THE OXIDATIVE-ADDITION OF SOME ORGANOSULFUR COMPOUNDS TO BIS(η^5-CYCLOPENTADIENYL)TITANIUM(II)DICARBONYL

by

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Ph.D. Stephen Arthur Morris Chemistry

ABSTRACT

$Cp_2Ti(CO)_2$, where Cp = η^5-cyclopentadienyl, reacted with RSSSR to give the catenated sulfur complexes $Cp_2Ti(SR)(SSR)$, where R = CMe_3, $CHMe_2$, CH_2Ph, p-C_6H_4Me and CPh_3. These complexes, except for R = CPh_3, reacted with $PhCH_2Br$ to give Cp_2TiBr_2, $PhCH_2SR$ and $PhCH_2SSR$ as major products. $Cp_2Ti(SR)(SSR)$ desulfurized slowly in solution and rapidly in the presence of Ph_3P, giving $Cp_2Ti(SR)_2$ and Ph_3PS, in addition to other species. Similarly, phth-SSR, where phth = phthalimide, oxidatively added to $Cp_2Ti(CO)_2$ to give $Cp_2Ti(X)(SSR)$, where X = phth and R = CMe_3, $CHMe_2$, CH_2Ph and p-C_6H_4Me. Solvolysis by MeOH and EtOH gave the species where X = OMe and OEt. In a similar manner Ph_3CSSCl added to $Cp_2Ti(CO)_2$ to give $Cp_2Ti(Cl)(SSCPh_3)$. Treatment of $Cp_2Ti(SR)(SSR)$ with (norbornadiene)$Mo(CO)_4$ gave the bridged dimers, $[Cp_2Ti(\mu\text{-}SR)(\mu\text{-}S_xR)Mo(CO)_4]$, where x = 1 and 2 and R = CMe_3 and $CHMe_2$. The complexes where x = 2 contained the rare iso-μ-η^1-SSR ligand. In solution at low temperatures the bridging thiolato and disulfano groups were predominantly transoid. At higher temperatures, a dynamic process that allowed averaging of cyclopentadienyl ring environments took place. ^1H NMR studies permitted evaluation of $\Delta G_c^{\ddagger}$ for the averaging process.

L'ADDITION OXYDANTE DE QUELQUES COMPOSÉS ORGANOSULFURÉS AU BIS(η^5-CYCLOPENTADIÉNYL)TITANIUM(II)DICARBONYLE

Ph.D. Stephen Arthur Morris Chimie

RÉSUMÉ

$Cp_2Ti(CO)_2$, où Cp = η^5-cyclopentadiényle a réagi avec RSSSR pour donner les complexes comportant un enchaînement d'atomes de soufre, $Cp_2Ti(SR)(SSR)$, où R = CMe_3, $CHMe_2$, CH_2Ph, p-C_6H_4Me et CPh_3. Ces complexes, sauf dans le cas où R = CPh_3, ont réagi avec $PhCH_2Br$ pour donner Cp_2TiBr_2, $PhCH_2SR$ et $PhCH_2SSR$ comme produits majeurs. Le complexe $Cp_2Ti(SR)(SSR)$ s'est désulfuré lentement en solution et rapidement en présence de Ph_3P pour donner $Cp_2Ti(SR)_2$ et Ph_3PS, en plus d'autres espèces. De façon similaire, des composés du type phth-SSR, où phth = phthalimide, se sont additionnés de façon oxydante à $Cp_2Ti(CO)_2$ pour donner $Cp_2Ti(X)(SSR)$, où X = phth et R = CMe_3, $CHMe_2$, CH_2Ph et p-C_6H_4Me. La solvolyse par MeOH et EtOH a donné les espèces où X = OMe et OEt. De même, PhC_3SSCl s'additionna à $Cp_2Ti(CO)_2$ pour donner $Cp_2Ti(Cl)(SSCPh_3)$. Le traitement de $Cp_2Ti(SR)(SSR)$ avec le (norbornadiène)$Mo(CO)_4$ a donné les dimères pontés [$Cp_2Ti(\mu$-SR)-(μ-S_xR)$Mo(CO)_4$] où x = 1, 2 et R = CMe_3 et $CHMe_2$. Les complexes où x = 2 contenaient le rare ligand iso-μ-η^1-SSR. En solution à de basses températures, les groupes pontants thiolato et disulfano sont transoïdes de façon prédominante. Aux plus hautes températures, un processus dynamique permettant l'obtention d'un signal moyen pour l'environnement

des anneaux cyclopentadiényles s'effectue. Des études en RMN-^{1}H ont permis l'évaluation du $\Delta G_c^{\ddagger}$ de ce processus.

To Gill

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LIST OF ABBREVIATIONS

Å	ångström (1 ångström = 10^{-10} m)
br	broad
$CHMe_2$	isopropyl
$p\text{-}C_6H_4Me$	4-methylphenyl (p-tolyl)
CH_2Ph	benzyl
CMe_3	tert-butyl
Cp	η^5-cyclopentadienyl
CPh_3	triphenylmethyl
Cy	cyclohexyl
dec	decomposed
dppe	1,2-bis(diphenylphosphino)ethane. $Ph_2PCH_2CH_2PPh_2$
Et	ethyl
GC	gas chromatography
Hz	Hertz
IR	infrared
J	coupling constant
L	ligand
m	medium
M	metal atom
Me	methyl
MeCp	η^5-methylcyclopentadienyl
Me_5Cp	η^5-pentamethylcyclopentadienyl
υ	absorption frequency
$\upsilon_{1/2}$	linewidth at half-height

NMR	nuclear magnetic resonance
Ph	phenyl
phth	phthalimido
ppm	parts per million
R	organic group
s	strong
THF	tetrahydrofuran
TMS	tetramethylsilane
w	weak

Abbreviations used to describe NMR peaks

ABq	AB quartet
d	doublet
m	multiplet
q	quartet
s	singlet
t	triplet

"Take a whiff on me that ain't no rose,
Roll up your window and hold your nose,
You don't have to look and you don't have to see,
'Cause you can feel it in your olfactory."

Loudon Wainwright III

"Dead Skunk"

CHAPTER I

GENERAL INTRODUCTION

In times past, sulfur was regarded as a product of the Gods. In the Book of Genesis, XIX, 24 we read: "Then the Lord poured down on Sodom and Gomorrha sulphur and fire from the Lord out of heaven"[1]. The Greek word θεῖον means sulfur and God.

Contemporary first exposure to sulfur often comes from the unappealing aroma of certain sulfur compounds. The sensitivity of the human nose to low molecular weight sulfur molecules may be due to natural selection, which developed this olfactory sensitivity as a way of protecting against the consumption of decaying food. Some of the products of biological decay are volatile sulfur compounds[2]. Defense secretions of malodorous sulfur compounds protect skunks from their predators[3].

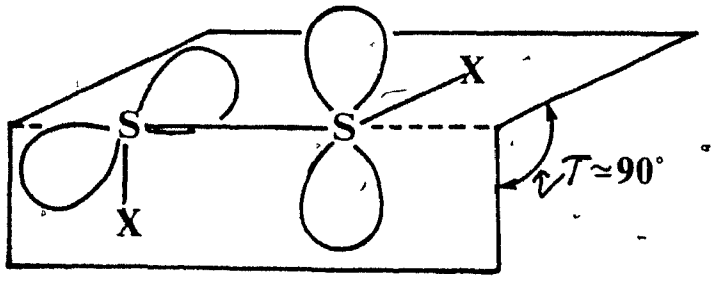
Sulfur has many effects on our lives. On the cellular level sulfur is important in amino acids and metalloenzymes[4]. Sulfur comprises 0.052% of the earth's crust making it the 16th most abundant element[5,6]. It often occurs in the native state and thus has been available to mankind throughout history. At present, over 100 million tonnes p.a. of sulfuric acid are produced, mostly from sulfur[6]. Other uses include: metal sulfides as heterogeneous catalysts[7]; sulfuration of polyolefins to form vulcanized rubber[8]; other sulfur-containing polymers[9]; energy-conversion devices based on metal sulfides[10]; electrical conductors such as tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane, the first organic metal[11]; and even construction materials[12]. The underlying function in many chemical applications is the "softness" and high polarizability of the sulfur atom.

Covalently bonded sulfur is a major contaminant of nearly all crude

fossil fuels[13]. This is undesirable because sulfur oxides which are produced during their combustion, are a major cause of acid rain[14]. Also, sulfur poisons the catalysts required for many industrial reactions, such as naptha reformation[7b,15].

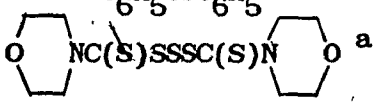
Sulfur has a propensity to catenate in all its forms[16,17,18]. Only carbon is superior to sulfur in its ability to combine with itself to form chains. The sulfur species, S_2, has chemical and physical properties analogous to those of oxygen[19]. The bond energy in O_2 is 498 kJ mol^{-1}; that for S_2 is 425 kJ mol^{-1}. The covalent single bond energy for O-O is 157 kJ mol^{-1} [5]; and for S-S is 265 kJ mol^{-1} [20]. Simple calculations thus show that O_2 is stable with respect to polymerization to a singly bonded species; S_2 is not and forms S_8. This difference in the behaviour of two Group 16 elements may be due to the low-lying unoccupied 4s and 3d orbitals of sulfur. Sulfur also tends to expand its valence shell using d-orbitals[21]. It is widely believed that the 4s and 3d orbitals participate in bonding in a manner similar to that of the 2s and 2p orbitals of carbon[19]. Double bond character can result from overlap of a lone pair in a 3p orbital with an empty 3d orbital on another sulfur atom[22].

The preferred dihedral angle between the two substituents of a simple disulfide is close to 90° (Table I.1). This value is a result of



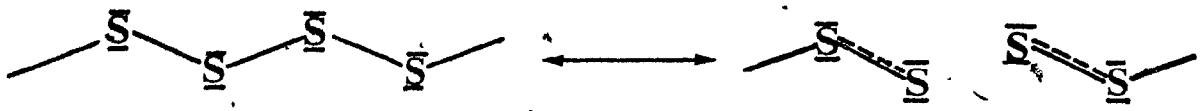
minimization of repulsion of lone pairs in adjacent 3p orbitals[23].

TABLE I.1: Dihedral Angles in Some XSSX Compounds

Compound	Dihedral Angle (τ)	Ref.
HSSH	90.6°	24
CH_3SSCH_3	84°	25
$C_6H_5SSC_6H_5$	96.2°	26
 [a]	101.5°	27
α-S_8	98.3°	28

[a] Transoid conformation.

The barriers to rotation about the S-S bond in a series of organic disulfides, $PhCH_2SSR$, are about 32 kJ mol^{-1} [29], and the free energy of activation increases with the bulk of the R groups. The initial S-S bond dissociation energies in a series of dialkyl polysulfides, RS_xR, where x = 2, 3 and 4, are approximately 285[30], 190[31] and 150[32] kJ mol^{-1}, respectively. The value for the bond dissociation energy in S_8 is 134 kJ mol^{-1} [33]. The lower values for $x \geq 3$ and S_8 can be explained by stabilization of the radicals formed, by π-bond resonance delocalization, as shown below[23]. The relative ease of chain scission



in higher polysulfides is consistent with formation of mixtures of di-, tri-, and tetrasulfides by thermal[34] or photolytic[35] disproportionation of organic trisulfides (Eq. I.1).

$$RSSSR \xrightarrow[h\upsilon]{\Delta \text{ or}} RSSR + RSSSR + RSSSSR \qquad (I.1)$$

Transition metal cations and sulfide anions are both considered to be "soft" species and consequently should have an affinity for one another. This qualitative approach explains at least in part the large number of binary metal sulfides[36] and the occurrence of sulfido (S^{2-})[37,38], thiolato (RS^-)[39] and to a lesser extent thioether (R_2S)[40] ligands, in inorganic and organometallic compounds. The coordinating ability of these ligands is related to the polarizibility of the lone pairs of the sulfur atom, which decreases in the order[40]

$$S^{2-} > RS^- > R_2S.$$

Addition of one sulfur atom to each of these ligand types gives disulfido (S_2^{2-}), disulfano (RSS^-), and dithioether (RSSR) ligands. However, these ligands are less common than the simpler ligands containing one sulfur atom. Examples of compounds containing such

sulfur ligands are shown in Table I.2, which clearly shows the structural diversity of sulfur containing complexes. Bonding modes increase as fewer organic groups are attached to the sulfur atom(s), due to the increased number of available lone pair electrons.

TABLE I.2: Known Geometries of RS_xR, RS_x^- and S_x^{2-}, where x = 1 or 2 and R = alkyl or aryl

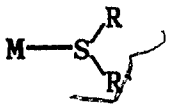
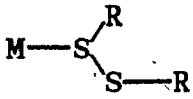
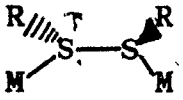
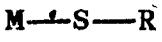
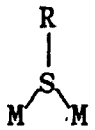
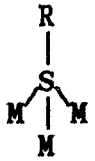
Structural type		Example[a]	Ref.
Ia		$(CO)_5Cr(SEt_2)$	41
Ib		$Pt_2Br_4(\mu\text{-}SEt_2)_2$	42
IIa		$[CpFe(CO)_2(PhSSMe)]BF_4$	43
IIb		$[Re_2Br_2(CO)_6](\mu\text{-}\eta^1\text{-}S_2Ph_2)$	44
IIIa		$Cp_2Ti(SPh)_2$	45
IIIb		$[Cp_2Ti(\mu\text{-}SCH_3)_2Mo(CO)_4]$	46
IIIc		$[Re(CO)_3(\mu_3\text{-}SMe)]_4$	47

TABLE I.2: (cont'd)

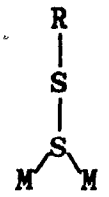
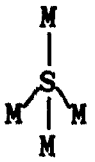
Structural type		Example[a]	Ref.
IVa	M—S—S—R	$CpW(CO)_3SS\text{-}p\text{-}C_6H_4Me$	48
IVb		$CpW(NO)(\eta^2\text{-}SSR)R$	49
IVc		$Mo_2(NC_6H_4Me)_2(S_2P(OEt)_2)_2S(O_2CMe)(\underline{iso}\text{-}\mu\text{-}\eta^1\text{-}SSEt)$	50
Va	M═S	$[NbS(SCH_2CH_2S)(SCH_2CH_2SCH_2CH_2S)]PPh_4$	51
Vb	M—S—M	$[(t\text{-}BuC_5H_4)_2Zr(\mu\text{-}S)]_2$	52
Vc	M═S═M	$K_{6.68}[MoO_4]_{0.34}[Mo_2(CN)_{12}(\mu\text{-}S)].5.32H_2O$	53
Vd	M═S═M	$[CpCr(CO)_2]_2(\mu\text{-}S)$	54
Ve		$[CpTi]_5(\mu_3\text{-}S)_6$	55
Vf		$Re_8(CO)_{32}(\mu_4\text{-}S)_4$	38
Vg		$PtOs_4(CO)_{13}(PPh_3)(\mu_4\text{-}S)$	56
Vh		$[(C_5H_4N)(CO)_6Fe_2]\text{-}\mu_4\text{-}S\text{-}[Fe_2(CO)_6S(C_5H_4N)]$	57

TABLE I.2: (cont'd)

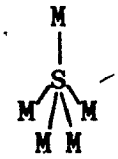
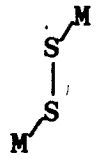
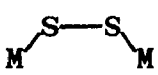
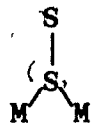
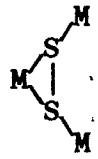
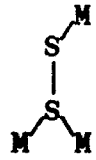
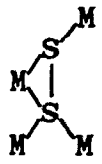
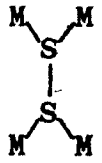
Structural type	Example[a]	Ref.
Vi		$Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4(PPh_3)]$	58
VIa		$[Me_5Cp]_2V(\eta^2\text{-}S_2)$	59
VIb		$Cp_2Fe_2(CO)(\mu\text{-}\eta^1,\eta^2\text{-}S_2)_2$	60
VIc		$[((NH_3)_5Ru)_2(\underline{anti}\text{-}\mu\text{-}\eta^1\text{-}S_2)]Cl_4$	61
VId		$MeCp_2V_2(\underline{syn}\text{-}\mu\text{-}\eta^1\text{-}S_2)_2S$	62
VIe		$Mo_3(S_2)_3S(\mu\text{-}\eta^2\text{-}S_2)_3$	63
VIf		$[Me_5Cp]_2Cr(S_2)(S)(\underline{iso}\text{-}\mu\text{-}\eta^1\text{-}S_2)$	64
VIg		$MeCp_4Ti_4(O)_2(S_2)(S)(\mu\text{-}\eta^1,\eta^2\text{-}S_2)$	65
VIh		$[CpFe]_4(S)_2(\mu\text{-}\eta^1\text{-}S_2)$	66

TABLE I.2: (cont'd)

Structural type		Example[a]	Ref.
VIi		$Mn_4(CO)_{15}(S_2)(\mu\text{-}\eta^1,\eta^2\text{-}S_2)$	67
VIj		$[Co_8(CO)_7S](\mu\text{-}\eta^1\text{-}S_2)$	68

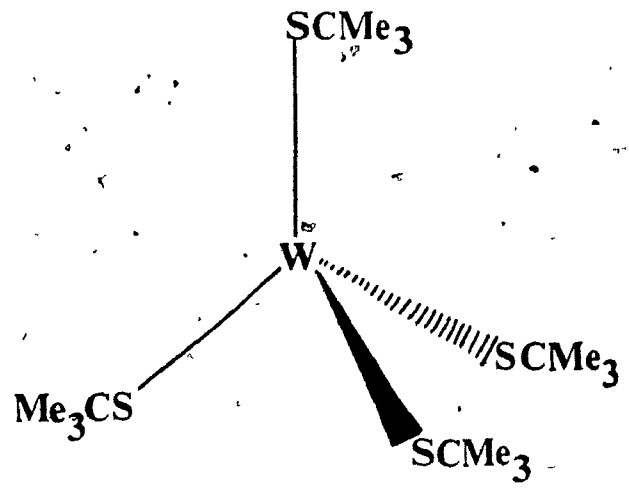
[a] The mode of sulfur bonding is described only for the structural type of interest.

The simplest systems are those containing thioethers which can function either as monodentate (Ia) or bidentate (Ib) ligands, as a result of two lone pairs on the sulfur atom. Thioethers are relatively poor σ-donors and π-acceptors, but a large number of complexes have been synthesized, particularly for Group 8-10 metals[40]. Complexes containing dithioether as a monodentate or bridging ligand are comparatively rare. Only a handful have been structurally characterized and are represented by the monodentate (IIa) and bridging (IIb) complexes as shown in Table I.2. Theoretically, other bonding modes should exist for RSSR, but have not yet been observed. This may be due in part to the ease of S-S bond cleavage by low oxidation state metals to give thiolate complexes[69]. In metallothioether complexes of the type, $L_xM(SR_2)$, where M is a "soft" metal, molecular orbital calculations did not detect

participation of the vacant d-orbitals of sulfur in metal to sulfur bonding[70].

Thiolate ligands can bind to metals in a variety of ways. The presence of three lone pairs of electrons on the thiolate anion, permits the formation of singly, doubly or triply bound systems, as shown by structural types IIIa-c.

Monomeric complexes of the type $[M(SR)_x]^{y-}$ were relatively rare until recently. These approximately tetrahedral species usually contain sterically demanding R groups, for example in $[M(SPh)_4]^{2-}$, where M = Fe, Cd, Zn, Mn, Co, Ni[71], $[Ti(S\text{-}2,4,6\text{-}C_6H_2(CHMe_2)_3)_4]^-$ [72], and $M(SCMe_3)_4$, where M = Mo[60] and W[73], as shown below. Bulky groups appear to be

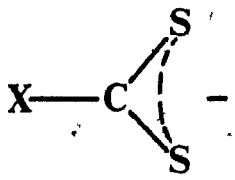


effective in preventing auto redox reactions such as Eq.I.2[72,74] and

$$[M(SR)_4]^- + RS^- \longrightarrow [M(SR)_4]^{2-} + 1/2\ RSSR \qquad (I.2)$$

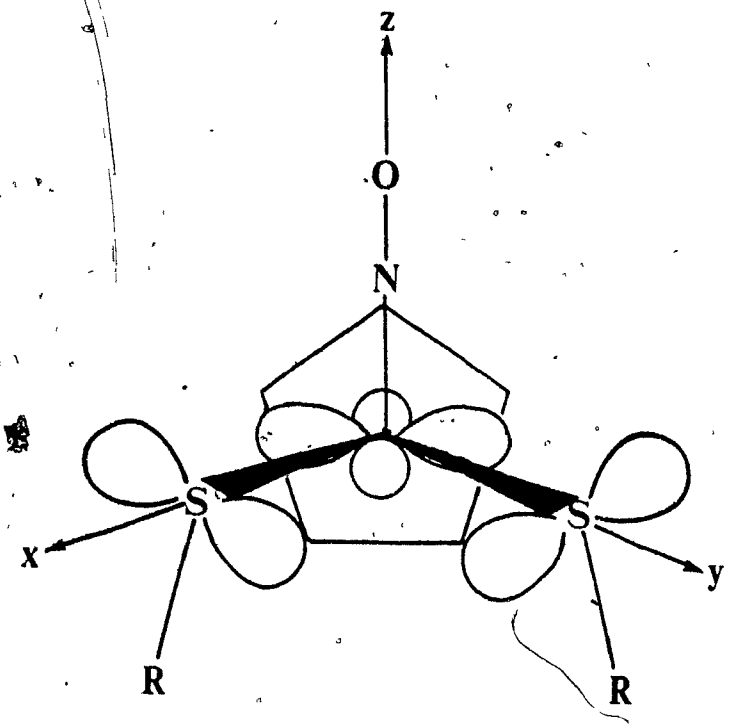
also prevent dimerization of the complexes. Numerous complexes containing the chelating ligand, dithiocarboxylate, are known and are

reviewed elsewhere[75]. A large number of complexes exist which contain

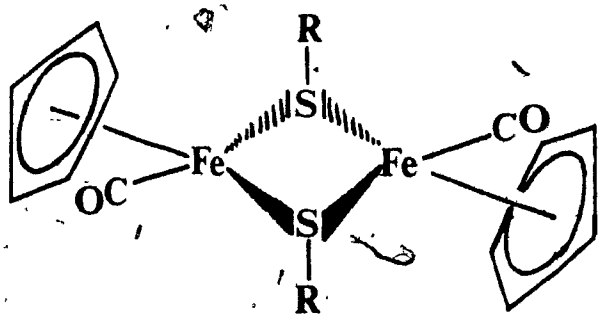


terminal thiolates in association with other ligand types. These mixed ligand complexes have been extensively reviewed[76]. Some representative examples are $[(O)Mo(SR)_4]$[77], <u>cis</u>-$(Ph_3P)_2Pt(SR)_2$[78], $CpW(CO)_3SR$[79], and $Cp_2Ti(SR)_2$[45].

Molecular orbital calculations by Hoffmann <u>et al</u>. suggest that sulfur donor atoms in terminal thiolates can contribute to the stability of 16 electron metal complexes[80]. For example, the species $CpMo(NO)(SPh)_2$ has unexpected stability for a 16 electron system. This has been contributed to $p\pi \longrightarrow d\pi$ donation from the thiolato ligand to an empty Mo $4d_{xy}$ orbital[81], as shown below.

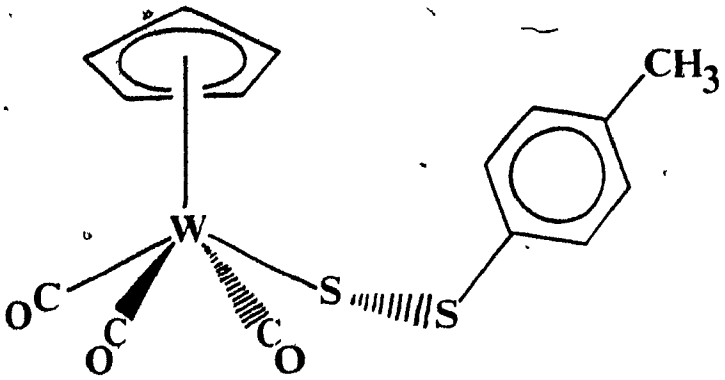


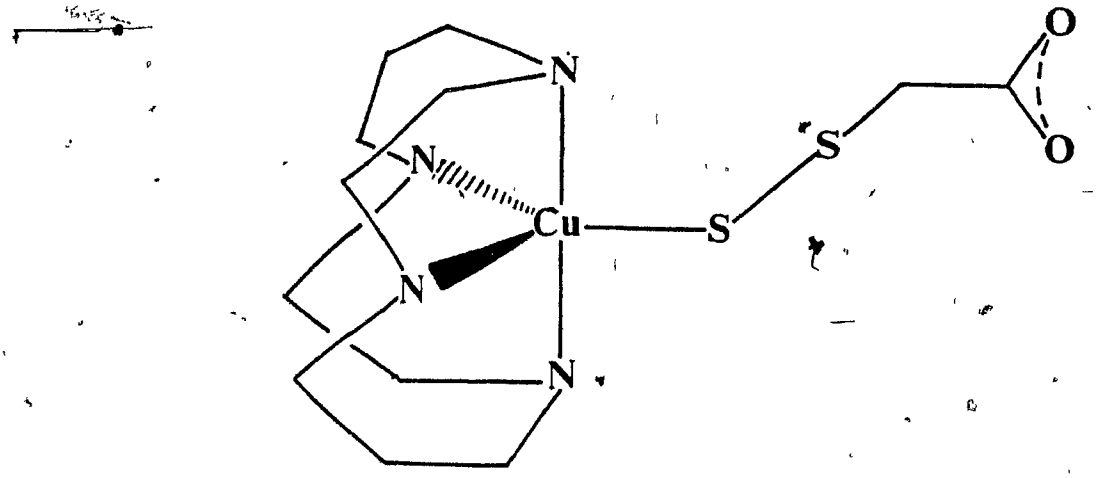
A dominant feature of metal thiolates is the tendancy to form bridged binuclear complexes. Compounds such as $[CpFe(CO)(\mu\text{-}SR)]_2$[82] and $[Cp_2Mo_2(\mu\text{-}SMe)_3(CO)_2]Br$[83] are examples of type IIIb. The sulfur atom



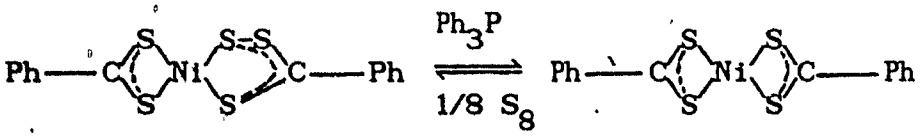
of a μ_2-bridging thiolato ligand still possesses a free lone pair of electrons available for donation to a third metal centre. Such a μ_3-bridging system may be symmetric as in $[Re(CO)_3(\mu_3\text{-}SMe)]_4$[47] (type IIIc) or asymmetric as in $[ZnMe(SCHMe_2)]_8$ where the Zn-S distances are 2.464, 2.489 and 2.346 Å [84]. Review articles have been published on both doubly and triply bridging thiolates and they will not be discussed further here[38,85].

The main thrust of this research was the synthesis of complexes containing the MSSR linkage, which is an analogue of organic disulfides, RSSR. This particular metallosulfur system has been little studied. Structurally characterized complexes containing a linear MSSR system of structural type IVa, are: $CpW(CO)_3SSR$[48]; cis-$(Ph_3P)_2Pt(C_8H_4NO_2)SSR$[48]; and a copper(II) disulfane, $Cu(tet\text{-}b)SSCH_2CO_2$[86]. The complexes $Cp_2Ti(SSCHMe_2)_2$[87] and $(Ph_3P)_2IrCl_2(CO)SSC_6F_5$[88] have also been reported.





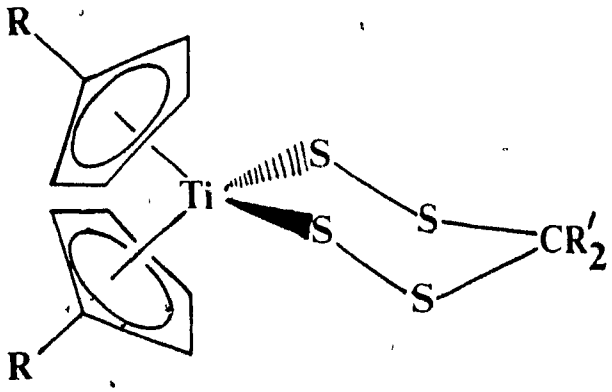
Cyclic systems containing an organodisulfano group include the complex $[Ni(S_2CC_6H_5)(S_3CC_6H_5)]$, which readily loses sulfur upon addition of Ph_3P, to give $[Ni(S_2CC_6H_5)_2]$[89]. Addition of sulfur reforms the disulfano linkage as shown in Eq. I.3. Labelling studies using ^{34}S



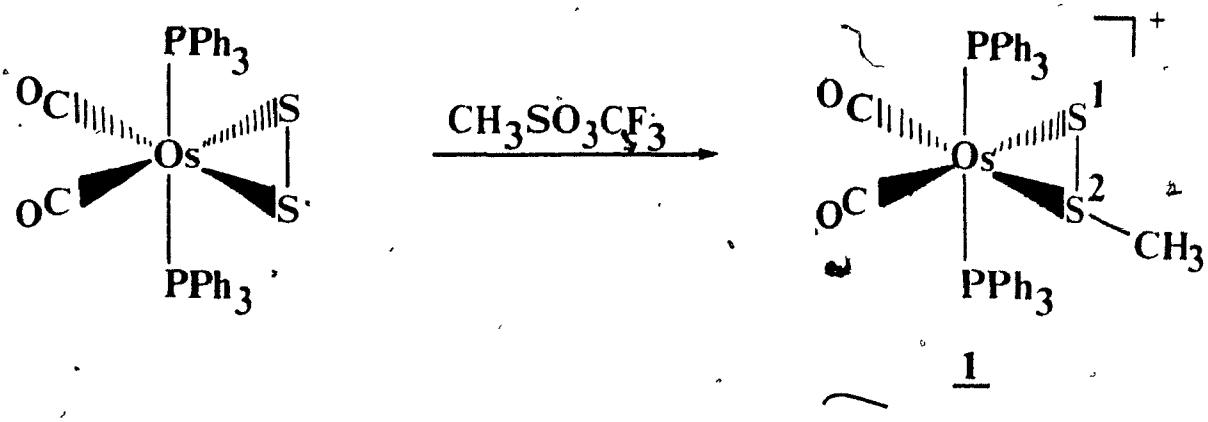
(I.3)

confirmed that the sulfur atom adjacent to the carbon atom was labile[89]. The complex $(\eta^5\text{-}C_5H_4R)_2TiS_4CR'_2$ [90] is similar to the titanium complex

mentioned above[87]. This cyclic species is not desulfurized by Ph_3P.

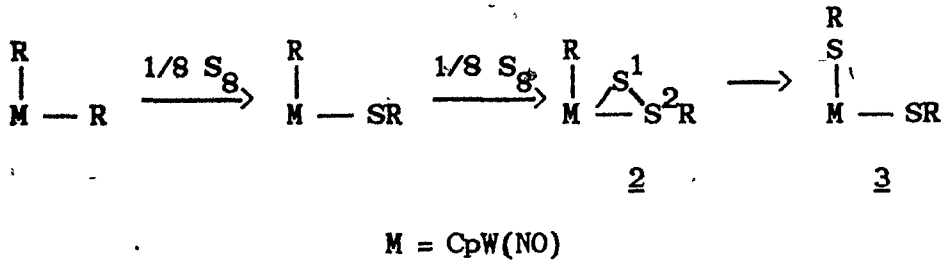


The RSS^- anion can also bind in an η^2 mode as shown in structural type IVb. Only two examples are known. The osmium complex $[Os(\eta^2\text{-SSMe})(CO)_2(PPh_3)_2]ClO_4$[91] (1) was formed by methylation of a coordinated disulfur ligand[92], as shown in Scheme I.1.



SCHEME I.1

The tungsten compound $CpW(NO)(\eta^2\text{-SSCH}_2SiMe_3)(CH_2SiMe_3)$[49] (2) was synthesized by sequential insertion of sulfur into M-R and M-SR bonds, as shown in Scheme I.2. The η^2-SSR unit in 2 ultimately rearranges in solution to form a bisthiolate complex, 3[93]. Both 1 and 2 attain an 18



M = CpW(NO)

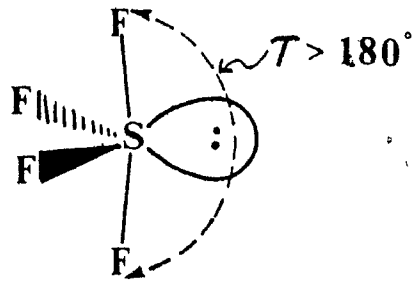
SCHEME I.2

electron configuration via side-on coordination of the η^2-SSR ligand[94]. Interestingly in 1 the Os-S^2 bond distance (2.426 Å) is shorter than that the Os-S^1 distance[91] (2.442 Å), whereas in 2 the W-S^2 distance (2.479 Å) is longer than the W-S^1 distance (2.452 Å)[49]. An iso-μ-η^1-SSR configuration has been postulated for a molybdenum dimer[50], as shown in structural type IVc in Table I.2, and is the only one of its kind. Unfortunately, a structural analysis has not been published. Other possible configurations of organodisulfano groups, as yet unreported, are possible due to the number of lone pairs on the RSS^- ligand.

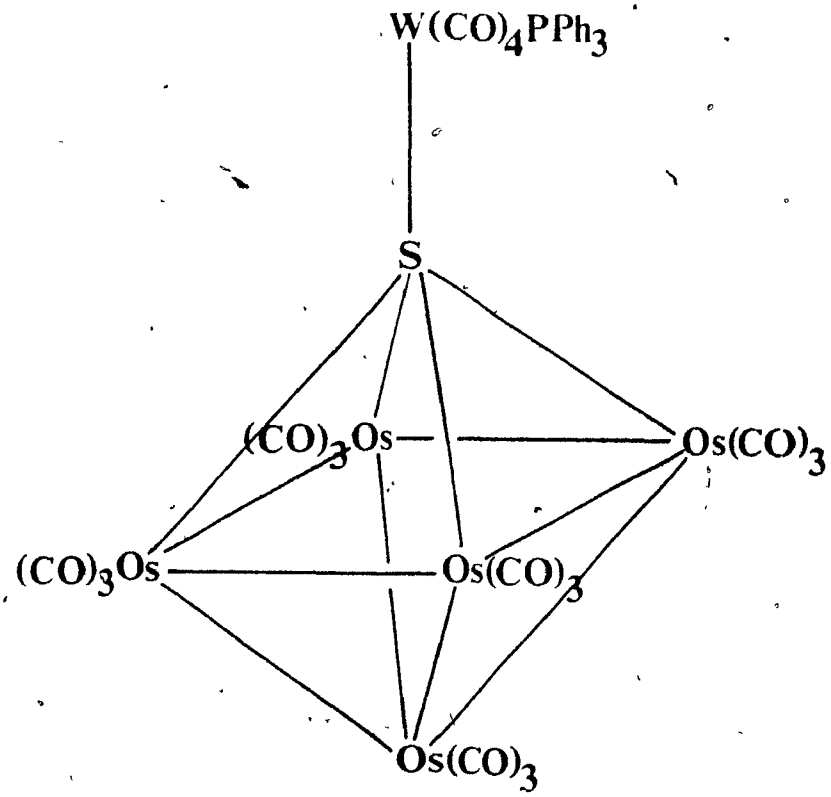
A single sulfur atom can act as a two (Va-b), four (Vc,Ve,Vg) and six (Vd,Vf,Vh-i) electron donor, which results in structural diversity[37] and preference for cluster compounds. The sulfur ligand may bond from one metal (M=S) up to five metal atoms ($M_5(\mu_5$-S)).

In counting electrons all bonding partners are regarded as neutral particles[38]. For example, structural type Vf can be considered as a MSM analogue of organic sulfides, RSR, with the two remaining lone pairs on S acting as two electron donors to each of the other two metal centres.

The sulfur atom is therefore a six electron donor. The sulfur atom in type Vg is considered as a four electron donor with a lone pair of electrons[58]. This is similar to SF_4[95]. The lone pair in type Vg acts



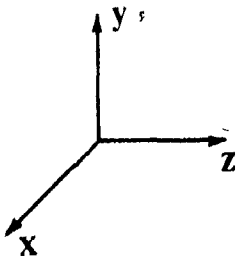
as a Lewis donor to form the unusual complex, $Os_5(CO)_{15}(\mu_5\text{-}S)$-$[W(CO)_4(PPh_3)]$, in which sulfur is in its highest known coordinative state[58], as shown in structural type Vi. The number and variety of

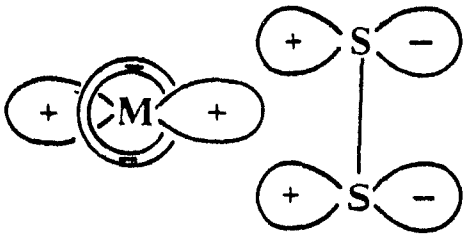


sulfido species are legion. The reader is directed to several reviews

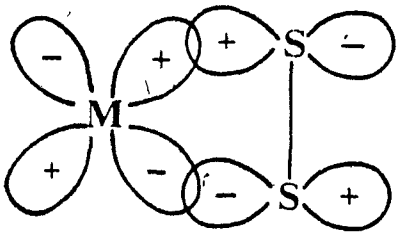
for further details[37,38,40,96].

Finally, the disulfido group is discussed, which has a staggering number of possible binding modes[97] (types VIa-j) many of which are extensions of the basic structures exhibited by RS_x^- and S^{2-} complexes. The simplest system is side-on-bound S_2 as shown in the complex $[Ir(dppe)_2S_2]^+$ [98]. It is proposed that the S_2 group binds to the metal centre by σ overlap of a metal $d_{z^2}+p_z$ hybrid with S_2 $\pi_{\|}$ and $p\sigma$ orbitals, and by in-plane π overlap of a S_2 $\pi_{\|}^*$ orbital with a metal p_x+d_{xz} hybrid[99], as shown in an approximate manner below.





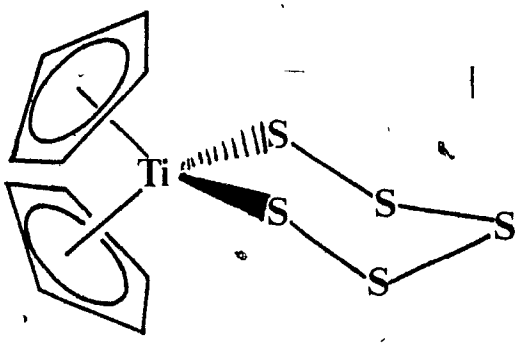
σ overlap, $\pi_{\|} \longrightarrow d_{z^2}+p_z$

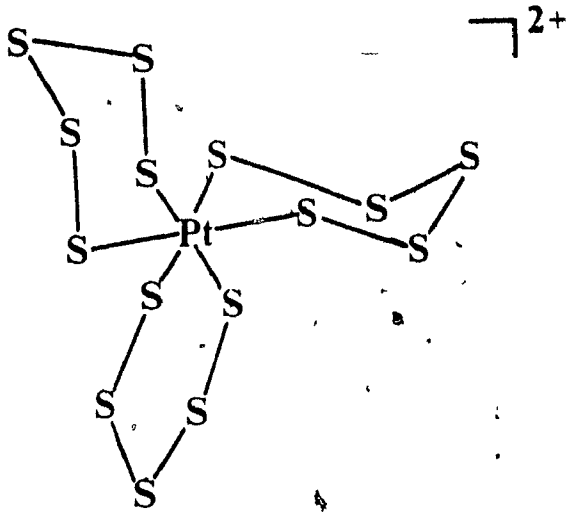


π overlap, $\pi_{\|}^* \longrightarrow p_x+d_{xz}$

Thus there appears to be no need to invoke S d-orbitals to explain M-S bonding in many MS_x, MS_xR or MS_xR_2 moieties, where x = 1 and 2, in contrast to the bonding between two sulfur atoms. A large number of disulfur complexes are described in the excellent article by Müller et al.[100]. Longer S_x^{2-} chains, where x > 2 occur in transition metal

polysulfides, and have been the subject of intense study[18]. Compounds such as $(NH_4)_2Pt(S_5)_3.2H_2O$[101] and Cp_2TiS_5[102] have been crucial in stimulating research in this field. The area has been recently reviewed[103].





Scope of the thesis

This work introduces some novel synthetic methods for the formation of MSSR species. Bis(η^5-cyclopentadienyl)titanium(IV) systems are studied because of the stability of compounds of the type Cp_2TiXY, and because of the availability of $Cp_2Ti(CO)_2$, a well known precursor to $Cp_2Ti(IV)$ complexes via oxidative-addition reactions. $Cp_2Ti(CO)_2$ reacts with RSSR to give $Cp_2Ti(SR)_2$. The reactions of $Cp_2Ti(CO)_2$ with organic compounds containing RSS-SR, RSS-N and RSS-Cl bonds to produce the desired disulfano linkage, are reported. The relevance of these products to other organometallic and inorganic sulfur containing complexes is discussed. The reactivity of the TiSSR group with selected nucleophiles and electrophiles is assessed. Useful methods for the characterization of metallosulfur systems are reported. The reactions of these systems with other complexes, leading to bridged dimers, are also described.

References

1. The Holy Bible, New Catholic Edition, Catholic Book Publishing Co., New York, 1957.
2. "Reactions of Organosulfur Compounds", by E. Block, Academic Press, Toronto, 1978.
3. "Organic Chemistry of Bivalent Sulfur", by E.E. Ried, Chemical Publishing Co., New York, 1960, Vol. I, p 16.
4. a) "Iron-Sulfur Proteins", ed. W. Lovenberg, Academic Press, Toronto, 1977, Vol. 3, Chapters 2 and 7.
   b) "The Peptides, Analysis, Synthesis and Biology", eds. E. Gross and J. Meienhoffer, Academic Press, Toronto, 1981, Vols. 1-3.
   c) V.K. Shah and W.J. Brill, Proc. Natl. Acad. Sci. U.S.A., 74, (1977), 3249.
5. Handbook of Chemistry and Physics, 67th Edition, CRC Press, Boca Raton, Florida, 1986.
6. "Sulfur, Energy and Environment", by B. Meyer, Elsevier, New York, 1977.
7. a) "Chemistry of Catalytic Processes", by B.C. Gates, J.R. Katzer and G.C.A. Schuit, McGraw-Hill, Toronto, 1979, pp 415-422.
   b) "Proceedings, Climax 5th International Conference on the Chemistry and Uses of Molybdenum", Polyhedron, 5, (1986), pp 145-232.
8. "Rubber Technology and Manufacture", ed. C.M. Blow, Butterworth, Toronto, 1971, pp 147-173.
9. a) E.J. Goethals in, "Topics in Sulfur Chemistry", eds. A. Senning and P.S. Magee, Georg Thieme, Stuttgart, 1977, Vol. 3, pp 1-62.

b) "New Uses of Sulfur", by J.R. West, A. C. S. Advances in Chemistry Series, 140, (1975).

10. V. Moss and D.A. Nole in, "Topics in Sulfur Chemistry", eds. A. Senning and P.S. Magee, Georg Thieme, Stuttgart, 1977, Vol. 3, pp 63-100.
11. F. Wudl, Acc. Chem. Res., 17, (1984), 227.
12. a) Chem. Eng. News, September, 1980, p 45.
    b) "Sulfur Construction Materials", by W.C. McBee, T.A. Sullivan and H.L. Fike, U.S. Dept. of the Interior, Bureau of Mines, 1985, Bulletin; 678.
13. C.-D. Czogalla and F. Boberg, Sulfur Reports, 3, (1983), 121.
14. a) G.M. Hidy, D.A. Hansen, R.C. Henry, K. Ganesan and J. Collins, J. Air Pollut. Control Assoc., 34, (1984), 333.
    b) "The Acid Rain Sourcebook", eds. T.C. Elliot and R.G. Schwieger, McGraw-Hill, Toronto, 1984.
15. a) "Catalyst Poisoning", by L.L. Hegedus and R.W. McCabe, Marcel Dekker Inc., New York, 1984.
    b) J. Oudar, Catal. Rev. Sci. Eng., 22, (1980), 171.
16. M. Schmidt, Angew. Chem. Int. Ed. Engl., 12, (1973), 445.
17. "Organic Chemistry of Bivalent Sulfur", by E.E. Ried, Chemical Publishing Co., New York, 1960, Vol. III, pp 362-462.
18. M. Draganjac and T.B. Rauchfuss, Angew. Chem. Int. Ed. Engl., 24, (1985), 742.
19. B. Meyer, Chem. Rev., 76, (1976), 367.
20. D.A. Johnson in, "Sulfur in Organic and Inorganic Chemistry", ed. A. Senning, Marcel Dekker Inc, New York, 1972, p 37.

21. a) R.S. Laitinen, T.A. Pakkanen and R. Steudel, J. Am. Chem. Soc., 109, (1987), 711.

b) A. Hinchliffe, J. Mol. Struct., 55, (1979), 127.

c) W.J. Pietro, M.M. Francl, W.J. Hehre, D.J. DeFrees, J.A. Pople and J.S. Binkley, J. Am. Chem. Soc., 104, (1982), 5039.

d) C.J. Marsden and B.J. Smith, J. Mol. Struct., 105, (1983), 385.

22. J.L. Kice in, "Sulfur in Organic and Inorganic Chemistry", ed. A. Senning, Marcel Dekker Inc., New York, 1972, p 155.

23. R. Steudel, Angew. Chem. Int. Ed. Engl., 14, (1975), 655.

24. G. Winnewisser, M. Winnewisser and W. Gordy, J. Chem. Phys., 49, (1968), 3465.

25. B. Beagley and K.T. McAloon, J. Chem. Soc., Faraday Trans., 67, (1971), 3216.

26. J.D. Lee and M.W.R. Bryant, Acta Crytallogr., Sect. B, 25, (1969), 2094.

27. a) S. Husebye, Acta Chem. Scand., 27, (1973), 756.

b) "Organic Chemistry of Sulfur", by S. Oae, Plenum Press, New York, 1977, p 334.

28. "The Structures of the Elements", by J. Donohue, Wiley, New York, 1974, p 324.

29. R.R. Fraser, G. Boussard, J.K. Saunders, J.B. Lambert and C.E. Mixan, J. Am. Chem. Soc., 93, (1971), 3822.

30. H. Mackle, Tetrahedron, 19, (1963), 1159.

31. T.L. Pickering, K.J. Saunders and A.V. Tobolsky in, "The Chemistry of Sulfides", ed. A.V. Tobolsky, Interscience, New York, 1968, p 71.

32. I. Kende, T.L. Pickering and A.V. Tobolsky, J. Am. Chem. Soc., 87, (1965), 5582.

33. T.K. Wiewiorowski, A. Parthasarathy and B.L. Slaten, J. Phys. Chem., 72, (1968), 1890.

34. D. Grant and J.R. van Wazer, J. Am. Chem. Soc., 86, (1964), 3012.

35. B. Milligan, D.E. Rivett and W.E. Savige, Aust. J. Chem., 16, (1963), 1020.

36. "Sulfide Catalysts, Their Properties and Applications", by O. Weisser and S. Landa, Pergammon Press, New York, 1973.

37. "Sulfur, its Significance for Chemistry, for the Geo-, Bio-, and Cosmosphere and Technology", eds. A. Müller and B. Kreba, Elsevier, New York, 1984, pp 121-139.

38. H. Vahrenkamp, Angew. Chem. Int. Ed. Engl., 14, (1975), 322.

39. Ref. 37, pp 141-165.

40. C.G. Kuehn and S.S. Isied, Prog. Inorg. Chem., 27, (1980), 153.

41. H.G. Raubenheimer, J.C.A. Boeyens and S. Lotz, J. Organomet. Chem., 112, (1976), 145.

42. D.L. Sales, J. Stokes and P. Woodward, J. Chem. Soc. (A), (1968), 1852.

43. P.M. Treichel, M.S. Schmidt, P.C. Nakagaki and E.K. Rublein, J. Organomet. Chem., 311, (1986), 193.

44. I. Bernal, J.L. Atwood, F. Calderazzo and D. Vitali, Gazz. Chim Ital., 106, (1976), 971.

45. E.G. Müller, S.F. Watkins and L.F. Dahl, J. Organomet. Chem., 111, (1976), 73.

46. G.R. Davies and B.T. Kilbourn, J. Chem. Soc. (A), (1971), 87.

47. W. Harrison, W.C. Marsh and J. Trotter, J. Chem. Soc., Dalton Trans., (1972), 1009.

48. A.G. Shaver, J. Hartgerink, R.D. Lai, P. Bird and N. Ansari, Organometallics, 2, (1983), 938.

49. S.V. Evans, P. Legzdins, S.J. Rettig, L. Sanchez and J. Trotter, Organometallics, 6, (1987), 7.

50. M.E. Noble, Inorg. Chem., 25, (1986), 3311.

51. K. Tatsumi, Y. Sekiguchi and A. Nakamura, J. Am. Chem. Soc., 108, (1986), 1358.

52. G. Ecker, T. Mühlenbernd, R. Benn and A. Rufinska, Organometallics, 5, (1986), 1023.

53. M.G.B. Drew, P.C.H. Mitchell and C.F. Pygall, J. Chem. Soc., Dalton Trans., (1979), 1213.

54. T.J. Greenhough, B.W.S Kolthammer, P. Legzdins and J. Trotter, Inorg. Chem., 18, (1979), 3543.

55. F. Bottomley, G.O. Egharevba and P.S. White, J. Am. Chem. Soc., 107, (1985), 4353.

56. R.D. Adams, J.E. Babin, R. Mathab and S. Wang, Inorg. Chem., 25, (1986), 1623.

57. G.L. Borgne and D. Grandjean, J. Organomet. Chem., 92, (1975), 381.

58. R.D. Adams, J.E. Babin and K. Natarajan, J. Am. Chem. Soc., 108, (1986), 3518.

59. S.A. Koch and V. Chebolu, Organometallics, 2, (1983), 350.

60. G. Giannotti, A.M. Ducourant, H. Chanaud, A. Chiaroni and C. Riche, J. Organomet, Chem., 140, (1977), 289.

61. R.C. Elder and M. Trkula, Inorg. Chem., 16, (1977), 1048.

62. C.M. Bolinger, T.B. Rauchfuss and A.L. Rheingold, Organometallics, 1, (1982), 1551.

63. A. Müller, S. Sarkar, R.G. Battacharyya, S. Pohl and M. Dartmann, Angew. Chem. Int. Ed. Engl., 17, (1978), 535.

64. H. Brunner, J. Wachter, E. Guggolz and M.L. Ziegler, J. Am. Chem. Soc., 104, (1982), 1765.

65. G.A. Zank, C.A. Jones, T.B. Rauchfuss and A.L. Rheingold, Inorg. Chem., 25, (1986), 1886.

66. P.J. Vergamini, G.J. Kubas, Prog. Inorg. Chem., 21, (1976), 261.

67. V. Küllmer, E. Röttinger and H. Vahrenkamp. J. Chem. Soc., Chem. Commun., (1977), 782.

68. D.L. Stevenson, V.R. Magnuson and L.F. Dahl, J. Am. Chem. Soc., 89, (1967), 3727.

69. a) K.L. Bradenburg, M.J. Heeg and H.B. Abrahamson, Inorg. Chem., 26, (1987), 1064.

b) C.-L. Lee, J. Chisholm, B.R. James, D.A. Nelson and M.A. Lilga, Inorg. Chim. Acta, 121, (1986), L7.

c) J.L. Davidson and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1975), 813.

70. a) A. Streitweiser, Jr. and S.P. Ewing, J. Am. Chem. Soc., 97, (1975), 190.

b) A. Streitweiser, Jr. and J.G. Williams, J. Am. Chem. Soc., 97, (1975), 191.

71. D. Swenson, N.C. Baenziger and D. Coucouvanis, J. Am. Chem. Soc., 100, (1978), 1932.

72. G.A. Sigel and P.P. Power, Inorg. Chem., 26, (1987), 2819.

73. M.L. Listermann, J.C. Dewan and R.R. Schrock, J. Am. Chem. Soc., 107, (1985), 7207.

74. a) R. Fikar, S.A. Koch and M. Millar, Inorg. Chem., 24, (1985), 3311.

b) S.A. Koch and M. Millar, J. Am. Chem. Soc., 105, (1983), 3362.

75. a) R.P. Burns, F.P. McCullough and C.A. McAuliffe, Adv. Inorg. Chem. Radiochem., 23, (1980), 211.

b) D. Coucouvanis, Prog. Inorg. Chem., 26, (1979), 301.

76. a) E.W. Abel and B.C. Crosse, Organomet. Chem. Rev., 2, (1967), 443.

b) S.E. Livingstone, Quart. Rev., 19, (1965), 386.

77. S.-L. Soong, V. Chebolu, S.A. Koch, T. O'Sullivan and M. Millar, Inorg. Chem., 25, (1986), 4068.

78. R.D. Lai and A.G. Shaver, Inorg. Chem., 20, (1981), 477.

79. J.L. Davidson and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1972), 107.

80. a) M. Kamata, K. Hirostu, T. Higuchi, K. Tasumi, R. Hoffmann, T. Yoshida and S. Otsuka, J. Am. Chem. Soc., 103, (1981), 5772.

b) M. Kamata, T. Yoshida, S. Otsuka, K. Hirotsu, T. Higuchi, M. Kido, T. Tatsumi and R. Hoffmann, Organometallics, 1, (1982), 227.

81. M.T. Ashby and J.H. Enemark, J. Am. Chem. Soc., 108, (1986), 730.

82. S.D. Killops and S.A.R. Knox, J. Chem. Soc., Dalton Trans., (1978), 1260.

83. M.B. Gomes de Lima, J.E. Guerchais, R. Mercier and F.Y. Pétillon, Organometallics, 5, (1986), 1952.

84. G.W. Adamson and H.M.M. Shearer, J. Chem. Soc., Chem. Commun., (1969), 897.

85. Ref. 37, P 141-165.

86. E. John, P.K. Bharadwaj, K. Krogh-Jespersen, J.A. Potenza and H.J. Schugar, J. Am. Chem. Soc., 108, (1986), 5015.

87. A.G. Shaver, J.M. McCall, P.H. Bird and N. Ansari, Organometallics, 2, (1983), 1894.

88. S.N. Battacharya, C.V. Senoff and F.S. Walker, Inorg. Chim. Acta, 44, (1980), L273.

89. a) J.P. Fackler, Jr., J.A. Fetchin and D.C. Fries, J. Am. Chem. Soc., 94, (1972), 7323.

b) J.P. Fackler, Jr., P.R. Del Niera, C. Campana and B. Trzcinska-Bancroft, J. Am. Chem. Soc., 106, (1984), 7883.

90. D.M. Giolando and T.B. Rauchfuss, Organometallics, 3, (1984), 487.

91. G.R. Clark and D.R. Russell, J. Organomet. Chem., 173, (1979), 377.

92. G.R. Clark, D.R. Russell, W.R. Roper and A. Walker, J. Organomet. Chem., 136, (1977), C1.

93. P. Legzdins and L. Sânchez, J. Am. Chem. Soc., 107, (1985), 5525.

94. D.H. Farrar, K.R. Grundy, N.C. Payne, W.R. Roper and A. Walker, J. Am. Chem. Soc., 101, (1979), 6577.

95. "Inorganic Chemistry, Principles of Structure and Reactivity", by J.E. Huheey, Harper and Row, London, 1975, p 125.

96. A. Müller, E. Diemann, R. Jostes and H. Bögge, Angew. Chem. Int. Engl., 20, (1981), 934.

97. A. Müller and W. Jaegermann, Inorg. Chem., 18, (1979), 2631.

98. W.D. Bonds, Jr. and J.A. Ibers, J. Am. Chem. Soc., 94, (1972),

3413.

99. A.P. Ginsberg, J.H. Osborne and C.R. Sprinkle, Inorg. Chem., 22, (1983), 254.

100. A. Müller, W. Jaegermann and J.H. Enemark, Coord. Chem. Rev., 46, (1982), 245.

101. a) K.A. Hofmann and F. Höchtlen, Ber., 36, (1903), 3090.

b) R.D. Gillard and F.L. Wimmer, J. Chem. Soc., Chem. Commun., (1978), 936.

c) A.E. Wickenden and R.A. Krause, Inorg. Chem., 8, (1969), 779.

102. a) E. Samuel, Bull. Soc. Chim. Fr., (1966), 3548.

b) H. Köpf, B. Block and M. Schmidt, Chem. Ber., 101, (1968), 272.

103. A. Müller and E. Diemann, Adv. Inorg. Chem., 31, (1987), 89.

CHAPTER II

THE SYNTHESES, CHARACTERIZATION AND REACTIONS OF

$(\eta^5\text{-}C_5H_4R)_2Ti(SR')(SSR'')$

Introduction

Few metal complexes containing a linear catenated sulfur ligand (ie. RS_x^-, where $x > 1$) have been prepared. This may in part be due to a lack of suitable synthetic approaches, since the analogous organic species, RS_yR, where $y = 1 - 6$ are common[1]. Recently the complexes, $CpW(CO)_3S_xR$, where $x = 2, 3$ and $R = CH_2Ph$, $p\text{-}C_6H_4Me$, were prepared by reaction of the sulfur-transfer reagent RS_{x-1}imide with $CpW(CO)_3SH$[2]. In a similar manner $Cp_2Ti(SH)_2$ gave $Cp_2Ti(SSCHMe_2)_2$ and $Cp_2Ti(SPh)(SSSPh)$, the latter a product of a rearrangement and containing the only structurally characterized organotrisulfano ligand[3]. Recently an alkyl disulfano copper(II) species (CuSSR) was isolated during model studies on the possible bonding modes in certain copper(II) enzymes[4]. The complex $CpW(NO)(CH_2SiMe_3)(SSCH_2SiMe_3)$, which contains an η^2-SSR ligand, was recently prepared by insertion of elemental sulfur into a W-C bond[5].

The bisthiolato complexes, $Cp_2Ti(SR)_2$, where R = alkyl, aryl and PCy_2, have been made by oxidative-addition of RSSR (2) to $Cp_2Ti(CO)_2$ (1)[6,7] and by other methods[8]. Sulfur-sulfur bond cleavage also occurs in the oxidation of 1 by S_8 to give Cp_2TiS_5[9]. Therefore it seemed reasonable to treat 1 with organic trisulfides, RSSSR (3), as a route to complexes of the type $Cp_2Ti(SR)(SSR)$.

Experimental

Reagents and Solvents

All manipulations were carried out under an atmosphere of prepurified nitrogen (Union Carbide) using standard techniques for handling air sensitive compounds[10], unless otherwise stated. All solvents were reagent grade with hexanes (bp 68-70°C), diethylether and toluene being refluxed over sodium/benzophenone, and CH_2Cl_2 being refluxed over P_2O_5. All solvents were freshly distilled under N_2 just prior to use. The NMR solvents C_6D_6, $CDCl_3$ and CD_2Cl_2 were dried over molecular sieves (Linde 4 Å). Benzylbromide (Kodak) was distilled; the fraction boiling at 100-107°C (41 mmHg) being retained. Phenyllithium (2.0M solution in cyclohexane/Et_2O), Cp_2TiCl_2 and the compounds di(tert-butyl)sulfide, di(isopropyl)sulfide, dibenzylsulfide, dibenzyldisulfide, di(p-tolyl)disulfide, dibenzyltrisulfide (3c) and triphenylphosphine (Aldrich) were used as received. Di(tert-butyl)-disulfide and di(isopropyl)disulfide (Fairfield) were also used as received. The unsymmetrical sulfides $RSCH_2Ph$, where R = CMe_3 (7a)[11] and $CHMe_2$ (7b)[12], were prepared by a standard method[13]. The triphenylmethyl substituted compounds Ph_3CSZ, where Z = H, CPh_3 and $SCPh_3$, were kindly supplied by Mr. Charles Williams. Di(isopropyl)trisulfide (3b) and di(p-tolyl)trisulfide (3d) were prepared by an extension of the route previously reported by Harpp et al.[14]. The yields of trisulfides were 67% for 3b (via benzimidazole), and 64% and 59% for 3d (via benzimidazole and 1,2,4 triazole, respectively). The compounds di(triphenylmethyl)trisulfide (3e), di(tert-butyl)trisulfide (3a)[15],

triphenylmethylchlorodisulfide[16] and the complexes $Cp_2Ti(SR)_2$, where R = CMe_3 (5a)[17], $CHMe_2$ (5b)[17], CH_2Ph (5c)[8c] and p-C_6H_4Me (5d)[8c], were prepared by literature methods. $RCp_2Ti(CO)_2$ (1), where R = H and Me, were synthesized by the method of Demersemen et al.[18].

Reaction products were identified in the following ways: organic sulfides by means of comparison of GC parameters and NMR spectra to those of authentic samples and where appropriate by means of their GC-mass spectra; disulfides by their GC-mass spectra; triphenylphosphine sulfide and $Cp_2Ti(SR)_2$ by comparison of the NMR and mass spectra to those of authentic samples.

Thin layer chromatography was performed using BDH 150F254 aluminum sheets. Deactivated alumina used for column chromatography was prepared by a published method[8a] using activated alumina (Anachemia 80-200 mesh).

Physical Measurements

^1H NMR spectra were measured on a Varian XL-200 spectrometer and all data are reported in ppm relative to TMS as an internal standard and are considered accurate to ± 0.05 ppm. All NMR spectra were measured at ambient temperature (19°C ± 2). Gas chromatography (GC) was performed on a Shimadzu GC-8APF instrument equipped with a flame ionization detector. The capillary column used was of 30 m × 0.25 mm I.D. with a 1 μm film of Polymethyl (5% Phenyl) Siloxane (coating (A)) bonded on fused silica. The temperature was raised at the rate of 20°C/min from 100 to 260°C, with a column N_2 flow rate of 0.5 mL/min. Gas chromatography/Mass spectrometry was carried out on a Hewlett-Packard 5984A spectrometer with a 2m × 2mm I.D. 6% OV101 Chromosorb W/HP column,

or on a Finnigan Model 700 Ion Trap Detector coupled to a Varian 3500 Gas Chromatograph (Column 30 m × 0.25 mm I.D. with a 0.25 μm film of coating (A) on fused silica). Mass spectrometry was performed by direct inlet at 70 eV on a Hewlett-Packard 5984A or on a DuPont 21-492B spectrometer using ion sources at 210°C or 250°C, respectively. Spectra are reported as: m/z, assignment, rel. int..

Visible spectra were recorded on a Unicam SP800 UV-visible spectrophotometer. Infrared spectra were measured using a Perkin-Elmer 457 or 297 spectrometer calibrated using the 1601 cm^{-1} band of polystyrene, and are reported in cm^{-1}. All reactions of $RCp_2Ti(CO)_2$ (1) with organic trisulfides were monitored, by following the decrease in intensity of the characteristic CO bands of 1 in the IR spectrum of the reaction solution.

Melting points were determined in sealed tubes under vacuum on a Thomas-Hoover Melting Point Apparatus, and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

Preparation of Bis(η^5-cyclopentadienyl)(tert-butylthiolato)(tert-butyldisulfano)titanium(IV), $Cp_2Ti(SCMe_3)(SSCMe_3)$ (4a).

$(Me_3C)_2S_3$ (3a) (4.99 g, 23.7 mmol) was added to a solution of $Cp_2Ti(CO)_2$ (1) (5.32 g, 22.7 mmol) in toluene (80 mL). The reaction mixture was stirred for 45 h to give a very intense emerald green solution, which was stripped to dryness. A NMR spectrum of the residue indicated that 4a accounted for 96% (integrated intensity) of the cyclopentadienyl containing products. The only other product was

$Cp_2Ti(SCMe_3)_2$ (5a). The residue was extracted with hexanes (10 × 50 mL) and the volume of the filtered extracts was reduced to 100 mL. Slow cooling to -78°C gave an intensely emerald green powder (5.33 g, 60%, mp 85-87°C (dec)).

Anal. (%): Calcd. for $C_{18}H_{28}S_3Ti$: C, 55.65; H, 7.26; S, 24.76. Found: C, 55.71; H, 7.37; S, 24.72.

^1H NMR (C_6D_6): δ5.91 (s, 10H, C_5H_5), 1.66 (s, 9H, $SC(CH_3)_3$), 1.42 (s, 9H, $SSC(CH_3)_3$).

^1H NMR ($CDCl_3$): δ6.20 (s, 10H, C_5H_5), 1.46 (s, 9H, $SC(CH_3)_3$), 1.32 (s, 9H, $SSC(CH_3)_3$).

^1H NMR (CD_2Cl_2): δ6.19 (s, 10H, C_5H_5), 1.43 (s, 9H, $SC(CH_3)_3$), 1.32 (s, 9H, $SSC(CH_3)_3$).

IR (KBr): 3080 (m), 2950 (s, br), 1435 (m), 1354 (m), 1150 (s), 1008 (m), 800 (s), 640 (s, br), 580 (s), 420 (m).

MS (NH_3 C.I.): 389 ($M^{+\bullet}+H^\bullet$, 13.7), 211 ($C_8H_{18}S_3^{+\bullet}+H^\bullet$ or $C_{10}H_{10}STi^{+\bullet}+H^\bullet$, 4.8).

Visible spectrum, $\lambda_{max}(CH_2Cl_2)$ = 570 nm (ε 3.30 × 10^3 L $mol^{-1}cm^{-1}$).

Preparation of Bis(η^5-methylcyclopentadienyl)(tert-butylthiolato)(tert-butyldisulfano)titanium(IV), $MeCp_2Ti(SCMe_3)(SSCMe_3)$ (4a')

$MeCp_2Ti(CO)_2$ (1.99 g, 7.59 mmol) was added to a solution of 3a (1.67 g, 7.94 mmol) in toluene (40 mL). As above, a residue was obtained which showed a NMR spectrum in which 4a' accounted for 94% of the methylcyclopentadienyl containing products. Extraction of the residue with hexanes (4 × 20 mL), concentration, and slow cooling to -78°C, gave an emerald green powder. The supernatant was decanted and

the powder dried under vacuum at -78°C. The powder was washed with hexanes (2 × 5 mL) at -78°C, and dried again at -78°C. Warming the product to -20°C gave a viscous oil (0.95 g, 30%). A second crop was similarly obtained from the supernatant (1.50 g, 47%) and was used as the analytical sample.

Anal. (%): Calcd. for $C_{20}H_{32}S_3Ti$: C, 57.67; H, 7.74; S, 23.09. Found: C, 57.60; H, 7.76; S, 23.16.

^1H NMR (C_6D_6): δ6.13 (m, 2H, C_5H_4), 6.06 (m, 2H, C_5H_4), 5.96 (m, 2H, C_5H_4), 5.70 (m, 2H, C_5H_4), 1.90 (s, 6H, $C_5H_4\underline{CH_3}$), 1.70 (s, 9H, $SC(CH_3)_3$), 1.44 (s, 9H, $SSC(CH_3)_3$).

^1H NMR (toluene d_8): δ6.05 (m, 2H, C_5H_4), 5.97 (m, 2H, C_5H_4), 5.90 (m, 2H, C_5H_4), 5.64 (m, 2H, C_5H_4), 1.89 (s, 6H, $C_5H_4\underline{CH_3}$), 1.63 (s, 9H, $SC(CH_3)_3$), 1.39 (s, 9H, $SSC(CH_3)_3$).

IR (KBr): 2910 (m), 1441 (w, br), 1360 (m), 1148 (m), 1029 (w, br), 809 (s), 642 (m, br), 589 (s), 418 (vw, br).

MS: 415 ($M^{+\bullet}-H^{\bullet}$, 2), 295 ($M^{+\bullet}-C_4H_9S_2^{\bullet}$, 24), 271 ($M^{+\bullet}-C_8H_{18}S^{\bullet}+H^{\bullet}$, 3), 239 ($M^{+\bullet}-C_8H_{18}S_2^{\bullet}-H^{\bullet}$, 14), 225 ($M^{+\bullet}-C_8H_{18}S_2^{\bullet}-CH^{\bullet}$, 4), 210 ($C_8H_{18}S_3^{+\bullet}$, 49).

Preparation of Bis(η^5-cyclopentadienyl)(isopropylthiolato)(isopropyldisulfano)titanium(IV), $Cp_2Ti(SCHMe_2)(SSCHMe_2)$ (4b)

$(Me_2CH)_2S_3$ (3b) (0.30 g, 1.65 mmol) in toluene (10 mL), was added via canula to a solution of 1 (0.29 g, 1.24 mmol) in toluene (50 mL) and the resulting solution was stirred for 16 h to give a deep purple solution. A 1 mL sample of this solution was stripped to dryness and the NMR spectrum of the residue indicated that 4b accounted for 93% of

the Cp containing products.

^{1}H NMR (C_6D_6): δ5.81 (s, 10H, C_5H_5), 3.76 (septet, 1H, J = 6.6 Hz, SCH), 3.11 (septet, 1H, J = 6.8 Hz, SSCH), 1.46 (d, 6H, J = 6.6 Hz, $SCH(\underline{CH}_3)_2$), 1.34 (d, 6H, J = 6.8 Hz, $SSCH(\underline{CH}_3)_2$).

The assignment of methine and methyl resonances in the NMR spectrum of 4b was confirmed by decoupling experiments. $Cp_2Ti(SCHMe_2)_2$ (5b) (δ5.75) and $Cp_2Ti(SSCHMe_2)_2$ (6b) (δ5.85) made up 3% and 4% respectively of the total integrated intensity in the Cp region and were assigned based upon their Cp and isopropyl resonances, which were identical to those of authentic samples or literature values[17a]. A pure sample of 4b could not be obtained due to persistent contamination with 5b and 6b after attempted purification.

Preparation of Bis(η^5-cyclopentadienyl)(benzylthiolato)(benzyldisulfano)titanium(IV), $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c)

$(PhCH_2)_2S_3$ (3c) (0.75 g, 2.69 mmol) in toluene (10 mL), was added via canula to a solution of 1 (0.63 g, 2.69 mmol) in toluene (50 mL) and the resulting solution was stirred for 43 h at 12°C, then allowed to rise to room temperature to give a deep purple solution. A NMR spectrum of the residue obtained upon drying of a 1 mL sample of this solution indicated that 4c accounted for 81% of the Cp and CH_2 containing products.

^{1}H NMR (C_6D_6): δ7.44 - 7.03 (m, 10H, C_6H_5), 5.71 (s, 10H, C_5H_5), 4.39 (s, 2H, SCH_2), 3.94 (s, 2H, $SSCH_2$).

The complexes $Cp_2Ti(SCH_2Ph)_2$ (5c) and $Cp_2Ti(SSCH_2Ph)_2$ (6c) [^{1}H NMR (C_6D_6): δ5.72 (s, 10H, C_5H_5), 3.97 (s, 4H, CH_2), phenyl region

obscured] made up 14% and 5%, respectively, of the total integrated intensity in the CH_2 region. A pure sample of 4c could not be obtained due to persistent contamination with 5c and 6c after attempted purification.

Preparation of Bis(η^5-cylcopentadienyl)(4-methylphenylthiolato)-(4-methylphenyldisulfano)titanium(IV), $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)(SS\text{-}p\text{-}C_6H_4Me)$ (4d)

$(p\text{-}C_6H_4Me)_2S_3$ (3d) (0.27 g, 0.97 mmol) was added to a solution of 1 (0.22 g, 0.94 mmol) in toluene (20 mL) at -20°C and the solution was stirred at -20°C for 9 h and then for 12 h at 5°C. The deep purple solution was stripped to dryness at room temperature. A NMR spectrum of the residue showed that 4d accounted for 84% of the Cp containing products. The only other signal in the Cp region was due to $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d). The residue was extracted with CS_2 (25 mL) at 0°C and the solution was filtered through Celite into a receiving vessel cooled to 0°C. The solvent was stripped at 0°C and the residue recrystallized from Et_2O (40 mL) at -20°C to give deep purple microcrystals (0.069 g, 16%, mp 136-138°C), which were stable to air for short periods.

Anal. (%): Calcd. for $C_{24}H_{24}S_3Ti$: C, 63.14; H, 5.30; S, 21.07. Found: C, 62.83; H, 5.50; S, 20.84.

^1H NMR (C_6D_6): δ7.64 - 6.98 (m, 8H, C_6H_4), 5.77 (s, 10H, C_5H_5), 2.11 (s, 3H, S-p-$C_6H_4\underline{CH_3}$), 2.03 (s, 3H, SS-p-$C_6H_4\underline{CH_3}$).

IR (KBr): 3104 (w), 3010 (w), 2920 (w), 2860 (w), 1486 (m), 1440 (m), 1178 (m), 1014 (m), 830 (s), 821 (s), 812 (s), 504 (w), 488 (w).

MS: 424 ($M^{+\cdot}-S^{\cdot}$, 2.4), 301 ($M^{+\cdot}-C_7H_7S_2^{\cdot}$, 27), 278 ($C_{14}H_{14}S_3^{+\cdot}$, 39), 246 ($C_{14}H_{14}S_2^{+\cdot}$, 100), 235 ($M^{+\cdot}-C_7H_7S_2^{\cdot}-C_5H_6^{\cdot}$, 7).

Preparation of Bis(η^5-cyclopentadienyl)(triphenylmethylthiolato)-(triphenylmethyldisulfano)titanium(IV), $Cp_2Ti(SCPh_3)(SSCPh_3)$ (4e)

$(Ph_3C)_2S_3$ (3e) (0.68 g, 1.17 mmol) was added to 1 (0.27 g, 1.15 mmol) in toluene (20 mL) and the solution was stirred for 32 h. The dark brown solution was stripped to dryness. A NMR spectrum of the residue showed that 4e accounted for 34% of Cp containing products. The other products were unidentified. Chromatography on activated alumina (2 × 20 cm), eluting with 1:9 CH_2Cl_2:hexanes, gave a colourless organic fraction and a slower moving purple band. Elution with CH_2Cl_2 gave the purple band which was stripped to dryness and washed with hexanes (2 × 2 mL) to give the product (0.17 g, 19%, mp 126-128°C).

Anal. (%): Calcd. for $C_{48}H_{40}S_3Ti$: C, 75.77; H, 5.30; S, 12.64. Found: C, 75.65; H, 5.49; S, 12.53.

^{1}H NMR (C_6D_6): δ7.74 - 7.10 (m, 30H, C_6H_5), 5.44 (s, 10H, C_5H_5).

^{1}H NMR (acetone d_6): δ7.50 - 7.26 (m, 30H, C_6H_5), 5.78 (s, 10H, C_5H_5).

^{1}H NMR ($CDCl_3$): δ7.50 - 7.21 (m, 30H, C_6H_5), 5.63 (s, 10H, C_5H_5).

IR (KBr): 3045 (w), 2944 (w, br), 1482 (w), 1468 (m), 1258 (w), 1076 (m, br), 1016 (m, br), 817 (s), 739 (m), 696 (s), 614 (w), 496 (w, br).

MS: 759 ($M^{+\cdot}-H^{\cdot}$, 0.42), 626 ($C_{44}H_{35}S_2^{+\cdot}-H^{\cdot}$, 0.2), 548 ($C_{38}H_{30}S_2^{+\cdot}-2H^{\cdot}$, 0.52), 409 ($C_{32}H_{25}^{+\cdot}$, 1.25).

Reaction of $Cp_2Ti(CO)_2$ (1) with $Ph_3CSSSCMe_3$ (3f)

3f (0.19 g, 0.48 mmol) was added to a solution of 1 (0.11 g, 0.47

mmol) and the solution was stirred for 28 h. The dark green solution was stripped to dryness and a NMR of the residue showed that $Cp_2Ti(SCPh_3)(SSCMe_3)$ (4f) and $Cp_2Ti(SCMe_3)(SSCPh_3)$ (4g) accounted for 45% and 4% respectively of the Cp containing products. The remainder of the Cp region consisted of a broad band from δ7.0 - 5,6 ppm due to unidentified products. Flash chromatography on activated alumina (1 × 20 cm), eluting with 50:50 CH_2Cl_2:hexanes, gave a single turquoise band. This band was collected and stripped to dryness and the NMR spectrum of the residue (0.026 g) showed that the mixture consisted of: 4f with 84% of the Cp region integrated intensity, ^1H NMR (C_6D_6): δ5.65 (s, 10H, C_5H_5), 1.41 (s, 9H, CH_3); and 4g with 16%, ^1H NMR (C_6D_6): δ5.69 (s, 10H, C_5H_5), 1.71 (s, 9H, CH_3). The phenyl regions were overlapping. No further attempts at seperation and isolation of the products were made.

Reaction of $Cp_2Ti(CO)_2$ (1) with RSSSR (3) in Refluxing Toluene

Since a similar procedure was followed for R = CMe_3 (3a), $CHMe_2$ (3b), CH_2Ph (3c) and p-C_6H_4Me (3d), only one example, R = p-C_6H_4Me, is described in detail. A solution of 3d (0.24 g, 0.86 mmol) in toluene (20 mL) was added via canula to a solution of 1 (0.20 g, 0.85 mmol) in toluene (50 mL). The reaction mixture was refluxed for 1.5 h after which the presence of a mixture of $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d) and $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)(SS\text{-}p\text{-}C_6H_4Me)$ (4d) was detected via TLC analysis. The solution was refluxed for a further 4 h to give a red-purple solution. A 2 mL sample was removed by syringe and was evaporated to dryness. The NMR spectrum (C_6D_6) of the residue indicated that 5d now accounted for 96% of the cyclopentadienyl resonances, the remainder being due to 4d.

R = $CHMe_2$. Similarly 1 and 3b after refluxing for 74 h gave a solution consisting of $Cp_2Ti(SCHMe_2)_2$ (5b) (85%) and $Cp_2Ti(SCHMe_2)(SSCHMe_2)$ (4b) (8%), in addition to other unidentified species.

R = CH_2Ph. 1 and 3c after refluxing for 15 h gave a solution consisting of $Cp_2Ti(SCH_2Ph)_2$ (5c) (88%) and $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c) (12%).

R = CMe_3. 1 and 3a after refluxing for 67 h resulted in an emerald green solution consisting predominantly of $(Me_3C)_2S_x$ (x = 2, 3) and a species with a very broad resonance in the region δ7.0 - 5.0 ppm. Bands assigned to traces of $Cp_2Ti(SCMe_3)(SSCMe_3)$ (4a) and $Cp_2Ti(SCMe_3)_2$ (5a) were detected. A substantial amount of brown powder was present as a precipitate (0.24 g, 48%), which was insoluble in toluene d_8 or $CDCl_3$. Anal. (%): Calcd. for $C_{10}H_{10}S_{1.50}Ti_{0.80}$: C, 55.45; H, 4.65; S, 22.20. Found: C, 55.42; H, 4.88; S, 22.23.

Reaction of $Cp_2Ti(CO)_2$ (1) with $(PhCH_2)_2S_3$ (3c) in Toluene d_8 at 80°C

A NMR sample was prepared containing 1 (41 mg, 0.18 mmol) and 3c (52 mg, 0.19 mmol) in toluene d_8 and was heated at 80°C for 48 h to give a purple solution. A NMR spectrum gave bands due to $Cp_2Ti(SCH_2Ph)_2$ (5c) (45%), $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c) (21%) and a very broad band of cyclopentadienyl resonances (34%) in the range δ6.5 - 5.9 ppm.

Thermal Desulfurization of $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c)

The complex 1 (1.82 g, 7.77 mmol) and $(PhCH_2)_2S_3$ (3c) (2.21 g, 7.94 mmol) were reacted, as described earlier, in toluene at 12°C to give (NMR analysis of a dried aliquot in C_6D_6) a mixture of $Cp_2Ti(SCH_2Ph)_2$ (5c) (28% by integration of the Cp region),

$Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c) (58%) and $Cp_2Ti(SSCH_2Ph)_2$ (6c) (14%), without residual 1. The toluene solution was then refluxed for 42 h, at which point neither 4c nor 6c could be detected by NMR. A band due to 5c (80%) was the major resonance in the cyclopentadienyl region, in addition to a broad band from δ6.4 - 5.8 ppm (20%). The solution was stripped to dryness, dissolved in 1:1 hexanes:CH_2Cl_2 and applied to a column of activated alumina (4 x 30 cm). Elution with hexanes (1.5 L) gave a colourless fraction which was stripped to dryness (0.20 g) and was shown by NMR to contain $(PhCH_2)_2S_x$, where x = 2 and 3. Elution with CH_2Cl_2 gave a red-purple band which was collected, stripped to dryness and then washed with pentane (5 x 100 mL), to give pure $Cp_2Ti(SCH_2Ph)_2$ (5c) (1.39 g, 42%). The pentane washings were stripped to dryness (0.90 g) and were shown by NMR to consist predominantly of $(PhCH_2)_2S_2$ with traces of $(PhCH_2)_2S_3$. Specific attempts to detect S_8 via TLC in all of the fractions collected, were unsuccessful.

Desulfurization of $Cp_2Ti(SR)(SSR)$ (4a-e) by Ph_3P

Two NMR samples, A and B, were prepared in C_6D_6 for each of 4a-e (toluene d_8 was used for 4d). For R = $CHMe_2$ (4b), CH_2Ph (4c) and p-C_6H_4Me (4d) the samples were generated *in situ*. For R = CMe_3 (4a) and CPh_3 (4e) pure samples were used.

A slight excess of one equivalent of Ph_3P was added to sample A. The NMR signals due to 4a-d decreased in intensity over several days concomitant with the increase in intensity of peaks due to $Cp_2Ti(SR)_2$ (5a-d), and Ph_3PS. None of the starting complex could be detected for R = CMe_3 after 11 days; $CHMe_2$ after 12 days; CH_2Ph after 3 days; and

p-C_6H_4Me after 1 day. For R = CMe_3, after 11 days the cyclopentadienyl signals due to $Cp_2Ti(SR)_2$ (5a) accounted for 22% of the integrated intensity in the Cp region, while a broad resonance in the region δ6.9 - 5.9 ppm accounted for the remainder. For R = $CHMe_2$, a similar result was obtained. For R = CPh_3, after 3.5 days the NMR signals due to the starting material had decreased (9%) concomitant with formation of a broad cyclopentadienyl resonance (91%) in the region δ6.9 - 5.6 ppm. Only a small amount of Ph_3PS was detected.

After the same period for the B samples the ratio $Cp_2Ti(SR)(SSR)$: $Cp_2Ti(SR)_2$ was 5:3 for R = CH_2Ph, and 2:1 for R = p-C_6H_4Me. No $Cp_2Ti(SCHMe_2)(SSCHMe_2)$ was detected after 12 days. For R = CMe_3, the cyclopentadienyl region consisted of a very broad signal in the region δ6.9 - 5.9 ppm (77%) and signals due to $Cp_2Ti(SCMe_3)(SSCMe_3)$ (7%) and $Cp_2Ti(SCMe_3)_2$ (16%). For R = CMe_3 and $CHMe_2$, in both samples A and B, significant quantities of R_2S_x, where x = 2 and 3 were observed. For R = CPh_3, in sample B after 3.5 days a precipitate had formed and NMR signals due to $Cp_2Ti(SCPh_3)_2$ (3%) and a broad band at δ6.9 - 5.5 ppm (97%) were observed. NMR signals due to $Cp_2Ti(SCPh_3)(SSCPh_3)$ were not detected.

Desulfurization of $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c) with Ph_3P, Preparative Scale

$(PhCH_2)_2S_3$ (3c) (1.20 g, 4.31 mmol) was added to a solution of 1 (1.01 g, 4.31 mmol) in toluene (40 mL) at 12°C and the reaction mixture was stirred for 50 h at 12°C followed by 20 h at 20°C, to give a deep purple solution. A 2 mL aliquot of the solution was stripped to

dryness. A ^1H NMR spectrum of the residue indicated a mixture of $Cp_2Ti(SCH_2Ph)_2$ (5c) (38%, integrated intensity of the Cp region), $Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$ (4c) (49%) and $Cp_2Ti(SSCH_2Ph)_2$ (6c) (13%). The solution contained no residual 1. A slight excess of Ph_3P was added to the reaction solution and stirring was continued at room temperature for 3 days. NMR analysis of a dried aliquot indicated that 5c and Ph_3PS were the major constituents, with traces of $(PhCH_2)_2S_x$ (x = 2, 3) also present. The reaction mixture was stripped to dryness. Chromatography on activated alumina (4 × 30 cm), eluting with 1:2 Et_2O:hexanes, gave two colourless fractions which were stripped to dryness and identified as: (i) a mixture of Ph_3P and $(PhCH_2)_2S_2$; and (ii) Ph_3PS (0.91 g, 72%). Elution with CH_2Cl_2 gave a red band which was collected and stripped to dryness giving red-purple microcrystals of 5c (1.12 g, 61%).

Desulfurization of $Cp_2Ti(SCMe_3)(SSCMe_3)$ (4a) by $Cp_2Ti(CO)_2$ (1)

1 (0.08 g, 0.33 mmol) was added to a solution of 4a (0.13 g, 0.33 mmol) in toluene (10 mL) giving an emerald green solution. The temperature of the reaction mixture was raised quickly and was stirred under reflux for 9 min. A red-brown solution was obtained which was stripped to dryness. The residue was extracted with hexanes (8 × 10 mL) until the extracts were colourless. These extracts were evaporated to dryness and a ^1H NMR spectrum indicated the presence of almost pure $Cp_2Ti(SCMe_3)_2$ (5a). The light brown residue remaining (0.09 g) was soluble in C_6D_6 and a NMR spectrum indicated the presence of a large number of sharp resonances in the cyclopentadienyl region in the range, δ7.2 - 5.7 ppm.

Anal. (%): Calcd. for $C_{10}H_{10}S_{0.78}Ti_{1.34}$: C, 54.75; H, 4.59; S, 11.40. Found: C, 54.34; H, 5.07; S, 11.65.

Reaction of $Cp_2Ti(SR)(SSR)$ (4a-e) with Benzylbromide

Toluene solutions of $Cp_2Ti(SR)(SSR)$ (the species, where R = CMe_3 (4a), $CHMe_2$ (4b), CH_2Ph (4c) and p-C_6H_4Me (4d), were prepared in situ as described above) were treated with two equivalents of $PhCH_2Br$ and then refluxed for 4 h to give orange-red solutions. A 2 mL sample of each was carefully concentrated, to avoid evaporation of volatile products, and was shown to contain Cp_2TiBr_2, $RSCH_2Ph$ (7a-d), $RSSCH_2Ph$ (8a-d), $(PhCH_2)_2S$ and $(PhCH_2)_2$ (for 4a only) by means of NMR and GC-mass spectral analysis. The reaction solutions were concentrated to about 30 mL and cooled at -16°C overnight to give Cp_2TiBr_2 as dark red crystals, which were collected by filtration and washed with a small quantity of Et_2O.

A toluene solution of $Cp_2Ti(SCPh_3)(SSCPh_3)$ (4e) was treated with two equivalents of $PhCH_2Br$ and was refluxed for 2 h to give an orange-red solution. In a similar manner, a mixture of $Cp_2Ti(SCPh_3)(SSCMe_3)$ (4f) and $Cp_2Ti(SCMe_3)(SSCPh_3)$ (4g) (prepared as described above) also gave an orange-red solution. Both reaction mixtures were carefully concentrated and were shown by NMR to contain Cp_2TiBr_2 and Cp_2TiS_5 as minor products, in addition to a very broad band in the region δ7.0 - 6.0 ppm and a great many organic products. Neither ^1H NMR nor GC-mass spectra were helpful in elucidation of the composition of the reaction mixture.

Preparation of Bis(η^5-cyclopentadienyl)bis(triphenylmethylthiolato)-titanium(IV), $Cp_2Ti(SCPh_3)_2$ (5e)

Phenyllithium (4.2 mL of a 2.0 M solution in cyclohexane/Et_2O, 8.4 mmol) was added by syringe to a solution of triphenylmethanethiol (2.12 g, 7.67 mmol) in THF (100 mL) and the solution was stirred at 0°C for 30 min. A solution of Cp_2TiCl_2 (0.64 g, 2.56 mmol) in THF (100 mL) was added dropwise to the solution of $LiSCPh_3$ over a period of 20 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for a further 3 h. The deep red solution was filtered through activated alumina (2 × 6 cm) and then stripped to dryness. The residue was extracted with CH_2Cl_2 (80 mL), the extracts were filtered through Celite and the filtrate was stripped to dryness to give a red powder. The powder was washed with Et_2O until the washings were very pale pink (80 mL) and was then dried under vacuum (0.60 g, 32%, mp 176-177°C (dec)).

Anal. (%): Calcd. for $C_{48}H_{40}S_2Ti$: C, 79.10; H, 5.53; S, 8.80. Found: C, 78.92; H, 5.41; S, 8.91.

^1H NMR (C_6D_6): δ7.71 - 7.05 (m, 30H, C_6H_5), 5.47 (s, 10H, C_5H_5).

^1H NMR ($CDCl_3$): δ7.39 - 7.11 (m, 30H, C_6H_5), 5.63 (s, 10H, C_5H_5).

IR (KBr): 3048 (w, br), 1579 (w), 1481 (w), 1439 (m), 1177 (w), 1076 (w), 1017 (m), 817 (s), 738 (s), 696 (s), 618 (m), 495 (w).

Preparation of Triphenylmethyl(tert-butyl)trisulfide, $Ph_3CSSSCMe_3$ (3f)

A solution of Me_3CSH (0.54 g, 5.99 mmol) in Et_2O (20 mL) was added over a period of 20 min to a suspension of Ph_3CSSCl (2.00 g, 5.83 mmol) in Et_2O (80 mL) at -78°C. The solution was allowed to warm slowly to

room temperature with stirring, over a period of 90 min. The solvent was stripped off and the residue was recrystallized from hexanes. Two crops of white microcrystals were obtained (1.15 g, 50%, mp 98-100°C).
^{1}H NMR (C_6D_6): δ7.58 - 6.98 (m, 15H, C_6H_5), 1.19 (s, 9H, CH_3).
^{1}H NMR ($CDCl_3$): δ7.33 - 7.25 (m, 15H, C_6H_5), 1.29 (s, 9H, CH_3).

Preparation of Unsymmetrical Benzylsulfides, $RSCH_2Ph$ (R = p-C_6H_4Me (7d) and CPh_3 (7e)[19])

The preparations of these sulfides were very similar and therefore only that for R = p-C_6H_4Me is given.

An aqueous solution (30 mL) of KOH (4.75 g, 84.8 mmol) was added over a period of 15 min to stirred neat p-MeC_6H_4SH (9.57 g, 77.0 mmol). To the reaction mixture was added $PhCH_2Br$ (13.18 g, 77.0 mmol) and the solution was stirred for 4 h at 60°C. The solution was extracted with CH_2Cl_2 (2 × 100 mL) in a seperatory funnel and the extracts were dried over Na_2SO_4 and filtered. Fractional distillation of the extracts gave 7d (13.12 g, 80%, bp 118-124°C at 0.45 mmHg, mp 43-44°C).

For R = CPh_3, KOH was added as a 1:1 H_2O:EtOH solution. Recrystallization from hexanes gave 7e (3.83 g, 79%, mp 87-89°C).

Results

The reaction between $Cp_2Ti(CO)_2$ (1) and RSSSR (3), where R = CMe_3 (3a), $CHMe_2$ (3b), CH_2Ph (3c), p-C_6H_4Me (3d) and CPh_3 (3e), in toluene, was monitored by observing the decrease in intensity of CO bands due to 1 in the infrared spectrum. For 3a-d the products consisted of mixtures of $Cp_2Ti(SR)(SSR)$ (4a-d), $Cp_2Ti(SR)_2$ (5a-d) and $Cp_2Ti(SSR)_2$ (6b,c), as shown in Eq. II.1. A similar result was obtained for the reaction of $MeCp_2Ti(CO)_2$ with 3a. The relative compositions of the product mixtures, as determined by NMR analysis, are given in Table II.1. In the reaction of 1 with 3e the complex $Cp_2Ti(SCPh_3)(SSCPh_3)$ (4e) was the only product identified by its NMR spectrum. The other species present gave a broad band of resonances in the Cp region at δ7.0 - 5.6 ppm. The

$$Cp_2Ti(CO)_2 + RSSSR \xrightarrow{-2CO} Cp_2Ti\begin{matrix}SSR\\SR\end{matrix} + Cp_2Ti\begin{matrix}SR\\SR\end{matrix} + Cp_2Ti\begin{matrix}SSR\\SSR\end{matrix} \qquad \text{(II.1)}$$

1 3a-d 4a-d 5a-d 6b,c

Major Product

reaction of 1 with the unsymmetrical trisulfide, $Ph_3CSSSCMe_3$ (3f), gave a mixture in which two species assigned to $Cp_2Ti(SCPh_3)(SSCMe_3)$ (4f) and $Cp_2Ti(SCMe_3)(SSCPh_3)$ (4g) were present, in addition to a broad band of resonances in the region δ7.0 - 5.6 ppm. The NMR spectral data for the complexes 4a-g, 5a-e and 6b are given in Table II.2.

The relative amounts of the products shown in Eq. II.1 depended on the R group and the reaction temperature. In general lower temperatures favoured 4, with the ratio of 4:5 being: 24 for 3a at 22°C; 31 for 3b at

TABLE II.1: Products of Oxidative-Addition of RSSSR to $Cp_2Ti(CO)_2$[a]

R		$Cp_2Ti(SSR)(SR)$	$Cp_2Ti(SR)_2$	$Cp_2Ti(SSR)_2$
CMe_3	3a	96	4	0
$CHMe_2$	3b	93	3	4
CH_2Ph	3c	81	14	5
p-C_6H_4Me	3d	84	16	0
CPh_3	3e	34[b]	0	0

[a] Percentage, based on NMR integration of the peaks due to Cp and/or R groups at the point in the reaction when all $Cp_2Ti(CO)_2$ was consumed, as determined by IR.

[b] The other products were in the form of a broad band in the region δ7.0 - 5.6 ppm, and were unassigned.

22°C; 5.8 for 3c at 12°C; and 5.3 for 3d at -20°C (Table II.1). The solubility and chromatographic properties of 4, 5 and 6 were very similar, making seperation difficult; however analytically pure samples of 4a, 4d and 4e were isolated by recrystallization or chromatography. Complexes 4b-e were intensely deep purple in colour while 4a was very dark emerald green. The bisthiolato complexes 5a-e were red. All disulfano species obtained were air-sensitive, but could be handled in air for short periods. The respective dithiolates 5b-d were relatively air-stable, whereas 5a and 5e decomposed slowly in air. Attempts to

TABLE II.2: ^{1}H NMR Data for $RCp_2Ti(SR')(S_xR'')$, where x = 1 and 2[a]

Complex		Assignment RCp	CH	CH_2	CH_3
$Cp_2Ti(SCMe_3)_2$	5a	5.89			1.64
$Cp_2Ti(SCMe_3)(SSCMe_3)$	4a	5.91			1.66 1.42
$MeCp_2Ti(SCMe_3)(SSCMe_3)$	4a'	6.13m 6.06m 5.96m 5.70m 1.90			1.70 1.44
$Cp_2Ti(SCHMe_2)_2$	5b	5.75	3.62[b]		1.43[b]
$Cp_2Ti(SCHMe_2)(SSCHMe_2)$	4b	5.81	3.76[c] 3.11[d]		1.46[c] 1.34[d]
$Cp_2Ti(SSCHMe_2)_2$[17a]	6b	5.85	3.21[e]		1.35[e]
$Cp_2Ti(SCH_2Ph)_2$[f]	5c	5.72		4.31	
$Cp_2Ti(SCH_2Ph)(SSCH_2Ph)$[g]	4c	5.71		4.39 3.94	
$Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$[h]	5d	5.72			2.12
$Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)(SS\text{-}p\text{-}C_6H_4Me)$[i]	4d	5.77			2.11 2.03
$Cp_2Ti(SCPh_3)_2$[j]	5e	5.47			
$Cp_2Ti(SCPh_3)(SSCPh_3)$[k]	4e	5.44			
$Cp_2Ti(SCPh_3)(SSCMe_3)$[l]	4f	5.65			1.41
$Cp_2Ti(SCMe_3)(SSCPh_3)$[l]	4g	5.69			1.71

[a] C_6D_6 in δ ppm, all peaks are singlets unless otherwise noted.
[b] J(H-H) = 6.9 Hz. [c] J(H-H) = 6.6 Hz. [d] J(H-H) = 6.8 Hz.
[e] J(H-H) = 6.7 Hz. [f] C_6H_5 = 7.45 - 7.05. [g] C_6H_5 = 7.44 - 7.03.
[h] C_6H_4 = 7.83, 7.00, AB quartet, J(H-H) = 8.1 Hz.
[i] C_6H_4 = 7.64 - 6.98. [j] C_6H_5 = 7.71 - 7.05. [k] C_6H_5 = 7.74 - 7.10.
[l] Combined C_6H_5 region = 7.72 - 6.95.

grow single crystals of 4 were unsuccessful possibly due to the presence of small quantities of RS_3R which were often observed. Polysulfides are sometimes used as softening agents in rubber and rubber substitutes[48].

Reaction of $Cp_2Ti(CO)_2$ (1) and 3b-d in refluxing toluene gave 5b-d as the major products, with the ratio of 4:5 being: 0.09 for 3b after 74 h; 0.14 for 3c after 15 h; and 0.04 for 3d after 5.5 h. Significant amounts of starting trisulfides 3b-d, were detected in these reactions. In the case of 3a only traces of 4a and 5a were detected in the NMR spectrum of the crude product; however a very broad band appeared in the cyclopentadienyl region in the range δ7.0 - 5.0 ppm together with strong peaks due to $(Me_3C)_2S_x$, where x = 2 and 3. When $Cp_2Ti(CO)_2$ (1) and 3c were reacted at 80°C in toluene d_8 for 48 h a similar broad band in the Cp region (δ6.5 - 5.9 ppm) was detected, in addition to resonances due to 5c and 4c. This latter reaction was also performed in toluene on a preparative scale (Eq. II.2) and the crude product mixture was

$$Cp_2Ti(CO)_2 + PhCH_2SSSCH_2Ph \xrightarrow{\Delta} Cp_2Ti(SCH_2Ph)_2 + ? \qquad \text{(II.2)}$$

1 3c 5c

chromatographed on a column specifically developed to seperate a standard sample consisting of 5c and S_8. Complex 5c was isolated, but no S_8 was detected, nor was S_8 detected in any of the reactions using sensitive TLC techniques previously developed for this purpose in this laboratory[49]. The species responsible for the broad band in the

cyclopentadienyl region did not survive the column. Various attempts were made to isolate the species causing the broad Cp region band without success.

When 1 and 3a were refluxed for 64 h in toluene an insoluble material was obtained, the elemental analysis of which is consistent with the empirical formula, $C_{10}H_{10}S_{1.50}Ti_{0.80}$. The rapid reaction between 1 and 4a also at reflux in toluene gave a fairly soluble substance exhibiting the characteristic broad band of resonances in the cyclopentadienyl region (δ7.2 - 5.7 ppm). Elemental analysis of this material is consistent with the empirical formula, $C_{10}H_{10}S_{0.78}Ti_{1.34}$. Recrystallizations of these materials were unsuccessful, as were mass spectra.

The NMR spectra of $Cp_2Ti(SR)(SSR)$ (4a-e), in C_6D_6 or toluene d_8, were monitored over time. Pure samples of 4a and 4e were used and the other samples prepared *in situ* contained the appropriate amounts of $Cp_2Ti(SR)_2$ (5b-d) and $Cp_2Ti(SSR)_2$ (6b,c), where applicable (Table II.1). The samples did not contain any residual 1.

For 4c and 4d peaks due to 5c and 5d, respectively, grew in intensity at the expense of the former until the ratio of 4:5 was: 5:3 for c after 3 days; and 2:1 for d after 1 day. The peaks due to the disulfano species 6c diminished in intensity more rapidly than 4c. The addition of approximately one equivalent of Ph_3P to the fresh solutions accelerated the loss of sulfur such that only 5c and 5d were detected after 3 and 1 day(s), respectively. Peaks due to Ph_3PS were observed. $Cp_2Ti(SCH_2Ph)_2$ (5c) and Ph_3PS were subsequently isolated from a larger scale reaction, in 61% and 72% yields, respectively.

For the NMR samples containing 4a and 4b without Ph_3P, the spectral changes were dominated by the growth of a broad band in the Cp region. While peaks due to 4a and 5a were detected, the broad band accounted for 77% of the integrated intensity in the Cp region after 11 days. After 3 days no 5b was observed, but 4b was still present (39%) and the broad band accounted for 48% of the intensity in the Cp region, while another sharp resonance tentatively assigned to $Cp_2Ti(SSCHMe_2)_2$ (6b) accounted for the remainder. For both 4a and 4b peaks due to RS_xR, where x = 2 and 3, were detected. In the presence of Ph_3P, the complex 4a was not detected after 11 days, while 5a accounted for 22% of the integrated intensity and the broad band made up the remainder. Peaks due to 4b, 5b and the broad band were detected in the relative intensities 1:1:2, respectively, after 3 days in the presence of Ph_3P. No 6b was observed after 3 days. For both 4a and 4b peaks due to Ph_3PS and RS_xR, where x = 2 and 3, were also observed. Attempts to desulfurize 4a cleanly using $MePh_2P$, Et_3P, Me_3P, $(Et_2N)_3P$ and CH_3NC led to intractable mixtures.

In the case of 4e without the presence of Ph_3P, a broad band in the Cp region (97%) dominated the spectrum after 3.5 days, only a trace of 5e was present (3%), and the solution was red in colour. In the presence of Ph_3P only a small quantity of Ph_3PS was detected after the same time. The Cp resonance due to 4e accounted for only 9% of the integrated intensity in the Cp region of a NMR spectrum of the purple solution, with the broad band making up the remainder.

Treatment of bisthiolato complexes of the type $Cp_2Ti(SR)_2$, where R = $CHMe_2$ (5b), CH_2Ph (5c), Ph (5f) and $(CH_2)_3CH_3$ (5g), with two equivalents of $PhCH_2Br$ in refluxing toluene, gives Cp_2TiBr_2 and the

appropriate sulfides $RSCH_2Ph$ (7b,c,f,g)[20]. Similar treatment of $Cp_2Ti(SR)(SSR)$ (4a-d) gave Cp_2TiBr_2 and the appropriate sulfides $RSCH_2Ph$ (7a-d) and disulfides $RSSCH_2Ph$ (8a-d), in approximately the expected ratio as determined by NMR and GC techniques (Table II.3). In addition, small quantities of the sulfide $(PhCH_2)_2S$ were observed for the reactions of 4a,b,d with $PhCH_2Br$. Dibenzyl was also detected by NMR and GC in the reaction with 4a. ^1H NMR values for the products of the reactions are shown in Tables II.3 and II.4. Control reactions involving refluxing 3a-d in toluene for 4 h with two equivalents of $PhCH_2Br$ showed no evidence for sulfides or disulfides. The calculated ratios for $RSCH_2Ph$:$RSSCH_2Ph$, as shown in Table II.3, have been corrected for the presence of $Cp_2Ti(SR)_2$ (5a-d) and $Cp_2Ti(SSR)_2$ (6b,c) which always accompany the in situ preparation of 4a-d, but which were easily measured by integration of the NMR spectrum.

The reaction of triphenylmethyl containing species 4e-g with two equivalents of $PhCH_2Br$ gave low yields of Cp_2TiBr_2 and Cp_2TiS_5[21] as detected by NMR, in addition to a mixture of organic products. GC-mass spectra of the mixtures showed the presence of Ph_3CH as the major component; however the instability and lack of volatility of compounds containing the triphenylmethyl group precludes the conclusion that Ph_3CH is indeed the major product in the crude reaction mixtures.

TABLE II.3: Products of Reaction of $Cp_2Ti(SR)(SSR)$ with $PhCH_2Br$

R		Products (%)[a]					$RSCH_2Ph/RSSCH_2Ph$	
		Cp_2TiBr_2[b]	$PhCH_2SR$	$PhCH_2SSR$	$(PhCH_2)_2S$	$(PhCH_2)_2$[c]	Calculated[d]	Found
CMe_3	4a	100	25	41	3	31	1.08	0.61
$CHMe_2$	4b	63	40	54	6	0	0.98	0.74
CH_2Ph	4c	66	60	40	NA	0	1.20	1.50
$p\text{-}C_6H_4Me$	4d	18[e]	64	35	1	0	1.38	1.83

[a] The percentage yield represents: the isolated yield for Cp_2TiBr_2; the calculated yield by ^1H NMR analysis of the crude reaction mixture immediately after completion of the reaction for all R groups, except R = CH_2Ph, which was calculated by GC comparison to known standards.

[b] ^1H NMR (C_6D_6): δ6.00 (s, C_5H_5).

[c] ^1H NMR (C_6D_6): δ7.17 - 6.96 (m, C_6H_5), 2.74 (s, CH_2).

[d] The calculated yields are corrected for the presence of 5 and 6 formed in the preparation of $Cp_2Ti(SR)(SSR)$ (Table II.1).

[e] Low yields of pure Cp_2TiBr_2 were obtained, due to cocrystallization of organometallic and organic products of the reaction.

TABLE II.4: ^{1}H NMR Data for RS_xR', where x = 1, 2 and 3[a]

Compound		Assignment				
		CH	CH_2	CH_3	C_6H_4	C_6H_5
$(Me_3C)_2S$				1.34		
$(Me_3C)_2S_2$				1.22		
$(Me_3C)_2S_3$	3a			1.27		
$(Me_2CH)_2S$		2.78[b]		1.16[b]		
$(Me_2CH)_2S_2$		2.79[b]		1.16[b]		
$(Me_2CH)_2S_3$	3b	3.00[b]		1.17[b]		
$(PhCH_2)_2S$	7c		3.34			7.14 - 7.07
$(PhCH_2)_2S_2$	8c		3.34			7.14 - 7.07
$(PhCH_2)_2S_3$	3c		3.72			7.09 - 7.05
$(p\text{-}C_6H_4Me)_2S_2$	d{			1.94 1.97	7.40, 6.75[c] 7.33, 6.75[e]	
$(p\text{-}C_6H_4Me)_2S_3$	3d d{			1.94 1.98	7.33, 6.75[f] 7.35, 6.73[f]	
$(Ph_3C)_2S$						7.75 - 7.00
$(Ph_3C)_2S_2$						7.75 - 6.90
$(Ph_3C)_2S_3$	3e					7.47 - 6.98
$Ph_3CSSSCMe_3$	3f			1.19		7.58 - 6.98
$PhCH_2SCMe_3$	7a		3.56	1.19		7.31 - 7.08
$PhCH_2SSCMe_3$[g]	8a		3.74	1.19		obscured
$PhCH_2SCHMe_2$	7b	2.58[h]	3.50	1.07[h]		7.22 - 7.06
$PhCH_2SSCHMe_2$[g]	8b	2.47[i]	3.62	1.05[i]		obscured

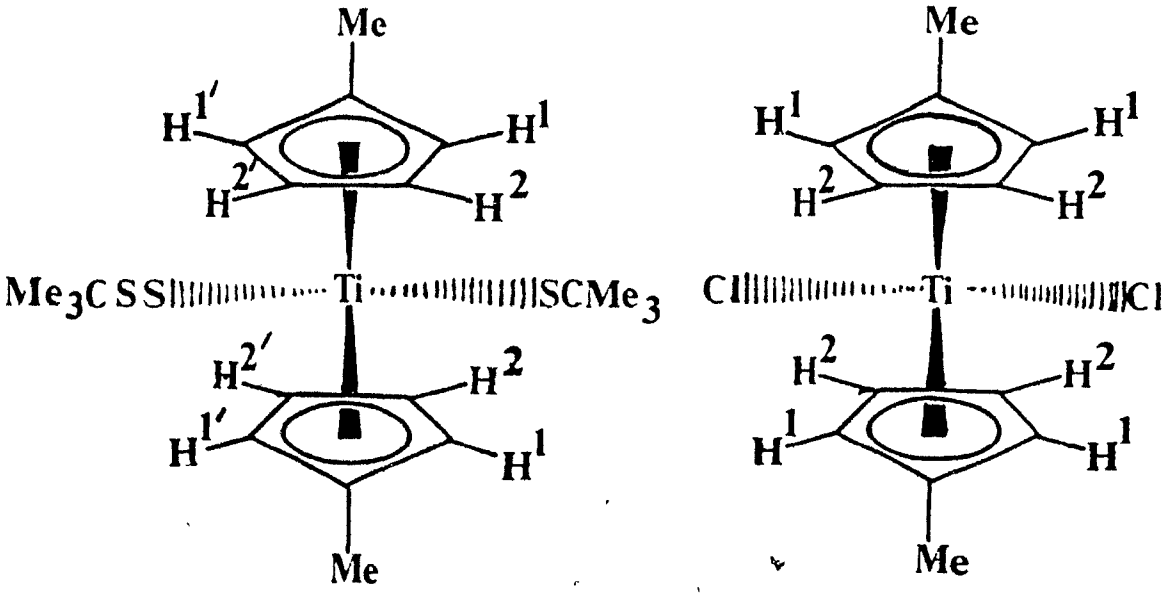
TABLE II.4: (cont'd)

Compound		Assignment				
		CH	CH_2	CH_3	C_6H_4	C_6H_5
$PhCH_2S$-p-C_6H_4Me	7d		3.81	1.99	7.19 - 6.78	
$PhCH_2SS$-p-C_6H_4Me[g]	8d		4.28	1.93	obscured	
$PhCH_2SCPh_3$	7e		3.39			7.65 - 7.00

[a] C_6D_6 in δ ppm unless otherwise noted. [b] J(H-H) = 6.8 Hz.
[c] AB q, J = 8.4 Hz. [d] Toluene d_8. [e] AB q, J = 8.3 Hz.
[f] AB q, J = 8.1 Hz.
[g] Obtained from the reaction of $Cp_2Ti(SR)(SSR)$ with $2PhCH_2Br$ and was not isolated. [h] J(H-H) = 6.7 Hz. [i] J(H-H) = 6.6 Hz.

Discussion

The presence of the novel TiSSR linkage in 4a-e is consistent with their physical and chemical properties. The complexes 4a-d display ^{1}H NMR spectra which are significantly different from those of closely related 5a-d, but which are in accordance with the unsymmetrical nature of 4a-d, with respect to the number and relative intensities of the peaks due to the Cp ligands and the two R groups (Table II.2). The NMR spectrum of the methyl substituted species, $MeCp_2Ti(SCMe_3)(SSCMe_3)$ (4a'), clearly shows the presence of two different sulfur containing ligands. The spectrum consists of two tert-butyl resonances as previously seen for 4a, a singlet due to equivalent methyl groups on the substituted cyclopentadienyl rings, and a total of four bands in the Cp region. The latter arises from the apparently diastereotopic environments of the ring protons, as shown below. By comparison, the complex $MeCp_2TiCl_2$, which can possess a mirror plane through the titanium and the MeCp rings, exhibits only two bands in the Cp region[22].



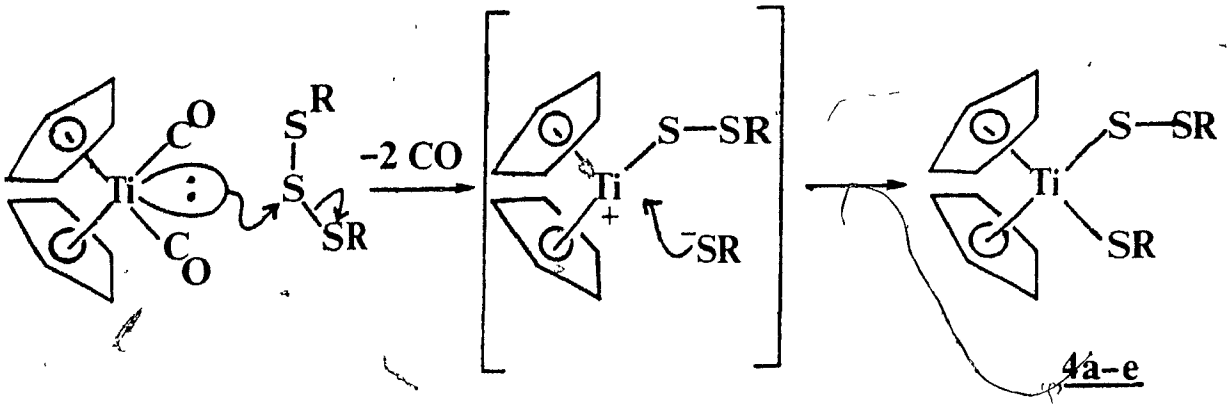
The NMR signals observed at high field for one of the R groups of the sulfur containing ligands in 4a-d are similar in chemical shift to those observed for RS_xR, where $x \geq 1$ (Table II.4), while the signals for the other R groups are similar to those observed for 5a-d. It seems reasonable to assume that the R groups of the disulfano ligand, SSR, account for the higher field peaks. The R groups of the thiolato ligand, SR, in 4a-d and 5a-d, are in lower field environments, presumably due to their closer proximity to the metal centre (Table II.2).

Qualitatively, it appears that the rate of oxidative-addition of RSSSR (3a-d) to 1 may be related to the electronegativity of the R substituent in the order,

$$\underset{\text{3d}}{p\text{-}C_6H_4Me} > \underset{\text{3c}}{CH_2Ph} > \underset{\text{3b}}{CHMe_2} > \underset{\text{3a}}{CMe_3}.$$

A number of mechanisms can be envisaged for the reaction which results in S-S bond cleavage in 3a-d. Since aryl thiolate anions are known to be better leaving groups than alkyl thiolates[23], the observed relative rates of reaction are consistent with a mechanism in which the stability of an intermediate thiolate anion plays an important role (Scheme II.1). This type of mechanism has previously been proposed by Floriani et al. for the reaction of 1 with disulfides, RSSR[6]. The oxidative-addition of RSSSR might also occur via initial dissociation of a CO ligand from 1[50]. The slow rates of oxidation of 1 by 3a and 3e may be caused by steric hinderance due to the large bulk of the tert-butyl and triphenymethyl

groups. In addition, the titanium sulfur bond strength may be smaller



SCHEME II.1

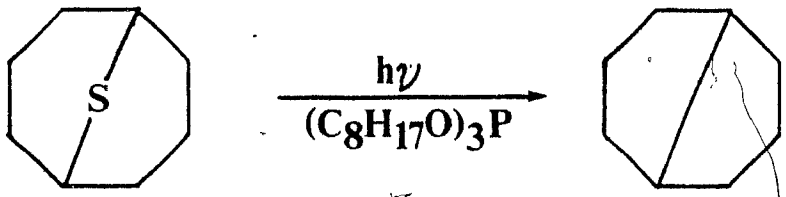
in these cases than for less sterically demanding thiolate ligands[24]. The spontaneous conversion of 4c,d to 5c,d (Eq. II.3) at room temperature in toluene is consistent with similar behaviour observed for $CpW(CO)_3SSR$[2] (Eq. II.4). The qualitative order of rates of S loss from 4a-d under thermal conditions, or in the presence of Ph_3P, are similar to those observed for the rates of oxidative-addition of 3a-d to 1, as discussed above.

$$\underset{\text{4c,d}}{Cp_2Ti(SR)(SSR)} \longrightarrow \underset{\text{5c,d}}{Cp_2Ti(SR)_2} \qquad \text{(II.3)}$$

$$CpW(CO)_3SSR \longrightarrow CpW(CO)_3SR \qquad \text{(II.4)}$$

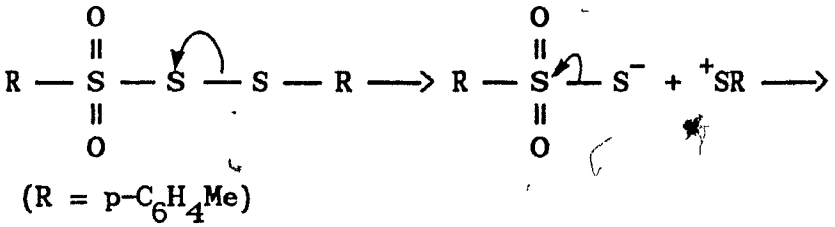
Some organosulfur compounds exhibit "spontaneous" loss of sulfur[25]. This has been observed to occur via thermal, photochemical, or solvent-related pathways[26]. For example, sulfur-bridged carbocycles can

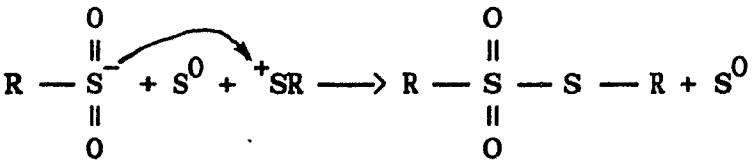
be induced to lose S via irradiation, using phosphite as a solvent, as shown in Eq. II.5 [27].



(II.5)

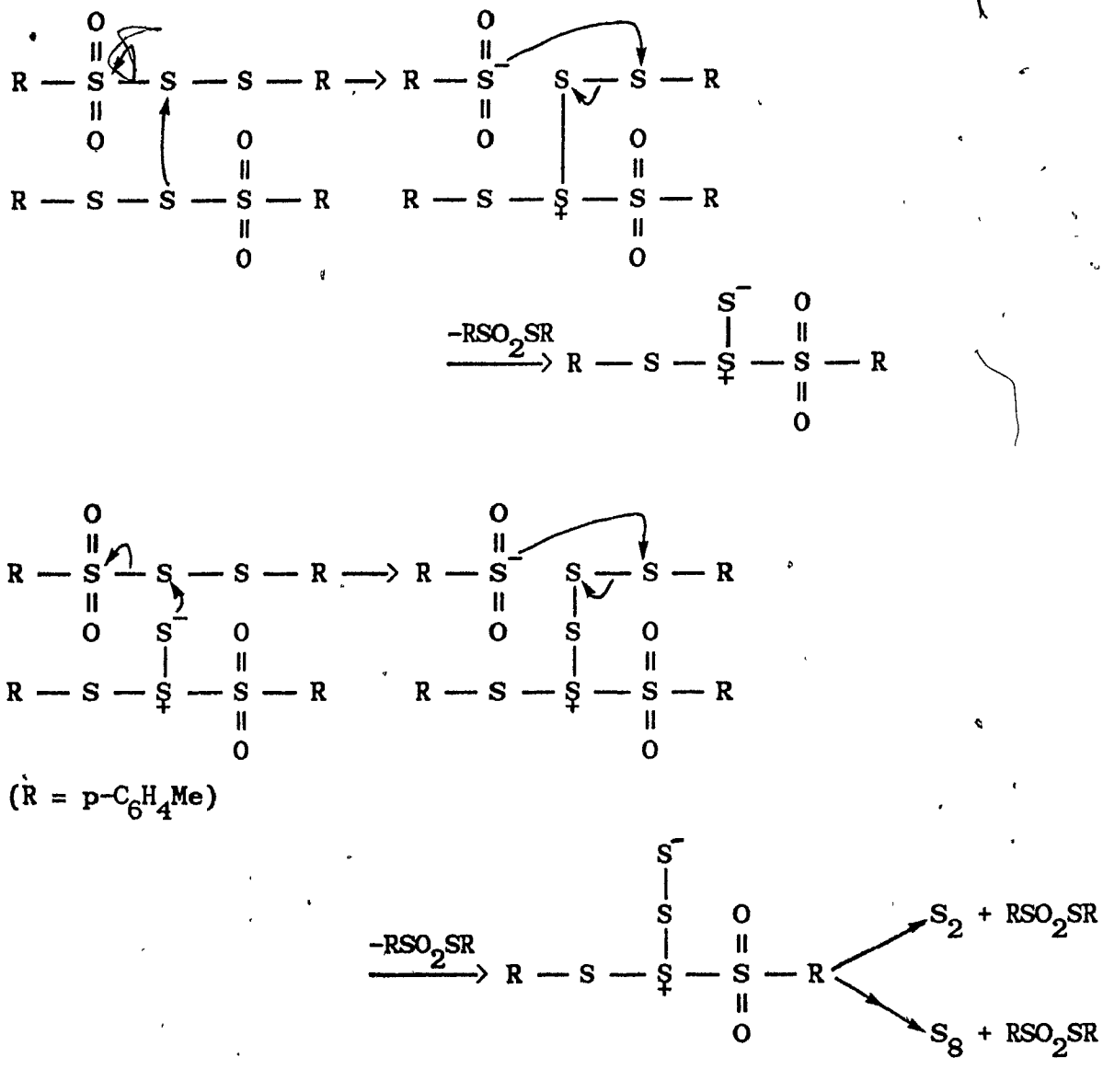
Certain sulfenic sulfonic thioahydrides have been found to undergo "spontaneous" desulfurization to thiosulfonates in polar solvents[26]. A mechanism involving solvent-stabilized sulfenium ions was proposed for this phenomenum, as shown in Scheme II.2. Elemental sulfur was





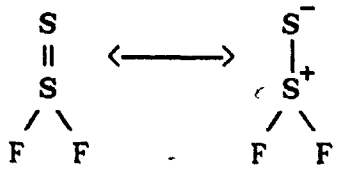
SCHEME II.2

recovered from this reaction. In light of recent considerations[28], this may not be an accurate picture and the mechanism of desulfurization may involve production of S_2 or S_8 rather than sulfur atoms (Scheme II.3)[25a,28].



SCHEME II.3

A branch-bonded sulfur intermediate is implicated. The release of S_2 or S_8, by acquisition of additional sulfur atoms, could then follow. Structures analogous to the thiosulfoxide intermediate have been presented in the literature[29], for example in S_2F_2[30].



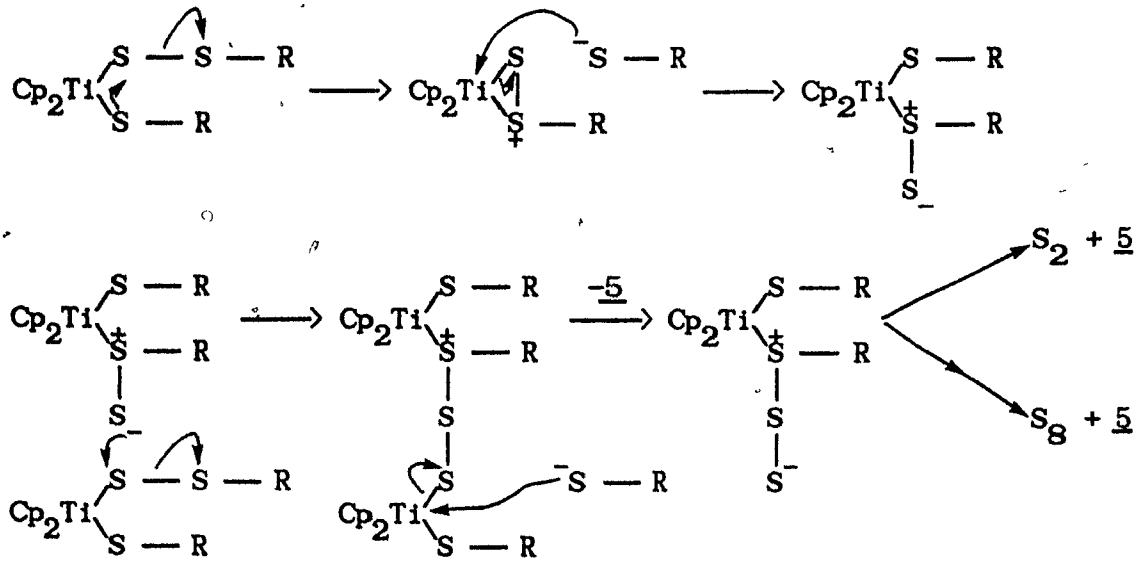
Solutions of 4a-c,e lose sulfur to give the respective dithiolates 5a-c,e. The reactions result in formation of other products: first, species that exhibit broad bands in the Cp region of the NMR spectrum; and also organic di- and trisulfides RS_xR, where x = 2 and 3. The broad band and the signals due to RS_xR tended to be of a larger integrated intensity compared to 5 when bulkier R groups were present. This may indicate that not only do sterically demanding R groups undergo oxidative-addition more slowly (as discussed above), but also favour loss of the sulfur-containing ligands to form RS_xR.

Some possible mechanisms for sulfur loss from the disulfano linkage in 4a-e are shown in Schemes II.4.A and B. Mechanisms involving homolytic scission of S-S bonds are not discussed since this normally occurs only under photolytic conditions or at temperatures greater than 180°C[31]. The mechanisms presented differ in initiation processes, but both implicate branch-bonded sulfur intermediates in later stages[25a,28]. In Scheme II.4.A initiation occurs via intramolecular attack of a sulfur lone-pair of the thiolato ligand in 4 onto the adjacent disulfano ligand and results in formation of a side-bound η^2-S_2R moiety. This type of sulfur bonding has been reported for the complex $[Os(\eta^2\text{-SSMe})(CO)_2(PPh_3)_2]ClO_4$[32]. In Scheme II.4.B intermolecular initiation occurs by attack originating from the sulfur adjacent to a R

group in a disulfano linkage. Attack of either of the terminal sulfurs of 4 on another molecule of 4 is also feasible, but would seem less likely since the effect of the metal centre should reduce the availability of these sulfur lone pairs. Both of mechanisms A and B involve attack of the anion RS^- on the metal centre. Sulfur readily forms compounds in which it has formally accepted electron density[33] and anionic sulfur species such as LiSR are often used in synthesis[17a]. The complex $Cp_4Ti_2S_6$, which exhibits a TiSSSTi unit, has been reported in the literature[34].

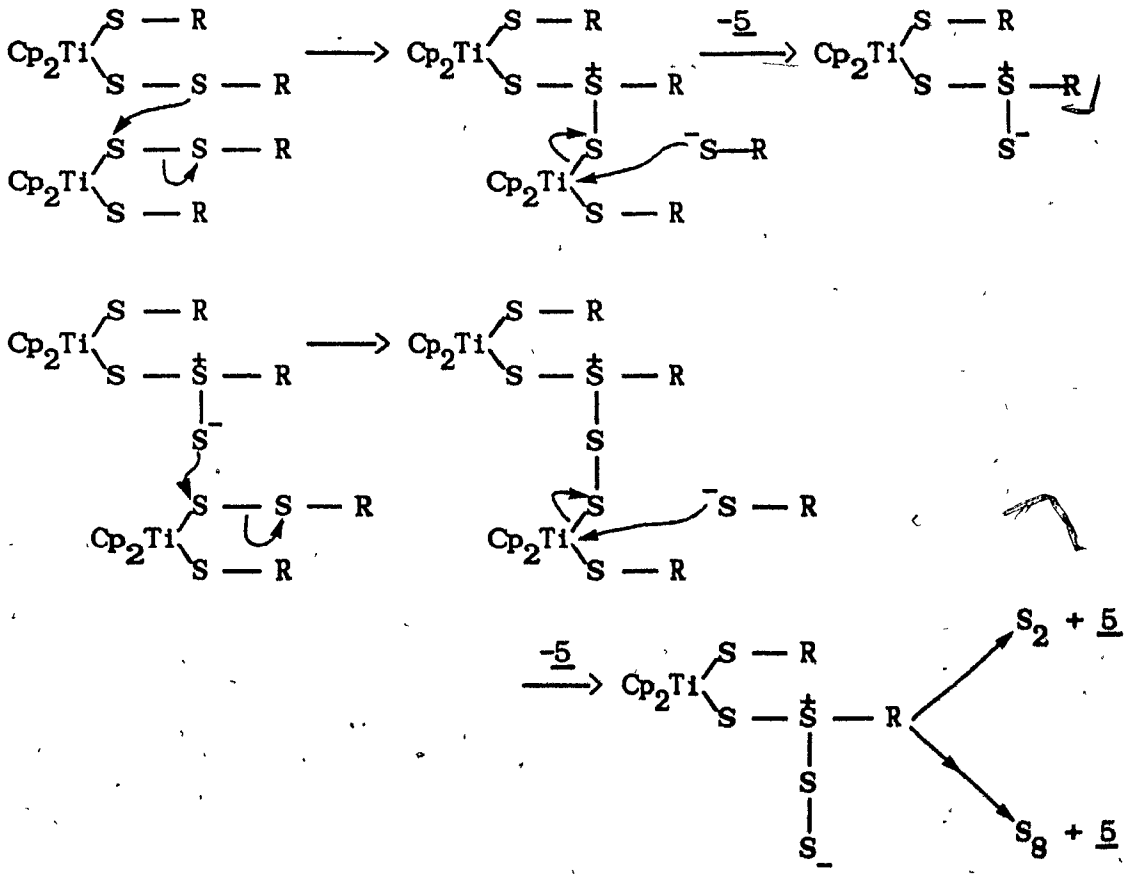
The net result of either of the mechanisms outlined above is loss of the S adjacent to the metal centre. Other possible schemes resulting

A. Intramolecular Initiation



SCHEME II.4.A

B. Intermolecular Initiation



SCHEME II.4.B

in loss of the S adjacent to the R group in the disulfano ligand would appear less likely, since either relatively unstable R^- species, or very rare anionic complexes of the type $Cp_2TiLL'^-$ [35], would probably result. Disulfur or S_8 are shown as products in Schemes II.4.A and B. However in the thermal desulfurizations of 4a-e elemental sulfur, S_8, was never detected as a product of the reactions. The fate of the sulfur lost from the disulfano linkage in 4 is discussed later.

Addition of Ph_3P to solutions of 4 resulted in clean desulfurizations, once again only for the complexes 4c,d, resulting in formation of 5c,d and $Ph_3P{=}S$ (Eq. II.6).

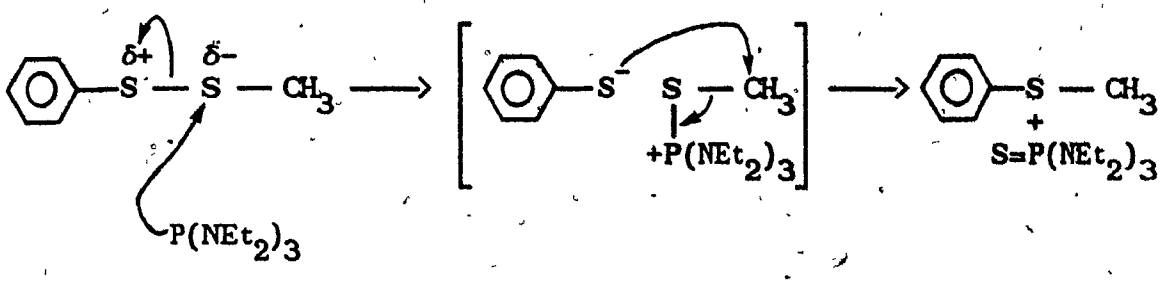
$$Cp_2Ti(SR)(SSR) + Ph_3P \longrightarrow Cp_2Ti(SR)_2 + Ph_3P{=}S \qquad (II.6)$$

4c,d — 5c,d

$$\underline{cis}\text{-}(Ph_3P)_2Pt(SSCH_2Ph)(phth) + Ph_3P \longrightarrow \underline{cis}\text{-}(Ph_3P)_2Pt(SCH_2Ph)(phth) + Ph_3P{=}S \qquad (II.7)$$

The enhanced S loss in the presence of a nucleophile is consistent with similar behaviour for $CpW(CO)_3SSR$[2] and $\underline{cis}\text{-}(Ph_3P)_2Pt(phth)(SSR)$[36], where phth = $NO_2C_8H_4$ (Eq. II.7). Sulfur abstraction from 4a,b,e is not clean and occurs with formation of 5a,b,e, in addition to species responsible for a broad band in the Cp region (~δ7.0 - 5.5 ppm) of the NMR spectrum.

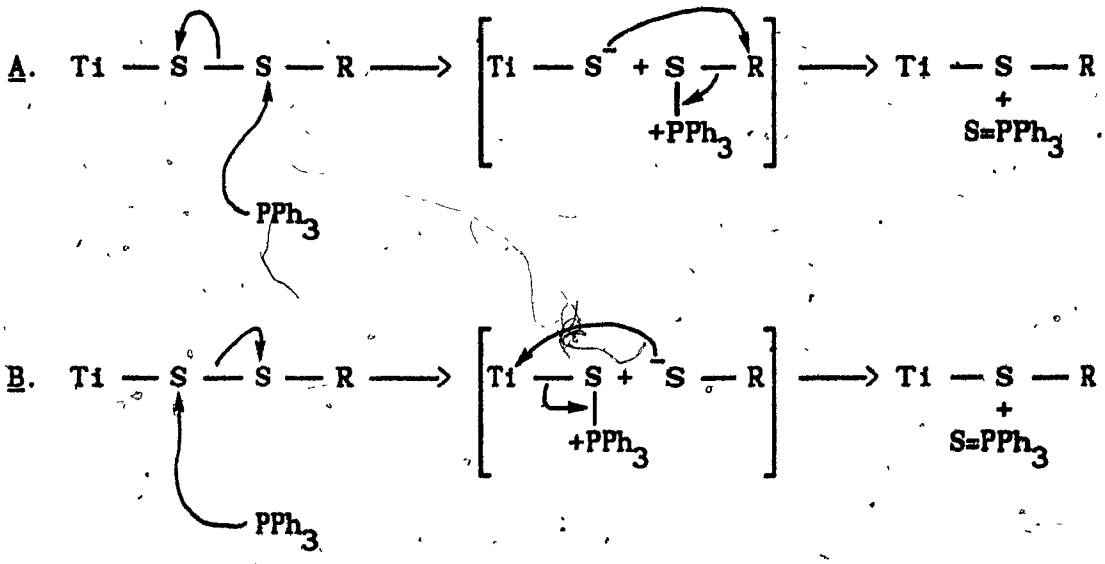
Organic disulfides RSSR, are not in general desulfurized by phosphines. Only acyl, thioacyl and vinylogous acyl disulfides are desulfurized by triphenylphosphine; benzyl and diethyl disulfides (among others) fail to react[37]. Previous studies have indicated that desulfurization of simple organic disulfides can occur on treatment with aminophosphines[38]. Desulfurization using $(Et_2N)_3P$ can be rationalized as nucleophilic attack on the more negatively polarized sulfur atom. Thus for $C_6H_5SSCH_3$ the observed products result from the attack on the sulfur adjacent to the methyl group (Scheme II.5) which is probably due



SCHEME II.5

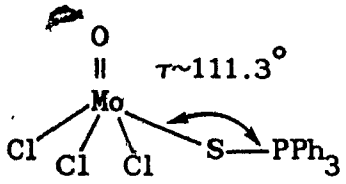
to the greater stability of the arylthiolate anion. S_N2 attack of the mercaptide then gives the sulfide and $(Et_2N)_3P{=}S$. This ionic mechanism has been suggested by Harpp et al.[38,39].

For S loss from 4a-e in the presence of Ph_3P a number of mechanisms are possible. By reasoning similar to that presented above, ionic mechanisms are considered, as shown in Scheme II.6. In the mechanism



SCHEME II.6

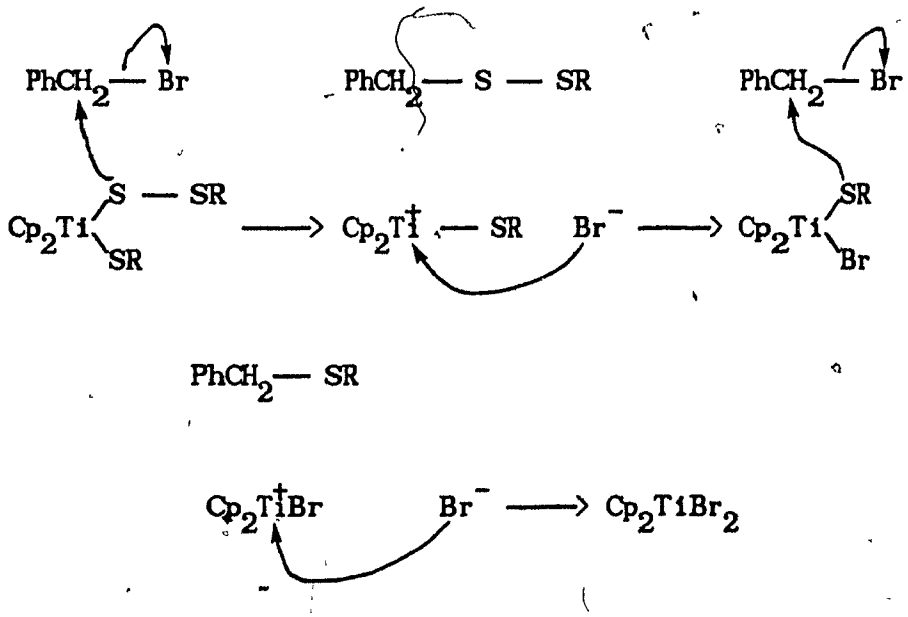
presented in Scheme II.6.A phosphine attack occurs on the S which might be expected to be the most negatively polarized sulfur atom. This type of attack is consistent with Scheme II.5. Scheme II.6.B which seems more feasible, but is as yet unproven, involves nucleophilic attack on the S adjacent to the metal centre, which would be expected to be the most positively polarized S atom. This attack would be favoured on electrostatic grounds. The proposed intermediates are similar to known compounds, for example, the thiolate anion[17a] and a metal bound triphenylphosphine sulfide ligand as observed in $[MoOCl_3(SPPh_3)]$ in which the Mo-S and P-S bond lengths are 2.460 and 2.041 Å, respectively[40].



The observed qualitative rates of desulfurization of 4a-d with Ph_3P show that loss of sulfur occurs faster with more electronegative R groups. Scheme II.6.B is consistent with this observation. Other mechanisms which result in S abstraction are discussed elsewhere[38,41]. The complex 4a is desulfurized only very slowly on addition of various nucleophiles. This result is in accordance with the behavior of $(Me_3C)_2S_2$ which does not lose sulfur even on addition of amino-phosphines[38,42], presumably due to the presence of bulky alkyl groups which hinder nucleophilic attack on sulfur.

Treatment of 4a-d with $PhCH_2Br$ gives Cp_2TiBr_2, and the

unsymmetrical sulfides $RSCH_2Ph$ (6a-d), and disulfides $RSSCH_2Ph$ (7a-d), in a ratio which is consistent with the presence of a $Cp_2Ti(SR)(SSR)$ species. This reaction represents a convenient method to characterize complexes containing thiolato and disulfano ligands. The $RSCH_2Ph$:$RSSCH_2Ph$ ratios found in the cases of 4c,d are too high (Table II.3) probably due to the conditions of the reaction (120°C), which tend to accelerate the conversion of 4c,d into 5c,d prior to reaction with $PhCH_2Br$. While 4a,b are more resistant to conversion into 5a,b, as shown in the NMR scale desulfurizations, the sulfides Me_3CSCH_2Ph (7a) and Me_2CHSCH_2Ph (7b) are somewhat volatile. Thus the lower ratios found for 4a,b may be due to loss of these sulfides during the concentration step of the work-up involved in NMR sample preparation. A possible mechanism for this ligand replacement reaction is shown in Scheme II.7.



SCHEME II.7

Complexes of the type, $Cp_2Ti(Cl)SR$, are known[8a]. Although initial attack on $PhCH_2Br$ by the disulfano ligand is depicted, attack by the thiolate ligand would be equally possible. A similar mechanism has been proposed for the reaction of $PhCH_2Br$ with the molybdenum persulfide species, $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$[43]. The sulfur atoms in $Cp_2Ti(SR)_2$ (5) have also been shown to be quite sensitive to electrophilic attack by acylchlorides (Eq. II.8)[6].

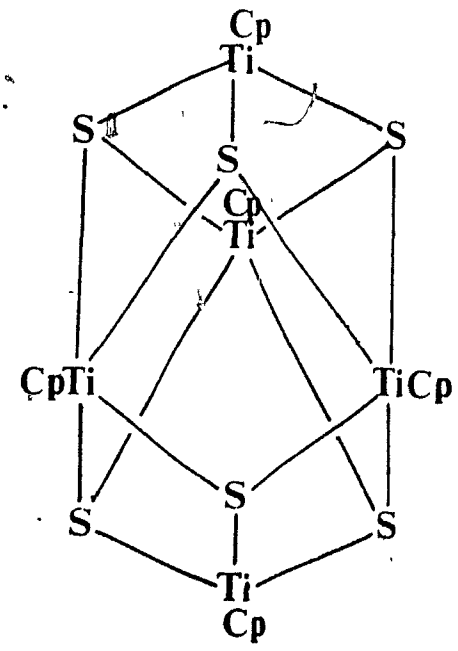
$$Cp_2Ti(SCH_2Ph)_2 + 2PhCH_2\overset{O}{\overset{\|}{C}}-Cl \longrightarrow Cp_2TiCl_2 + 2PhCH_2\overset{O}{\overset{\|}{C}}-SCH_2Ph \quad (II.8)$$

Minor quantities of other organic compounds were observed in the reactions of 4a-d with $PhCH_2Br$ (Table II.3). More dibenzylsulfide was detected in the reactions of 4a,b than in 4d. This is surprising since 4a,b react more slowly with $PhCH_2Br$ to give Cp_2TiBr_2, than other R groups. Reflux of 4a,b alone in toluene gave materials which may contain a bridging sulfur moiety Ti-S-Ti (as discussed below) which might lead to $(PhCH_2)_2S$ on reaction with $PhCH_2Br$. Dibenzyl was observed in significant quantities in the reaction of 4a with $PhCH_2Br$. It is known that alkyl and alkylaryl halides, RX, are reduced by many low-valent transition metal compounds, often via organometallic intermediates. Mixtures of RH and R-R are commonly formed in proportions depending on the specific halide, metal, ligands and conditions used[44]. For example, it has been reported that vanadocene, Cp_2V, reduces benzyl chloride to bibenzyl[45] (Eq. II.9). The organic trisulfide, 3a, was observed as a

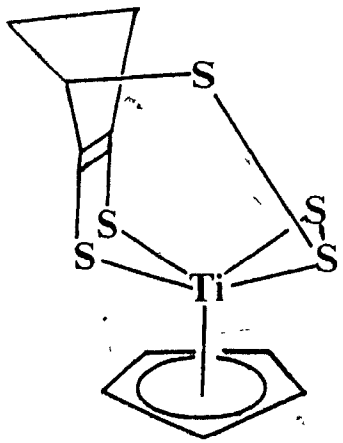
$$Cp_2V + PhCH_2Cl \longrightarrow Cp_2VCl + 1/2PhCH_2CH_2Ph \qquad (II.9)$$

minor product of the reaction of 4a with $PhCH_2Br$. One can envisage the reductive-elimination of 3a from 4a to form a reactive "titanocence" intermediate which might then react with $PhCH_2Br$ to form bibenzyl.

In the thermal and Ph_3P desulfurizations of 4a-c,e broad bands in the NMR spectra were observed, generally in the region δ7.0 - 5.5 ppm. The width and integrated intensity of this band varied with reaction conditions and R group. The breadth of the band might be due to paramagnetism and/or polymeric cyclopentadienyl titanium species. A cyclopentadienyl titanium sulfido cluster has been observed from the reaction of $Cp_2Ti(CO)_2$ with H_2S in toluene at 80°C[46]. The structure of this pentanuclear compound, $(CpTi)_5S_6$, is based upon a distorted trigonal bipyramid of titanium atoms. Sulfur bridges the triangular faces of the cluster (Note: Ti-Ti bonds are omitted for clarity). This



species is paramagnetic and very soluble in toluene. A monomeric cyclopentadienyl titanium(IV) sulfide which exhibits broad and complex resonances has been synthesized by reflux of Cp_2TiS_5 in xylenes[47]. Migration of the π-complexed organic fragment to the inorganic sulfur ligand occurred to give β-$C_{10}H_{10}S_5Ti$.



The reaction of 1 with 3a or 4a in refluxing toluene produced insoluble or soluble products, respectively. Elemental analyses and physical properties of the products indicate that both species contain a $C_{10}H_{10}$ moiety and that the titanium and sulfur ratios vary from 1.5:0.8 (insoluble material) to 0.78:1.34 (soluble material). The soluble material exhibited the typical broad band in the Cp region, as seen in many of the reactions of 4a-e. Apparently, 1 abstracts a sulfur atom from the disulfano linkage in 4a to form 5a and the soluble material. Since the latter does not analyse for "Cp_2TiS", Cp exchange and perhaps rearrangement of Cp and S ligands has occurred. Similar transformations might also occur to give the insoluble product in the reaction of 1 with 3a. The structures of both species (or mixtures of species) are not

known. However, the possibility of S attack on the Cp ring and the presence of Ti-S-Ti linkages, cannot be excluded even in the sulfur "deficient" material. The similarity of the NMR spectrum of the soluble product, to that of the broad bands obtained in the NMR spectra of the products of other reactions of 4a-e, might indicate that similar species are present in both cases.

If indeed the thermal desulfurizations of 4a-e result in formation of S_2 as shown in Scheme II.4, one would expect S_8 to form (Eq. II.10).

$$4\,S_2 \longrightarrow 1/8\ S_8 \qquad \text{(II.10)}$$

However, elemental sulfur, S_8, is not observed in these reactions. S_2 is known to be more reactive than S_8[25b], and thus might react with the organometallic complexes present in solutions of 4a-c,e, to form paramagnetic and/or polymeric species that give the broad band in the Cp region of the NMR spectra. This hypothesis cannot be proven at present.

References

1. a) "Organic Chemistry of Bivalent Sulfur", by E.E. Ried, Chemical Publishing Co., New York, 1960, Vols. II and III.
   b) B.D. Vineyard, J. Org. Chem., 31, (1966), 601.
   c) I. Kende, T.L. Pickering and A.V. Tobolsky, J. Am. Chem. Soc., 87, (1965), 5582.
   d) A.W. Mott and G. Barany, Sulfur Letters, 2, (1984), 137.
   e) D. Grant and J.R. van Wazer, J. Am. Chem. Soc., 86, (1964), 3012.
2. A.G. Shaver and J. Hartgerink, Can. J. Chem., 65, (1987), 1190.
3. A.G. Shaver, J.M. McCall, P.H. Bird and N. Ansari, Organometallics, 2, (1984), 1894.
4. E. John, P.K. Bharadwaj, K. Krogh-Jespersen, J.A. Potenza and H.J. Schugar, J. Am. Chem. Soc., 108, (1986), 5015.
5. S.V. Evans, P. Legzdins, S.J. Rettig, L. Sanchez and J. Trotter, Organometallics, 6, (1987), 7.
6. G. Fachinetti and C. Floriani, J. Chem. Soc., Dalton Trans., (1974), 2433.
7. L. Gelmini and D.W. Stephan, Organometallics, 6, (1987), 1515.
8. a) R.S.P. Coutts, J.R. Surtees, J.M. Swan and P.C. Wailes, Aust. J. Chem., 19, (1966), 1377.
   b) S.A. Giddings, Inorg. Chem., 6, (1967), 849.
   c) H. Köpf and M. Schmidt, Z. Anorg. Allg. Chem., 340, (1965), 139.
9. E.G. Müller, J.L. Petersen and L.F. Dahl, J. Organomet. Chem., 111, (1976), 91.
10. "The Manipulation of Air-Sensitive Compounds", by D.F. Shriver, McGraw-Hill, New York, 1969, Chap. 7.

11. H. Rheinboldt, F. Mott and E. Motzkus, J. Prakt. Chem., 134, (1932), 257.

12. I.J. Büchi, M. Prost, H. Eichenberger and R. Lieberherr, Helv. Chim. Acta, 35, (1952), 1527.

13. Ref. 1a), Vol.II, p 24.

14. D.N. Harpp, K. Steliou and T.H. Chan, J. Am. Chem. Soc., 100, (1978), 1222.

15. a) T. Nakabayashi, J. Tsurugi and T. Yabuta, J. Org. Chem., 29, (1964), 1236.

b) A. Schöbert and A. Wagner in "Methoden der Organischen Chemie", ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1955, p 87.

c) Ref. 1a), Vol.III, p 388.

16. D.N. Harpp and D.K. Ash, Int. J. Sulfur Chem., Part A, 1, (1971), 211.

17. a) J.M. McCall, Ph.D. Thesis, McGill University, (1983).

b) S.A. Giddings, U.S. Pat. No. 3,030,395, (1962); Chem. Abstr., 57, (1962), 9881.

18. a) B. Demersemen, G. Bouquet and M. Bigorgne, J. Organomet. Chem., 101, (1975), C24.

b) G.A. Zank and T.B. Rauchfuss, Organometallics, 3, (1984), 1191.

19. C.B. Boyce, R.J.G. Searle and P.J. Williams, Ger. Offen. (Pat.) No. DE1963070, (1970).

20. A. Desjardins, Summer Research Project, Chemistry Dept., McGill University, (1985).

21. H. Köpf, B. Block, M. Schmidt, Chem. Ber., 101, (1968), 272.

22. J.L. Petersen and L.F. Dahl, J. Am. Chem. Soc., 97, (1975), 6422.

23. "Organic Chemistry of Sulfur", ed. S. Oae, Plenum Press, New York, 1977.

24. M.J. Calhordo, M.A.A.F. de C.T. Carrondo, A.R. Dias, A.M.T.S. Domingos, J.A.M. Simoes and C. Teixeira, Organometallics, 5, (1986), 660.

25. a) E. Lutz and J.-F. Biellmann, Tetrahedron Lett., 26, (1985), 2789.
b) K. Steliou, Y. Gareau and D.N. Harpp, J. Am. Chem. Soc., 106, (1984), 799.
c) B.M. Trost and S.D. Ziman, J. Org. Chem., 38, (1973), 932.
d) "Extrusion Reactions", by B.P. Stark and A.J. Duke, Pergammon Press, London, 1967, pp 91-107.

26. D.N. Harpp, D.K. Ash and R.A. Smith, J. Org. Chem., 44, (1979), 4135.

27. E.J. Corey and E. Block, J. Org. Chem., 5, (1969), 1233.

28. D.N. Harpp in, "Perspectives in the Organic Chemistry of Sulfur", eds. B. Zwanenburg and A.J.H. Klunder, Elsevier, New York, 1987, pp 1-22.

29. G.W. Kutney and K. Turnbull, Chem. Rev., 82, (1982), 333.

30. a) B. Solowki and H. Bock, Inorg. Chem., 16, (1977), 665.
b) R.D. Brown, G.P. Pez and M.F. O'Dwyer, Aust. J. Chem., 18, (1965), 627.

31. Ref. 23, pp 43 and 368.

32. G.R. Clark and D.R. Russell, J. Organomet. Chem., 173, (1979), 377.

33. "Organic Chemistry of Bivalent Sulfur", by E.E. Ried, Chemical Publishing Co., New York, 1960, Vol.I, p 262.

34. C.M. Bolinger, T.B. Rauchfuss and S.R. Wilson, J. Am. Chem. Soc.,

103, (1981), 5620.

35. "Organometallic Chemistry of Titanium, Zirconium and Hafnium", by P.C. Wailes, R.S.P. Coutts and H. Weigold, Academic Press, New York, 1974.

36. A.G. Shaver, J. Hartgerink, R.D. Lai, P. Bird and N. Ansari, Organometallics, 2, (1983), 938.

37. a) A.Schönberg and M. Barakat, J. Chem. Soc., (1949), 892.

b) F. Challenger and D. Greenwood, J. Chem. Soc., (1950); 26.

c) C. Moore and B. Trego, Tetrahedron, 18, (1962), 205.

38. D.N. Harpp and J.G. Gleason, J. Am. Chem. Soc., 93, (1971), 2437.

39. D.N. Harpp, J.G. Gleason and J.P. Snyder, J. Am. Chem. Soc., 90, (1968), 4181.

40. P.M. Boorman, C.D. Garner, F.E. Mabbs and T.J. King, J. Chem. Soc., Chem. Commun., (1974), 663.

41. a) D.K. Ash, Ph.D. Thesis, McGill University, (1973).

b) R.D. Lai, Ph.D. Thesis, McGill University, (1981).

42. Ref. 1a), Vol. III, pp 391-392.

43. D.N. Harpp and J.G. MacDonald, Tetrahedron Lett., 25, (1984), 703.

44. T.A. Cooper, J. Am. Chem. Soc., 95, (1973), 4158.

45. H.J. de Liefde Meijer, M.J. Janssen and G.J.M. van der Kerk, Recl.: J.R. Neth. Chem. Soc., 80, (1961), 831.

46. a) F. Bottomley, G.O. Egharevba and P.S. White, J. Am. Chem. Soc., 107, (1985), 4353.

b) F. Bottomley, D.F. Drummond, G.O. Egharevba and P.S. White, Organometallics, 5, (1986), 1620.

47. D.M. Giolando and T.B. Rauchfuss, J. Am. Chem. Soc., 106, (1984),

6455.

48. Ref. 1a), Vol. III, p 392.

49. 9:1 hexanes:CH_2Cl_2.

50. G.T. Palmer, F. Basolo, L.B. Kool and M.D. Rausch, J. Am. Chem. Soc., 108, (1986), 4417.

CHAPTER III

THE SYNTHESES AND CHARACTERIZATION OF

$(\eta^5\text{-}C_5H_5)_2Ti(X)(SSR)$.

WHERE X = PHTH, OR' AND Cl

Introduction

Sulfur-rich complexes which contain a sulfur-sulfur bond may play an important role in hydrodesulfurization[1], redox enzymes[2] and energy storage[3]. Consequently, a better understanding of polysulfur-metal chemistry would be of interest.

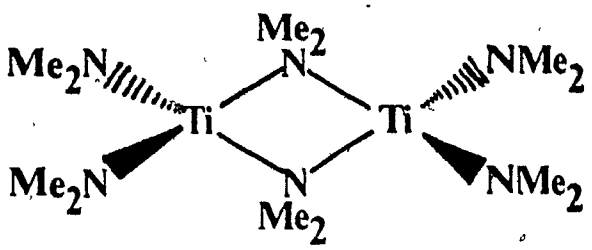
The preceeding chapter presented the preparation of disulfano complexes via oxidative-addition of the sulfur-sulfur bond of organic trisulfides. There have been a few reports of oxidative-addition of sulfur-nitrogen[4] and sulfur-chlorine[5] bonds to Ti(II) species. This chapter presents the reactions of RS_yX with $Cp_2Ti(CO)_2$ (1) to give $Cp_2Ti(X)(S_yR)$, where: y = 1, 2 and X = phth; and y = 2 and X = Cl. The subsequent reactions of $Cp_2Ti(phth)(SSR)$ with R'OH, where R' = Et and Me, are described. Thus it is appropriate at this point to briefly discuss the chemistry of titanium N- and O- bonded complexes.

Amido and Imido Complexes of Titanium

Titanium amides are very numerous[6]. Complexes of the type $Ti(NR_2)_x$, where x = 3, 4 and R = alkyl[7], aryl[8], are obtained by treating the appropriate titanium chloride with lithium amides[9] (Eq. III.1).

$$TiCl_x + xLiNR_2 \longrightarrow Ti(NR_2)_x + xLiCl \qquad (III.1)$$

Heteroleptic amides, $Ti(NR_2)_x(NR'_2)_{3-x}$, where x = 1 and 2, are also known[6]. Titanium(IV) amides are monomeric, whereas titanium(III) species are dimeric, except when R is a bulky group such as $SiMe_3$[7c,10].



Significant Ti-Ti interaction is proposed for $[Ti(NMe_2)_3]_2$, in which the amido groups were shown to undergo rapid exchange at room temperature[7b].

Titanium(IV) amides react with H_2O, alcohols[11], thiols[12] and even acidic hydrocarbons such as cyclopentadiene[13] (Eqs. III.2 and 3).

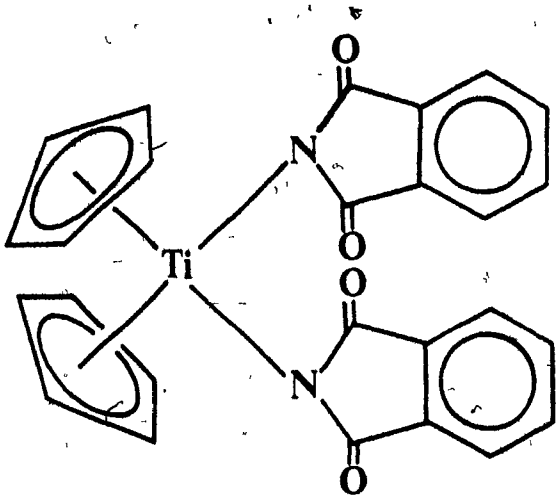
$$Ti(NR_2)_4 + 4HA \longrightarrow MA_4 + 4R_2NH \qquad (III.2)$$

A = OR' and SR'

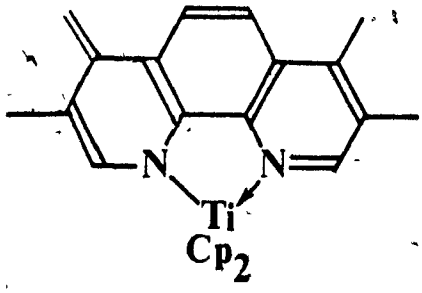
$$Ti(NMe_2)_4 + C_5H_6 \longrightarrow CpTi(NMe_2)_3 + Me_2NH \qquad (III.3)$$

Titanium(III) amides tend to disproportionate to $Ti(II)(NR_2)_2$ and $Ti(IV)(NR_2)_4$[7b].

The complexes $Cp_2Ti(NMe_2)_x$ have been prepared from Cp_2TiCl_x, where x = 1 and 2, using $LiNMe_2$[7b,14]. The yellow species $Cp_2Ti(imido)_2$ have been reported by Issleib and Bätz[15], via reaction of Cp_2TiCl_2 with alkali metal derivatives of pyrrole, indole, carbazole and phthalimide. However, attempts to repeat this preparation have been unsuccessful[16]. Although bonding of the imido group through the nitrogen atom was proposed[15], no structural evidence was produced. A fully characterized example of the Cp_2Ti moiety binding to two nitrogen atoms is found in the substituted phenanthroline complex shown below, which was formed by



reaction of $Cp_2Ti(CO)_2$ with 3,4,7,8-tetramethyl-1,10-phenanthroline[17]. Cyclopentadienyl titanium amides also react with weak acids such as



alcohols, thiols and terminal acetylenes[18] (Eqs. III.4 and 5).

$$[Cp_2Ti(NMe_2)]_2 + 2EtOH \longrightarrow [Cp_2Ti(OEt)]_2 + 2Me_2NH \qquad (III.4)$$

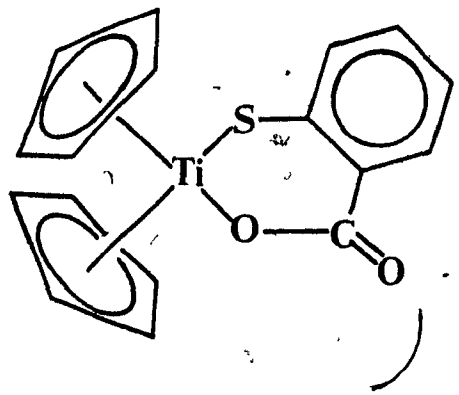
$$MeCpTi(NMe_2)_3 + PhC{\equiv}CH \longrightarrow MeCpTi(C{\equiv}CPh)(NMe_2)_2 + Me_2NH \qquad (III.5)$$

Alkoxide and Aryloxide Complexes of Titanium

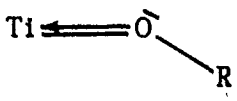
Complexes containing the titanium-oxygen bond have been heavily studied[19], due in part to the industrial applications of metal

alkoxides, which include: Zeigler-Natta olefin polymerization catalysts[20]; Meerwein-Ponndorf-Verley redox catalysts; polymer hydrogenation catalysts[21]; accelerators for the drying of paints and inks; and in heat resistant paints[22].

Sulfur and oxygen atoms are simultaneously bound to titanium in the carboxylate species shown below[23].



The alkoxide ligand has generally been recognized as a one electron donor in metal complexes. However, recently reported molecular structures of $Cp_2Ti(Cl)(OEt)$ and the dimer $[CpTiCl_2]_2O_2C_2(CH_3)_4$, gave evidence for π-donation by alkoxide ligands[24]. It is suggested that the oxygen atom donates three electrons to the metal centre, with the alkoxy ligand exceeding the chloro group in π-donor ability. It is proposed



that $Cp_2Ti(Cl)(OEt)$ achieves an effective 18 electron configuration by this oxygen π-bonding[24].

Complexes of the type $Cp_2Ti(Cl)(OR)$, where R = alkyl, aryl[20,25],

and $Cp_2Ti(OR)_2$, where R = alkyl[26], aryl[27], are monomeric, relatively stable and have been reviewed elsewhere[23,28].

Experimental

Materials and Methods

All manipulations carried out and all solvents used, were as described in Chapter II. Methanol and ethanol were both distilled over Mg turnings under anhydrous conditions. The reagents N-(isopropyldithio)phthalimide (9b), N-(benzyldithio)phthalimide (9c), N-(4-methylphenyldithio)phthalimide (9d), were made by published procedures[29]. N-(tert-butyldithio)phthalimide (9a) was received as a gift from Mr. Dominic Ryan. The compounds, N-(isopropylthio)-phthalimide (15b), N-(benzylthio)phthalimide (15c) and N-(4-methylphenylthio)phthalimide (15d) were kindly supplied by Ms. Bernadette Soo Lum, Mr. Riccardo Turrin and Mr. Pierre-Yves Plouffe, respectively. These compounds were made by a literature method[30]. Triphenylmethylchlorodisulfide was made by the method of Harpp and Ash[31]. Other compounds and materials used were prepared as described in Chapter II.

Reaction products were identified by ^{1}H NMR comparison to authentic samples of $Cp_2Ti(SR)_2$, where R = CH_2Ph and p-C_6H_4Me[32], Cp_2TiCl_2, dibenzyldisulfide, phthalimide, triphenylphosphine, triphenylphosphine sulfide (Aldrich) and di(isopropyl)disulfide (Fairfield). All physical measurements were determined in a manner similar to that described previously.

Preparation of Bis(η^5-cyclopentadienyl)(phthalimido)(tert-butyldisulfano)titanium(IV), $Cp_2Ti(NO_2C_8H_4)(SSCMe_3)$ (10a)

N-(tert-butyldithio)phthalimide (9a) (1.72 g, 6.44 mmol) was added

to a solution of $Cp_2Ti(CO)_2$ (1) (1.51 g, 6.44 mmol) in toluene (25 mL) at 22°C. The reaction mixture was stirred for 44 h to give a purple solution. A deep purple powder (1.76 g, 61%, mp 163-165°C) was obtained after filtration, washing (Et_2O, 10 mL) and vacuum-drying.

Anal. (%): Calcd. for $C_{22}H_{23}NO_2S_2Ti$: C, 59.32; H, 5.20; S, 14.39. Found: C, 59.26; H, 5.27; S, 14.48.

^1H NMR ($CDCl_3$): δ7.64 - 7.49 (m, 4H, C_6H_4), 6.35 (s, 10H, C_5H_5), 1.49 (s, 9H, CH_3).

IR (toluene): 1664 (υ_{C-O}).

Preparation of Bis(η^5-cyclopentadienyl)(phthalimido)(isopropyldisulfano)titanium(IV), $Cp_2Ti(NO_2C_8H_4)(SSCHMe_2)$ (10b)

N-(isopropyldithio)phthalimide (9b) (1.21 g, 4.78 mmol) was added to a solution of 1 (1.12 g, 4.78 mmol) in toluene (20 mL) and the reaction mixture was stirred for 44 h. A deep purple powder (0.88 g, 43%, mp 128-130°C) was obtained after filtration, washing (Et_2O, 3 x 10 mL) and vacuum-drying.

Anal. (%): Calcd. for $C_{21}H_{21}NO_2S_2Ti$: C, 58.46; H, 4.91; S, 14.86. Found: C, 60.94; H, 4.92; S, 12.60.

^1H NMR ($CDCl_3$): δ7.61 - 7.48 (m, 4H, C_6H_4), 6.32 (s, 10H, C_5H_5), 3.31 (septet, 1H, J = 6.8 Hz, CH) 1.43 (d, 6H, J = 6.8 Hz, CH_3).

IR (toluene): 1663 (υ_{C-O}).

Preparation of Bis(η^5-cyclopentadienyl)(phthalimido)(benzyldisulfano)-titanium(IV), $Cp_2Ti(NO_2C_8H_4)(SSCH_2Ph)$ (10c)

N-(benzyldithio)phthalimide (9c) (1.40 g, 4.65 mmol) was added to a

solution of 1 (1.09 g, 4.65 mmol) in toluene (40 mL) and the reaction mixture was stirred for 8.5 h. A red-purple powder (0.83 g, 37%, mp 138-140°C) was obtained after filtration, washing (hexanes, 2 x 5 mL) and vacuum-drying.

Anal. (%): Calcd. for $C_{25}H_{21}NO_2S_2Ti$: C, 62.63; H, 4.41; S, 13.37. Found: C, 62.50; H, 4.49; S, 13.38.

^1H NMR ($CDCl_3$): δ7.61 - 7.47 (m, 4H, C_6H_4), 7.40 - 7.29 (m, 5H, C_6H_5), 6.20 (s, 10H, C_5H_5), 4.20 (s, 2H, CH_2).

IR (toluene): 1665 (υ_{C-O}).

Preparation of Bis(η^5-cyclopentadienyl)(phthalimido)(4-methylphenyldisulfano)titanium(IV), $Cp_2Ti(NO_2C_8H_4)(SS\text{-}p\text{-}C_6H_4Me)$ (10d)

N-(4-methylphenyldithio)phthalimide (9d) (1.48 g, 4.92 mmol) was added to a solution of 1 (1.15 g, 4.92 mmol) in toluene (40 mL) and the reaction mixture was stirred for 28 h. A purple powder (0.79 g, 34%, mp 146-149°C) was obtained after filtration, washing (hexanes, 2 x 5 mL) and vacuum-drying.

Anal. (%): Calcd. for $C_{25}H_{21}NO_2S_2Ti$: C, 62.63; H, 4.41; S, 13.37. Found: C, 62.02; H, 4.29; S, 13.27.

^1H NMR ($CDCl_3$): δ7.64 - 7.51 (m, 4H, $NO_2C_8H_4$), 7.43, 7.16 (ABq, 4H, J = 7.8 Hz, C_6H_4Me), 6.40 (s, 10H, C_5H_5), 2.36 (s, 3H, CH_3).

IR (toluene): 1651 (υ_{C-O}).

Preparation of Bis(η^5-cyclopentadienyl)(ethoxy)(tert-butyldisulfano)-titanium(IV), $Cp_2Ti(OEt)(SSCMe_3)$ (13a)

N-(tert-butyldithio)phthalimide (9a) (1.67 g, 6.23 mmol) was added

to a solution of 1 (1.46 g, 6.23 mmol) in toluene (25 mL) and the reaction mixture was stirred for 47 h. Filtration, washing (Et_2O, 10 mL), and vacuum-drying gave a deep purple powder of which NMR analysis indicated the presence of pure 10a. Addition of the powder to EtOH (35 mL) followed by stirring for 20 min, gave a dark orange solution which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4 x 6 cm), eluting with CH_2Cl_2, gave an orange band which was collected. A dark orange oil (1.24 g, 58%) was obtained after stripping the band to dryness.

Anal. (%): Calcd. for $C_{16}H_{24}OS_2Ti$: C, 55.80; H, 7.02; S, 18.62. Found: C, 55.63; H, 7.11; S, 18.72.

^1H NMR ($CDCl_3$): δ6.14 (s, 10H, C_5H_5), 4.23 (q, 2H, J = 6.8 Hz, CH_2), 1.37 (s, 9H, $C(CH_3)_3$), 1.00 (t, 3H, J = 6.8 Hz, $CH_2\underline{CH_3}$).

^1H NMR (C_6D_6): δ5.88 (s, 10H, C_5H_5), 4.16 (q, 2H, J = 6.8 Hz, CH_2), 1.50 (s, 9H, $C(CH_3)_3$), 1.06 (t, 3H, J = 6.8 Hz, $CH_2\underline{CH_3}$).

IR (KBr): 3090 (w), 2940 (m, br), 1718 (w, br), 1650 (w, br), 1430 (m), 1355 (m), 1095 (s, br), 1056 (s), 1009 (m), 908 (m), 800 (s), 712 (w), 560 (m), 400 (m).

MS: 344 ($M^{+\cdot}$, 1.5), 242 ($C_{10}H_{10}TiS_2^{+\cdot}$, 2.7), 223 ($M^{+\cdot}-C_4H_9S_2^{\cdot}$, 21), 210 ($C_{10}H_{10}TiS^{+\cdot}$, 1.2), 205 ($M^{+\cdot}-C_4H_9S_2^{\cdot}-H_2O^{\cdot}$, 5.5), 178 ($C_{10}H_{10}Ti^{+\cdot}$, 10).

Preparation of Bis(η^5-cyclopentadienyl)(ethoxy)(isopropyldisulfano)-titanium(IV), $Cp_2Ti(OEt)(SSCHMe_2)$ (13b)

N-(isopropyldithio)phthalimide (9b) (1.10 g, 4.35 mmol) was added to a solution of 1 (1.02 g, 4.35 mmol) in toluene (15 mL) and the reaction mixture was stirred for 48 h. Filtration, washing (Et_2O,

5 × 10 mL), and vacuum-drying, gave a deep purple powder of which NMR analysis indicated that 10b was the major constituent, with a trace of phthalimide also present. Addition of the powder to EtOH (35 mL) followed by stirring for 10 min, gave a dark orange solution which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4 × 6 cm), eluting with CH_2Cl_2, gave an orange band which was collected. Stripping of the band to dryness gave a dark orange powder (0.47 g, 33%, mp 61-63°C).

Anal. (%): Calcd. for $C_{15}H_{22}OS_2Ti$: C, 54.54; H, 6.71; S, 19.41. Found: C, 54.36; H, 6.80; S, 19.19.

^1H NMR ($CDCl_3$): δ6.13 (s, 10H, C_5H_5), 4.25 (q, 2H, J = 7.0 Hz, CH_2), 2.86 (septet, 1H, J = 6.8 Hz, CH), 1.32 (d, 6H, J = 6.8 Hz, $CH(\underline{CH_3})_2$), 1.01 (t, 3H, J = 7.0 Hz, $CH_2\underline{CH_3}$).

^1H NMR (C_6D_6): δ5.83 (s, 10H, C_5H_5), 4.14 (q, 2H, J = 6.9 Hz, CH_2), 3.01 (septet, 1H, J = 6.8 Hz, CH), 1.43 (d, 6H, J = 6.8 Hz, $CH(\underline{CH_3})_2$), 1.02 (t, 3H, J = 6.9 Hz, $CH_2\underline{CH_3}$).

IR (KBr): 3100 (w), 3070 (m), 2950 (m), 2910 (w), 2820 (m), 1432 (m), 1360 (m, br), 1095 (s), 1058 (s), 1008 (m), 910 (m), 800 (s), 560 (s), 404 (m).

MS: 330 ($M^{+\bullet}$, 2.0), 298 ($M^{+\bullet}-S^{\bullet}$, 0.2), 265 ($M^{+\bullet}-S_2H^{\bullet}$, 0.8), 254 ($M^{+\bullet}-C_3H_8S^{\bullet}$, 4.1), 223 ($M^{+\bullet}-C_3H_7S_2^{\bullet}$, 34), 210 ($C_{10}H_{10}TiS^{+\bullet}$, 40), 178 ($C_{10}H_{10}Ti^{+\bullet}$, 39).

Preparation of Bis(η^5-cyclopentadienyl)(ethoxy)(benzyldisulfano)-titanium(IV), $Cp_2Ti(OEt)(SSCH_2Ph)$ (13c)

N-(benzyldithio)phthalimide (9c) (1.24 g, 4.12 mmol) was added to a

solution of 1 (0.98 g, 4.12 mmol) in toluene (40 mL) and the reaction mixture was stirred for 26 h. Filtration and vacuum-drying gave a red-purple powder of which NMR analysis indicated that 10c was the major constituent, with a trace of phthalimide also present. Addition of the powder to EtOH (35 mL) followed by stirring for 30 min gave a dark brown-orange solution which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4 × 6 cm), eluting with CH_2Cl_2, gave an orange band which was collected. Stripping of the band to dryness gave a brown powder (0.44 g, 28%, mp 84-86°C).

Anal. (%): Calcd. for $C_{19}H_{22}OS_2Ti$: C, 60.31; H, 5.86; S, 16.94. Found: C, 60.15; H, 5.80; S, 17.10.

^1H NMR ($CDCl_3$): δ7.36 - 7.31 (m, 5H, C_6H_5), 6.11 (s, 10H, C_5H_5), 4.30 (q, 2H, J = 7.0 Hz, $\underline{CH_2}CH_3$), 3.83 (s, 2H, $\underline{CH_2}Ph$), 1.05 (t, 3H, J = 7.0 Hz, CH_3).

^1H NMR (C_6D_6): δ7.38 - 6.96 (m, 5H, C_6H_5), 5.77 (s, 10H, C_5H_5), 4.13 (q, 2H, J = 6.9 Hz, $\underline{CH_2}CH_3$), 3.95 (s, 2H, $\underline{CH_2}Ph$), 1.00 (t, 3H, J = 6.9 Hz, CH_3).

IR (KBr): 3078 (w), 2960 (w, br), 2630 (w), 1488 (w), 1430 (m), 1366 (w), 1343 (m), 1048 (s, br), 1010 (s), 900 (m), 795 (s, br), 686 (m), 558 (s), 472 (m), 406 (m).

MS: 378 ($M^{+\cdot}$, 0.0).

Preparation of Bis(η^5-cyclopentadienyl)(ethoxy)(4-methylphenyldisulfano)titanium(IV), $Cp_2Ti(OEt)(SS\text{-}p\text{-}C_6H_4Me)$ (13d)

N-(4-methylphenyldithio)phthalimide (9d) (1.95 g, 6.48 mmol) was added to a solution of 1 (1.52 g, 6.48 mmol) in toluene (40 mL) and the

reaction mixture was stirred for 23 h. Filtration and vacuum-drying gave a purple powder of which NMR analysis indicated that 10d was the major constituent, with a trace of phthalimide also present. Addition of the powder to EtOH (35 mL) followed by stirring for 45 min gave a dark brown-orange solution which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4 x 6 cm), eluting with CH_2Cl_2, gave a brown band which was collected. Stripping of the band to dryness gave a brown powder (0.85 g, 35%, mp 104-106°C).

Anal. (%): Calcd. for $C_{19}H_{22}OS_2Ti$: C, 60.31; H, 5.86; S, 16.94. Found: C, 60.17; H, 5.85; S, 17.05.

^1H NMR ($CDCl_3$): δ7.40, 7.07 (ABq, 4H, J = 8.2 Hz, C_6H_4), 6.12 (s, 10H, C_5H_5), 4.18 (q, 2H, J = 6.8 Hz, CH_2), 2.30 (s, 3H, $C_6H_4CH_3$), 0.95 (t, 3H, J = 6.8 Hz, CH_2CH_3).

^1H NMR (C_6D_6): δ7.72, 7.00 (ABq, 4H, J = 8.0 Hz, C_6H_4), 5.80 (s, 10H, C_5H_5), 4.11 (q, 2H, J = 6.8 Hz, CH_2), 2.10 (s, 3H, $C_6H_4CH_3$), 0.98 (t, 3H, J = 6.8 Hz, CH_2CH_3).

IR (KBr): 3070 (w), 2955 (w), 2840 (w), 1478 (w), 1432 (m), 1362 (m), 1348 (m), 1264 (w), 1090 (s), 1062 (s, br), 1008 (s), 914 (m), 794 (s, br), 562 (m), 480 (m), 390 (w).

Preparation of Bis(η^5-cyclopentadienyl)(methoxy)(4-methylphenyldisulfano)titanium(IV), $Cp_2Ti(OMe)(SS\text{-}p\text{-}C_6H_4Me)$ (13e)

N-(4-methylphenyldithio)phthalimide (9d) (1.62 g, 5.38 mmol) was added to a solution of 1 (1.26 g, 5.38 mmol) in toluene (40 mL) and the reaction mixture was stirred for 18 h. Filtration, washing (hexanes, 2 x 5 mL), and vacuum-drying gave a purple powder of which NMR analysis

indicated that 10d was the major constituent, with a trace of phthalimide also present. Addition of the powder to MeOH (35 mL) followed by stirring for 10 min gave a dark orange solution which was taken to dryness in vacuo. Flash chromatography on deactivated alumina (4.x 30 cm), eluting with 50:50 CH_2Cl_2:Et_2O, gave an orange band which was collected. Stripping of the band to dryness gave an orange oil (0.59 g, 30%), which was recrystallized from Et_2O at -16°C to give dark orange microcrystals (mp 87-89°C) that were used as the analytical sample.

Anal. (%): Calcd. for $C_{18}H_{20}OS_2Ti$: C, 59.33; H, 5.53; S, 17.60. Found: C, 59.44; H, 5.42; S, 17.67.

^1H NMR ($CDCl_3$): δ7.39, 7.08 (ABq, 4H, J = 8.2 Hz, C_6H_4), 6.14 (s, 10H, C_5H_5), 3.94 (s, 3H, OCH_3), 2.30 (s, 3H, $C_6H_4\underline{CH_3}$).

^1H NMR (C_6D_6): δ7.67, 6.98 (ABq, 4H, J = 8.2 Hz, C_6H_4), 5.78 (s, 10H, C_5H_5), 3.88 (s, 3H, OCH_3), 2.08 (s, 3H, $C_6H_4\underline{CH_3}$).

IR (KBr): 3088 (w), 2891 (w), 2773 (w), 1470 (m), 1420 (m), 1282 (w), 1240 (w), 1065 (s, br), 997 (m), 790 (s, br), 506 (m), 470 (m).

Preparation of Bis(η^5-cyclopentadienyl)(chloro)(triphenylmethyldisulfano)titanium(IV), $Cp_2Ti(Cl)(SSCPh_3)\cdot 1/2\ CH_2Cl_2$ (11)

Ph_3CSSCl (1.64 g, 4.79 mmol) was added to a solution of 1 (1.12 g, 4.79 mmol) in toluene (30 mL) at -78°C. The temperature of the stirred reaction mixture was allowed to rise slowly to 22°C over a period of 2.5 h. A deep purple powder was obtained after filtration and washing (hexanes, 2 x 10 ml). Addition of the washings to the mother-liquors with cooling to -16°C, gave a second crop of powder. Flash

chromatography on deactivated alumina (1 x 6 cm), eluting with CH_2Cl_2, gave a purple band. The band was stripped to dryness, then recrystallized from CH_2Cl_2 layered with hexanes, to give a deep purple powder (1.48 g, 54%, mp 155-157°C (dec)). Once again the powder was recrystallized at room temperature from CH_2Cl_2 (10 mL) layered with hexanes (30 mL). Dark orange crystals were obtained that were used as the analytical sample.

Anal. (%): Calcd. for $C_{29}H_{25}S_2ClTi.1/2\ CH_2Cl_2$: C, 62.88; H, 4.65; S, 11.38. Found: C, 63.14; H, 4.65; S, 11.71.

^1H NMR ($CDCl_3$): δ7.47 - 7.19 (m, 15H, C_6H_5), 6.12 (s, 10H, C_5H_5).

^1H NMR (C_6D_6): δ7.72 - 6.98 (m, 15H, C_6H_5), 5.72 (s, 10H, C_5H_5).

IR (KBr): 3108 (m, sh), 3050 (m, br), 1588 (w, br), 1484 (m), 1442 (m), 1268 (w), 1183 (w), 1078 (w), 1016 (m), 820 (s), 737 (s), 700 (s), 620 (w), 501 (m).

MS: 520/518 ($M^{+\bullet}$-2H$^\bullet$, 0.39/0.28), 482 ($M^{+\bullet}$-2H$^\bullet$-HCl$^\bullet$, 0.96), 448 ($M^{+\bullet}$-2H$^\bullet$-HCl$^\bullet$-$H_2S^\bullet$, 0.96), 409 ($M^{+\bullet}$-2H$^\bullet$-HCl$^\bullet$-$H_2S^\bullet$-$C_3H_3^\bullet$, 1.03).

Addition of Ph_3P to $Cp_2Ti(OEt)(SSR)$, where R = CMe_3 (13a) and p-C_6H_4Me (13d), in C_6D_6

Two NMR samples, A and B, were prepared in C_6D_6 for each of 13a and 13d. A slight excess of one equivalent of Ph_3P was added to sample A.

R = CMe_3 (13a). No changes in the NMR signals were observed in either sample A or B over a period of 5 days.

R = p-C_6H_4Me (13d). The NMR signals due to 13d in sample A decreased in intensity concomitant with an increase in intensity of peaks due to $Cp_2Ti(OEt)(S\text{-}p\text{-}C_6H_4Me)$ (14).

^{1}H NMR (C_6D_6): δ5.77 (s, C_5H_5); 4.25 (q, J = 6.8 Hz, CH_2), 2.18 (s, $C_6H_4\underline{CH_3}$), 1.10 (t, J = 6.8 Hz, $CH_2\underline{CH_3}$), the aryl regions were obscured.

$Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d) was also detected. After 5 days the relative proportions of 13d:14:5d were 17:49:34. In addition, peaks due to Ph_3PS were observed. In sample B no spectral changes were observed over a period of 5 days.

Reaction of $Cp_2Ti(CO)_2$ (1) with Phth-SR, where R = $CHMe_2$ (15b) and CH_2Ph (15c): Preparation of $[Cp_2Ti(NO_2C_8H_4)]_n$ (16)

R = $CHMe_2$. N-(isopropylthio)phthalimide (15b) (1.47 g, 6.65 mmol) was added to a solution of 1 (1.56 g, 6.65 mmol) in toluene (40 mL). The reaction mixture was stirred for 47 h, at which point no residual 1 was present, as determined by an IR spectrum of the supernatant solution. Filtration gave a turquoise powder and an orange filtrate. Washing (toluene, 2 x 5 mL), and vacuum-drying gave the powder as the analytical sample (0.38 g, 18%, mp 209-211 °C (dec)).

Anal. (%): Calcd. for $C_{18}H_{14}NO_2Ti$: C, 66.68; H, 4.35; S, 0.00. Found: C, 66.89; H, 4.24; S, 0.00.

IR (toluene): 1582 (υ_{C-O}).

MS: 324 ($M^{+\bullet}$, 64), 259 ($M^{+\bullet}-C_5H_5^{\bullet}$, 100), 230 ($M^{+\bullet}-C_5H_5^{\bullet}-CHO^{\bullet}$, 40), 215 ($M^{+\bullet}-C_5H_5^{\bullet}-CO_2^{\bullet}$, 18), 188 ($M^{+\bullet}-C_5H_5^{\bullet}-NC_2O_2H^{\bullet}$, 24), 178 ($C_{10}H_{10}Ti^{+\bullet}$, 6).

The orange filtrate was stripped to dryness. A NMR spectrum of the residue indicated that $Cp_2Ti(phth)(SCHMe_2)$ (17b) was the major constituent (80% of the integrated intensity in the Cp region).

^{1}H NMR ($CDCl_3$): δ7.62 - 7.48 (m, 4H, C_6H_4), 6.31 (s, 10H, C_5H_5), 4.75

(septet, 1H, J = 6.6 Hz, CH), 1.57 (d, 6H, J = 6.6 Hz, CH_3).

In addition, peaks attributed to $(Me_2CH)_2S_2$ and phthalimide were detected.

R = CH_2Ph. In a manner similar to above, addition of N-(benzylthio)phthalimide (15c) (1.46 g, 5.43 mmol) to a solution of 1 (1.27 g, 5.43 mmol) in toluene (40 mL), resulted in formation of 16 (0.35 g, 20%). The red-orange filtrate was stripped to dryness. A NMR spectrum of the residue indicated that $Cp_2Ti(phth)(SCH_2Ph)$ (17c) was the major constituent (80% of the integrated intensity in the Cp region). ^1H NMR ($CDCl_3$): δ6.35 (s, 10H, C_5H_5), 5.42 (s, 2H, CH_2), the aryl regions were obscured.

In addition, peaks attributed to $Cp_2Ti(SCH_2Ph)_2$ (20%), $(PhCH_2)_2S_2$ and phthalimide were detected.

Results

The complex $Cp_2Ti(CO)_2$ (1) cleaved a S-N bond in toluene solutions of phth-SSR (9a-d) to give the complexes $Cp_2Ti(phth)(SSR)$ (10a-d), where phth = phthalimido, as shown in Eq. III.6. The novel disulfano

$$Cp_2Ti(CO)_2 + \text{phth-SSR} \xrightarrow{-2CO} Cp_2Ti(phth)(SSR) \qquad \text{(III.6)}$$

1 + 9a-d

10a: R = CMe_3

10b: R = $CHMe_2$

10c: R = CH_2Ph

10d: R = p-C_6H_4Me

complexes precipitated from the reaction mixtures over periods ranging from 8.5 h (10c) to 44 h (10a) in yields of 34-61%. They could not be recrystallized or chromatographed due to decomposition in solution and in the solid state under N_2. Satisfactory microanalytical results were obtained for all of complexes 10a-d. The compounds were slightly soluble in toluene, insoluble in hexanes and diethylether, and dissolved with decomposition in CH_2Cl_2. The ^1H NMR spectra were consistent with their formulation (Table III.1). The phthalimido ligand resonances appeared as a symmetric multiplet at higher field than in phth-S_xR, where x = 1 and 2, and in free phthalimide (δ7.9 - 7.7 ppm in $CDCl_3$). The chemical shifts of the methine and methylene resonance of 10b,c are shifted to higher field than those of their analogues $Cp_2Ti(phth)(SR)$ (17b,c).

The carbonyl stretching vibrations in IR spectra (benzene solutions) of organic phthalimido derivatives, phth-R[33], and sulfur

TABLE III.1: Spectroscopic Data for $Cp_2Ti(phth)(S_xR)$, where x = 1 and 2

			^1H NMR Assignment[a]							
R	x		C_5H_5	CH	CH_2	CH_3	C_6H_4	C_6H_5	phth	IR(ν_{C-O})[b]
CMe_3	2	10a	6.35s			1.49s			7.64-7.49m	1664
$CHMe_2$	2	10b	6.32s	3.31sept[c]		1.43d[c]			7.61-7.48m	1663
CH_2Ph	2	10c	6.20s		4.20s			7.40-7.29m	7.61-7.47m	1665
p-C_6H_4Me	2	10d	6.40s			2.36s	7.43, 7.16 ABq[d]		7.64-7.51m	1651
$CHMe_2$	1	17b	6.31s	4.75sept[e]		1.57d[e]			7.62-7.48m	
CH_2Ph[f]	1	17c	6.35s		5.42s					

[a] In $CDCl_3$ in δ ppm. s = singlet, d = doublet, ABq = AB quartet, sept = septet, m = multiplet.
[b] Toluene in cm^{-1}. [c] J = 6.8 Hz. [d] J = 7.8 Hz. [e] J = 6.6 Hz.
[f] Phenyl and phth regions obscured by impurity peaks.

transfer reagents, phth-SSR[29] (9a-d) (Table III.2), appear as two bands in the region 1720-1750 cm^{-1}, with the higher frequency band being of much lower intensity. The bands are shifted to 1585-1620 cm^{-1} in the phthalimido anion[33]. The IR spectra (toluene) of 10a-d (Table III.1) showed a single strong υ_{C-O} stretching vibration in the region 1651-1665 cm^{-1}. The spectra were of low concentration solutions due to the low solubilities of 10a-d. Freshly made toluene solutions of 10a-d exhibited a υ_{C-O} band due to phthalimide (1746 cm^{-1}) after less than 10 min in an IR cell.

If the reaction of 1 with 9a-d was not performed under rigorously inert atmospheric conditions, or if slightly impure 1 was used, the products 10a-d were contaminated by phthalimide. However, using very pure 1 required longer reaction times. For the synthesis of 10c the precipitated product had to be collected prior to total consumption of 1 due to instability of the former over periods longer than 8.5 h.

Treatment of $MeCp_2Ti(CO)_2$ with 9d gave an intractable pale orange powder, the NMR spectrum of which indicated the presence of MeCp and phth groups in the ratio 1:1.

$Cp_2Ti(CO)_2$ (1) was readily oxidized by Ph_3CSSCl in toluene at -78°C, and after evaporation of solvent gave a crude product, which gave a NMR spectrum consistent with $Cp_2Ti(Cl)(SSCPh_3)$ (11) as the major Cp containing species. In addition, weak peaks due to Cp_2TiCl_2 (12) and other unidentified Cp containing species were observed. Recrystallization gave 11 contaminated with 12. Flash chromatography on deactivated alumina, using CH_2Cl_2 as the eluant, gave pure 11 as determined by its NMR spectrum and elemental analysis. The reaction of

TABLE III.2: Spectroscopic Data for phth-S_xR, where x = 1 and 2

R	x		^{1}H NMR Assignment[a] CH	CH_2	CH_3	C_6H_4	C_6H_5	IR(υ_{C-O})[b]
CMe_3	2	9a			1.42s			1742
	1	15b	3.48sept[c]		1.29d[c]			1742
$CHMe_2$	2	9b	3.36sept[d]		1.39d[d]			1742
	1	15c		4.12s			7.87-7.19m	1743
CH_2Ph	2	9c		4.31s			7.55-7.28m	1741
	1	15d			2.32s	7.63, 7.17 ABq[e]		1743
p-C_6H_4Me	2	9d			2.29s	7.48, 7.12 ABq[f]		1745

[a] $CDCl_3$ in δ ppm. Phthalimido region omitted. s = singlet, d = doublet, ABq = AB quartet, sept = septet, m = multiplet.

[b] Toluene in cm^{-1}. Only the more intense band is listed. [c] J = 6.6 Hz. [d] J = 6.5 Hz.

[e] J = 7.9 Hz. [f] J = 8.0 Hz.

Ph_3CSSCl with 1 in toluene at room temperature gave a reduced yield of 11. Complex 11 is air-stable for months and is soluble in CH_2Cl_2 and toluene, giving intensely purple coloured solutions.

Treatment of 10a-d with ethanol and 10d with methanol gave $Cp_2Ti(OR')(SSR)$ (13a-e) in high yields, as shown in Eq. III.7.

$$Cp_2Ti(phth)(SSR) \xrightarrow{R'OH} Cp_2Ti(OR')(SSR) + phth\text{-}H \qquad (III.7)$$

10a-d

13a: R = CMe_3; R' = Et

13b: R = $CHMe_2$; R' = Et

13c: R = CH_2Ph; R' = Et

13d: R = p-C_6H_4Me; R' = Et

13e: R = p-C_6H_4Me; R' = Me

Treatment of 10d with one equivalent of $PhCH_2OH$ in toluene, produced an intractable mixture, of which a NMR spectrum ($CDCl_3$) gave resonances attributable to $Cp_2Ti(OCH_2Ph)(SS\text{-}p\text{-}C_6H_4Me)$ [δ6.20 (s, 10H, C_5H_5), 5.17 (s, 2H, CH_2), 2.25 (s, 3H, CH_3), aryl regions obscured], in addition to unidentified products.

The highest yields of 13a-e (28-58%, based upon 1) were obtained by allowing the oxidative-addition reactions of 9a-d to 1 to proceed to completion, as indicated by the absence of υ_{C-O} bands of 1 in the IR spectrum of the reaction solution, and then adding EtOH. Flash chromatography on deactivated alumina separated 13a-e from phthalimide, to give the analytical sample after work-up. 13b-e were air-stable powders, 13a was an oil and all complexes were air-stable in $CDCl_3$ and C_6D_6.

^{1}H NMR spectral data for 13a-e are given in Table III.3. The peaks due to Cp and R groups are similar in chemical shift to those of the analogous species 10a-d. The signals due to ethoxy groups were considerably shifted to lower field relative to free EtOH. The infrared spectra of 13a-e gave a broad band in the region 506-562 cm^{-1}, which is the approximate frequency expected for a ν_{Ti-O} stretching vibration[22,34] (Table III.3).

Triphenylphosphine does not react with 13a, but with 13d over a period of 5 days led to partial desulfurization, giving the complex $Cp_2Ti(OEt)(S\text{-}p\text{-}C_6H_4Me)$ (14) with concomitant formation of Ph_3PS, as detected by ^{1}H NMR spectroscopy. In addition, peaks due to $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d) and unreacted 13d were observed. The resonances due to the bisthiolato complex 5d grew in intensity only in the latter stages of the reaction.

The reactions in toluene of $Cp_2Ti(CO)_2$ (1) with phth-SR, where R = $CHMe_2$ (15b), CH_2Ph (15c) and $p\text{-}C_6H_4Me$ (15d), gave different results than those observed with 9a-d. The reactions of 15b and 15c with 1 gave a very sparingly soluble, air-sensitive, turquoise powder, 16, of which the elemental analysis was consistent with the empirical formula $C_{18}H_{14}NO_2Ti$. The mass spectrum of 16 gave ions and a fragmentation pattern consistent with $Cp_2Ti(phth)$. The powder was only sparingly soluble in C_6D_6 and exhibited a broad band of resonances in the region δ7.5 - 6.2 ppm in the NMR spectrum. Immediate reaction occurred upon solvolysis in $CDCl_3$, giving a dark red solution exhibiting a large number of sharp peaks in the Cp region (δ6.7 - 6.3 ppm) of the NMR spectrum. An infrared spectrum of a very dilute toluene solution of 16

TABLE III.3: Spectroscopic Data for $Cp_2Ti(OR')(SSR)$

Complex		^1H NMR Assignment[a] C_5H_5	CH	CH_2	CH_2'	CH_3	CH_3'	C_6H_4 or C_6H_5	Solvent	IR(ν_{Ti-O})[b]
$Cp_2Ti(OCH_2CH_3')$-		6.14s		4.23q[e]		1.37s	1.00t[e]		c	
$(SSC(CH_3)_3)$	13a	5.88s		4.16q[e]		1.50s	1.06t[e]		d	560
$Cp_2Ti(OCH_2CH_3')$-		6.13s	2.86sept[e]	4.25q[f]		1.32d[e]	1.01t[f]		c	
$(SSCH(CH_3)_2)$	13b	5.83s	3.01sept[e]	4.14q[g]		1.43d[e]	1.02t[g]		d	560
$Cp_2Ti(OCH_2CH_3')$-		6.11s		4.30q[f]	3.83s		1.05t[f]	7.36–7.31m	c	
$(SSCH_2'Ph)$	13c	5.77s		4.13q[g]	3.95s		1.00t[g]	7.38–6.96m	d	558
$Cp_2Ti(OCH_2CH_3')$-		6.12s		4.18q[e]		2.30s	0.95t[e]	7.40, 7.07 ABq[h]	c	
$(SS\text{-}p\text{-}C_6H_4CH_3)$	13d	5.80s		4.11q[e]		2.10s	0.98t[e]	7.72, 7.00 ABq[i]	d	562
$Cp_2Ti(OCH_3')$-		6.14s				2.30s	3.94s	7.39, 7.08 ABq[h]	c	
$(SS\text{-}p\text{-}C_6H_4CH_3)$	13e	5.78s				2.08s	3.88s	7.67, 6.98 ABq[h]	d	506

[a] In δ ppm. s = singlet, d = doublet, t = triplet, q = quartet, ABq = AB quartet, sept = septet, m = multiplet.

[b] KBr in cm^{-1}. [c] $CDCl_3$. [d] C_6D_6.

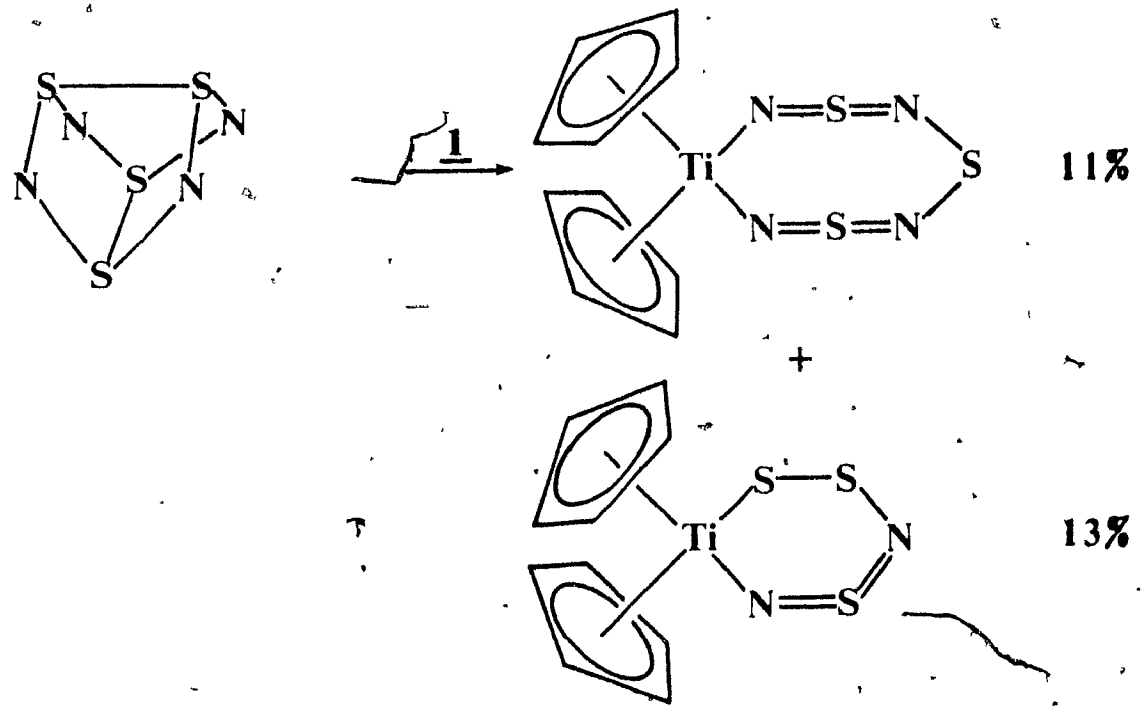
[e] J = 6.8 Hz. [f] J = 7.0 Hz. [g] J = 6.9 Hz. [h] J = 8.2 Hz. [i] J = 8.0 Hz.

showed a single weak band at 1582 cm^{-1}, which is 80 cm^{-1} and 140 cm^{-1} lower than the band assigned to the ν_{C-O} stretching vibration in 10a-d (Table III.1) and 15b-d (Table III.2), respectively. 16 decomposed very rapidly in toluene and phthalimide was detected within minutes by its IR spectrum.

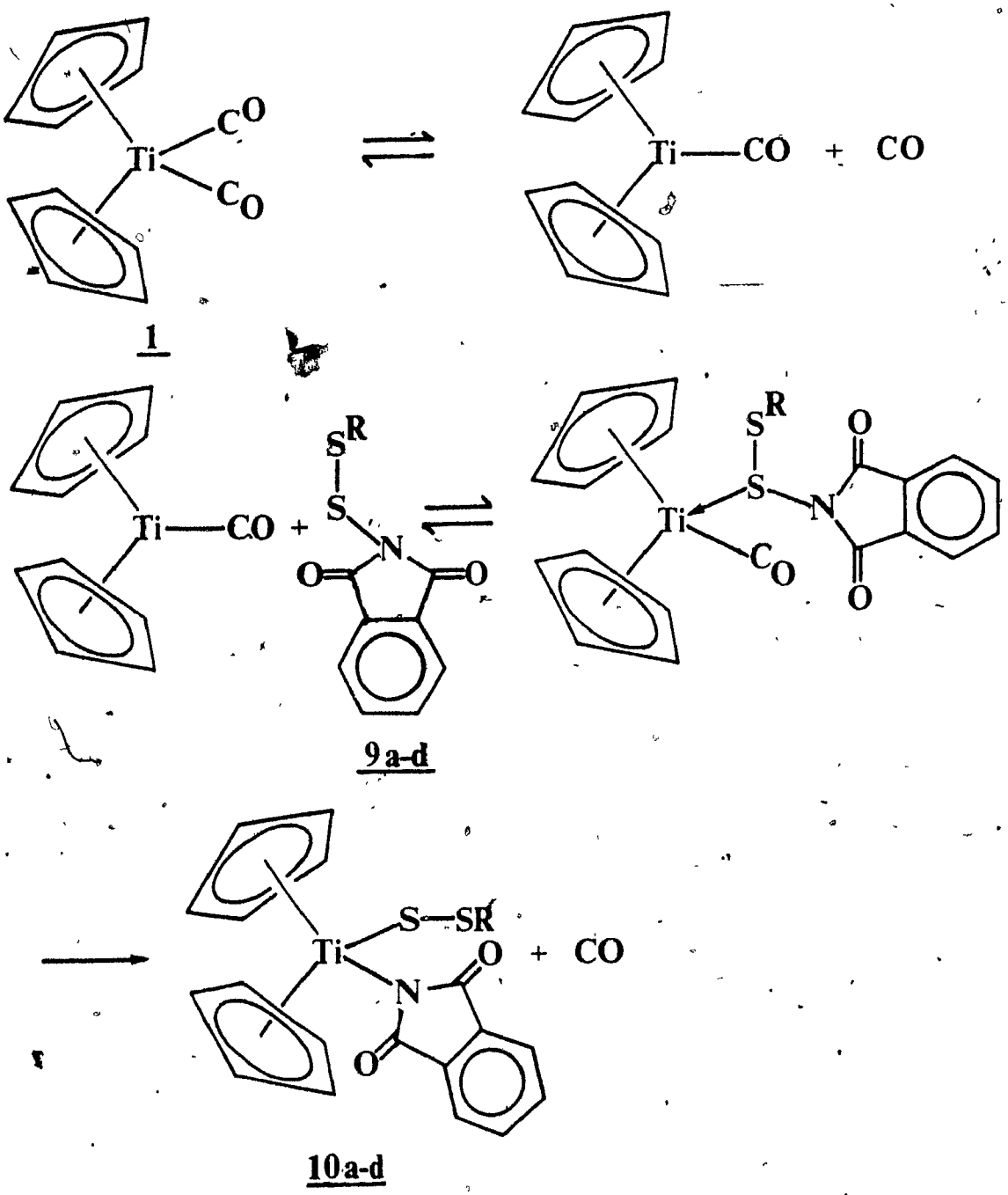
An orange filtrate obtained after collection of the powder, 16, was stripped to dryness. A NMR spectrum of the residue showed resonances consistent with the presence of phthalimide, RSSR and $Cp_2Ti(phth)(SR)$, where R = $CHMe_2$ (17b) and CH_2Ph (17c). The latter could not be separated from phthalimide. The reaction of 1 and 15d gave very impure $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d).

Discussion

The complexes $Cp_2Ti(X)(SSR)$, where X = phth (10a-d) and Cl (11), were formed via oxidative-addition of a S-X bond to $Cp_2Ti(CO)_2$ (1). Previous workers have shown that phth-SSR can oxidatively add to $(Ph_3P)_2Pt(C_2H_4)$ to form cis-$(Ph_3P)_2Pt(phth)(SSR)$[35] and can also give $CpW(CO)_3SSSR$ on reaction with $CpW(CO)_3SH$[36]. The oxidation of 1 with tetrasulfur tetranitride was shown to give at least two products[4].



The CO ligands in 1 are easily displaced[23]. Substitution by ketones, aldehydes, acyl halides, carboxylic acids and haloalkanes have been reported[37]. Recent work by Basolo et al. indicates that dissociation of a carbonyl ligand is the first step in the reaction[38]. Thus, the reaction of phth-SSR with 1 may proceed via initial coordination of a sulfur atom to the titanium centre of the highly coordinatively unsaturated species $Cp_2Ti(CO)$, as shown in Scheme III.1.



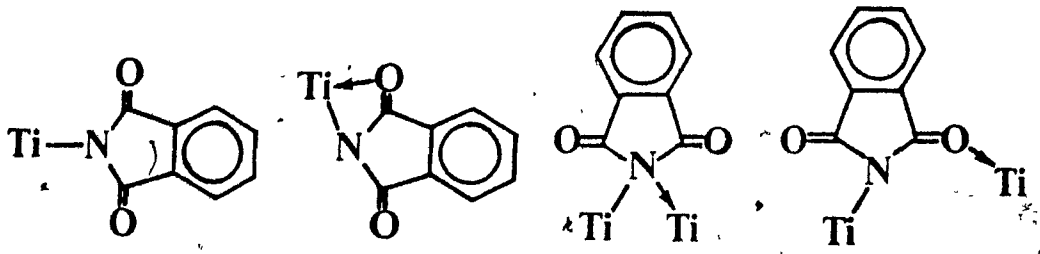
SCHEME III.1

The products 10a-d are fairly unstable. This must be due to the presence of the phthalimido ligand, since the analogous thiolates, $Cp_2Ti(SR)(SSR)$ (Chapter II), and alkoxides, 13a-e, are more stable. Homolytic scission of the N-Br bond in N-bromosuccinimide is well

documented[39]. Homolysis of the N-Ti bond may account for the occurrence of phthalimide in solutions and precipitates of 10a-d. NMR and IR spectroscopic data are consistent with a linear TiSSR linkage and coordination of the phthalimido group through the nitrogen atom. However, no splitting of carbonyl absorptions was observed, which is in contrast to the pattern of υ_{C-O} absorptions expected for coordination of an imido group involving no metal-oxygen interactions[33,35]. Therefore, bidentate coordination of the phthalimido group in 10a-d to titanium using both oxygen and nitrogen atoms, cannot be ruled out.

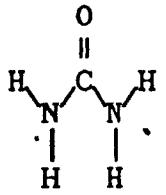
Interestingly, the oxidative-additions of phth-SR (15b,c) to 1 gave turquoise powders, 16, which exhibited broad ^{1}H NMR resonances consistent with a d^1 Ti(III) species. Compounds such as $[Cp_2TiCl]_2$[40] and $[Cp_2Ti(NMe_2)]_2$[7b] are paramagnetic dimers with chlorine and nitrogen atoms bridging between the metal centres. The value of the υ_{C-O} stretching vibration in 16 is close to that of the phthalimido anion[33]. Since a poorly resolved IR spectrum was obtained due to the insoluble nature of 16, it was not possible to discern if a lower intensity, higher frequency υ_{C-O} band was present, as might be expected for a phthalimido ligand bound only through a nitrogen atom[33,35].

The phthalimido group has three sites available for coordination, but due to structural limitations all three donor atoms cannot coordinate to the same metal atom[41]. Some possible monodenate and bidentate phthalimido coordination modes are presented below. It is well known that as a result of coordination through the carbonyl oxygen, the double bond character between carbon and oxygen is reduced[42]. The molecular structure of cis-$(Ph_3P)_2$Pt(phth)(SSR) shows no Pt-O



I II III IV

interaction[35]. However, a decrease in the ν_{C-O} stretching vibration is observed compared to that of phth-SSR[43], indicating reduced C-O bond order. Urea can bind to a metal centre via the nitrogen or the oxygen



atom[53]. The unused lone pair on the nitrogen atom of the phthalimido ligand in structural type I might thus be expected to exhibit some nucleophilic character, thereby permitting formation of type III, as shown above.

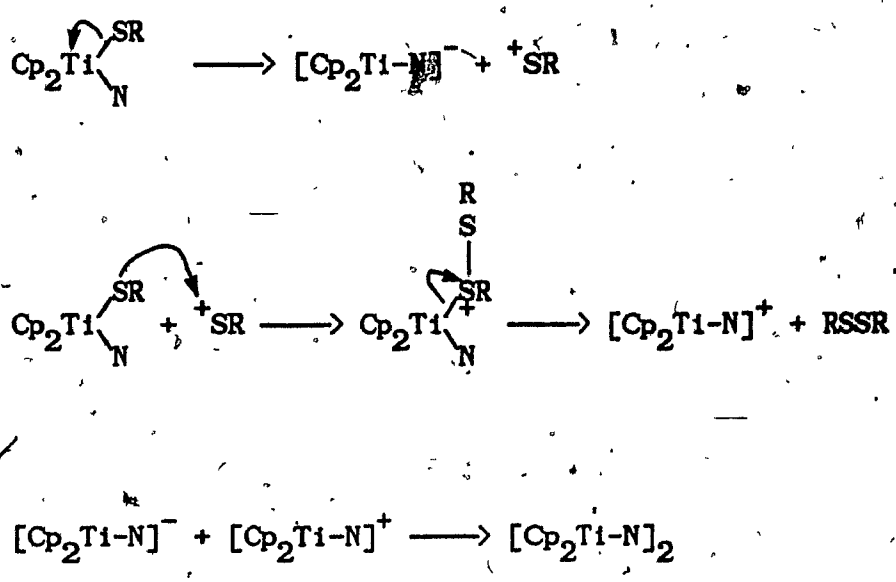
The lack of additional data on 16 prevents an unequivocal assignment of structure. However, it seems probable that the species is of the type, $[Cp_2TiX]_n$, where X = phth and n ≥ 2, with the bridging phthalimido groups acting as in either of structural types III or IV. Polymeric complexes, for example where X = O and $S(CH_2)_nS$, have been discussed in the literature[23].

The mother-liquors left after removal of 16, contained the expected

thiolato complexes $Cp_2Ti(phth)(SR)$ (17b,c), in addition to approximately 0.5 equivalents of RSSR. The formation of organic disulfides likely accompanied the reduction of the Ti(IV) species, 17b,c, to 16. The accessiblity of various oxidation states is relatively easy for titanium[23,44]. The disulfano complexes 10b,c do not produce organic tetrasulfides.

Three speculative mechanisms for reduction of 17b,c are presented in Scheme III.2. $[Cp_2Ti(phth)]_n$ (16), is depicted as dimeric, i.e. n = 2, but values of n > 2 are also possible. The ^1H NMR resonances of alkylthiolate groups in 17b,c are shifted to lower field than those

A. RS^+ cation



SCHEME III.2

B. $RS^{\bullet}$ radical

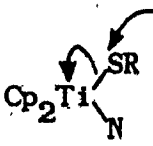
$$Cp_2Ti(SR)N \longrightarrow [Cp_2Ti\text{-}N]^{\bullet} + {}^{\bullet}SR$$

$$2RS^{\bullet} \longrightarrow RSSR$$

$$2[Cp_2Ti\text{-}N]^{\bullet} \longrightarrow [Cp_2Ti\text{-}N]_2$$

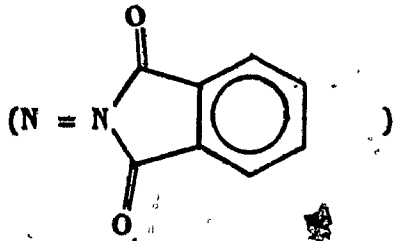
C. RS^{-} anion

$$Cp_2Ti(SR)N \longrightarrow [Cp_2Ti\text{-}N]^{+} + {}^{-}SR$$



$$Cp_2Ti(SR)N + {}^{-}SR \longrightarrow [Cp_2Ti\text{-}N]^{-} + RSSR$$

$$[Cp_2Ti\text{-}N]^{+} + [Cp_2Ti\text{-}N]^{-} \longrightarrow [Cp_2Ti\text{-}N]_2$$



(N = N)

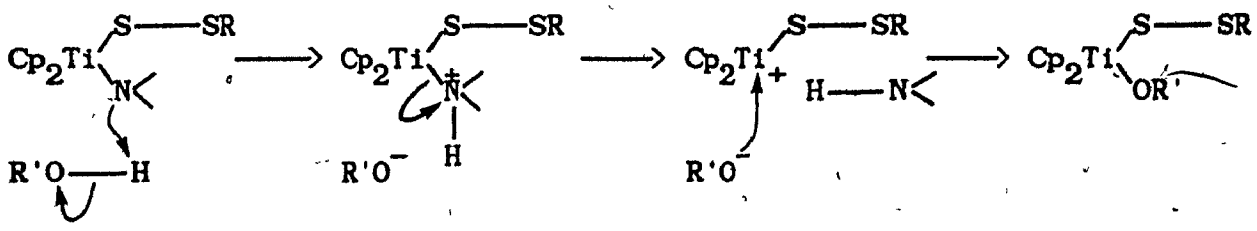
SCHEME III.2 (cont'd)

of 10b,c perhaps suggestive of loss of RS^{+} as the first step in reduction of 17b,c, as shown in Scheme III.2.A. Radicals of the type

$RS_x^{\bullet}$, where $x \geq 2$, are more stable than $RS^{\bullet}$ due to resonance stabilization on a catenated sulfur chain[46]. Thus Scheme III.2.B seems an unlikely mechanism since the first and probably slowest step in the analogous reduction of $Cp_2Ti(phth)(SSR)$ (10a-d) would be more favourable than that of $Cp_2Ti(phth)(SR)$ (17b,c), and reaction of 10a-d does not appear to occur. Scheme III.2.C cannot be ruled out since anionic sulfur species such as LiSR are known[47].

The subtle effects of ligand substitution in complexes 10a-d and 17b,c is further illustrated by the attempted synthesis of $MeCp_2Ti(phth)(SS\text{-}p\text{-}C_6H_4Me)$. Methyl substitution on the cyclopentadienyl ring will increase the ligand to metal electronic donation, thereby heightening metal basicity[48]. Increased electron density on the metal centre may cause formation of the observed products, which consist of a predominant Cp containing species, tentatively assigned as $MeCp_2Ti(phth)_2$.

The reactions of 10a-d with EtOH are acid-base displacements of the phthalimido ligands. The mechanism may involve initial protonation of the nitrogen atom, as shown below in Scheme III.3. Another possibility



SCHEME III.3

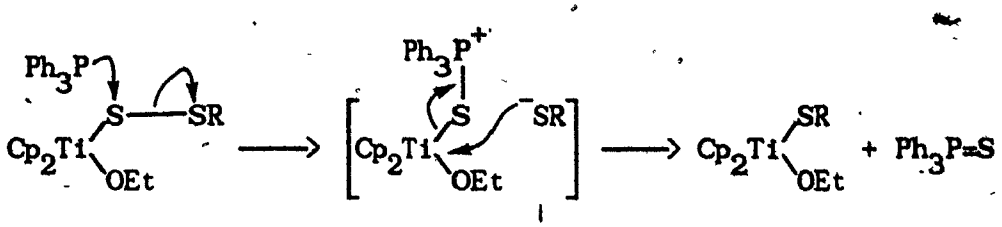
involves S_N2 attack by the oxygen lone pair of ethanol on the titanium

atom, leading to an 18 electron intermediate prior to loss of phthalimide[49].

The alkoxide complexes 13a-e show upfield shifts in their NMR spectra for the Cp and RSS ligands, relative to 10a-d (Tables II.1 and 3), as would be expected for replacement of an electron withdrawing phthalimido group by an alkoxide ligand. The R groups of the disulfano ligand are in a similar high field environment to those observed for organic disulfides, RSSR. The possibility of π-bond donation by alkoxide and even disulfano ligands in 13a-e cannot be ruled out[24]. 13c was examined by variable temperature NMR spectroscopy and no evidence for an η^2-SSR coordination mode was found.

The addition of Ph_3P to solutions containing 13a or 13d resulted in sulfur abstraction from the disulfano ligand, only in the case of R = p-C_6H_4Me. Nucleophilic attack on the TiSSR moiety of 13a thus appears to be inhibited by the presence of a bulky tert-butyl group. This phenomenon was observed in the attempted desulfurization of $Cp_2Ti(SCMe_3)(SSCMe_3)$ by Ph_3P and other nucleophiles (Chapter II). Also, the desulfurization of 13d may be favoured by the greater electron withdrawing properties of p-tolyl vis-à-vis tert-butyl groups, which would help stabilize an intermediate thiolate anion. A possible mechanism for sulfur abstraction is shown in Scheme III:4. The complex, $Cp_2Ti(S\text{-}p\text{-}C_6H_4Me)_2$ (5d) was also observed as a product of addition of Ph_3P to 13d. However, no evidence for $Cp_2Ti(OEt)_2$, a possible product of disproportionation of 14, was observed. Previous workers have noted unsuccessful attempts to synthesize $Cp_2Ti(OEt)_2$[50].

The oxidative-addition of Ph_3CSSCl to 1 occurs with relative ease,



13d

R = p-C_6H_4Me

14

SCHEME III.4

as might be expected for cleavage of the reactive sulfur-chlorine bond[5]. The product $Cp_2Ti(Cl)(SSCPh_3)$ (11) is relatively stable towards decomposition compared to 10a-d and 13a-e. The thiolato complexes $Cp_2Ti(Cl)(SR)$, where R = CMe_3, $CHMe_2$[47], Me, Et, Ph and CH_2Ph[51], are known. Pentafluorophenylchlorodisulfide adds to Vaska's complex via S-Cl bond cleavage to give $(Ph_3P)_2IrCl_2(CO)(SSC_6F_5)$[52].

References

1. a) S.C. Schuman and H. Shalit, Catal. Rev., 4, (1970), 245.
   b) A.I. Hadjikyriacou and D. Coucouvanis, Inorg. Chem., 26, (1987), 2400.
2. a) L.E. Bennet, Prog. Inorg. Chem., 18, (1973), 1.
   b) A. Müller, Angew. Chem. Int. Ed. Engl., 17, (1978), 279.
   c) A. Müller, W. Eltzer and N. Mohan, Angew. Chem. Int. Ed. Engl., 18, (1979), 168.
3. M.S. Whittingham, Prog. Solid. St. Chem., 12, (1978), 41.
4. C.G. Marcellus, R.T. Oakley, W.T. Pennington and A.W. Cordes, Organometallics, 5, (1986), 1395.
5. G. Fachinetti and C. Floriani, J. Chem. Soc., Dalton Trans., (1977), 2297.
6. "Metal and Metalloid Amides", by M.F. Lappert, P.P. Power, A.R. Sanger and R.C. Srivastava, Ellis Horwood, London, 1980.
7. a) E.C. Alyea, D.C. Bradley, M.F. Lappert and A.R. Sanger, J. Chem. Soc., Chem. Commun., (1969), 1064.
   b) M.F. Lappert and A.R. Sanger, J. Chem. Soc. (A), (1971), 874.
   c) D.C. Bradley and R.G. Copperthwaite, J. Chem. Soc., Chem. Commun., (1971), 764.
8. A. Nicco and J. Aboulafia, French Patent 1,358,503, (1964).
9. D.C. Bradley and I.M. Thomas, Proc. Chem. Soc., (1959), 225.
10. C. Airoldi and D.C. Bradley, Inorg. Nucl. Chem. Lett., 11, (1975), 155.
11. I.M. Thomas, Can. J. Chem., 39, (1961), 1386.
12. D.C. Bradley and P.A. Hammersley, J. Chem. Soc. (A), (1967), 1894.

13. G. Chandra and M.F. Lappert, J. Chem. Soc. (A), (1968), 1940.

14. G. Chandra and M.F. Lappert, Inorg. Nucl. Chem. Lett., 1, (1965), 83.

15. K. Issleib and G. Bätz, Z. Anorg. Allg. Chem., 369, (1969), 83.

16. Personal communication, R. Turrin and A.G. Shaver.

17. D.R. Corbin, W.S. Willis, E.N. Duesler and G.D. Stucky, J. Am. Chem. Soc., 102, (1980), 5969.

18. a) M.F. Lappert and A.R. Sanger, J. Chem. Soc. (A), (1971), 1314.

b) D.R. Gray and C.H. Brubaker Jr., Inorg. Chem., 10, (1971), 2143.

19. "The Organic Chemistry of Titanium", by R. Feld and P.L. Cowe, Butterworth, London, 1965.

20. M.P. Mack and G.T. Berge, Ger. Offen. (Pat.) No. DE3409754 A1, (1983).

21. a) Y. Kishimoto and T. Masubuchi, Japanese Pat. No. 61/28507 A2 [86/28507], (1986).

b) Y. Kishimoto and H. Morita, Ger. Offen. (Pat.) No. DE3401983 A1, (1984).

c) C. Lassau, R. Stern and L. Sajus, Ger. Offen. (Pat.) No. DE1944382, (1970).

22. "Metal Alkoxides", by D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Academic Press, New York, 1978.

23. "Organometallic Chemistry of Titanium, Zirconium and Hafnium", by P.C. Wailes, R.S.P. Coutts and H. Weigold, Academic Press, New York, 1974.

24. J.C. Huffman, K.G. Moloy, J.A. Marsella and K.G. Caulton, J. Am. Chem. Soc., 102, (1980), 3009.

25. a) A.N. Nesmeyanov, O.V. Nogina and A.M. Berlin, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., (1961), 804.

b) A.N. Nesmeyanov, O.V. Nogina, A.M. Berlin, A. Girshovich and G.V. Shatalov, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., (1961), 2008.

26. T. Blackmore, M.I. Bruce, P.J. Davidson, M.Z. Iqbal and F.G.A. Stone, J. Chem. Soc. (A), (1970), 3153.

27. a) K. Andrä, J. Organomet. Chem., 11, (1968), 567.

b) A.R. Dias, M.S. Salema and J.A.M. Simoes, J. Organomet. Chem., 222, (1981), 69.

28. M.D. Curtis, S. Thanedar and W.M. Butler, Organometallics, 3, (1984), 1855.

29. D.N. Harpp and D.K. Ash, Int. J. Sulfur Chem. (A), 1, (1971), 57.

30. M. Behforouz and J.E. Kerwood, J. Org. Chem., 34, (1969), 51.

31. D.N. Harpp and D.K. Ash, Int. J. Sulfur Chem. (A), 1, (1971), 211.

32. H. Köpf and M. Schmidt, Z. Anorg. Allg. Chem., 340, (1965), 139.

33. T. Matsuo, Bull. Chem. Soc. Japan, 37, (1964), 1844.

34. H. Kriegsmann and K. Licht, Z. Elektrochem., 62, (1958), 1163.

35. A.G. Shaver, J. Hartgerink, R.D. Lai, P. Bird and N. Ansari, Organometallics, 2, (1983), 938.

36. A.G. Shaver and J. Hartgerink, Can. J. Chem., 65, (1987), 1190.

37. a) G. Fachinetti and C. Floriani, J. Chem. Soc., Dalton Trans., (1974), 2433.

b) ibid, (1977), 2297.

c) ibid, (1979), 792.

d) G. Fachinetti and C. Floriani, J. Am. Chem. Soc., 100, (1978),

1921.

e) G. Fachinetti, C. Brian, C. Floriani, A. Chiesi-Villa and C. Gaust, Inorg. Chem., 17, (1978), 2995.

38. G.T. Palmer, F. Basolo, L.B. Kool and M.D. Raush, J. Am. Chem. Soc., 108, (1986), 4417.

39. R.H. Mitchell, Y.-H. Lai and R.V. Williams, J. Org. Chem., 44, (1979), 4733.

40. R. Jungst, D. Sekutowski, J. Davis, M. Luly and G. Stucky, Inorg. Chem., 16, (1977), 1645.

41. S.C. Jain and R. Rivest, J. Inorg. Nucl. Chem., 31, (1969), 399.

42. a) S.C. Jain and R. Rivest, J. Inorg. Nucl. Chem., 29, (1967), 2787.

b) S.C. Jain and R. Rivest, Can. J. Chem., 41, (1963), 2130.

c) W.E. Bull, S.K. Madan and J.E. Willis, Inorg. Chem., 2, (1963), 303.

d) C.S. Kraihanzel and S.C. Grenda, Inorg. Chem., 4, (1965), 1037.

43. R.D. Lai, Ph.D. Thesis, McGill University, (1981).

44. "Chemistry of Organo-Zirconium and -Hafnium Compounds", by D.J. Cardin, M.F. Lappert and C.L. Raston, John Wiley, Toronto, 1986, pp 18-19.

45. a) H. Mackle, Tetrahedron, 19, (1963), 1159.

b) I. Kende, T.L. Pickering and A.V. Tobolsky, J. Am. Chem. Soc., 87, (1965), 5582.

46. R. Steudel, Angew. Chem. Int. Ed. Engl., 14, (1975), 655.

47. J.M. McCall, Ph.D. Thesis, McGill University, (1983).

48. a) S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini,

Inorg. Chem., 23, (1984), 1739.

b) J.L. Robbins, N. Edelstein, B. Spencer and J.C. Smart, J. Am. Chem. Soc., 104, (1982), 1882.

49. J. Besançon, S. Top, J. Tirouflet, Y. Dusausey, C. Lecomte and J. Protas, J. Organomet. Chem, 127, (1977), 153.

50. a) S.A. Giddings, Inorg. Chem., 6, (1967), 849.

b) Ref. 23, p 74.

51. R.S.P. Coutts, J.R. Surtees, J.M. Swan, and P.C. Wailes, Aust. J. Chem., 19, (1966), 1377.

52. S.N. Bhattacharya, C.V. Senoff and F.S. Walker, Inorg. Chim. Acta, 44, (1980), L273.

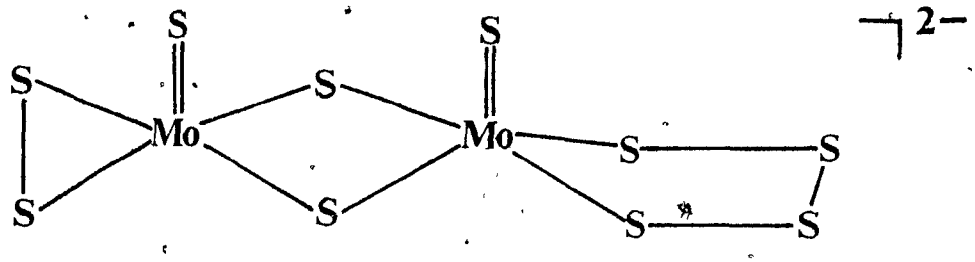
53. R.B. Penland, S. Mizushima, C. Curran and J.V. Quagliani, J. Am. Chem. Soc., 79, (1957), 1575.

CHAPTER IV

THE SYNTHESES, CHARACTERIZATION AND VARIABLE TEMPERATURE ^{1}H NMR STUDIES OF $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}SR)(\mu\text{-}S_xR)Mo(CO)_4]$, WHERE x = 1 AND 2

Introduction

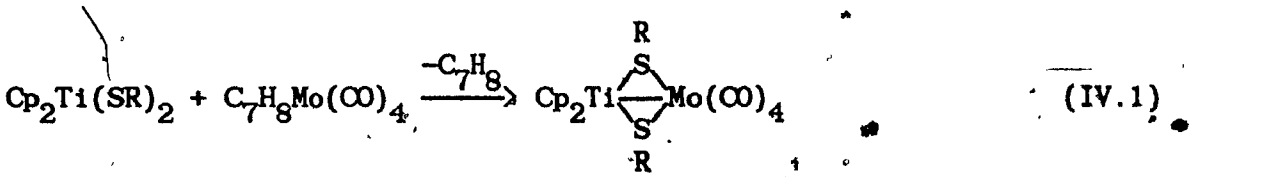
Interest in molybdenum sulfur compounds is due in part to the widespread use of sulfided molybdenum/Al_2O_3 based hydrodesulfurization catalysts[1,2] and to the presence of molybdenum and sulfur in the active component of certain enzymes. Even "simple" binary molybdenum polysulfides have a variety of compositions. In these systems the sulfide (S^{2-}), disulfide (S_2^{2-}) and tetrasulfide (S_4^{2-}) groups can appear as ligands in complex anions such as $[(S_4)_2MoS]^{2-}$, $[Mo_2S_{12}]^{2-}$ [3] and $[Mo_2S_{10}]^{2-}$ [3,4], illustrated below.



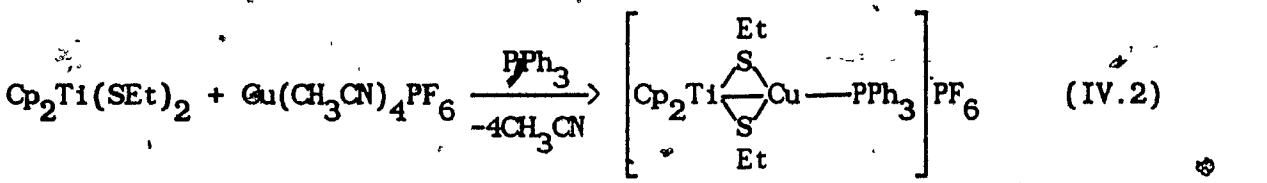
Studies on nitrogenase enzymes have suggested that a molybdenum atom is present in a cluster containing Fe and S atoms[5]. Edmundson et al. have postulated that a protein bound disulfano anion, RSS^-, undergoes nucleophilic attack during the catalytic cycle of xanthine oxidase[6], another molybdenum containing enzyme[7]. The relevance of low oxidation states of Mo to biology is uncertain, although Mo(II) and Mo(III) may be involved during the catalytic cycle of nitrogenase[8].

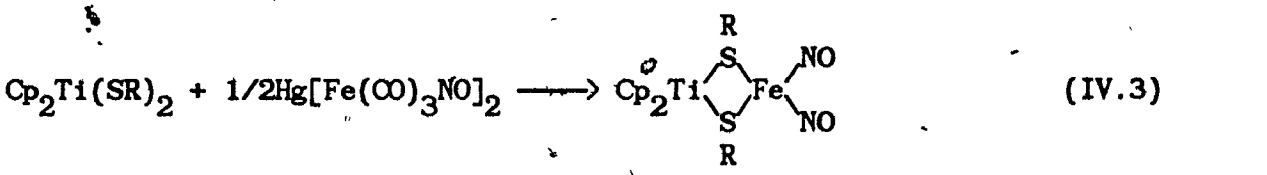
Reactivity studies on well-defined Mo-S complexes might give a basic understanding of the interactions of organosulfur compounds on molybdenum sulfide surfaces[9] and to the nature of active sites in molybdenum containing enzymes. The availability of $Cp_2Ti(SR)(SSR)$ (4) suggested combining this species with molybdenum precursors. Dimeric

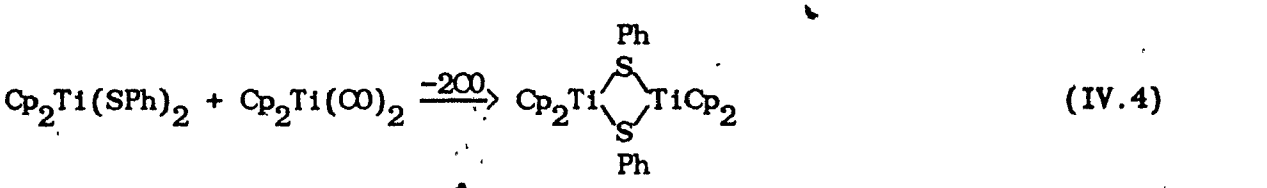
titanium species containing bridging thiolate ligands are common, for example, $[Cp_2Ti(\mu\text{-}SR)_2ML_x]$, where: R = H[10], Me, Ph[11] and ML_x = $Mo(CO)_4$ (19) (Eq. IV.1); R = Et and ML_x = $Cu(PPh_3)$[12] (Eq. IV.2); R = Me, Ph and ML_x = $Fe(NO)_2$[13] (Eq. IV.3); and R = Ph and ML_x = $TiCp_2$[14] (Eq. IV.4).



C_7H_8 = norbornadiene







The dimers shown in Eqs. IV.1 and 2 have been postulated to contain metal-metal bonds, based upon electronic absorption spectra and crystallographic studies which gave Ti-Mo and Ti-Cu bond distances as 3.321 Å and 2.803 or 2.840 Å, respectively[12,15], consistent with single

bonds. The diamagnetism exhibited by the dimer shown in Eq. IV.3 was interpreted as evidence for Ti-Fe interaction[13].

There are no structurally characterized examples of a bridging polysulfano ligand, RS_x, where $x > 1$. Noble has recently described a complex containing a RSS ligand bridging two Mo(V) atoms[16]. Conformational isomers were observed via variable temperature ^1H and ^{31}P NMR, consistent with the assignment of a μ-η^1-SSR bridge. Accordingly, the reactions of $Cp_2Ti(SR)(SSR)$ (4) with $C_7H_8Mo(CO)_4$ were investigated as a possible route to heterobimetallic dimers bridged by RS and RSS ligands.

Experimental

Materials and Methods

All manipulations carried out and all solvents used, were as described in Chapter II. $Cp_2Ti(SCMe_3)(SSCMe_3)$ (4a) and an impure sample of $Cp_2Ti(SCHMe_2)(SSCHMe_2)$ (4b) were prepared according to the procedures described previously. The complexes $Cp_2Ti(SR)_2$[17], where R = CMe_3 (5a) and $CHMe_2$ (5b), and $C_7H_8Mo(CO)_4$[18] were prepared by literature methods.

Physical Measurements

^1H NMR spectra were measured on a Varian XL-300 spectrometer and all data are reported in ppm relative to TMS. Referencing was achieved using the δ2.09 ppm pentet of residual toluene d_7 and are considered accurate to $\pm$ 0.05 ppm. All NMR spectra were measured at ambient temperature (292K $\pm$ 2) unless otherwise indicated. Variable temperature controllers calibrated with methanol and ethylene glycol gave temperatures that are considered accurate to $\pm$ 0.5K. The coalescence temperatures were estimated visually from the recorded spectra and are considered accurate to within $\pm$ 2K of their true values. This was taken into account in the estimation of error limits for the calculated $\Delta G_c^{\dagger}$ values. Following the experiments the integrity of the samples was rechecked at ambient temperatures.

The desorption chemical ionization (NH_3) mass spectrum was obtained on a ZAB-HS spectrometer (VJ Analytical, England) at the McGill University Biomedical Mass Spectrometry Unit. The spectrum is reported as: m/z, assignment, rel. int. All other physical measurements were

determined in a manner similar to that described in Chapter II.

Preparation of Bis(η^5-cyclopentadienyl)titanium(μ-tert-butylthiolato)-(μ-tert-butyldisulfano)molybdenumtetracarbonyl, [$Cp_2Ti(\mu\text{-}SCMe_3)$-$(\mu\text{-}SSCMe_3)Mo(CO)_4$]. (18a)

$C_7H_8Mo(CO)_4$ (0.30 g, 1.00 mmol) was added to a stirred solution of $Cp_2Ti(SCMe_3)(SSCMe_3)$ (4a) (0.39 g, 1.00 mmol) in toluene (50 mL) and the reaction mixture was stripped to an oil at 10°C over a period of 50 min. Fresh toluene (50 mL) at 10°C was added to the oily dark green residue and the solvent stripped again. The process was repeated a further 3 times in order to remove liberated C_7H_8. The oil was extracted with hexanes (5 x 50 mL). The solution was filtered through Celite and the filtrate collected in a flask cooled to 0°C. The solution was concentrated to a volume of 100 mL and slowly cooled to -78°C. The supernatant was decanted, leaving a dark green powder that melted on warming slowly to room temperature under vacuum, to give a viscous green oil (0.35 g, 59%).

Anal. (%): Calcd. for $C_{22}H_{28}O_4S_3TiMo$: C, 44.30; H, 4.73; S, 16.13. Found: C, 44.18; H, 4.92; S, 16.24.

^1H NMR (toluene d_8): δ5.63 - 5.00 (m, 10H, C_5H_5), 1.56 (s, 9H, $SC(CH_3)_3$), 1.43 (s, 9H, $SSC(CH_3)_3$).

^1H NMR (CD_2Cl_2): δ5.90 - 5.50 (m, 10H, C_5H_5), 1.69 (s, 9H, $SC(CH_3)_3$), 1.58 (s, 9H, $SSC(CH_3)_3$).

Visible spectrum, $\lambda_{max}(CH_2Cl_2)$ = 573 nm (ϵ 3.99 x 10^3 L mol^{-1} cm^{-1}).

Preparation of Bis(η^5-cyclopentadienyl)titanium(bis(μ-tert-butyl-thiolato))molybdenumtetracarbonyl, $[Cp_2Ti(\mu\text{-}SCMe_3)_2Mo(CO)_4]$, (19a)

$Cp_2Ti(SCMe_3)_2$ (5a) (0.19 g, 0.53 mmol) was added to a solution of $C_7H_8Mo(CO)_4$ (0.16 g, 0.53 mmol) in toluene (20 mL) and the reaction mixture was stirred for 2 h, then stripped to 2 mL in volume. Fresh toluene (20 mL) was added to the dark purple oil and the solvent was stripped again. This process was repeated a further 17 times. The residue was dissolved in toluene (50 mL) and an IR spectrum of an aliquot of the solution showed almost complete consumption of $C_7H_8Mo(CO)_4$. Finally, the solution was reduced in volume to 5 mL and hexanes (10 mL) was added, leading to precipitation of a deep purple powder. The powder was collected by filtration and washed (hexanes, 2 x 2 mL) to give the product (0.19 g, mp >275°C). The mother-liquors were stripped to dryness and washed (hexanes, 2 x 2 mL) to give a further quantity of powder (0.06 g) for a combined yield of 84%. Recrystallization from toluene (3 mL) layered with hexanes (10 mL) gave the analytical sample as deep purple microcrystals.

Anal. (%): Calcd. for $C_{22}H_{28}O_4S_2TiMo$: C, 46.81; H, 5.00; S, 11.36. Found: C, 46.88; H, 5.05; S, 11.46.

^1H NMR (toluene d_8): δ5.25 (s, 10H, C_5H_5), 1.58 (s, 18H, CH_3).

Preparation of Bis(η^5-cyclopentadienyl)titanium(bis(μ-isopropyl-thiolato))molybdenumtetracarbonyl, $[Cp_2Ti(\mu\text{-}SCHMe_2)_2Mo(CO)_4]$ (19b)

$Cp_2Ti(SCHMe_2)_2$ (5b) (0.92 g, 2.80 mmol) was added to a solution of $C_7H_8Mo(CO)_4$ (0.83 g, 2.77 mmol) and the red-purple reaction mixture was stirred for 2 h, then stripped to 2 mL in volume. Fresh toluene (50 mL)

was added to the dark purple oil and the solvent was stripped again. This process was repeated a further 8 times. The residue was dissolved in toluene (50 mL) and an IR spectrum of an aliquot of this solution did not show the characteristic ν_{C-O} bands due to $C_7H_8Mo(CO)_4$. Finally, the volume of the solution was reduced to 10 mL, leading to precipitation of a deep purple powder. This was collected by filtration and washed with hexanes (3 x 5 mL) to give the product as a deep purple powder (1.00 g, 67%, mp 193-195°C). Addition of the hexanes washings to the mother-liquors with cooling to -16°C, gave a further quantity of 19b (0.07g, 5%).

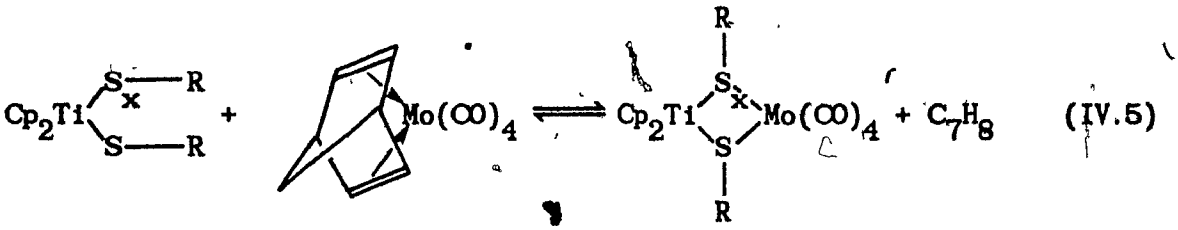
Anal. (%): Calcd. for $C_{20}H_{24}O_4S_2TiMo$: C, 44.79; H, 4.51; S, 11.95. Found: C, 44.82; H, 4.47; S, 11.80.

^1H NMR (toluene d_8): δ5.04 (s, 10H, C_5H_5), 2.57 (septet, 2H, J = 6.5 Hz, CH), 1.58 - 1.50 (broad d, 12H, J = 6.5 Hz, CH_3).

MS: 510 ($M^{+\bullet}$-CO$^\bullet$, 4.5), 452 ($M^{+\bullet}$-CO$^\bullet$-$SC_3H_7^\bullet$ +$NH_3^\bullet$, 1.4), 435 ($M^{+\bullet}$-CO$^\bullet$-$SC_3H_7^\bullet$, 8.2), 411 ($M^{+\bullet}$-$C_3O^\bullet$-$SC_3H_7^\bullet$, 20), 383 ($M^{+\bullet}$-$C_4O_2^\bullet$ -$SC_3H_7^\bullet$, 2.6).

Results

The reactions between $Cp_2Ti(SR)(SSR)$, where R = CMe_3 (4a) and $CHMe_2$ (4b), or $Cp_2Ti(SR)_2$, where R = CMe_3 (5a) and $CHMe_2$ (5b), with $C_7H_8Mo(CO)_4$, were monitored by IR spectroscopy (toluene solution) by observing the decrease in intensity of the sharp CO band at 2038 cm^{-1} due to $C_7H_8Mo(CO)_4$. Solvent-stripping, solvent-addition cycles were employed to remove free norbornadiene produced in the reactions, which appeared to be in equilibrium with the products (Eq. IV.5).



(IV.5)

x = 2, 4a,b

x = 1, 5a,b

x = 2, 18a,b

x = 1, 19a,b

The crude yields of 18a and 19a,b were virtually quantitative, as determined by ^1H NMR analysis of residues of the evaporated reaction mixtures, prior to recrystallization. Complex 18a was isolated at -78°C as a dark green powder, that was very soluble in all common solvents and melted under vacuum at approximately -20°C. These properties may be due in part to traces of $(Me_3C)_2S_3$ (3a), which were invariably present due to the method of preparation of 4a. In contrast to the preparation of 18a, the dimers 19a,b precipitated easily from toluene or toluene/hexanes solutions and recrystallization gave 19a,b as fairly air-stable microcrystals.

The formulations of $[Cp_2Ti(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)Mo(CO)_4]$ (18a) and $[Cp_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$, where R = CMe_3 (19a) and $CHMe_2$ (19b), were based upon microanalytical and ^1H NMR and IR spectroscopic data (Tables IV.1 and 2). The υ_{C-O} stretching vibrations corresponded to that described for cis-$Mo(CO)_4L_2$ (C_{2v}; IR active modes = $2A_1$, B_1 and B_2)[19]. In addition, the visible spectrum of 18a (λ_{max} = 573 nm) was similar to that of 4a (λ_{max} = 570 nm).

A mixture of $[Cp_2Ti(\mu\text{-}SCHMe_2)(\mu\text{-}SSCHMe_2)Mo(CO)_4]$ (18b) (76% of the integrated intensity in the Cp region of a NMR spectrum), and 19b (24%) and other minor non-Cp containing species, was obtained via reaction of an impure sample of 4b with $C_7H_8Mo(CO)_4$, by a method similar to that described for 18a and 19a,b. The solubility and chromatographic properties of 18b and 19b were very similar, making separation difficult. Complex 18b was identified by variable temperature ^1H NMR spectroscopy, and the Cp region exhibited similar peak changes to that observed for 18a (Table IV.1).

Both 18a and 18b converted to 19a and 19b, respectively, under thermal or chromatographic conditions. Thus, in order to slow down sulfur loss the preparations of 18a,b were performed at 10°C.

The reactions of 4a,b with $C_7H_8W(CO)_4$ required much longer reaction times and did not give products indentifiable as analogues of 18a,b. In addition, reactions of 4a with $W(CO)_5THF$[20], $Mo(CO)_5THF$[20], $(COD)PtMe_2$[21], $(PhCN)_2PtCl_2$[22], $HgCl_2$[23], $(Ph_3P)_2Ni(CO)_2$[24], $CpCo(CO)_2$[24], $Cu(CH_3CN)_4PF_6$[25] and $[(COD)Ir(THF)_2]BF_4$[26], also gave intractable products.

TABLE IV.1: ^{1}H NMR Data for $[Cp_2Ti(\mu\text{-}SR)(\mu\text{-}S_xR)Mo(CO)_4]$ and $Cp_2Ti(SR)(S_xR)$, where x = 1 and 2[a]

Temperature	Assignment (δ ppm)							
	204K					250K		
Complex	C_5H_5	S-CH	SS-CH	$S\text{-}CH_3$	$SS\text{-}CH_3$	C_5H_5	$S\text{-}CH_3$	$SS\text{-}CH_3$
18a[b]						5.56(s)cis	1.55(s)[c]	1.42(s)[c]
						5.38(s)trans		
						5.09(s)trans		
						4.95(s)cis		
19a						5.19(s)	1.56(s)	
18b[b]	5.21(s)cis[d]	3.19(s)trans[e]	2.69(s)trans[e]	1.48(s)trans[e]				
	5.13(s)trans			1.38(s)trans[e]				
	4.83(s)trans			1.33(s)trans[e]				
				1.27(s)trans[e]				
19b	4.90(s)trans	2.40(br)trans		1.82(br)trans				
	4.87(s)cis	2.27(br)cis		1.79(br)cis				
	4.82(s)cis			1.25(br)cis				
				1.10(br)trans				
4a[b]						5.84	1.65	1.42
5a						5.82	1.63	
4b[b]	5.70	3.67[i]	3.17[j]	1.50[k]	1.39[k]			
5b	5.64	3.57[i]		1.49[i]				

TABLE IV.1: (cont'd)

Temperature	Assignment (δ ppm)									
	292K					328K				
Complex	C_5H_5	S-CH	SS-CH	S-CH_3	SS-CH_3	C_5H_5	S-CH	SS-CH	S-CH_3	SS-CH_3
18a[b]	5.31(br)			1.56(s)	1.43(s)	5.31(br)			1.56(s)	1.43(s)
19a	5.25(s)			1.58(s)		5.30(s)			1.60(s)	
18b[b]	5.14(br)	3.18(s)[f]	2.55(s)[g]	1.55(br)		5.18(br)	3.20(s)[f]	2.63(s)[g]	1.55(br)	
19b	5.04(s)	2.57(s)[g]		1.53(br)[h]		5.01(s)	2.62(s)[g]		1.54(s)[g]	
4a[b]	5.86			1.61	1.39	5.88			1.57	1.36
5a	5.85			1.60		5.87			1.57	
4b[b]	5.77	3.70[f]	3.04[l]	1.40[f]	1.31[l]	5.79	3.71[f]	3.01[l]	1.37[f]	1.30[l]
5b	5.71	3.59[f]		1.39[f]		5.74	3.58[f]		1.36[f]	

TABLE IV.1: (cont'd)

[a] s = sharp, br = broad. All mononuclear species 4a,b and 5a,b exhibited sharp resonances unless noted otherwise. The solvent was toluene d_8. [b] At 328K, S loss was negligible on return to room temperature if the sample was run quickly. An impure sample was used for 4b.

[c] cis isomer tert-butyl peaks were not observed.

[d] Other cis peak was obscured by impurities.

[e] J = 6.6 Hz.

[f] J = 6.7 Hz.

[g] J = 6.5 Hz.

[h] broad doublet, J = 6.5 Hz.

[i] J = 6.4 Hz.

[j] J = 6.3 Hz.

[k] Coupling constants could not be measured due to peak broadening and to overlapping with impurity signals.

[l] J = 6.8 Hz.

TABLE IV.2: ν_{C-O} Data for $[Cp_2Ti(\mu\text{-}SR)(\mu\text{-}S_xR)Mo(CO)_4]$, where x = 1 and 2, and Related Compounds[a]

Complex	$CHCl_3$	hexanes	toluene
18a	2015, 1904(br)	2016, 1943, 1936, 1916	2011, 1923(sh), 1906
19a	2011, 1910(br)	2013, 1932(sh), 1914	2006, 1905(br)
19b	2008, 1902(br)	2016, 1928, 1918, 1911	2006, 1925, 1902
x = 1, R = Me[b]	2071, 2016, 1918, 1903		
x = 1, R = Ph[b]	2018, 1930, 1912, 1899		
$C_7H_8Mo(CO)_4$	2040, 1951, 1889	2045, 1958, 1915	2038, 1946, 1893

[a] All peaks are strong, br = broad, sh = shoulder. Frequency in cm^{-1}.
[b] Ref. 11.

Variable Temperature ^1H NMR Spectra

The NMR spectra of 18a and 18b were closely examined from 204K to 328K in toluene d_8. At higher temperatures conversion to 19a and 19b,

respectively, occurred. Pure samples of 19a and 19b were studied from 182K to 357K, also in toluene d_8. Table IV.1 lists ^{1}H NMR spectral data at chosen temperatures for all complexes studied. Only slight shifting of resonances with temperature was observed.

The NMR spectrum of 18a at 328K exhibited a broad singlet ($\upsilon_{1/2}$ = 9.4 Hz) in the Cp region (Figure IV.1) and a pair of sharp singlets of equal intensity in the tert-butyl region. The latter did not change upon cooling from 328K to 204K. However, the Cp peak broadened and collapsed upon cooling and at 292K exhibited a broad signal with $\upsilon_{1/2}$ = 115 Hz. At temperatures below 307K a pair of Cp singlets of equal intensity appeared and sharpened upon further cooling. Two additional weak signals of equal intensity were observed below 250K. The two pairs of resonances appeared in the ratio 24:1 at 250K and 19:1 at 227K, based upon the respective integrated intensities. Their line shapes changed at approximately the same temperature, indicating similar coalescence temperatures.

The variable temperature spectra of 18b were complicated by signals due to 19b. The signals due to the latter complex are described in detail later. At high temperatures (328K) 18b exhibited a broad singlet in the Cp region ($\upsilon_{1/2}$ = 14.4 Hz) (Appendix 1). In addition, the methine region showed resolved multiplets at δ3.20 and 2.63 ppm due to bridging thiolato and disulfano ligands, respectively. The methyl region exhibited a broad multiplet ($\upsilon_{1/2}$ = 11 Hz) at δ1.55 ppm (Table IV.I). The Cp peak broadened and collapsed upon cooling and at 292K exhibited a very broad signal with $\upsilon_{1/2}$ = 115 Hz. At temperatures below

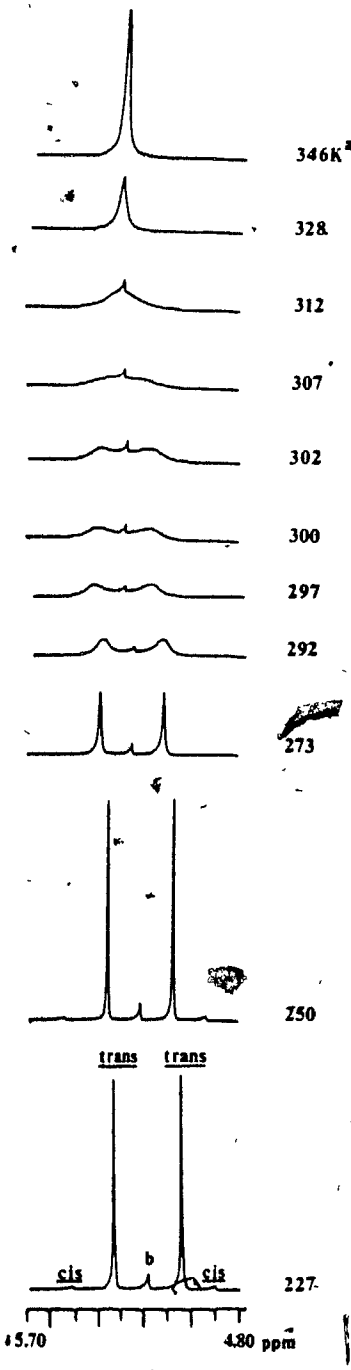


Figure IV.1: Cp Region of the ^1H NMR Spectra of $[Cp_2Ti(\mu\text{-}SCMe_3)(\mu\text{-}SSCMe_3)Mo(CO)_4]$ (18a). from 227K to 346K in Toluene d_8.

[a] Decomposition was detected by NMR on cooling of the solution to room temperature.

[b] $[Cp_2Ti(\mu\text{-}SCMe_3)_2Mo(CO)_4]$ (19a) was present as an impurity.

273K a pair of Cp singlets of equal intensity appeared and sharpened upon further cooling. The linewidths of each singlet were different throughout the temperature range examined, although their integrated intensities were always equal. For example, at 250K the linewidths, $\upsilon_{1/2}$, were 2 Hz and 10 Hz for the low and high field signals, respectively. At 204K an additional peak was observed, which was slightly downfield from the others. The CH and CH_3 regions of 18b remained complex at all temperatures examined (Appendix 2) and exhibited unresolved peaks below 204K.

Complex 19a exhibited single sharp resonances due to Cp and tert-butyl groups over all of the temperature range studied. For 19b, at high temperatures (357K) the Cp region exhibited a sharp singlet, and the methine and methyl regions showed a septet and a doublet, respectively. Cooling the sample caused broadening and collapse of all the signals. Two new methyl peaks of equal intensity began to appear below 264K (Figure IV.2). As the sample was cooled further, an additional peak shifted out from under the higher field peak and the three peaks began to sharpen. At the lowest temperatures an additional peak could be detected as a shoulder of the lower field peak. The relative ratio of the inner to outer methyl peaks was approximately 1:1.5 by integration at 204K. The methine region septet broadened and collapsed with cooling and then split into two unresolved peaks of unequal intensity below 233K (Figure IV.3). The sharp Cp singlet broadened, collapsed and a total of three new peaks in the approximate ratio 5:1:1 appeared at 204K (Figure IV.4).

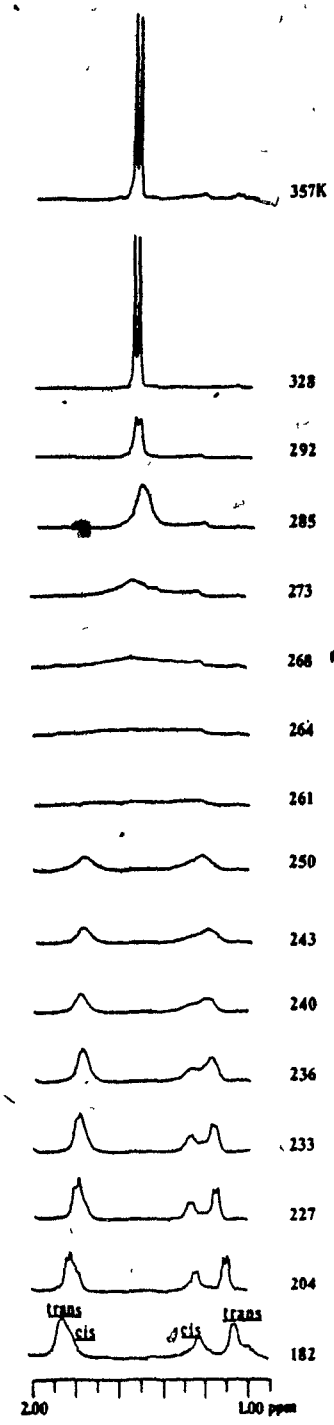


Figure IV.2: CH_3 Region of the ^1H NMR Spectra of $Cp_2Ti(\mu\text{-}SCHMe_2)_2Mo(CO)_4]$ (19b), from 182K to 357K in Toluene d_8.

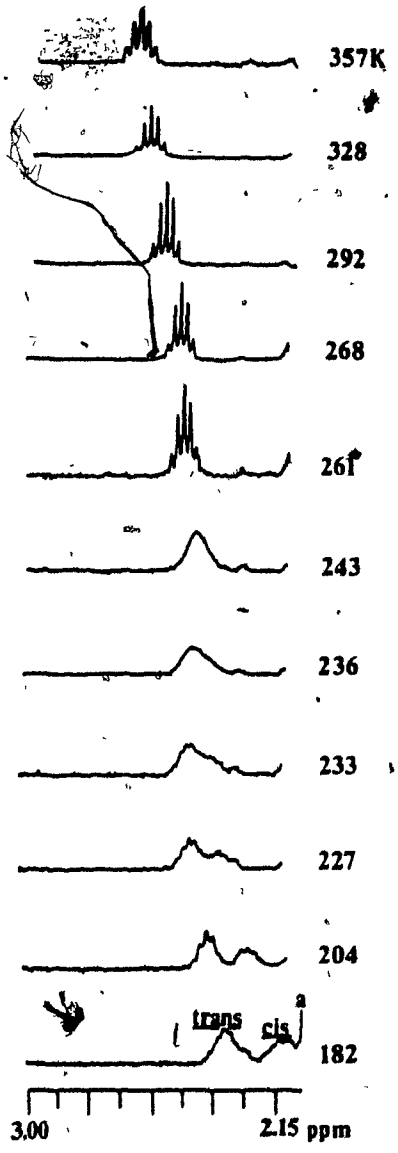


Figure IV.3: CH Region of the ^1H NMR Spectra of $[Cp_2Ti(\mu\text{-}SCHMe_2)_2\text{-}Mo(CO)_4]$ (19b), from 182K to 357K in Toluene d_8.

[a] Solvent peak, residual toluene d_7.

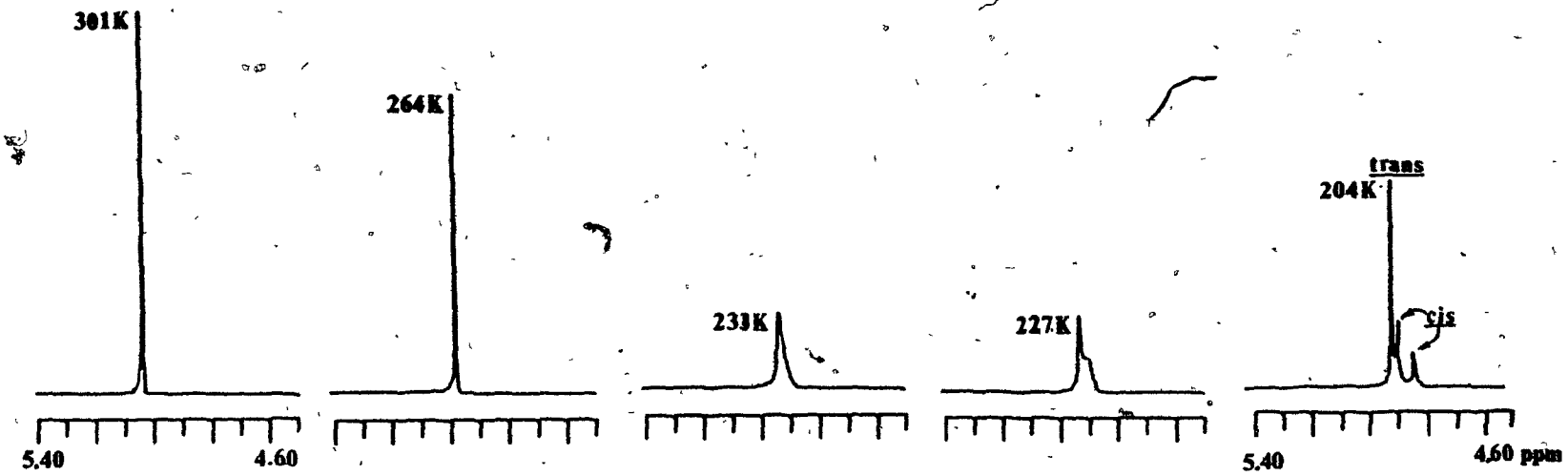


Figure IV.4: Cp Region of the ^1H NMR Spectra of $[Cp_2Ti(\mu\text{-}SCHMe_2)_2Mo(CO)_4]_n$ (19b), from 204K to 301K in Toluene d_8.

Coalescence temperatures (T_c), chemical shift differences in Hertz ($\Delta\nu$) at the low temperature limits, and calculated free energies of activation at coalescence temperatures ($\Delta G_c^{\ddagger}$) for 18a,b and 19b are given in Table IV.3.

TABLE IV.3: T_c, $\Delta\upsilon$ and $\Delta G_c^{\ddagger}$ values for the Averaging Process in $[Cp_2Ti(\mu\text{-}SR)(\mu\text{-}S_xR)Mo(CO)_4]$, where x = 1 and 2[a]

	T_c (K)			$\Delta\upsilon$ (Hz)			$\Delta G_c^{\ddagger}$ (kJ mol^{-1})		
Coalescing Group / Complex	C_5H_5[b]	SCH	$SCH(\underline{CH}_3)_2$	C_5H_5[b]	SCH	$SCH(\underline{CH}_3)_2$	C_5H_5	SCH	$SCH(\underline{CH}_3)_2$
<u>18a</u>[c]	307			86.4[d]			62		
<u>18a</u>[e]	304			63.4[f]			62		
<u>18b</u>[c]	298			89.8[g]			60		
<u>19b</u>[c]		233[h]	264[i]		55.8[j]	239.4[j]		47	51

[a] The T_c and $\Delta\upsilon$ values could not be obtained for all ligand types, due to spectral complexity and thus are left blank where applicable. <u>Tert</u>-butyl signals did not undergo broadening and collapse at any of the temperatures studied and are therefore not discussed.

[b] Based upon coalescence of <u>trans</u> isomer peaks. [c] Solvent = toluene d_8.

[d] In the low temperature limiting spectrum (L.T.L.S.) at 250K. [e] Solvent = CD_2Cl_2.

[f] In the L.T.L.S. at 226K. [g] In the L.T.L.S. at 204K.

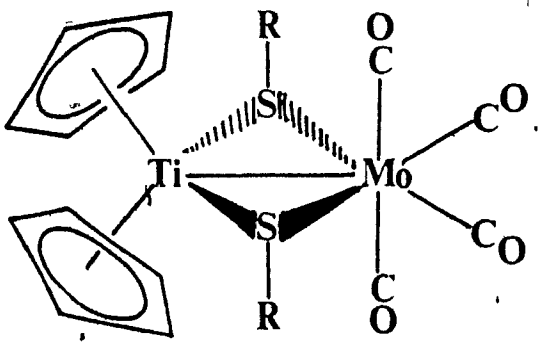
[h] Based upon coalescence of <u>trans</u> and <u>cis</u> isomer peaks.

[i] Based upon coalescence of the two peaks above 243K, each peak representing averaged signals.

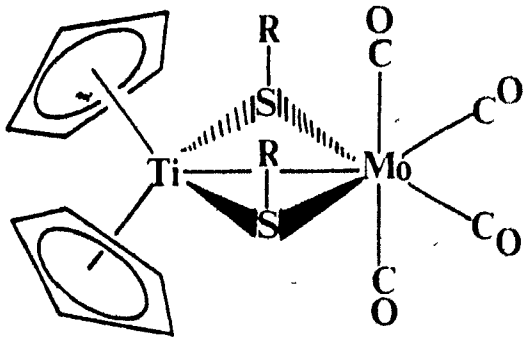
[j] In the L.T.L.S. at 182K.

Discussion

The analytical and spectroscopic properties of 18a,b and 19a,b are consistent with their formulation as $[Cp_2Ti(\mu\text{-}SR)(\mu\text{-}SSR)Mo(CO)_4]$ and $[Cp_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$, respectively. The latter complexes are analogues of others reported for R = H[10], Me and Ph[11], which contain planar four membered rings and a Ti-Mo single bond, as shown by X-ray molecular structure analysis[15]. Based upon ^1H NMR spectroscopy, other workers



trans-19



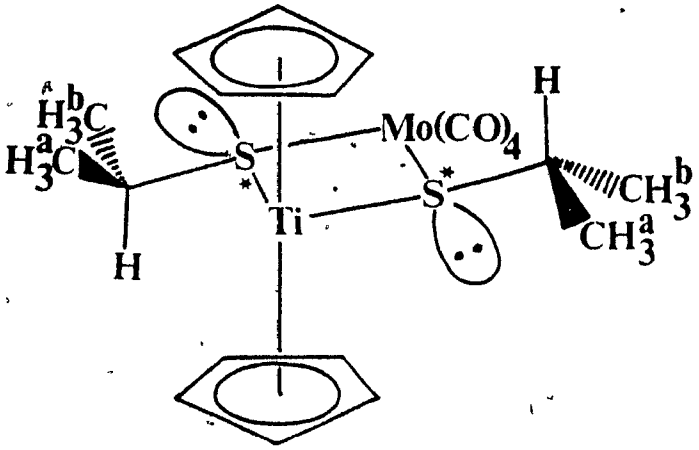
cis-19

have shown that 19 exhibits geometrical isomerism in solution[10,11]. Trans and cis isomers were present and gave one Cp resonance and two Cp resonances, respectively. The cis isomer found in the solid[15], predominated in solution[11]. For 19, where R = Me, coalescence of the Cp resonances occurred above room temperature[11]. The interconversion of trans and cis isomers in the analogue of 19, $[Cp_2Ti(\mu\text{-}SH)_2W(CO)_4]$, was studied by DNMR and a complete band shape analysis of the spectra obtained at various temperatures, gave activation parameters for the isomerization process, which was 76 kJ mol^{-1} at the coalescence temperature of 357K[10].

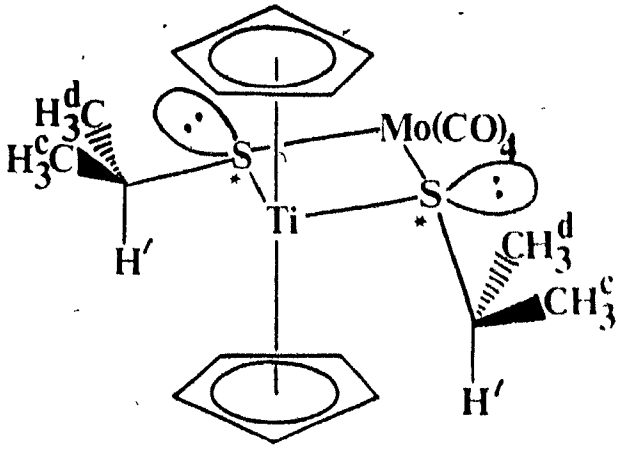
In light of the above, 19a,b would be expected to have a planar 4-membered ring core structure. The bridged bis(thiolato) complexes 19a,b contain alkyl groups which are sterically more demanding than those previously observed in this type of complex. Even when R = Me significant steric interaction between the thiolate ligands and Cp groups occurs[15]. The single sharp Cp resonance observed in solution at all temperatures for 19a is consistent with the presence of only the less sterically demanding trans isomer. Molecular models suggest that the trans isomer would be most favoured. It seems unlikely that the Cp ligand environments of 19a are exchanging rapidly at the lowest temperatures, since 18a,b and 19b were found to be in the slow-exchange region below 228K.

Complex 19b exhibited 3 sharp Cp peaks at 204K, consistent with the presence of a mixture of trans and cis isomers in the ratio 5:2. Each sulfur atom in 19b constitutes a chiral centre as a result of the tetrahedral arrangement of its adjacent groups and lone pair, as shown below. An isopropyl group in a chiral molecule has diastereotopic methyl groups and can therefore give 2 methyl doublets, but only 1 methine septet in a NMR spectrum[27]. The presence of two chiral centres in 19b results in 4 methyl peaks and two methine peaks in ratios which are consistent with the higher abundance of the trans isomer (Figures IV.2 and 3).

Interestingly, even in the slow-exchange region all of the isopropyl signals of 19b are still broad. The loss of coupling in the methyl and methine regions was not as pronounced for the isopropyl groups of 18b. This difference may result because the isopropyl groups



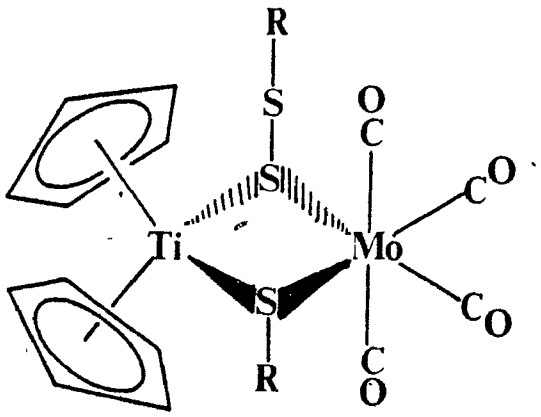
trans-19b



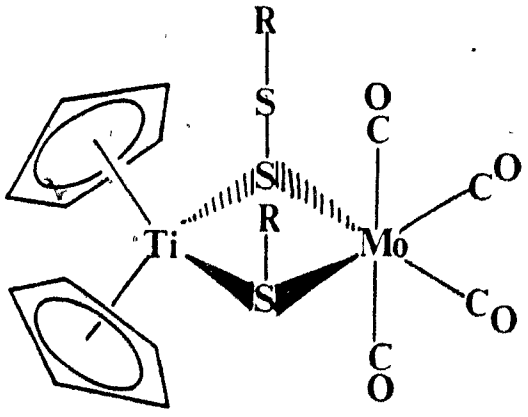
cis-19b

of 19b experience a greater restricted rotation, due perhaps to a more compact arrangement of alkyl groups around the TiL_2Mo core structure, where L = bridging ligand. Interaction of Cp and isopropyl groups can be envisaged.

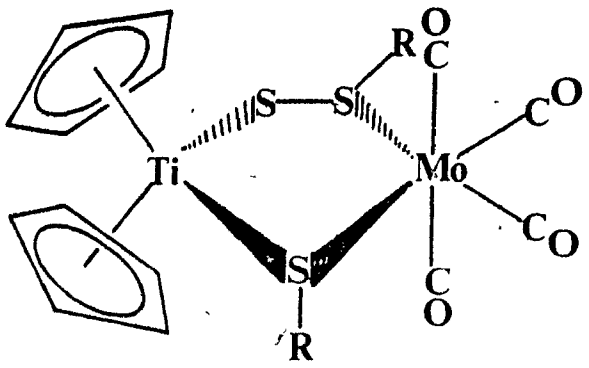
In 18a and 18b the organodisulfano ligand can bridge to give either a 4-membered ring with a μ-η^1-SSR linkage, or a 5-membered ring with a μ-η^1-SSR linkage, as shown below. Assignment of NMR signals to the



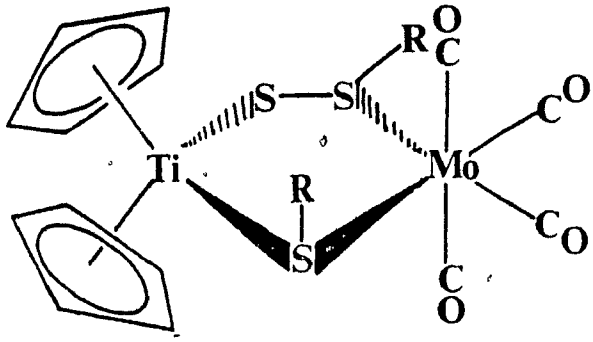
4-membered trans-18a,b



4-membered cis-18a,b



5-membered trans-18a,b

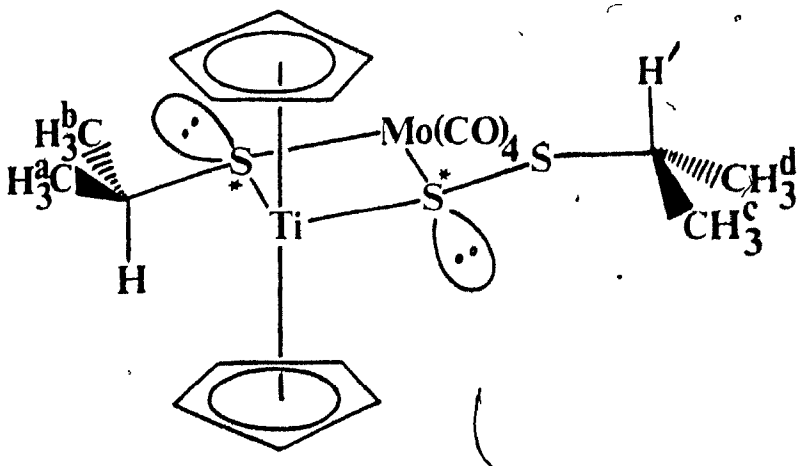


5-membered cis-18a,b

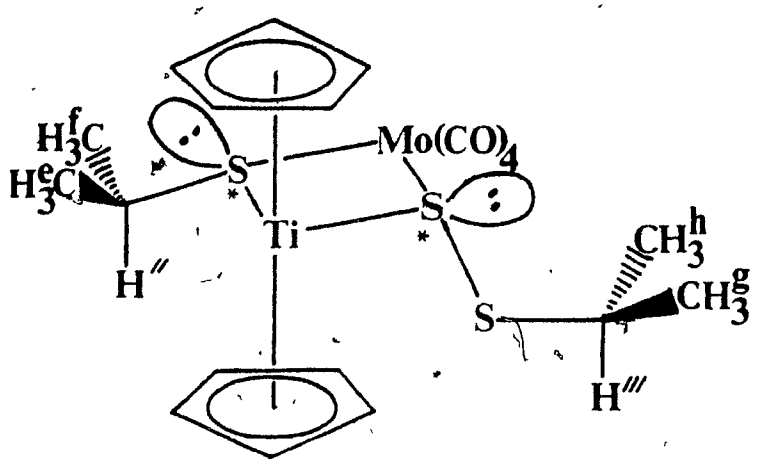
trans and cis isomers of 18a,b does not require prior knowledge of ring size, since similar patterns should be expected for both 4- and 5-membered rings.

Complex 18a exhibits an intense pair and a weak pair of Cp signals at 250K (the slow-exchange region). The assignment of the intense signals to the molecule containing a trans arrangement of tert-butyl groups, is based upon two considerations. First, molecular models indicate that the tert-butyl groups, due to their large steric bulk, might be expected to favour the trans isomer. Second, the chemical shift seperation of the intense pair of Cp peaks is less than that for the weak Cp peaks. A greater chemical shift difference might reasonably be expected between the two Cp ligands of the cis isomer since one Cp ligand is adjacent to two tert-butyl groups, whereas the other Cp ligand is in a relatively unencumbered environment. This effect has previously been observed in bis(η^5-cyclopentadienyl)titanium systems[28]. The tert-butyl signals for 18a are relatively uninformative throughout the temperature range studied.

By analogy to 18a, the pair of Cp signals for the trans isomer of 18b might be expected to have a smaller chemical shift seperation than those of the cis isomer. The Cp region of a NMR spectrum of 18b at 204K (Appendix 1) exhibited a peak slightly downfield from the others. This peak is tentatively assigned to one of the two expected Cp peaks of the cis isomer, the other peak assumed as being obscured by peaks due to 19b and the trans isomer of 18b. This assumption permits calculation of the ratio of the trans to cis isomers of 18b, which was approximately 3:1 at 204K. Thus, the trans isomer tended to be the most abundant geometrical isomer for 18a,b and 19a,b. Each sulfur bridge in both isomers of 18b constitutes a chiral centre, as shown below. Theoretically, the trans isomer of 18b should give 4 pairs of methyl doublets and two methine septets in the NMR spectrum, due to the presence of diastereotopic isopropyl groups on the thiolato and disulfano ligands. Similarly, a further different 4 pairs of methyl doublets and two methine septets would be expected for the cis isomer of 18b. However, due in part to peaks caused by impurities, 18b showed only a poorly resolved set of



trans-18b

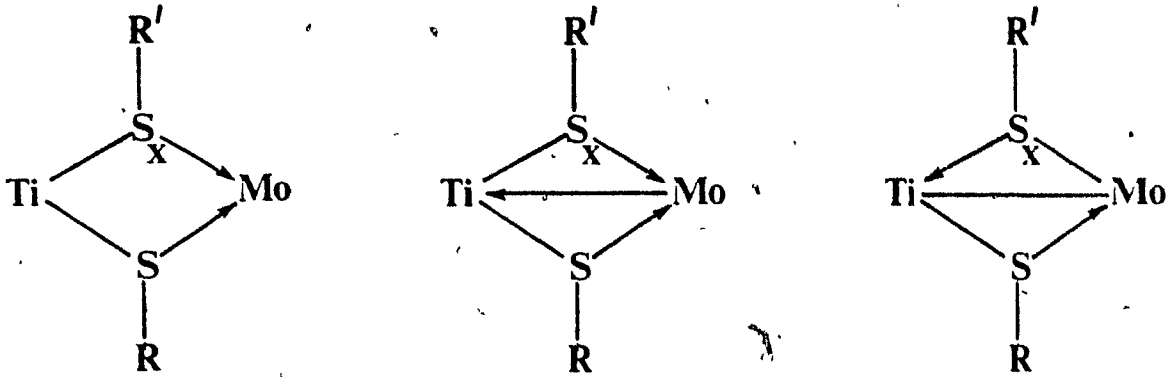


cis-18b

four pairs of methyl doublets, plus other minor peaks, at 227K (Appendix 2). Comparison of integrated intensities of CH_3 and Cp regions indicates that the major CH_3 signals might correspond to the 4 methyl doublets expected for the trans isomer of 18b.

The Cp signals of the trans isomer of 18b show different linewidths over most of the temperature range studied. The upfield Cp signal is the broader. Restricted rotation of this Cp ligand can be envisaged, due to interaction with an isopropylthiolato group on the same side of the dimer ring. The alkyl group of the isopropyldisulfano group of trans-18b might not be expected to interact as strongly with the other Cp ligand, since the alkyl group would be further displaced from the TiL_2Mo core structure.

The bonding in the complexes can be formulated in a number of ways. On dimer formation an upfield shift in the NMR spectrum of approximately 0.7 ppm was observed for the Cp resonances and little change was found for the chemical shift of the R groups (Table IV.1). A similar shift



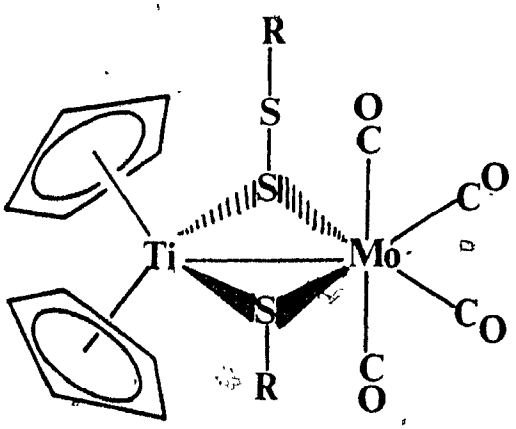
I II III

R' = R or SR

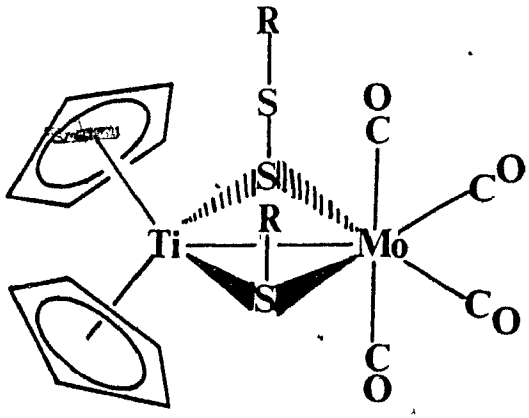
was observed on formation of $[Cp_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$ (19) from $Cp_2Ti(SR)_2$, where R = H[10], Me, Ph[11]. Therefore, structural type I can be excluded as a bonding possibility, since the depicted sulfur to molybdenum σ-donation would be expected to decrease the electron density on associated groups, thereby causing a downfield shift for Cp and R proton resonances. The shifts appear to indicate that electron donation to Ti is occurring and thus participation of structural types II and III in the actual bonding seems feasible. Electron donation from Mo $\longrightarrow$ Ti would help titanium attain an 18 electron configuration.

The Ti-Mo internuclear distance in 18a,b would be expected to be greater in a 5-membered ring than in a 4-membered ring. A planar 5-membered ring is unlikely due to its facile distortion[29] and a puckered ring should cause a decrease in molybdenum to titanium orbital overlap compared to a planar 4-membered ring[30]. These two effects would reduce Mo to Ti electron donation and cause the Cp resonances in the NMR spectrum of 18a,b to be at lower field compared to those of 19a,b. However, the Cp resonances of 18a,b and 19a,b experience similar

chemical shift environments. It therefore seems reasonable to assume that 18a and 18b exist as mixtures of trans and cis 4-membered rings, with iso-μ-η^1-SSR and μ-SR bridges between metal-metal bonded centres, as shown below. Molecular models of $[Cp_2Ti(\mu\text{-SR})(\text{iso-}\mu\text{-}\eta^1\text{-SSR})\text{-}Mo(CO)_4]$ (18a,b) suggest less steric interaction between the R group of an organodisulfano linkage and the $Mo(CO)_4$ moiety, in a 4-membered ring than in a 5-membered ring.



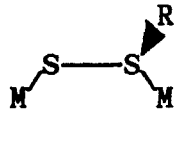
trans-18a,b



cis-18a,b

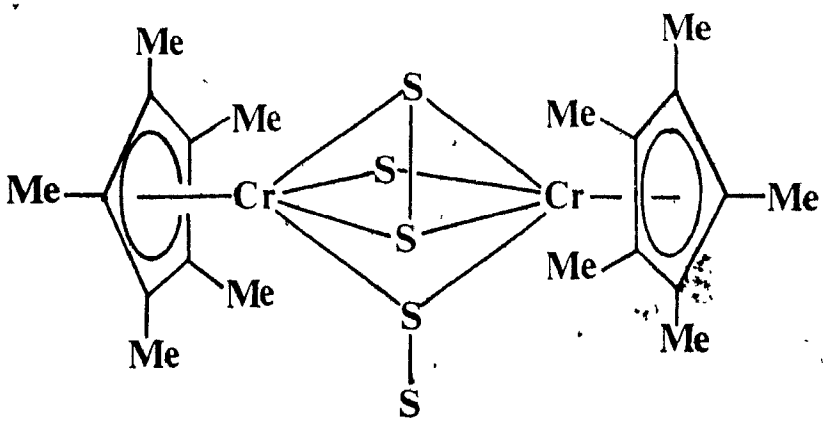
Bridging organodisulfano ligands, μ-SSR, are a rarity. Only one example has been reported and is believed to exist in an iso-μ-η^1-SSR coordination mode, bridging between two molybdenum centres[16]. An

iso-μ-η^1

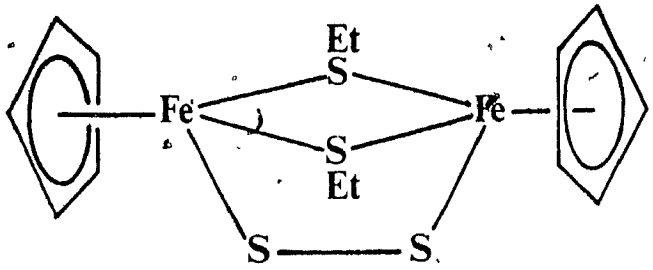


syn-μ-η^1

alternate bridging system is the syn-μ-η^1-SSR coordination mode. The analogous disulfur geometries, on which this nomenclature is based[31], have been observed in the complexes $Me_5Cp_2Cr(S_2)_2S$[32] and $\{CpFe(\mu\text{-}SEt)\}_2S_2$[33], as shown below. The alkylperoxidic complex

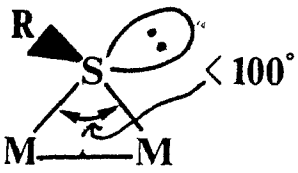


iso-μ-η^1



syn-μ-η^1

$[Cl_3CCO_2Pd\text{-}OOCMe_3]_4$, which contains an iso-$\mu$-$\eta^1$-$OOCMe_3$ ligand, has been structurally characterized[34]. Thiolato bridged complexes containing a metal-metal bond typically have a distorted tetrahedral environment around the bridging sulfur atom[15,35]. A similar arrangement can be anticipated for 18a,b and 19a,b.

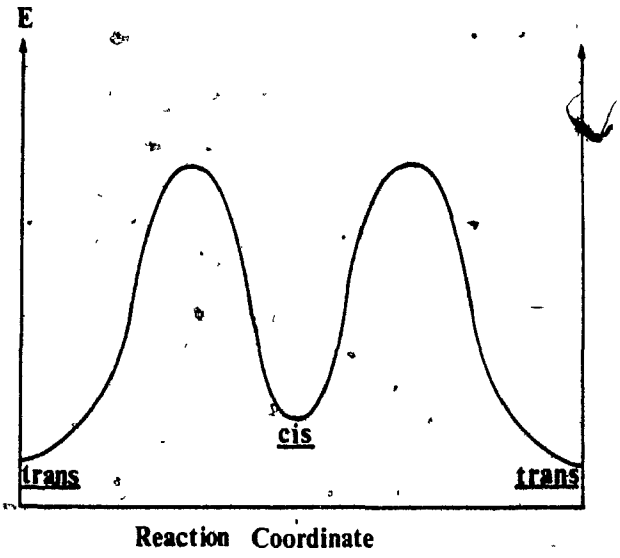


The free energy of activation at the coalescence temperature $\Delta G_c^{\ddagger}$ (in kJ mol^{-1}) for coalescence of singlets or multiplets, is often carried out using the Eyring equation, as shown below[27,36].

$$\Delta G_c^{\ddagger} = 1.914 \times 10^{-2} T_c[9.972 + \log(T_c/\Delta\upsilon)] \qquad \text{(IV.6)}$$

T_c is the coalescence temperature in K and $\Delta\upsilon$ is the chemical shift difference in Hertz for a pair of coalescing signals in the low temperature limiting spectrum. Calculation of $\Delta G_c^{\ddagger}$ for coalescence of the Cp signals in 18a,b and the CH_3 and CH signals in 19b is based upon two assumptions. First, since both trans and cis isomers are observed in solution by NMR spectroscopy, it is reasonable to assume that interconversion of trans isomers occurs via a cis isomer and vice versa. The application of Eq. IV.6 to cases were two equivalent transition states are separated by an energy minimum, as shown below for 18 and 19, introduces errors to $\Delta G_c^{\ddagger}$ which may amount to $\pm$ 2 kJ mol^{-1} for 18a,b and at least $\pm$ 4.2 kJ mol^{-1} for 19b. The errors inherent in Eq. IV.6 when it is applied to complex systems, is discussed by Sandström[37].

Calculation of $\Delta G_c^{\ddagger}$ for 18a,b can now be reduced to analysis of coalescence of the pair of intense trans isomer Cp singlets, and for 19b to analysis of coalescence of the pairs of CH_3 or CH signals[27,36] (Table IV.3). The values of $\Delta G_c^{\ddagger}$ are identical for 18a, at two



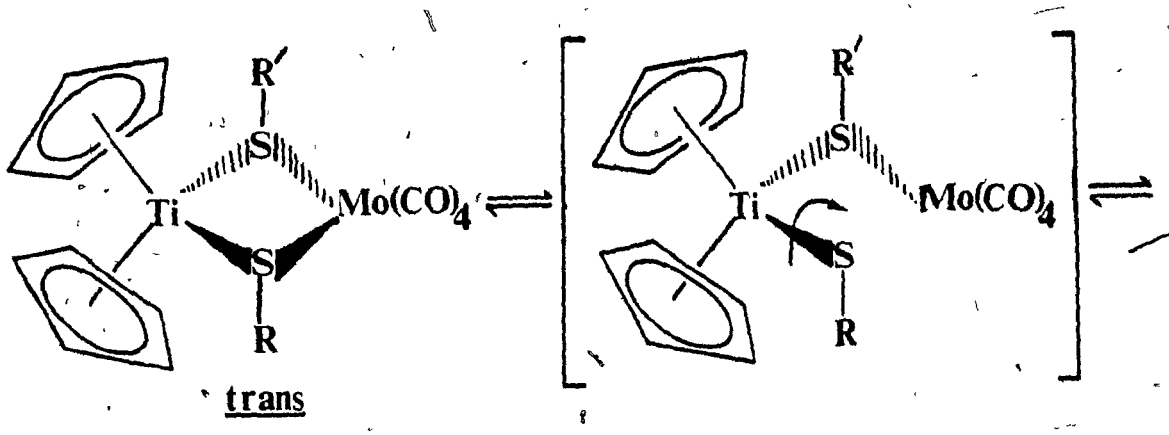
concentrations in toluene d_8 and in CD_2Cl_2, as expected for an intramolecular process which does not involve large changes in the dipole moment of the fluxional molecule[27]. The value of $\Delta G_c^{\ddagger}$ for 18b is within the range of error of that for 18a. The lower $\Delta G_c^{\ddagger}$ value for methine compared to methyl signals of 19b may arise from an artificially low $\Delta\nu$ value for the coalescence of methine signals, since the chosen low temperature limiting spectrum for the methine signals may not exhibit a constant maximum value of $\Delta\nu$. Therefore, the $\Delta G_c^{\ddagger}$ value for the methine peaks of 19b is considered less accurate than that for the methyl peaks. However, both these $\Delta G_c^{\ddagger}$ values fall within the range of error expected in these systems.

The $\Delta G_c^{\ddagger}$ value for 19b is significantly lower than the values calculated for 18a,b and may result from the comparatively more compact arrangement of thiolate groups in the former, which might cause partial distortion of the ground state geometry, thereby permitting easier

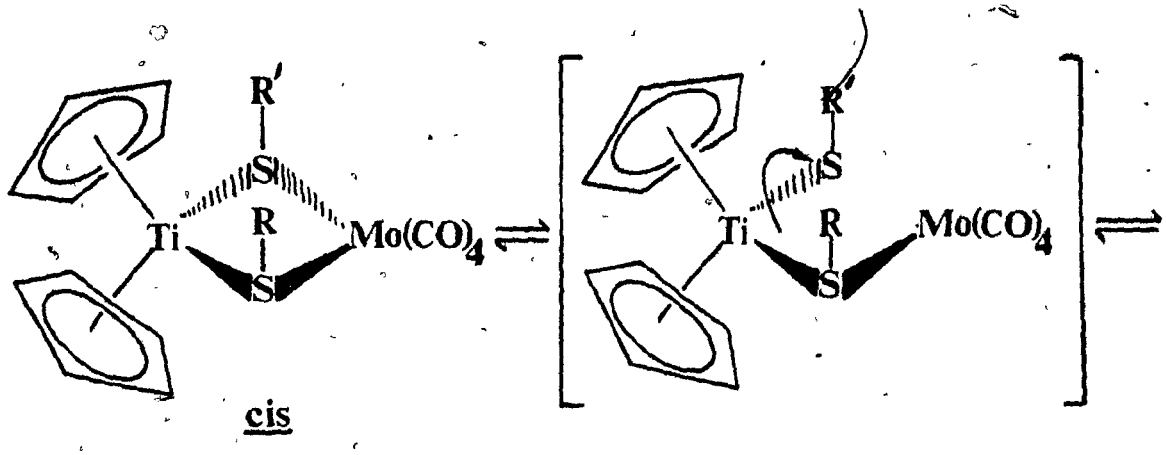
attainment of transition state structures during the isomerization process. However this reasoning is merely speculative.

The Cp signal averaging process in 18a,b and 19b must occur by inversion of configuration at the bridging sulfur atoms. This process would also exchange the methine and the diastereotopic methyl groups of 18b and 19b. The mechanism of S inversion may involve either metal-sulfur bond dissociation-rotation-recombination (Scheme IV.1), or inversion via a trigonal planar state (Scheme IV.2). Comparison with data published for similar complexes shows that the averaging process at the high temperature limit for 18a,b and 19b, most likely occurs via a trigonal planar state: $[Fe_2(CO)_5L(\mu\text{-}SCMe_3)_2]$[38], L = CO, $\Delta G_c^{\ddagger}$ = 77 kJ mol^{-1} and L = Ph_3P, $\Delta G_c^{\ddagger}$ = 66 kJ mol^{-1}; trans-$[CpRu(CO)(\mu\text{-}SCH_2Ph)]_2$[39], $\Delta G_c^{\ddagger}$ = 58.7 kJ mol^{-1}; $[Cp_2Ti(\mu\text{-}SEt)_2Cu(PPh_3)]$[12], $\Delta G_c^{\ddagger}$ = 71 kJ mol^{-1}.

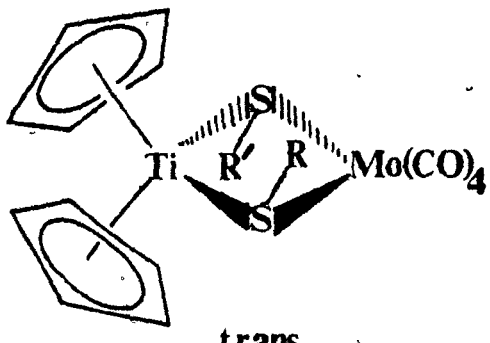
In general, the rates of sulfur inversion for metal bound thiolates are about 10^{18} times faster than inversion at sulfur in sulfoxides (which are also tricoordinate). This may be due to the presence of a metal, which might allow more facile inversion through the intermediate planar trigonal state due to stabilization by overlap of metal d-orbitals with the sulfur lone pairs[40].



trans



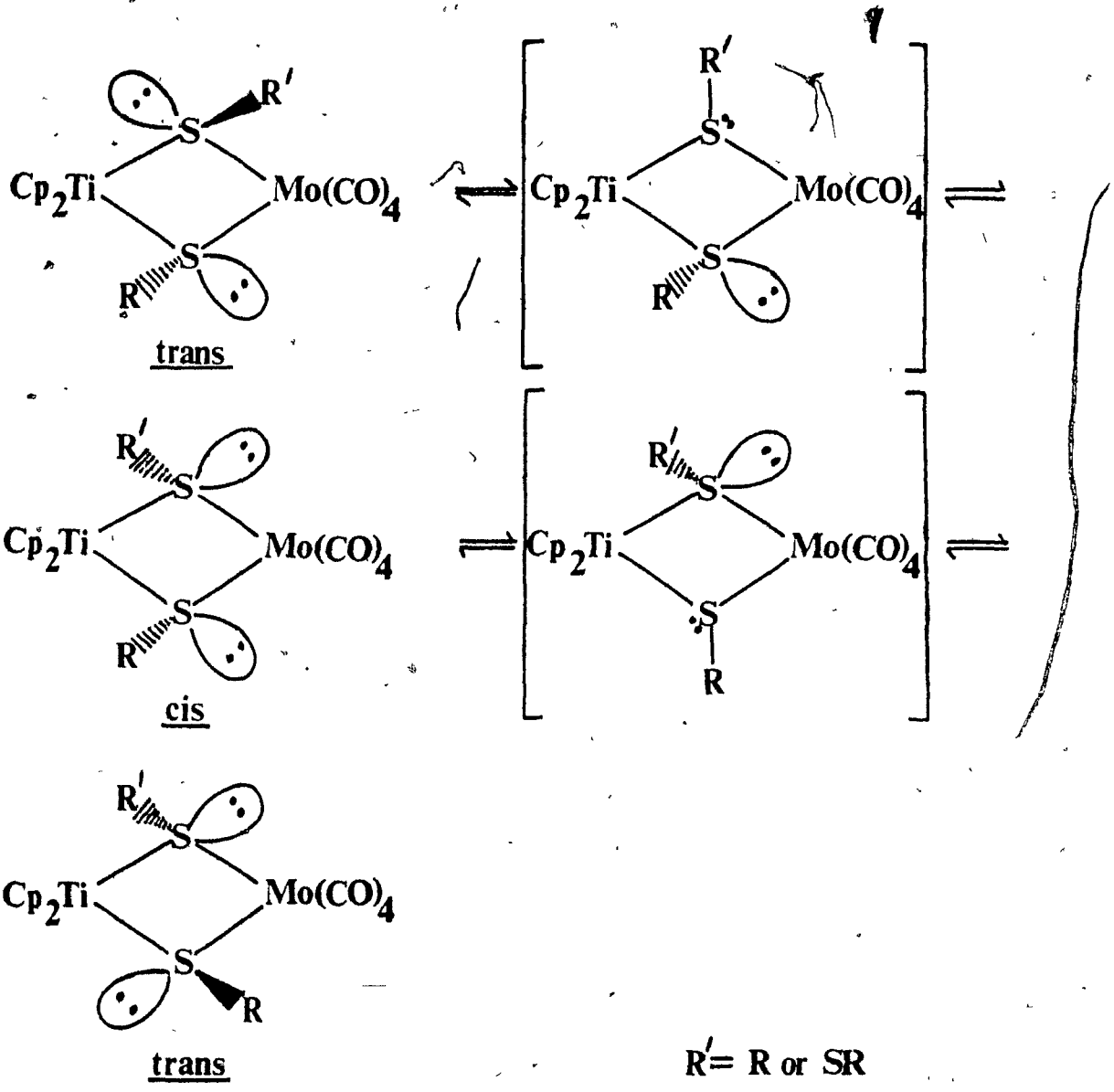
cis



trans

R′=R or SR

SCHEME IV.1



SCHEME IV.2

References

1. F.E. Massoth, Adv. Catal., 27, (1978), 265.
2. a) A.E. Hargreaves and J.R.H. Ross, J. Catal., 56, (1979), 363.
   b) F.E. Massoth and C.L. Kibby, J. Catal., 47, (1977), 300.
   c) P. Desikan and C.H. Amberg, Can. J. Chem., 42, (1964), 843.
3. M. Draganjac, E. Simhon, L.T. Chan, M. Kanatzidis, N.C. Baenziger and D. Coucouvanis, Inorg. Chem., 21, (1982), 3321.
4. W. Clegg, G. Christou, C.D. Garner and G.M. Sheldrick, Inorg. Chem., 20, (1981), 1562.
5. a) S.P. Cramer, W.O. Gillum, K.O. Hodgson, L.E. Mortenson, E.I. Stiefel, J.R. Chisnell, W.J. Brill and V.K. Shah, J. Am. Chem. Soc,, 100, (1978), 3814.
   b) D. Coucouvanis, A. Salifoglou, M.G. Kanatzidis, A. Simopoulous and A. Kostikas, J. Am. Chem. Soc., 109, (1987), 3807.
6. D. Edmundson, V. Massey, G. Palmer, L.M. Beauchman III and G.B. Elion, J. Biol. Chem., 247, (1972), 1597.
7. S.P. Cramer, H.B. Gray and K.V. Rajagopalan, J. Am. Chem. Soc., 101, (1979), 2772.
8. E.I. Stiefel, Prog. Inorg. Chem., 22, (1977), 1.
9. a) G.J. Kubas and R.R. Ryan, J. Am. Chem. Soc., 107, (1985), 6138.
   b) C.J. Casewit and M. Rakowski DuBois, J. Am. Chem. Soc., 108, (1986), 5482.
10. C.J. Ruffing and T.B. Rauchfuss, Organometallics, 4, (1985), 524.
11. P.S. Braterman, V.A. Wilson and K.K. Joshi, J. Chem. Soc. (A), (1971), 191.
12. T.A. Wark and D.W. Stephan, Inorg. Chem., 26, (1987), 363.

13. M. Sato and T. Yoshida, J. Organomet. Chem., 94, (1975), 403.

14. G. Fachinetti and C. Floriani, J. Chem. Soc., Dalton Trans., (1974), 2433.

15. G.R. Davies and B.T. Kilbourn, J. Chem. Soc. (A), (1971), 88.

16. M.E. Noble, Inorg. Chem., 25, (1986), 3311.

17. a) J.M. McCall, Ph.D. Thesis, McGill University, (1983), p 75.

b) S.A. Giddings, U.S. Pat. No. 3,030,395; Chem. Abstr., 57; (1962), 9881.

18. M.A. Bennett, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961), 2037.

19. a) G.R. Dobson, R.C. Taylor and T.D. Walsh, Inorg. Chem., 6, (1967), 1929.

b) M.Y. Darensbourg and D.J. Darensbourg, J. Chem. Educ., 47, (1970), 33.

20. a) W. Strohmeier, Angew. Chem. Int. Ed. Engl., 3, (1964), 730.

b) J. Hartgerink, M.Sc. Thesis, McGill University, (1981), p 15.

21. a) H.C. Clark and L.E. Manzer, J. Organomet. Chem., 59, (1973), 411.

b) C.R. Kristner, J.H. Hutchinson, J.R. Doyle and J.C. Storlie, Inorg. Chem., 2, (1963), 1255.

22. "The Chemistry of Platinum and Palladium", by F.R. Hartley, John Wiley, Toronto, 1973, p 462.

23. Purchased from Fisher Ltd.

24. Purchased from Strem Chemicals Inc.

25. G.J. Kubas, Inorg. Synth., 19, (1979), 90.

26. R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93, (1971), 3089.

27. "Dynamic NMR Spectroscopy", by J. Sandström, Academic Press, Toronto, 1982.

28. C. Aitken, Ph.D. Thesis, McGill University, (1986).

29. a) K. Tamagawa, R.L. Hilderbrandt and Q. Shen, J. Am. Chem. Soc., 109, (1987), 1380.

b) A. Kutoglu, Z. Anorg. Allg. Chem., 390, (1972), 195.

30. a) A.T. McPhail and G.A. Sim, J. Chem. Soc. (A), (1968), 1858.

b) L.F. Dahl, E. Rodulfo de Gil and R.D. Feltham, J. Am. Chem. Soc., 91, (1969), 1653.

31. C.M. Bolinger, T.B. Rauchfuss and A.L. Rheingold, Organometallics, 1, (1982), 1551.

32. H. Brunner, J. Wachter, E. Guggolz and M.L. Ziegler, J. Am. Chem. Soc., 104, (1982), 1765.

33. a) G.J. Kubus, T.G. Spiro and A. Terzis, J. Am. Chem. Soc., 95, (1973), 273.

b) A. Terzis and R. Rivest, Inorg. Chem., 12, (1973), 2132.

34. H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer and R. Weiss, J. Am. Chem. Soc., 102, (1980), 1047.

35. a) J.J. Bonnet, P. Kalck and R. Poilblanc, Inorg. Chem., 16, (1977), 1514.

b) J.J. Bonnet, A. Thorez, A. Maisonnat, J. Galy and R. Poilblanc, J. Am. Chem. Soc., 101, (1979), 5940.

36. G. Binsch and H. Kessler, Angew. Chem. Int. Ed. Engl., 19, (1980), 411.

37. Ref. 27, pp 96-97.

38. G. Natile, L. Maresca and G. Bor, Inorg. Chim. Acta, 23, (1977),

37.

39. S.D. Killops and S.A.R. Knox, J. Chem. Soc., Dalton Trans., (1978), 1260.

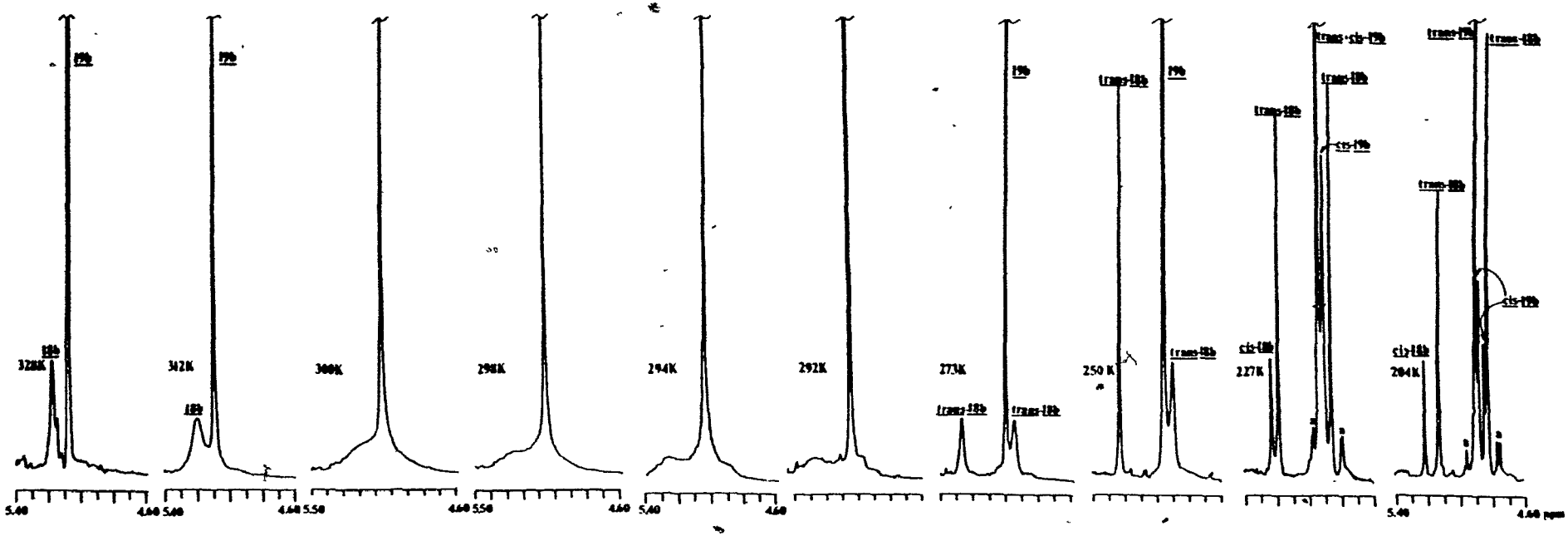
40. P.C. Turley and P. Haake, J. Am. Chem. Soc., 89, (1967), 4617.

CONCLUSIONS

Contributions to Original Knowledge

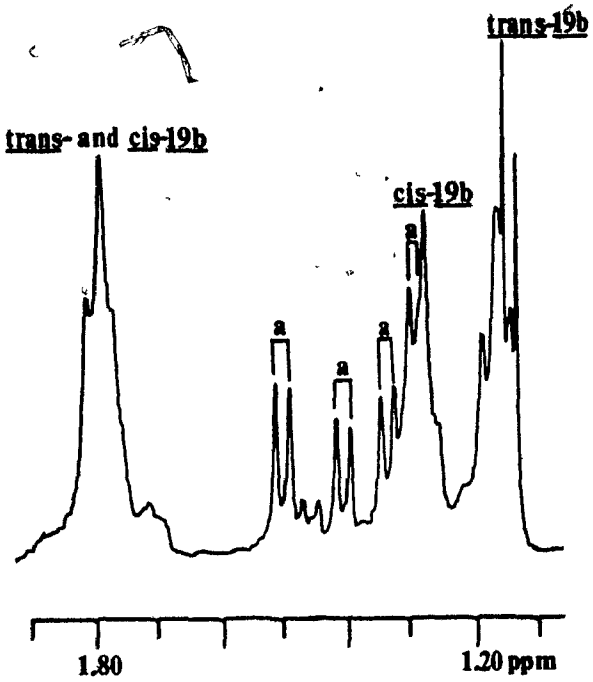
1. The new complexes $Cp_2Ti(X)(SSR)$ contain rare disulfano ligands, RSS^-. They were prepared via oxidative-addition of the S-X bond in RSSX to $Cp_2Ti(CO)_2$, where X = RS^-, phthalimido and Cl^-.
2. The reactions of $Cp_2Ti(SR)(SSR)$, where R = CMe_3, $CHMe_2$, CH_2Ph, p-C_6H_4Me and CPh_3 include:
   a) spontaneous loss of sulfur to give $Cp_2Ti(SR)_2$ and, usually, polymeric and/or paramagnetic species;
   b) desulfurization by the nucleophile Ph_3P, to give $Cp_2Ti(SR)_2$ and Ph_3PS;
   c) cleavage by the electrophile $PhCH_2Br$ to form Cp_2TiBr_2, $PhCH_2SR$ and $PhCH_2SSR$.
3. The complexes $Cp_2Ti(phth)(SSR)$, where R = CMe_3, $CHMe_2$, CH_2Ph and p-C_6H_4Me, react with R'OH to give $Cp_2Ti(OR')(SSR)$, where R' = Et and Me.
4. The sulfur ligands in $Cp_2Ti(SR)(SSR)$, where R = CMe_3 and $CHMe_2$, displace norbornadiene from $C_7H_8Mo(CO)_4$ to give heterobimetallic species of the type $[Cp_2Ti(\mu\text{-}SR)(\underline{iso}\text{-}\mu\text{-}\eta^1\text{-}SSR)Mo(CO)_4]$, which contain the rare bridging disulfano ligand. Variable temperature ^1H NMR spectroscopy permitted evaluation of $\Delta G_c^{\dagger}$ for a sulfur inversion process which interconverts the <u>trans</u> and <u>cis</u> isomers of this dimer.

APPENDICES



Appendix 1: Cp Region of the ^1H NMR Spectra of $[Cp_2Ti(\mu\text{-}SCHMe_2)(\mu\text{-}SSCHMe_2)Mo(CO)_4]$ (18b). from 204K to 328K in Toluene d_8.

[a] unidentified impurities.



Appendix 2: CH_3 Region of the ^1H NMR Spectrum of $[Cp_2Ti(\mu\text{-}SCHMe_2)(\mu\text{-}SSCHMe_2)Mo(CO)_4]$ (18b) at 227K in Toluene d_8.

[a] trans isomer of 18b.