were assigned to the metal carbonyl stretching modes of the monothione complex $\{Cp_2Mo_2(CO)_4(p\text{-}Me_2NC_6H_4C(S)C_6H_4NMe_2\text{-}p)\}$, 54e.

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with Thiosantonin

A mixture of 0.494 g (1 mmol) of the metal carbonyl and 0.59 g(2.3 mmol) of thiosantonin in benzene (70 ml) was refluxed with stirring for 21 hours. At the end of the reaction there still was a small amount of $\{Cp_2Mo_2(CO)_6\}$ and the colour of the solution had changed from dark red to brownish green.

The solution was rotary evaporated to give a brown-green solid which was then dissolved in a minimum of chloroform and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Elution with chloroform gave unreacted $\{Cp_2Mo_2(CO)_6\}$ followed by a fluffy brown solid. The latter was dissolved in a minimum of 1:1 diethyl ether/pentane solvent mixture. Evaporation of some of the solvent resulted in appearance of a greyish brown solid. The supernant solution was then discarded and the solid dried to give 0.23 g (33%) of rather unstable powdery solid of $\{Cp_2Mo_2(CO)_4$ (thiosantonin)} , 63, m.p. 134°C. Analytical, infrared and ^1H NMR data is recorded in Tables 2, 3 and 4 respectively.

Reaction of $\{Cp_2Mo_2(CO)_6\}$ with $\Delta^{1,4}$-Androstadiene-3-Thione-17-One

The thioketone (0.601 g, 2 mmol) was reacted with the molybdenum carbonyl in the same manner as thiosantonin. The solvent was then evaporated to a green-brown solid. This was then redissolved in a minimum amount of benzene and placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with benzene gave a yellowish green solid. Thin layer chromatography indicated that the mixture contained several minor and one major components. Repeated purification by passing the solution of the mixture through silica gel and eluting with benzene gave a yellow-green viscous solid. Recrystallisation of the solid from pentane gave 0.23 g (31%) of the powdery yellow-green rather unstable solid of $\{Cp_2Mo_2(CO)_4(\Delta^{1,4}$-androstadiene-3-thione-17-one)}, 64, m.p. 161°C. Analytical, infrared and ^1H NMR data are recorded in Tables 2, 3 and 4 respectively.

Reaction of $\{Cp_2W_2(CO)_6\}$ with $(p\text{-}CH_3OC_6H_4)_2C{=}S$

A solution of 1 g (1.5 mmol) of $\{Cp_2W_2(CO)_6\}$ and 0.4g (1.5 mmol) of $(p\text{-}CH_3OC_6H_4)_2CS$ in dry benzene was irradiated until all the thione had reacted (29 hours). However a considerable amount of $\{Cp_2W_2(CO)_6\}$ was still present.

The solvent was then evaporated to leave a reddish brown solid. This was then dissolved in about 10 ml of benzene and placed on a column of silica gel(60-200 mesh, Baker analysed reagent).

Elution with benzene/hexane (1:1) gave 0.214 g of unreacted $\{Cp_2W_2(CO)_6\}$. Further elution with 1:1 hexane/benzene or benzene afforded a brown viscous solid. The solid was then dissolved in a minimum amount of diethyl ether. An equal volume of hexane was added. Slow evaporation of diethyl ether resulted in the appearance of a brown solid. Then the supernant solution was

discarded and the crystals dried to give 0.297 g (29%) of dark-grey powdery solid of $\{Cp_2W_2(CO)_4(p\text{-}CH_3OC_6H_4OCH_3\text{-}p)\}$, 54g, m.p. 172°C (dec.). Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Reaction of $\{Cp_2W_2(CO)_6\}$ with $(p\text{-}CH_3C_6H_4)_2CS$

A solution of 1 g (1.5 mmol) of the tungsten carbonyl and 0.68 g (3 mmol) of 4,4'-dimethylthiobenzophenone in benzene (80 ml) was irradiated until all the thione was consumed (79 hours). The colour of the solution had changed from purple to brown.

Evaporation of solvent gave a dark brown semi-solid. This was then dissolved in a minimum amount of benzene and placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 1:2 benzene/hexane gave 0.06 g of a light red solid. The infrared spectrum revealed the presence of the starting material, $\{Cp_2W_2)CO)_6\}$, and an unknown component, which showed an absorption band at 1812 cm^{-1}(s). Due to the small size of the sample no further purification was done.

Elution with hexane/benzene (1:1) gave a brown-green solution. Using TLC it was found to contain four very poorly resolved components. Removal of solvent gave 0.9 g of a greenish brown viscous solid. All attempts to separate the components failed. However an infrared spectrum (in CCl_4) gave absorption bands at 1956(w), 1927(vs, sh), 1852(s) and 1813 cm^{-1}(w) which were assigned to the monothione complex

$\{Cp_2W_2(CO)_4(p\text{-}CH_3C_6H_4C(S)C_6H_4CH_3\text{-}p)\}$, 54j, by comparing with the infrared data of 54g and 54c (vide supra), both of which have already been characterised.

Reaction of $\{Cp_2W_2(CO)_6\}$ with Thiocamphor

A solution of 1 g (1.5 mmol) of the tungsten carbonyl and 0.506g (3 mmol) of thiocamphor in benzene (70 ml) was refluxed for 14 hours. No reaction was observed.

The reaction mixture was then transferred to a quartz vessel and irradiated until all the $\{Cp_2W_2(CO)_6\}$ was consumed (117 hours). The colour of the solution had changed from red to brown. The solvent was concentrated and then placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Elution of a brown band with 1:1 benzene/hexane gave a brown viscous solid, which was found (by TLC) to contain several organic (colourless) components in addition to one brown component. None of them was isolated and characterised.

A second mixture was obtained on further elution. It consisted of three minor (colourless) components and one major(brown) component. The mixture was then passed through a column of silica gel (60-200 mesh, Baker analysed reagent).

Slow elution with benzene gave a brown semi-solid which was then recrystallised from hexane to give 0.34 g (29%) of a brick red powdery solid of $\{Cp_2W_2(CO)_4(\text{thiocamphor})\}$, 69, m.p. 198°C. $\nu C{\equiv}O$ (KBr) : 1942(ms), 1910(vs), 1839(vs), 1786(m). Analytical data, infrared (solution) and ^1H NMR data are recorded in Tables 2,3 and 4 respectively.

Preparation of $\{CpMo(CO)_2\}_2$

A solution of 1 g (2 mmol) of $\{CpMo(CO)_3\}_2$ in p-xylene (40 ml) was refluxed until there was no or very little change in the extent of the reaction on further refluxing (6 hours). The reaction was followed by either TLC or the observation of a strong $\nu C{\equiv}O$ (in p-xylene) absorption band of $\{Cp_2Mo_2(CO)_6\}$ at 1958 cm^{-1} in comparison to the $\nu C{\equiv}O$ (in p-xylene) absorption bands of $\{Cp_2Mo_2(CO)_4\}$ around 1900 and 1860 cm^{-1}.

The solution was then cooled to 0^oC (in an ice bath). Dark-red crystals formed over a period of one hour. Then the solution (A) was decanted leaving crystals behind. The solid was then washed with 2 portions of hexane (20 ml) and dried under vacuum to yield 0.2 g of $Cp_2Mo_2(CO)_4$ containing a trace of $\{CpMo(CO)_3\}_2$.

The solution (A) was then placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 1:5 benzene/hexane yielded 0.005 g of $\{Cp_2Mo_2(CO)_6\}$.

Elution with benzene yielded 0.43 g of a flaky orange solid containing a trace of $\{CpMo(CO)_3\}_2$.

Addition of the two batches gave a total yield of about 0.63 g (73%) of $\{CPMo(CO)_2\}_2$. $\nu C{\equiv}O$(K Br): 1891(m), 1843(s). Literature:[52a] $\nu C{\equiv}O$ (iso-octane) : 1889, 1859 cm^{-1}.

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with $(p\text{-}CH_3OC_6H_4)_2CS$

A solution of 1.5 g (3 mmol) of $\{Cp_2Mo_2(CO)_6\}$ was refluxed in m-xylene (50 ml) until there was no change in the ratio between $\{CpMo(CO)_3\}_2$ and $\{Cp_2Mo_2(CO)_4\}$ on further refluxing (59 hours). The solution was cooled to room temperature.

A benzene solution of 0.69 g (2.3 mmol) of $(p\text{-}CH_3OC_6H_4)_2CS$ was then added to the molybdenum carbonyl solution. After about 6 minutes there was no unreacted thione in the reaction mixture, and the colour changed from orange to dark brown. The reaction was then stirred for one hour at room temperature. Evaporation of benzene left the crude product in m-xylene. This was then placed on a column of silica gel (60-200 mesh, Baker analysed regent).

Elution with 1:1 benzene/hexane gave a brownish red solid which was found to contain some unreacted $\{CP_2Mo_2(CO)_6\}$ in addition to a black mass possibly decomposed products of unreacted $\{CpMo(CO)_2\}_2$.

Elution with benzene gave a brown viscous solid. It was dissolved in a minumum of 1:1 diethyl ether/hexane. Evaporation of ether (under vacuum, 20°C) gave rise to the appearance of brown-green crystals. Crystals were then filtered and dried to give 1.238 g (78%) of 54a. Infrared and ^1H NMR data were found to be similar to those found earlier on (Tables 3 and 4).

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with Φ_2CS

A solution of 0.5 g (1 mmol) of $\{Cp_2Mo_2(CO)_6\}$ in n-octane (30 ml) was refluxed until there was no change in the concentration

of $\{CpMo(CO)_2\}_2$ in relation to $\{CpMo(CO)_3\}_2$ on further refluxing (23.5 hours). The crude product solution was cooled to room temperature, and then a benzene solution of 0.4 g (2 mmol) of thiobenzophenone was added. The reaction mixture immediately changed from an orange to brown. Neither the $\{Cp_2Mo_2(CO)_6\}$ nor the $\{CpMo(CO)_2\}_2$ was seen on the TLC plate.

Benzene was then evaporated to leave an octane solution of the crude product. This was then placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 5:1 hexane/benzene gave 0.173 g of unreacted thione.

Elution with 1:1 benzene/hexane yielded a brown viscous solid. Recrystallisation from hexane gave 0.51 g (81 %) of a brown crystalline solid of $\{Cp_2Mo_2(CO)_4(\Phi_2CS)\}$, 54b, m.p. 145°C (dec.). Analytical data are listed in Table 2. Infrared and ^1H NMR data(Tables 3 and 4) were found to be identical to those found earlier on for the same complex (see above).

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with $(p\text{-}CH_3C_6H_4)_2CS$

To a stirred benzene solution of 0.20 g (0.46 mmol) of $\{CpMo(CO)_2\}_2$ was added 0.226g (1 mmol) of $(p\text{-}CH_3C_6H_4)_2CS$. The colour of the solution immediately changed from orange to brown. Stirring was continued for 30 minutes after which the solvent was evaporated to give a brown semi-solid. This was dissolved in a minimum amount of benzene and placed on a column of alumina (80-200 mesh, A-540, Fisher Scientific Company).

Elution with 1:1 hexane/benzene gave a brown viscous solid which was recrystallised from pentane to give 0.20 g (66%) of greenish brown crystals of $\{Cp_2Mo_2(CO)_4(p\text{-}CH_3C_6H_4C(S)\ C_6H_4CH_3\text{-}p)\}$, 54c. Infrared and ^1H NMR data (Tables 3 and 4) and melting point were similar to those found above.

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with $p\text{-}CH_3OC_6H_4C(S)\Phi$

A solution of 0.99 g (2 mmol) of $\{CpMo(CO)_3\}_2$ in toluene (60 ml) was refluxed until there was no apparent change in the concentration of both $\{CpMo(CO)_2\}_2$ and $\{Cp_2Mo_2(CO)_6\}$ (13 hours). The solution was then cooled to room temperature after which a benzene solution of 1 g (4.4 mmol) of 4-methroxythiobenzophenone was added to it. Immediately the colour of the solution changed from orange to brown. The stirring was continued for 8 hours, after which the solvent was evaporated to leave just enough to keep the product in solution. The solution was then placed on the column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 5:1 hexane/benzene gave a trace amount of $\{Cp_2Mo_2(CO)_6\}$. Unreacted thione (0.558 g) was eluted with 1:9 benzene/hexane.

Elution with benzene yielded a brown viscous solid, which was then recrystallised from hexane to give 0.993 g (77%) of a brown powdery solid of $\{Cp_2Mo_2(CO)_4(p\text{-}CH_3OC_6H_4C(S)\Phi)\}$, 54d. Infrared, ^1H NMR and melting point were found to be similar to those obtained above (Tables 3 and 4).

Reaction of $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_2\}_2$ with $p\text{-}CH_3OC_6H_4C(S)\Phi$

A solution of 1 g (1.9 mmol) of $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6\}$ was refluxed in p-xylene (50 ml) until most of the starting material was converted to $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4\}$ (6 hours). The reaction mixture was cooled to room temperature following which 0.93 g (4 mmol) of $p\text{-}CH_3OC_6H_4C(S)\Phi$ was added. Immediately after the addition of the thione the colour of the solution changed from orange to brown. The reaction mixture was stirred for 27 hours after which the resulting solution was placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 9:1 hexane/benzene gave a mixture of blue unreacted thione and some colourless unidentified components.

Elution using benzene gave a brown solution together with some thione. The solvent was then reduced (by evaporation under vacuum) to about 20 ml and the mixture was then passed through the column again. All the thione was eluted with 9:1 hexane/benzene. This was then followed by the elution of the brown compound with benzene. On evaporation of solvent a mixture of brown and colourless (solid) was obtained.

The purification was repeated on a column of alumina (80-200 mesh, Baker analysed reagent). Elution with 1:1 benzene/hexane gave a viscous solid. Recrystallisation from hexane gave 0.6818 g (53%) of a brown powdery solid of $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4 - (p\text{-}CH_3OC_6H_4C(S)\}$, 66, m.p. 137°C. Infrared and ^1H NMR data (Tables 3 and 4) were found to be similar to those of 54d.

Reaction of $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_2\}_2$ with Adamantanethione

A solution of 0.60 g (1.1 mmol) of $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6\}$ was refluxed in p-xylene (40 ml) until there was no change in the amount of product on further heating (47 hours). The solution was cooled to room temperature and then passed through a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 1:1 hexane/benzene gave unreacted $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_6\}$. Using the same solvent a mixture of unreacted $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_3\}_2$ and $\{(h^5\text{-}C_6H_4CH_3)Mo(CO)_2\}_2$ was eluted. Evaporation of solvent gave an orange viscous solid (A). Then with benzene a mixture of starting material and $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_2\}_2$ was eluted. Let this be portion B.

To portion B a benzene solution of 0.162 g (0.98 mmol) of adamantanethione was added, the colour of the solution changing from orange to green. The solution was concentrated to about 10 ml and then chromatographed on silica gel (60-200 mesh, Baker analysed reagent).

Elution with 3:1 hexane/ benzene gave unreacted $\{(h^5\text{-}C_5H_4CH_3)Mo(CO)_3\}_2$.

Elution with 1:1 benzene/hexane yielded a green viscous solid. Recrystallisation from hexane gave 0.155 g (25%) of a green powdery solid of $\{(h^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4(\text{adamantanethione})\}$, 67, m.p. 178°C. Infrared and ^1H NMR data are recorded in Tables 3 and 4 respectively. The former are especially similar to those obtained for 56.

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with Thiocamphor

A solution of 1 g (2 mmol) of $\{CpMo(CO)_3\}_2$ in p-xylene (50 ml) was refluxed until most of the starting material had been converted to $\{CpMo(CO)_2\}_2$ (20 hours). The solution was then allowed to cool to room temperature after which a benzene solution of 0.673g (4 mmol) of thiocamphor was added. The colour of the solution immediately changed from orange to green-brown. The stirring was continued for 1 hour. Benzene was evaporated and the residual solution was chromatographed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 9:1 hexane/benzene gave a small amount of unidentified product.

Elution with 1:1 hexane/benzene gave a dark green shiny fluffy solid. Recrystallisation from hexane yielded 0.907 g (75%) of dark green crystals of $\{Cp_2Mo_2(CO)_4(\text{thiocamphor})\}$, 58, m.p. 190°C. Infrared and proton NMR data(Tables 3 and 4) were found to be similar to those obtained for the same complex earlier on.

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with $(p\text{-}FC_6H_4)_2CS$

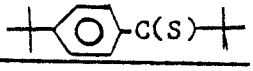
A solution of 1 g (2 mmol) of $\{Cp_2Mo_2(CO)_6\}$ was refluxed in p-xylene (50 ml) until there was no or very little starting material left (9.5 hours). The solution was cooled to room temperature, and a benzene solution of 1.59 g (5.5 mmol) of 4,4'-difluorothiobenzophenone was added. Immediately the colour changed from orange-brown to dark brown.

The reaction mixture was stirred for four hours, following which benzene was evaporated leaving the crude product in p-xylene. The solution was then placed on a column of alumina (80-200 mesh, A-540).

Using hexane all the p-xylene was eluted. No thioketone was recovered from the column despite the fact that it was present when the solution was placed on the column.

Elution with hexane/benzene (1:1) gave a brown semi-solid. The semi-solid was then dissolved in a minimum amount of diethyl ether and to the resulting solution was added twice the volume of pentane. On reduction of the volume of the solution greyish green crystals appeared. These were then washed with pentane and dried to give 0.179 (13%) of dark green crystalline solid of $\{Cp_2Mo_2(CO)_4(p\text{-}FC_6H_4C(S)C_6H_4F\text{-}p)\}$, 54f, m.p. 175°C. Analytical, infrared and proton NMR data are listed in Tables 2, 3 and 4 respectively.

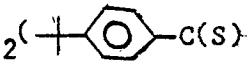
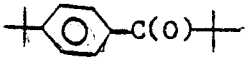
Elution with benzene gave a red-purple semi-solid. Recrystallisation from hexane yielded 0.161 g (9%) of red-purple crystals of $\{Cp_2Mo_2(F\text{-}C_6H_4C(S)C_6H_4\text{-}F)\}$, 55f, m.p. 170°C(dec.). Analytical, infrared and proton NMR data are recorded in Tables 2, 3 and 4 respectively.

Reaction of $\{Cp_2Mo_2(CO)_4\}$ with 

A solution of 1 g (2 mmol) of $\{Cp_2Mo_2(CO)_4\}$ in p-xylene (50 ml) was refluxed until most of the starting was converted to

{ $Cp_2Mo_2(CO)_4$} (9 hours). The solution was cooled to room temperature. Then 1.39 g (5.9 mmol) of the thioketone was added and the reaction mixture was stirred for 12 hours. The solution was placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 4:1 hexane/benzene gave 0.12 g of unreacted { $Cp_2Mo_2(CO)_6$ }. Further elution with 4:1 hexane/benzene gave unreacted $Cp_2Mo_2(CO)_4$, followed by 0.556 g of unreacted thione.

Elution with benzene resulted in 0.58 g of semi-solid. Recrystallisation from pentane (at 0°C) gave 20 mg (2%) of brown crystalline solid of {Cp_2Mo_2( -C(S) }, 61, m.p.180°C(dec.). Infrared and proton NMR data are listed in Tables 3 and 4 respectively. The complex was obtained as a mixture possibly with  so that the yield was estimated from proton NMR data. Also no analytical data was obtained.

Reaction of {$CP_2Mo_2(CO)_4$} with Fc$\overset{S}{\overset{\|}{C}}$-┼
(Fc=ferrocenyl group, ┼=$C(CH_3)_3$)

0.5 g (1 mmol) of {$Cp_2Mo_2(CO)_6$} was dissolved in p-xylene (50 ml) and the solution was refluxed for 10 hours. Then a benzene solution of 0.646 g (2.2 mmol) of FcC(S)┼ was added to the cooled solution. The reaction was stirred for 21 hours, after which benzene was evaporated. The resulting solution was then placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 5:1 hexane/benzene gave unreacted unreacted { $Cp_2Mo_2(CO)_6$ } (0.08 g) followed by 0.48 g of FcC(S)┼.

Elution with benzene gave a viscous brown solid. An infrared spectrum (in CCl_4) of the solid showed $\nu C\equiv O$ absorption bands at 1957(w), 1934(vs), 1864(m) and 1815 cm^{-1}(w), typical of complexes of general formula $\{Cp_2Mo(CO)_4L\}$, (cf 54a), where L is thione. This therefore, was indicative of the presence of $\{Cp_2Mo_2(CO)_4(FcC(S)-\!\!+\}$, 62.

It was found (by TLC) that the brown solid also contained some other components apart from 62. Unsuccessful attempts were made to obtain pure 62.

Reaction of $\{CpMo(CO)_2\}_2$ with $\Delta^{1,4}$-androstadiene-3-thione-17-one

From 1 g (2mmol) of $\{Cp_2Mo_2(CO)_6\}$ in p-xylene (40 ml) the complex $\{Cp_2Mo_2(CO)_4\}$ was made in the similar way as described above.

To the crude complex a benzene solution of 0.75 g (2.4 mmol) of $\Delta^{1,4}$-androstadiene-3-thione-17-one was added. Immediately the colour of the solution changed from orange to brown-yellow. The reaction mixture was stirred for one hour. Then benzene was evaporated to leave a solution of the crude product in p-xylene. This was then placed on a column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with benzene gave 17 mg of a brown viscous solid of possibly $\{Cp_2Mo_2(CO)_4L\}$, where L is probably $\Delta^{1,4}$-androstadiene-3, 17-dithione. The infrared spectrum of the above monothione complex showed $\nu C\equiv O$ absorption bands at 1957(w), 1934(vs), 1871(s) and

1829(w) cm^{-1} (in CCl_4), typical of complexes of general structure $\{Cp_2Mo_2(CO)_4L\}$ (where L=thione, M=Mo or W). The absence of the νC=O absorption band led to the above suggestion about the structure of the ligand. ^1H NMR ($CDCl_3$): δ5.41 (s, broad, Cp), 0.7-3.00 (complex, saturated C-H), 3.73-4.43 (complex, define C C-H of thione).

Using methylene chloride as eluant yielded a brown viscous solid. Recrystallisation of the solid from pentane resulted in 0.861 g (59%) of a powdery brownish yellow solid of $\{Cp_2Mo_2(CO)_4L\}$, 64, where L is $\Delta^{1,4}$-androstadiene-3-thione-17-one. Infrared and ^1H NMR data (Table 3 and 4) were found to be similar to those obtained earlier on. Carbon-13 NMR data are listed in Table 5.

Reaction of $\{Cp_2W_2(CO)_4\}$ with Φ_2CS

A solution of 1.02 g (1.5 mmol) of $\{CpW(CO)_3\}_2$ in p-xylene (40 ml) was refluxed until there was no or very little change in the extent of formation of $\{Cp_2W_2(CO)_4\}$ when heating was prolonged (20.5 hours).

The reaction mixture was left to cool to room temperature after which a benzene solution of 1.07 g (5.4 mmol) of thiobenzophenone was added. Immediately the colour of the solution changed from orange to deep brown. The reaction mixture was stirred for one hour, benzene was then removed and the remaining solution was placed on a column of silica gel (60-200 mesh, Baker, analysed reagent).

Elution with 9:1 hexane/benzene gave 0.70 g of unreacted thiobenzophenone.

Elution with 1:1 hexane/benzene yielded a brown semi-solid. This was then recrystallised from hexane to give 0.8224 g (64%) of a brown crystalline solid of $\{Cp_2W_2(CO)_4(\Phi_2CS)\}$, 54h, m.p. 182°C. Analytical, infrared and ^1H NMR data are listed in Tables 2, 3 and 4 respectively.

Reaction of $\{Cp_2W_2(CO)_4\}$ with $(p\text{-}CH_3C_6H_4)_2CS$

A solution of 0.80 g (1.2 mmol) of $\{Cp_2W_2(CO)_6\}$ in toluene (50 ml) was refluxed for about 11 hours. No reaction was observed. Toluene was then distilled off and replaced with nearly an equal amount of m-xylene. The reaction mixture was then refluxed until there was no increase in the concentration of $\{Cp_2W_2(CO)_4\}$ when heating was prolonged (82 hours).

After cooling to room temperature a benzene solution of 0.453 g (2 mmol) of $(p\text{-}CH_3C_6H_4)_2C{=}S$ was added to the solution. immediately the colour of the reaction mixture changed from orange to brown. The mixture was stirred for 12 hours after which benzene was removed by evaporation and the solution was placed on the column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 3:1 hexane/benzene gave 0.20 g of unreacted thione.

Elution with 1:1 hexane/benzene yielded a brown viscous solid. The solid was then recrystallised from hexane to give 0.847 g (84%) of powdery grey solid of $\{Cp_2W_2(CO)_4(p\text{-}CH_3C_6H_4C(S)C_6H_4CH_3\text{-}p)\}$, 54j, m.p. 140°C. Analytical, imfrared and proton NMR data are recorded in Tables 2, 3 and 4 respectively.

Reaction $\{Cp_2W_2(CO)_4\}$ with $p\text{-}CH_3OC_6H_4C(S)\Phi$

A solution of 1 g (1.5 mmol) of $\{Cp_2W_2(CO)_6\}$ in p-xylene (50 ml) was refluxed until most of the starting material had been transformed into $\{CP_2W_2(CO)_4\}$ (45 hours). The solution was then allowed to cool to room temperature. With stirring a benzene solution of 0.6712 g (2.9 mmol) of thione was added. The colour of the solution immediately changed from light to deep brown. The reaction was continued for one hour after which benzene was evaporated off to leave a p-xylene solution of the crude product, which was then placed on the column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 1:9 benzene/hexane yielded 0.045 g of unreacted $\{Cp_2W_2(CO)_6\}$.

Elution with benzene resulted in a brown semi-solid, which was then recrystallised from hexane to give a greyish brown solid (0.312 g; 26%) of $\{Cp_2W_2(CO)_4(p\text{-}CH_3OC_6H_4C(S)\Phi)\}$, 54k, m.p. 149°C (dec.). Analytical, infrared and proton NMR data are listed in Tables 2, 3 and 4.

Reaction of $\{Cp_2W_2(CO)_4\}$ with adamantanethione)

A solution of 0.94 g (1.4 mmol) of $\{Cp_2W_2(CO)_6\}$ in p-xylene (60 ml) was refluxed until most of the starting material was transformed into $\{Cp_2W_2(CO)_4\}$ (48 hours). Then the solution was allowed to cool to room temparature. A benzene solution of 0.50 g (3 mmol) of adamantanethione was added to the crude intermediate solution.

The colour of the reaction mixture changed from orange-brown to green. The solution was then stirred for 12 hours, after which benzene was evaporated to leave a p-xylene solution of the crude product. This was then placed on the column of silica gel (60-200 mesh, Baker analysed reagent).

Elution with 5:1 hexane/benzene gave 0.06 g of unreacted $\{Cp_2W_2(CO)_6\}$.

Elution with 9:1 benzene/hexane yielded a green semi-solid. Recrystallisation of the solid from pentane resulted in 0.805 g (73%) of dark green crystals of $\{Cp_2W_2(CO)_4$(adamantanethione)$\}$, 68, m.p. 232°C (dec.). Analytical, infrared and proton and carbon-13 NMR data are listed in Tables 2, 3, 4 and 5 respectively.

X-ray Analysis

The complex $C_{24}H_{26}O_4Mo_2S$, M_r = 602.4, forms brown prismatic crystals which are monoclinic, space group $P2_1$, with a = 15.607(2), b = 10.280(2), c = 7.993(2) Å, β= 109.86(3)°, V = 1206.1 Å^3, Z = 2; D_c = 1.66, D_m = 1.69 g cm^{-3} (by flotation in bromobenzene/iodobenzene), $F(000)$ = 604, μ(CuKα) = 97.10, μ(MoKα) = 11.24 cm^{-1}.

The X-ray measurements were carried out on a four-circle Picker diffractometer using a crystal fragment, 0.10x0.26x0.44 mm, mounted along b^*. The unit cell paramenters were derived from the angular settings of six high-order axial reflections measured with Cu radiation { $\lambda(K\alpha_1)$ = 1.54050, $\lambda(K\alpha_2)$ = 1.54434 Å}. The intensity data were measured with Nb filtered Mo-radiation using the θ-2θ scan procedure at a 2θ speed of 2° min^{-1}. The 2θ scan ranges were 1.9° for 2θ 10°, 2.0° for 2θ = 10-50°, 2.4° for 2θ = 50-55°, and the background was measured for 10 sec at the start and end of each scan. The (003) and (400) reflections were monitored at regular intervals for scaling, and showed a variation of less than 3%. Reflections with net counts $<$100 or $<$5% of their background counts were categorized as unobserved. Thus, of the 2932 independent reflections with $2\theta \leq 55°$, 2690 (92%) were observed. The net intensities were corrected for Lorentz and polarization effects and for absorption.

The structure was determined by the heavy-atom method and the atomic parameters were refined by block-diagonal least squares. All hydrogen atoms, except one from each of the three methyl groups,

were located on difference Fourier maps and their parameters were refined isotropically. Scattering factors were taken from the "International Tables for X-ray Crystallography"[67] and the molybdenum and sulfur curves were corrected for anomalous dispersion. Throughout the refinement the function $\sum \underline{w}(|\underline{F}_o| - |\underline{F}_c|)^2$ was minimized and the following weighting scheme was used during the final stages: $\underline{w} = \underline{w}_1\underline{w}_2$, where $\underline{w}_1 = 1$ for $|\underline{F}_o| \leqslant 35$, $\underline{w}_1 = 35/|\underline{F}_o|$ for $|\underline{F}_o| > 35$, $\underline{w}_2 = \sin^2\theta/0.07$ for $\sin^2\theta < 0.07$, $\underline{w}_2 = 1$ for $\sin^2\theta \geqslant 0.07$. Two very strong reflections, (020) and (110), and all unobserved reflections were assigned zero weights. After the final cycle the average parameter shift equalled 0.1σ and the largest one 1.2σ. The agreement index $\underline{R}'$ ($\sum \underline{w}\Delta\underline{F} / \underline{wF}_o$) is 0.034 and the weighted index $\underline{R}'$ ($\sum \underline{w}\Delta\underline{F}^2/\sum \underline{wF}_o^2$) is 0.032 for the 2690 observed reflections. The absolute configuration assumed in the refinement and shown in the figures is that derived from d-camphor. The final difference Fourier map showed no distinctive features. A list of observed and calculated structure amplitudes is available[68].

Legends for the Figures

(1) Stereoscopic view of the complex showing 20% probability ellipsoids.

(2) Bond lengths (Å) and valence angles (°). The root mean squares of the estimated standard deviations of the bond lengths are: Mo-Mo, 0.001; Mo-S, 0.002; Mo-C, 0.009;

S-C, 0.006; C-O, 0.010; C-C, 0.012 in the bicyclic camphane and 0.02 Å in the cyclopentadienes. The corresponding values for the angles are 0.1° if the three atoms are Mo or S, 0.2° if two of the atoms are Mo or S, 0.4° if only one of the atoms is Mo or S, 0.7° for Mo-C-O and C-C-C of the bicyclic camphane, and 1° for C-C-C in the cyclopentadienes. The C-H lengths are in the range 0.60-1.17 Å and their mean is 0.93 Å.

APPENDIX I: TREATMENT OF RAW KINETIC DATA

Assume that in solution an equilibrium depicted by Scheme XX does exist. If X is the major or only component in the solid state then on dissolving either 54d or 58 in a suitable solvent such as chloroform X will convert to Y until an equilibrium is reached. Consider the proton NMR cyclopentadienyl resonance signals of 58 in Figure 4 . Starting with the peak at lowest field let the four resonance signals be labelled A, B, C and D respectively. At a particular temperature, peaks A and C are supposed to decrease and B and D are supposed to increase with time. Sometimes this trend is not consistent resulting in all the resonance signals either decreasing or increasing in intensity over certain time intervals although the ratios between the peaks may have expected values.

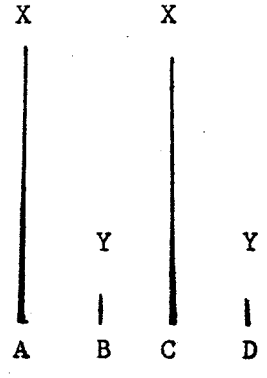


Figure 13: A sketch of proton NMR cyclopentadienyl signals of 58 at low temperature ($\simeq -40^{\circ}C.$) before equilibration (in $CDCl_3$).

This problem may be corrected as follows. Assume that at any time t the sum of the intensities of the resonance signals due to X and Y is constant. Then at any time t and temperature T for an ideal case equations (8), (9) and (10) hold. In this case equation (9) may be used. Note that A_t, B_t, C_t and D_t are

$$A_t + B_t + C_t + D_t = \text{constant} = Q_1 \tag{8}$$

$$A_t + B_t = \text{constant} = Q_2 \tag{9}$$

$$C_t + D_t = \text{constant} = Q_2 \tag{10}$$

intensities of resonance signals A, B, C and D respectively at time t. Then the average of Q_2 may be found for each temperature. This is followed by adjusting values of A_t and B_t such that equation (11) holds, where A'_t and B'_t are respectively new values of A_t and B_t at time t and Q is the average value of the quantities $A_t + B_t$ over all the time intervals at temperature T. The procedure for finding

$$A'_t + B'_t = Q \tag{11}$$

$$A'_t = \left(\frac{A_t}{A_t+B_t}\right) Q = [X]_t \tag{12}$$

$$B'_t = \left(\frac{B_t}{A_t+B_t}\right) Q = [Y]_t \tag{13}$$

the values of A'_t and B'_t is illustrated by equations (12) and (13) respectively. Finally the values of A'_t and B'_t are assigned to $\{X\}_t$ and $\{Y\}_t$ respectively. These are the averaged values of $\{X\}_t$ and $\{Y\}_t$ that are used in determining the rate constants using equations (1) and (2).

APPENDIX II: COMMENTS ON ERROR ANALYSIS

Estimation of rate constants, energies of activation and Arrhenius constants, together with their uncertainties were obtained by the least squares method.[70, 71] The uncertainty in resonance signal intensity was estimated to be ±1.1 whereas that in temperature was assumed to be ±1.5K (for a methanol standard).

Standard deviations of $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were estimated by the method of propagation of variance[72], from equations (7), (5) and (18) respectively. For example, the following is how the expression (equation (17)) for the estimation of the standard deviation of the Gibb's energy of activation was derived.

Gibb's free energy may be obtained from equation (7) or (14). In equation (7) k_B , k and h are the Bottzmann, rate and

$$\Delta G^{\neq} = RT\ln\left(\frac{k_B T}{kh}\right) \qquad (7)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \qquad (14)$$

Plank's constants respectively. Let σ_G, σ_k, σ_T and σ_S be estimates of standard deviations of Gibb's free energy of activation, rate constant, enthalpy of activation, temperature and entropy of activation respectively. By method of propagation of error we obtain from equations (7) and (14) equations (15) and (16) respectively, where r_{kT} is the correlation coefficient between the error in temperature and that in rate constant, etc. Correlation coefficients vary between -1 and +1 inclusive.

$$\sigma_{G7}^2 = (RT \frac{\sigma_k}{k})^2 + \{R (\ln (\frac{k_B T}{kh}) + 1) \sigma_T \}^2 +$$

$$2\left[R^2 T \{ \ln (\frac{k_B T}{hk}) + 1 \} \{\frac{\sigma_T \sigma_k r_{kT}}{k}\}\right] \quad (15)$$

It was found that by varying the correlation coefficients equation (9) could be approximated to equation (17), which was

$$^2_{G8} = \sigma_H^2 + (T \sigma_S)^2 + (\Delta S^{\neq} \sigma_T)^2 + 2\{ (T \Delta S^{\neq} \sigma_S \sigma_T r_{ST})$$

$$- (T \sigma_S \sigma_H r_{HS}) - (\Delta S^{\neq} \sigma_T \sigma_H r_{HT})\} \quad (16)$$

$$\sigma_G^2 = (RT \frac{\sigma_k}{k})^2 + \{R (\ln (\frac{k_B T}{kh}) + 1) \sigma_T\}^2 \quad (17)$$

$$\Delta S^{\neq} = \{ \ln A - \ln (\frac{k_B T}{h}) - 1 \} R \quad (18)$$

then used for the estimation of the standard deviations of Gibb's free energies of activation.

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