THE SYNTHESIS AND CHARACTERIZATION OF ORGANOMETALLIC POLYSULFANES AND POLYSELENANES OF TITANIUM(IV), ZIRCONIUM(IV), AND HAFNIUM(IV)

by

© James M. McCall

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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POLYSULFANO AND POLYSELENANO DERIVATIVES OF THE GROUP IVB METALS

Ph.D. James M. McCall Chemistry

THE SYNTHESIS AND CHARACTERIZATION OF ORGANOMETALLIC POLYSULFANES AND POLYSELENANES OF TITANIUM(IV), ZIRCONIUM(IV), AND HAFNIUM(IV)

Abstract

The complexes $Cp_2M(SH)_2$, where M = Ti and Zr, have been prepared and treated with S_8 and $>N-S_x-N<$, where >N = benzimidazolyl, phthalimidyl and x = 1, 2, to give the metallacyclohexasulfanes Cp_2MS_5. Reaction of $Cp_2Ti(SH)_2$ with >N-SR, where >N = phthalimidyl, succinimidyl, gave the complexes $Cp_2Ti(S_2R)_2$ (R = $CHMe_2$) and $Cp_2Ti(SR)(S_3R)$ (R = Ph, 4-C_6H_4Me). The thiolates $Cp_2Ti(Cl)SR$ and $Cp_2Ti(SR)_2$ (R = $CHMe_2$, CMe_3, Ph, 4-C_6H_4Me) were prepared for comparison. Treatment of the complexes Cp_2MCl_2 with anhydrous solutions of Li_2E_x gave the complexes Cp_2ME_5, where M = Ti, Zr, Hf and E = S, Se. The compounds $(RCp)_2TiS_5$ (R = Me, $SiMe_3$), $CH_2Cp_2TiS_5$, and $(Me_5Cp)CpTiS_5$ were prepared similarly. Reaction of Li_2S_x with $(Me_5Cp)_2MCl_2$ gave the metallacyclotetrasulfanes $(Me_5Cp)_2MS_3$. The complex $Cp_2Ti[S(CH_2)_3S]$ was synthesized. Variable temperature ^1H NMR studies established the barriers ($\Delta G^{\ddagger}$) for ME_x and TiS_2C_3 ring reversal in the above complexes. The crystal structures of $Cp_2Ti(SPh)(S_3Ph)$, Cp_2MS_5, and $(Me_5Cp)_2TiS_3$ are discussed.

Ph.D. James M. McCall Chimie

SYNTHESES ET CARACTERISATIONS DES POLYSULFANES ET POLYSELENANES ORGANOMETALLIQUES DE TITANE(IV), DE ZIRCONIUM(IV) ET DE HAFNIUM(IV)

Résumé

Les complexes $Cp_2M(SH)_2$, où M = Ti et Zr, ont été préparés et traités avec S_8 et $>N-S_x-N<$, où $>N$ = benzimidazolyle, phtalimidyle et x = 1, 2, pour donner les métallacyclohexasulfanes Cp_2MS_5. L'action de >N-SR sur $Cp_2Ti(SH)_2$, où >N = phtalimidyle, succinimidyle, a donné les complexes $Cp_2Ti(S_2R)_2$ (R = $CHMe_2$) et $Cp_2Ti(SR)(S_3R)$ (R = Ph, $4-C_6H_4Me$). Les thiolates $Cp_2Ti(Cl)SR$ et $Cp_2Ti(SR)_2$ (R = $CHMe_2$, CMe_3, Ph, $4-C_6H_4Me$) ont été préparés pour la comparaison. Le traitement des complexes Cp_2MCl_2 avec des solutions anhydres de Li_2E_x a donné les complexes Cp_2ME_5, où M = Ti, Zr, Hf et E = S, Se. Les composés $(RCp)_2TiS_5$ (R = Me, $SiMe_3$), $CH_2Cp_2TiS_5$ et $(Me_5Cp)CpTiS_5$ ont été préparés de façon analogue. L'action de Li_2S_x sur $(Me_5Cp)_2MCl_2$ a donné les métallacyclotétrasulfanes $(Me_5Cp)_2MS_3$. Le complexe $Cp_2Ti[S(CH_2)_3S]$ a été synthétisé. Les études RMN du proton à températures variables ont permis de déterminer les barrières ($\Delta G^{\ddagger}$) d'inversion de cycle pour ME_x et pour TiS_2C_3 dans les complexes ci-dessus. Une étude de la structure cristalline de $Cp_2Ti(SPh)(S_3Ph)$, Cp_2MS_5 et $(Me_5Cp)_2TiS_3$ est incluse.

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To my

Mother and Father

and

S.-D.C.

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$>N-S_x-N<$

Bz-S-Bz	1,1'-thiobisbenzimidazole
$Bz-S_2-Bz$	1,1'-dithiobisbenzimidazole
Phth-S-Phth	1,1'-thiobisphthalimide
$Phth-S_2-Phth$	1,1'-dithiobisphthalimide

>N-SR

Phth-SR	N-(alkylthio or arylthio)phthalimide
Succ-SR	N-(alkylthio or arylthio)succinimide
Cp	η-cyclopentadienyl, $\eta-C_5H_5$
MeCp	η-methylcyclopentadienyl, $\eta-C_5H_4Me$
Me_3SiCp	η-trimethylsilylcyclopentadienyl, $\eta-C_5H_4SiMe_3$
Me_5Cp	η-pentamethylcyclopentadienyl, $\eta-C_5Me_5$
CH_2Cp_2	1,1'-methylenebis(η-cyclopentadienyl), $CH_2(\eta-C_5H_4)_2$
dmpe	1,2-bis(dimethylphosphino)ethane, $Me_2PCH_2CH_2PMe_2$
dppe	1,2-bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PMe_2$

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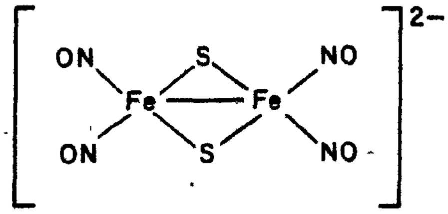
1. GENERAL INTRODUCTION

Sulfur

Preamble

Naturally occurring sulfur was a substance greatly praised by the ancients. Pliny the Elder remarked in the first century A.D. that there were four types of sulfur, each kind having its own specific applications. Native sulfur, then referred to as "live" sulfur, was the only one used for medicinal purposes. The other three forms were used for the bleaching of fabrics and in the preparation of lamp wicks.[1] The concept that metals were formed by the combination of sulfur and mercury was well established by the 13th century.[2] Indeed, it was thought that silver and gold resulted from the transmutation of minerals over thousands of years. Minerals themselves were considered to be "coagulated" sulfur and mercury.[2] However, alchemists were able to shorten this time span: " by the subtlety of the artist, transmutation of this kind is made in one day or in a brief space of time."[2] In the same way, Paracelsus proposed in the 16th century that metals were composed of the "three principles": mercury, sulfur and salt.[3] Finally in 1803 John Dalton defined sulfur as an element and assigned its atomic weight relative to hydrogen.[4]

The interaction of sulfur compounds with metals was studied by W.C. Zeise (1789-1847).[5] Although he is perhaps best known for his isolation of $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ (1827),[6] one of the first reported organometallic compounds, he also discovered potassium ethyl xanthate (1822) and its copper(I) salt, and ethanethiol (1834) and its mercury(II) salt. Other long-known sulfur-containing inorganic compounds such as Roussin's "red salts" containing the $Fe_2(\mu\text{-}S)_2(NO)_4^{2-}$ dianion (1) (1858)[7-9] and salts of the $[Pt(S_5)_3]^{2-}$ dianion (2) (1903)[10] have been reexamined recently.[11-14]



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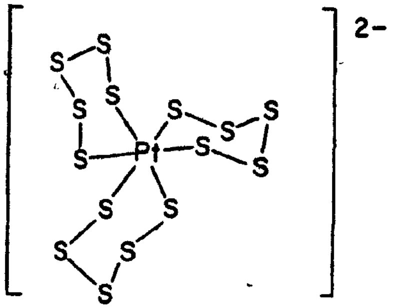

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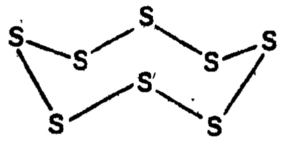
The first realization of the importance of catenation in sulfur chemistry resulted from early solution molecular weight determinations of elemental sulfur. These studies, conducted in the early 1900's, suggested that each sulfur molecule was composed of eight sulfur atoms.[15] The crystal structure determination in 1935 established the familiar crown shape of the S_8 molecule (3).[16] Its crystal structure has been investigated numerous times.[17] Over the



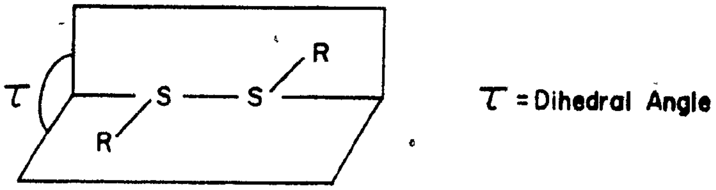
3

years chemists have discovered several more sulfur allotropes, ranging from the simple diatomic S_2 molecule to the S_{20} ring.

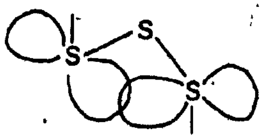
There are several series of inorganic acyclic compounds that are based on varying members of catenated sulfur atoms. These include the sulfanes H_2S_x (x = 1-8), the halosulfanes such as S_xBr_2 and S_xCl_2 (x = 1-8), sulfur amides $(R_2N)_2S_x$ (R = alkyl group, x = 1-4), polythionate dianions $S_x(SO_3)_2^{2-}$ (x = 1-4) and cyanogen polysulfides $S_x(CN)_2$ (x = 1-8).[18] A large number of cyclic sulfur diimides of the type $(HN)_2S_6$ are known. All of them have the crown-shaped eight-membered ring structure[19] found for S_8 and, depending on the location of the NR groups, contain three to six catenated sulfur atoms.

Organic polysulfides are well known as cyclic and acyclic molecules. Those containing up to six catenated sulfur atoms have been studied crystallographically. Chain-like dianions of the type S_x^{2-} (x = 2-5) have been studied in aqueous solution. Their relative stabilities depend markedly on the pH. The pentasulfide ion is the main species in acidic solution; S_2^{2-} predominates only in very alkaline solutions, and the others predominate in solutions of intermediate acidity.[20] In covalent compounds the sulfur chains can be formally regarded as oxidized or reduced, depending on the electronegativity of the attached groups. For example, the acyclic sulfanes H_2S_x formally have the S_x chain in the -2 oxidation state while the chlorosulfanes S_xCl_2 formally possess S_x^{+2} units.[21]

In order to develop an appreciation of the structural aspects of catenated sulfur compounds it is useful to establish some reference values. Electron-pair repulsions and steric interferences are at a minimum in H_2S_2 so that reference values may be set as follows:[22] S-S bond distance, 2.055 Å; dihedral angle, 90.6°. A value for the ideal bond angle at sulfur of 92.2° is obtained from H_2S.[22] Similar values are found for the polysulfide ions S_x^{2-}, but the ideal distances and angles are rarely observed. Even in covalent polysulfanes substituents other than hydrogen can markedly affect all of these parameters. Dihedral angles ranging from *ca*. 74° to 105° are known for organic disulfides.[23] In four- and five-membered cyclic disulfides these

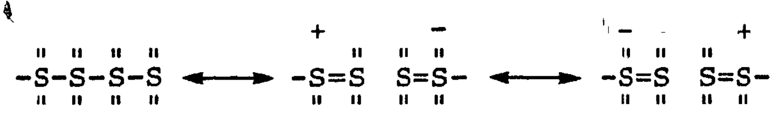


angles are compressed from the optimum value of ca. 90°. This compression increases electron-pair repulsions and consequently increases the S-S bond length.[22] For longer sulfur chains and for sulfur rings the optimum dihedral angle may be larger or smaller than 90° and the optimum bond angle larger than ca. 90°. A steric interaction of lone pairs on the next-but-one sulfur atoms has been proposed as an explanation.[22] The parameters for helical



(polymeric) sulfur should probably be used as a standard for higher order polysulfides.[24] The bond length, bond angle, and dihedral angle established crystallographically[25] for helical sulfur are 2.066 Å, 106°, and 85.3°, respectively.

In many sulfur allotropes and in compounds containing long sulfur chains an alternation of long and short sulfur-sulfur bonds is observed. Steudel et al.[22,26] have suggested that if a sulfur-sulfur bond is elongated due to a steric effect of substituents or due to unusual dihedral angle (as in strained rings) then the adjacent bonds will shorten in compensation. Contributions from resonance structures 4 and 5 may be important in such cases.[27]



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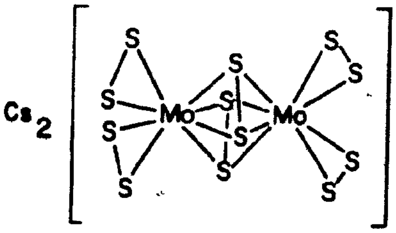
This thesis is concerned with organometallic compounds that contain catenated sulfur atoms. While organic polysulfides are common there are comparatively few examples in which a polysulfur chain is bonded to a metal atom. In the following pages the chemistry of polysulfur species known to coordinate to metal atoms are discussed with respect to their reduced, neutral, and oxidized states.

The S_2 Linkage

Paramagnetic disulfur is unstable in the liquid or solid state under normal conditions.[28] It has, however, been well characterized in the vapour.[29] At 1000 K and less than one torr (133.322 Pa) of pressure, sulfur vapour is essentially only S_2.[24] The precise identity of the blue[21] or purple[28] solids obtained when sulfur vapour is quenched in liquid nitrogen is in doubt. However, Meyer et al. have reported[29] that S_2 can be isolated in frozen rare gas matrices via deposition of a molecular beam of S_2 or by photolysis of S_2Cl_2. An alternative, perhaps more convenient, source of S_2 molecules is the dinuclear cluster $Cs_2[Mo_2(S_2)_6]$ (6). Heating this compound to 150°C reportedly generated molecular

S_2 via a reductive elimination process [reduction of Mo(V) and oxidation of S_2^{2-}].[30] The disulfur molecules were then studied spectroscopically in inert matrices. The S_2 triplet



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diradical has also been studied by ESR[31] and Raman[32] spectroscopies. Other spectroscopic studies[33] have established a ground-state bond length of 1.887 Å. This significant shortening from the value for H_2S_2 (2.055 Å)[22] is indicative of multiply-bonded sulfur atoms.

Isolated S_2^+ or S_2^{2+} have not been studied, unless one considers compounds such as S_2Cl_2 which formally contain the dication.[30] However, several groups have investigated the green radical anion S_2^- and the colourless dianion S_2^{2-}. Alkali halide crystals containing the former species as a dopant have been studied by ESR spectroscopy.[34] Both green S_2^- and blue S_3^- have been detected in ultramarines where the relative proportions of S_2^- to S_3^- vary with the colour of the ultramarine.[35]

The dianion S_2^{2-} is known in a large number of inorganic and, formally at least, organic and organometallic compounds. The free ion has been characterized crystallographically in salts such as SrS_2[36] and BaS_2.[37] Although the sulfur-sulfur bond length is somewhat dependent on the cation present, it is always significantly longer than in non-ionic compounds [e.g., 2.126(9) Å in BaS_2 <u>versus</u> 2.055 Å in H_2S_2[22]]. The increase in the bond length as neutral S_2 is reduced to S_2^- and S_2^{2-} is thought to be due to the antibonding character of the highest occupied molecular orbitals.[22]

The syntheses of metal complexes containing S_2 as a ligand have used sulfur reagents in three oxidation states:[30] (i) neutral S_8, (ii) substances such as S_2Cl_2 that formally act as sources of S_2^{2+}, and (iii) the disulfide ion S_2^{2-}. The first two synthetic methods effect oxidation of the metal with concomitant reduction of sulfur (i.e., oxidative addition) while the third method involves no net change in the oxidation state of the metal. Application of these reagents to inorganic and organometallic substrates has provided an enormous number of complexes containing the metal-bound disulfur moiety. In this respect disulfur has been referred to as the most versatile simple ligand with respect to its known coordination geometries.[30] Covalently bonded metal-disulfido complexes are best thought of as formally containing the S_2^{2-} moiety rather than the neutral molecule.[30] Because of reduced lone-pair repulsions in coordinated disulfur compared to the free disulfide ion (as in alkali metal or alkaline earth salts) the sulfur-sulfur bond lengths are expected, and indeed are found, to be shorter in metal-disulfido complexes.[30] Those types of metal-S_2 bonding geometries that to date have been demonstrated crystallographically are shown in Figure 1.[30] Typical examples are $Cs_2[Mo_2(S_2)_6]$ (6)[38] where the S_2^{2-} ligand is bonded "side-on", $(Me_5Cp)_2Cr_2S_5$ (7)[39] where it is bridging in a "side-on" and "end-on" fashion, and $Cp_2Mn_2(CO)_4S_2$ (8)[40] where it is only bridging "end-on".

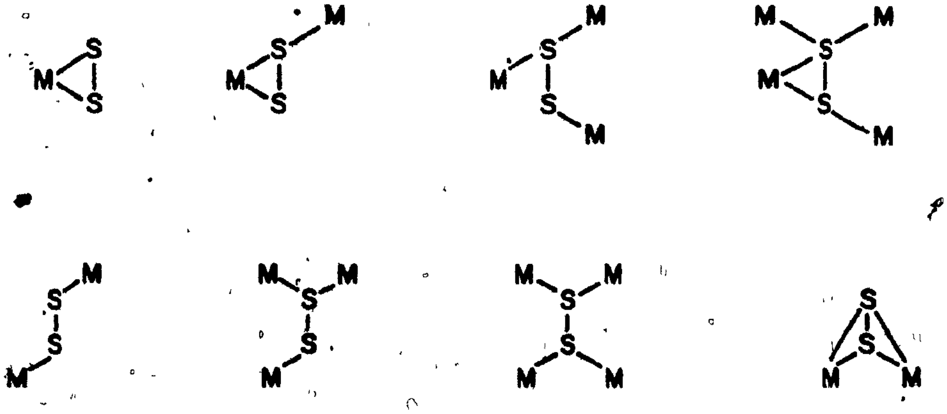
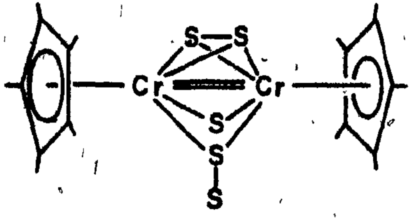


Figure 1. Bonding modes of S_2



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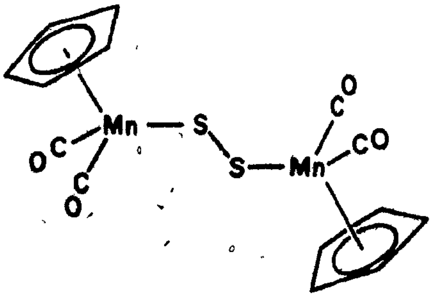

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A vast number of organic disulfides, R-SS-R, are known. However, few molecules such as 8 which contain the metal-SS-metal linkage are known. Other inorganic examples include $K_6[(CN)_5CoS_2Co(CN)_5]$,[41] $Li_4[(H_2O)_5CrS_2Cr(H_2O)_5]$,[42] and $[(NH_3)_5RuS_2Ru(NH_3)_5]X_4$ ($X^- = Cl^-, Br^-, PF_6^-$).[43,44] The crystal structure[45] of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4 \cdot 2H_2O$ established a trans planar RuSSRu arrangement (i.e., a dihedral angle about the S-S bond of 180°) and an S-S bond distance of 2.014(1) Å. Spectral data were consistent with the disulfur ligand behaving as a supersulfide ion (S_2^-),[45] and suggested a major contribution from the resonance structures 9 and 10. The neutral organometallic complex 8 had a

$$\mathrm{Ru}^{2+}\,\cdot\mathrm{S}\overset{\cdots}{-}\mathrm{S}^{-}\ \mathrm{Ru}^{3+} \longleftrightarrow \mathrm{Ru}^{3+}\ {}^{-}\mathrm{S}\overset{\cdots}{-}\mathrm{S}\ \mathrm{Ru}^{2+}$$

9 10

slightly shorter S-S bond [2.007(6) Å][40] which can be compared with the corresponding distances in neutral S_2 (1.887 Å),[33] S_2^{2-} [2.126(9) Å in BaS_2],[37] and organic disulfides (2.02 - 2.07 Å).[40] Some double-bond character in the S-S bond has been postulated.[40] Sulfur-sulfur bond lengths in transition metal disulfur complexes of the types shown in Figure 1 lie in the range 2.01 - 2.09 Å.[30]

Perhaps the most common bonding mode of S_2 to metal centers though is "side-on". This bonding mode is also known for the other Group VIA diatomic ligands O_2 and

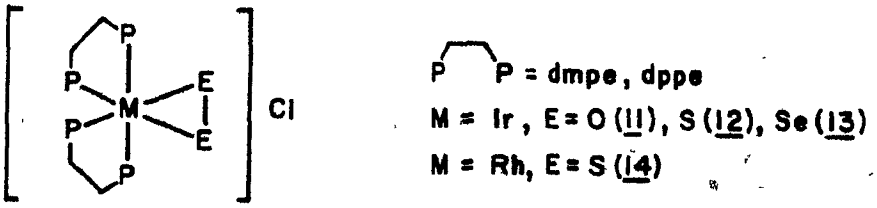
Se_2. The complex ions $[Ir(E_2)(dppe)_2]^+$ [where dppe = 1,2-bis(diphenylphosphino)ethane] have been prepared for E = O (<u>11</u>),[46-49] S (<u>12</u>),[50-53] and Se (<u>13</u>)[50,51] <u>via</u> the direct treatment of $[Ir(dppe)_2]Cl$ with the chalcogen (eq. 1).

$$[Ir(dppe)_2]Cl \;+\; A \longrightarrow [IrE_2(dppe)_2]Cl \qquad (1)$$

$$A = O_2,\ S_8,\ \text{red Se}$$

$$E = O\ (\underline{11}),\ S\ (\underline{12}),\ Se\ (\underline{13})$$

The rhodium complex $[RhS_2(dmpe)_2]Cl$ [where dmpe = 1,2-bis-(dimethylphosphino)ethane] (<u>14</u>) has also been prepared in an analogous fashion. However, $Rh(PPh_3)_3X$ (X = Cl, Br) reacted with sulfur to give the tetrameric products $[Rh(PPh_3)S_3X]_4$.[51] With $Rh(AsPh_3)_3Cl$ only oligomeric $[Rh(AsPh_3)S_2Cl]_n$ was obtained (n not specified).[51] Similarly, reaction of $M(CO)_2(PPh_3)_3$ with the chalcogens gave the complexes $ME_2(CO)_2(PPh_3)_2$ [M = Ru, E = O (<u>15</u>),[54] S (<u>16</u>);[55] M = Os, E = O (<u>17</u>);[54] S (<u>18</u>),[55] Se (<u>19</u>)[56]] (eq. 2). Cyclopentadienyl-metal complexes containing the η^2-S_2 ligand



<u>11</u> - <u>14</u>

$$M(CO)_2(PPh_3)_3 \; + \; A \longrightarrow ME_2(CO)_2(PPh_3)_2 \; + \; Ph_3PE \qquad (2)$$

$A = O_2$, S_8, red Se

M = Ru, E = O (15), S (16)

M = Os, E = O (17), S (18), Se (19)

include, for example, Cp_2NbE_2Cl [E = O,[57] S[58]]. The molybdenum complex 20 has also been prepared according to eq. 3.[59]

$$Cp_2MoCl_2 \; + \; Na_2S_2 \longrightarrow \underset{20}{Cp_2MoS_2} \qquad (3)$$

Metal-coordinated dioxygen can display an oxidizing nature[60] (eq. 4)[61] or can be attacked by electrophiles[62] (eq. 5). Coordinated disulfur or diselenium is also subject

$$(Ph_3P)_2Pt(O_2) \; + \; 3PPh_3 \longrightarrow (PPh_3)_3Pt \; + \; 2(Ph_3P)_2PtO \qquad (4)$$

$$(Ph_3P)_2Pt(O_2) \; + \; Ph_3CBr \longrightarrow (PPh_3)_2PtBr(OOCPh_3) \qquad (5)$$

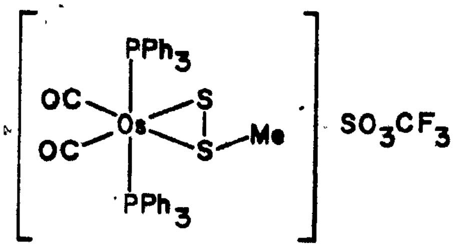
to attack by electrophiles.[56] For example, alkylation of 12 can be achieved using methyl fluorosulfonate (eq. 6)[52] and that of 18 and 19 using methyl triflate (methyltrifluoromethylsulfonate) (eqs. 7 and 8).[55,56] The X-ray structural

$$\underset{12}{IrS_2(dppe)_2Cl} \xrightarrow[\text{2) } NH_4PF_6]{\text{1) } MeSO_3F} Ir(\eta^2\text{-}S_2Me)(dppe)_2(PF_6)_2 \qquad (6)$$

$$\underset{\underline{18}}{\mathrm{Os(S_2)(CO)_2(PPh_3)_2}} + \mathrm{MeSO_3CF_3} \longrightarrow \underset{\underline{21}}{\mathrm{[Os(\eta^2\text{-}S_2Me)(CO)_2(PPh_3)_2]SO_3CF_3}} \qquad (7)$$

$$\underset{\underline{19}}{\mathrm{Os(Se_2)(CO)_2(PPh_3)_2}} \xrightarrow[\text{2) NaClO}_4]{\text{1) MeSO}_3\text{CF}_3} \underset{\underline{23}}{\mathrm{[Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]ClO_4}} \qquad (8)$$

determination of 21[55,63] established the bonding mode of the S_2Me ligand. Subsequent treatment[55] of 21 with iodide ion gave an unstable solid which was tentatively identified as $Os(\eta^1\text{-}S_2Me)I(CO)_2(PPh_3)_2$ (22). The selenium analogues were appreciably more stable. Treatment of 23 or



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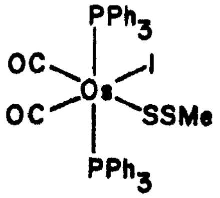

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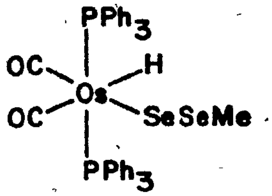
$[Os(\eta^2\text{-}Se_2Me)(CO)(CNR)(PPh_3)_2]ClO_4$ ($R = 4\text{-}C_6H_4Me$) with $NaBH_4$ gave the hydrido complexes $Os(\eta^1\text{-}Se_2Me)H(CO)_2(PPh_3)_2$ (24) and $Os(\eta^1\text{-}Se_2Me)H(CO)(CNR)(PPh_3)_2$, respectively, as stable crystalline solids.[56] The analogous reaction with 21 gave an unstable solid which evolved a gas.[56] A similar



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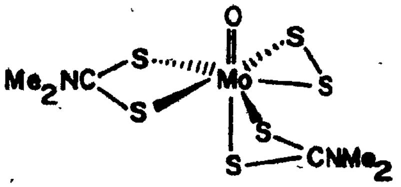
alkylation of $MoOS_2[S_2CNMe_2]_2$ (25) with $MeSO_3F$ gave $MoO(SSMe)(S_2CNMe_2)_2SO_3F$.[52] However, the spectral data for this compound could not distinguish between an η^1-SSMe or an η^2-S_2Me type of coordination.



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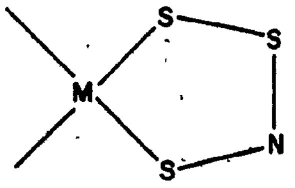
The trisulfur nitrido compounds of the type 26 are a class of inorganic complexes in which the metal-S_2



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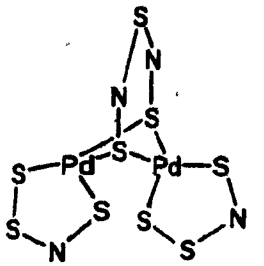
linkage has been incorporated into a ring. Many examples of these have been prepared, some of which, such as $Pd_2(S_3N)_2(S_3N_2)$ (27) and $Co(NO)_2(S_3N)$ (28), have been structurally characterized.[64,65] Both contain nonplanar MS_3N



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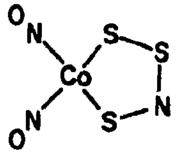

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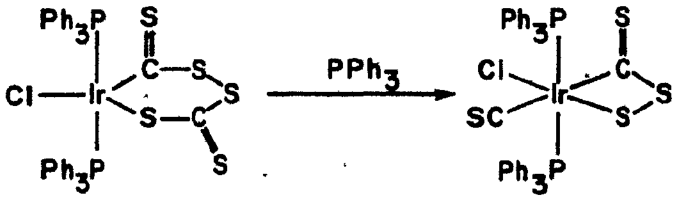
rings with normal[40] (*ca.* 2.00 Å) sulfur-sulfur bond lengths.

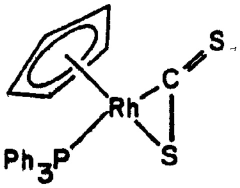
Complexes containing the CS_3^{2-} ligand are known. Kubota and Carey[66] reported the reaction of $(Ph_3P)_2Ir(N_2)Cl$ with CS_2 which gave $(Ph_3P)_2IrClC_2S_5$ (tentative structure 29). Desulfurization by triphenylphosphine gave $(Ph_3P)_2IrCl(CS)(CS_3)$ (30) (eq. 9). In a similar fashion $CpRh(PPh_3)_2$ (31) reacted



(9)

29 30

with excess CS_2 to give a mixture of $CpRh(PPh_3)(CS_2)$ and $CpRh(PPh_3)(CS_3)$ having proposed structures 32 and 33, respectively.[67] Interestingly, 31 reacted with elemental sulfur to give $CpRh(PPh_3)S_5$ (proposed structure 34).[67]



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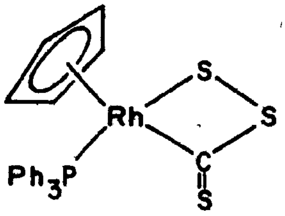

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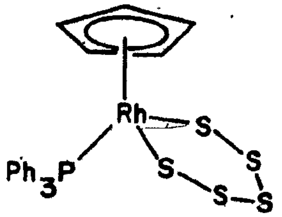

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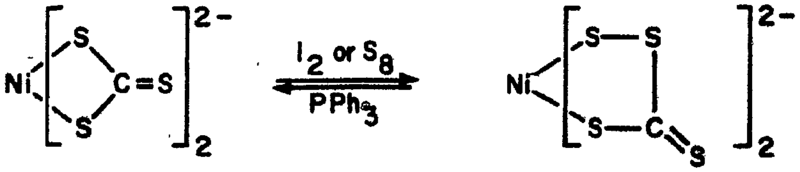
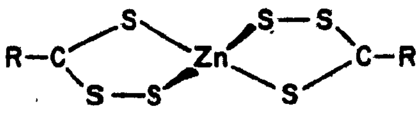
Coucouvanis and Fackler[68-70] reported the synthesis of several nickel, palladium, and platinum complexes containing the trithiocarbonate ligand such as $(Ph_4As)_2Ni(CS_3)_2$ and $[(PhCH_2)Ph_3P]_2Ni(CS_3)_2$. Treatment of the latter complex with iodine or sulfur gave the perthiocarbonato complex $[(PhCH_2)Ph_3P]_2Ni(CS_4)_2$. Desulfurization with triphenylphosphine gave back the trithiocarbonate derivative (eq. 10).



(10)

Similarly, M(dtb)$_2$ (M = Zn, Ni; dtb = dithiobenzoate) and M(4-dtc)$_2$ (M = Zn, Ni; 4-dtc = 4-dithiocumate) reacted either thermally or photochemically with sulfur to give "sulfur-rich" complexes such as 35 and 36 (R = C_6H_5 and $4\text{-}C_6H_4CHMe_2$).[68-70] Reaction of $FeCl_3$ with 35 (R = $4\text{-}C_6H_4Me$) gave the six-coordinate iron complex 37.[71]



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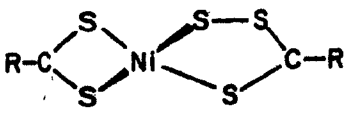

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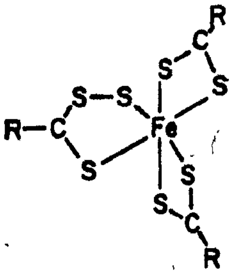

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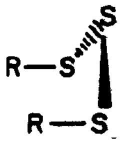
The S_3 Linkage

Like disulfur, trisulfur (also known as thiozone)[72] is unknown under normal conditions but has been characterized in the vapour[73-75] and liquid[76,77] states and has been trapped in low temperature matrix isolation experiments.[76,77] The structure of S_3 is still in doubt although the established bent chain structures of the isoelectronic molecules O_3, SO_2, and S_2O lend support to a similar structure.[24] At 440°C and 10 torr (1333.22 Pa), sulfur vapour has a deep red colour due to S_3 present in 10-20% concentration.[76,77] Photolysis of S_3Cl_2 in an organic glass at 77 K [76] or in a rare-gas matrix at 20 K [76] is the best way to prepare this allotrope for spectroscopic examination.[28]

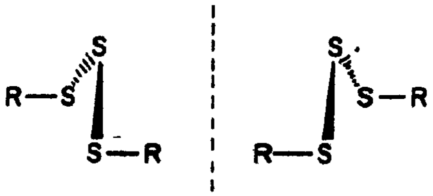
Aside from mass spectrometric observations, S_3^+ is unknown. The dication is similarly unknown. However, the singly as well as doubly reduced ions have been well studied. The blue S_3^- radical anion, along with the S_4N^- ion, have recently been implicated as the sources of the blue colour of solutions of sulfur in liquid ammonia.[78] The S_3^- anion has also been detected in solutions of alkali polysulfides in dimethylformamide or in hexamethylphosphoramide.[79] The existence of S_3^- doped into crystals and its presence in ultramarines was mentioned in the preceding section. The bent structure assigned to it on the basis of vibrational spectral studies is in accord with theoretical predictions.[80]

The trisulfide ion (S_3^{2-}) is quite stable at high pH in aqueous solution.[24] It has been crystallographically characterized in the anhydrous barium[36] and strontium[37] salts and most recently in $Na_2S_3\cdot NH_3$.[81] In these salts the S–S bond distance in the bent dianion ranges from 2.05 Å to 2.08 Å while the angle varies from 106.5° to 114.9°. It has been noted[79] that this angle is particularly sensitive to counterion and crystal packing forces. The sodium,[82] potassium,[83] and barium[84] salts have also been the subject of thorough infrared and Raman spectroscopic studies.

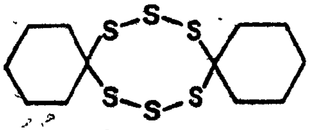
Acyclic compounds containing a covalently bonded S_3 chain can exist in <u>cis</u> or <u>trans</u> conformations with respect to the S_3 chain.[85] The <u>trans</u> conformation is enantiomorphic. Both conformers have been characterized crystallographically.[23] Cyclic and acyclic organic trisulfides are well known, although the former, such as <u>38</u>,[86,87] <u>39</u>,[88,89] and <u>40</u>,[90] are much rarer.



cis



trans



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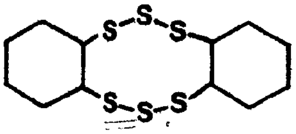

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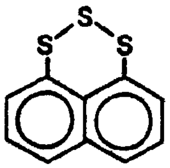

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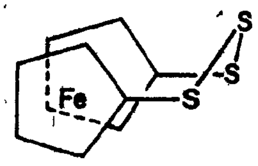
Compared to the diversity of bonding types established for S_2 in transition metal clusters[30] the bonding modes of S_3 are simple. A ferrocene derivative, 1,2,3-trithia[3]ferrocenophane (<u>41</u>), was prepared in 1969.[91,92] It has since been characterized by X-ray crystallography[93] and extensively studied by variable temperature NMR spectroscopy.[91,92,94-98] The selenium-containing analogue of <u>41</u> and the related 1,2,3-trithia[3]cobalticiniumophane hexafluorophosphate (<u>42</u>) have also been prepared and their fluxional behaviour in solution examined.[98]



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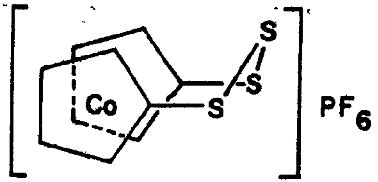
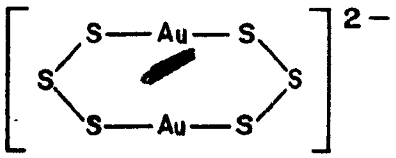


<u>42</u>

There are relatively few compounds known that contain the S_3 moiety directly bonded through the sulfur atoms to metal centers. A rare inorganic example is $(NH_4)AuS_3$. This salt was first prepared in 1903 from Au_2Cl_2 and ammonium polysulfides[10,99] but largely ignored until its inclusion in a recent review[100] on metallacyclopolysulfanes. A dinuclear structure with an eight-membered

$Au_2S_6^{2-}$ ring has been proposed (43).[101] Organometallic



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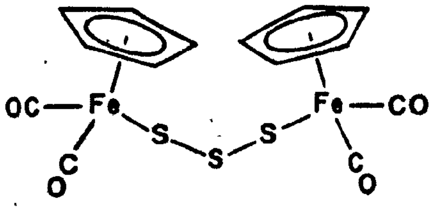
examples are somewhat more numerous. An organoiron complex having an FeS_3Fe linkage, $[CpFe(CO)_2]_2(\mu\text{-}S_3)$ (44), has been prepared and characterized crystallographically.[102] Two



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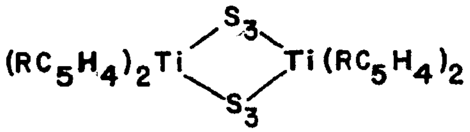
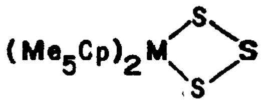
titanium-group trisulfanes have been reported: $[Cp_2Ti(\mu\text{-}S_3)]_2$ (45)[103] and $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46).[103] The synthesis and characterization of the complexes $(Me_5Cp)_2MS_3$ [where M = Ti (47), Zr (48), Hf (49)] is a major result of the research to be described in this thesis in a subsequent chapter.[104] The unsubstituted cyclopentadienyl analogue Cp_2TiS_3 has also been reported[105] but never firmly established. Attempts at duplicating its synthesis have been unsuccessful.[106]



45 R = H

46 R = Me



47 M = Ti

48 M = Zr

49 M = Hf

The S_4 Linkage

Tetrasulfur, like the lower molecular weight allotropes, has been identified in the vapour state by mass spectrometry, although it was thought to form via dimerization of S_2 molecules.[75] At 450°C and 20 torr (2666.44 Pa), considered to be the best conditions to observe the molecule, it constitutes 20% of sulfur vapour.[76,77] The gas phase structure of S_4 has not yet been firmly established. Possible structures include a chain, a ring, a branched form, or even a cage (Figure 2).[24] Theoretical calculations are not consistent in their predictions of the relative stabilities of these forms.[107-109] More experimental information on the structure of S_4 should contribute greatly to its theoretical understanding.[80] Liquid sulfur is reported to contain S_4 as a component.[76] Red tetrasulfur can be generated in situ by photolysis of S_4X_2 (X = Cl, Br) in an organic glass at 77 K or in a krypton matrix at 20 K,[76,77] or by the dimerization of S_2 molecules in a krypton matrix.[73]

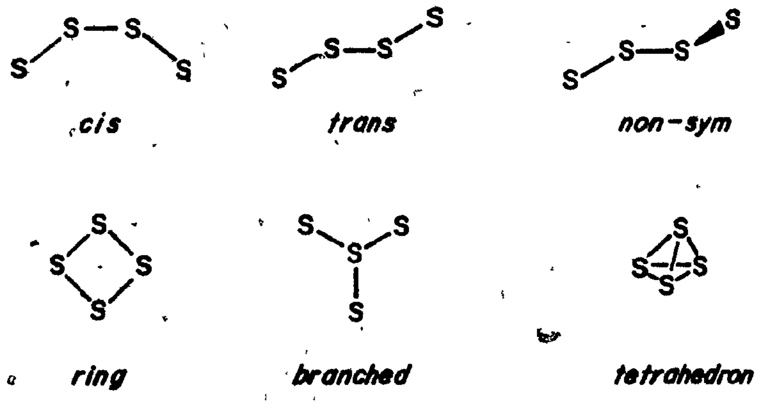
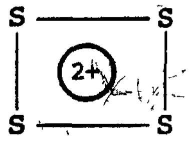


Figure 2. Possible structures of S_4

The chemistry of the oxidized and reduced S_4 species is quite well developed. The colourless diamagnetic[21] dication S_4^{2+} (50) has been prepared via various strongly oxidizing methods.[110] The similarity of its Raman and ultraviolet spectra to those of the square planar Se_4^{2+} cation immediately suggested an analogous structure.[111] Recent crystal structures of $(S_7I)_4S_4(AsF_6)_6$ and $S_4(AsF_6)_2 \cdot 0.6SO_2$ confirmed this conclusion.[112] The radical cation



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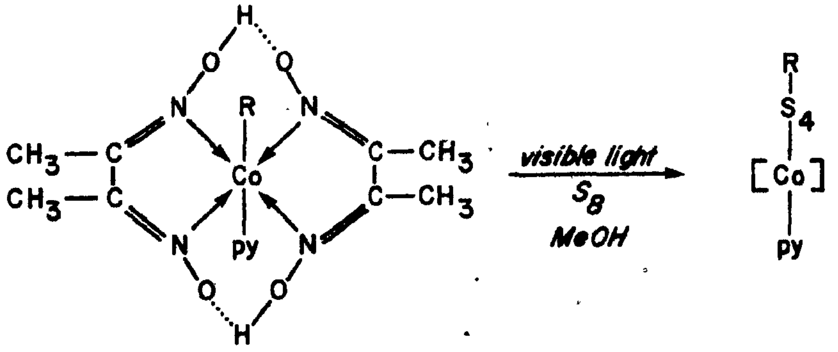
S_4^+ has been invoked to explain the paramagnetism observed for liquid SO_2 solutions of $S_8(Sb_2F_{11})_2$ via the equilibrium

$S_8^{2+} \rightleftharpoons 2S_4^{+}$.[113] However, more recent ESR studies[114] have established that the paramagnetism is due to S_5^{+}, not to S_4^{+}, although small concentrations (< 1%) of S_4^{+} could not be completely ruled out.[115] ESR measurements have detected S_4^{+} during the reaction of sulfur and chlorine in an NaCl-$AlCl_3$ melt[116] and in solutions of sulfur or sulfur-containing compounds in molten KCl/LiCl or KCNS.[117]

The tetrasulfide dianion S_4^{2-} is well known in both aqueous solutions and the solid state. Simple inorganic salts that contain this acyclic bent ion are numerous; Na_2S_4[118] and $BaS_4 \cdot H_2O$[119] have been characterized crystallographically. In addition, Na_2S_4 and K_2S_4 have been the subject of Raman and infrared spectroscopic studies in the solid and molten states as well as in aqueous solutions.[82,83] The salt $NH_4[CuS_4]$ has received some attention recently as a purported example of a metallacyclopentasulfide species MS_4^{-}.[100] The original synthesis via the treatment of copper(II) sulfate with aqueous ammonium polysulfides[10] has been extended to other salts of the $[CuS_4]^{-}$ ion. Investigations by Gattow and Rosenberg[120] on $M'CuS_4$ (M'^{+} = NH_4^{+}, K^{+}, Rb^{+}, Cs^{+}), however, established the presence of tetrahedral, four-coordinate copper(I) ions as well as S_4^{2-} chains. Consequently, the existence of the discrete cyclic CuS_4^{-} ion is in doubt.

A number of inorganic compounds containing a covalently bonded S_4 moiety have been synthesized. Both chain-like and cyclic bonding modes are known. A metal-S_4-alkyl linkage has been incorporated into several alkylcobaloximes (51) by photochemical methods[121] (eq. 11, where py = pyridine, R = a cyclic or acyclic alkyl group). Reduction with $NaBH_4$ gave the alkyl tetrasulfides RS_4R along with some H_2S. If CH_3I was present during the reduction, RS_4R, H_2S, and methyl(pyridinato)cobaloxime were isolated.[121] Additional products from eq. 11 included dimeric species of the type py-[Co]-S_4-[Co]-py (52). A free-radical mechanism (eq. 12) was proposed.[121] Other macrocyclic cobalt complexes



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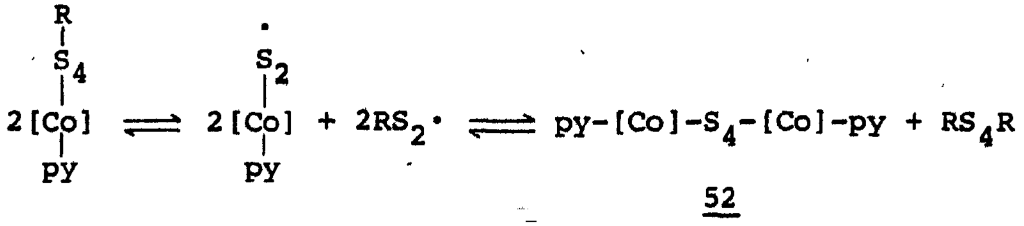
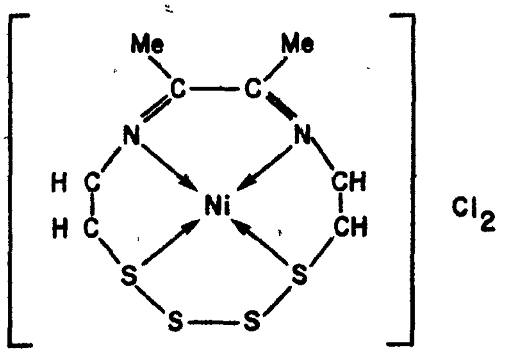


$$2\,\underset{\underset{py}{|}}{\overset{\overset{R}{|}}{\overset{S_4}{|}}}{[Co]} \rightleftharpoons 2\,\underset{\underset{py}{|}}{\overset{\overset{\bullet}{S_2}}{|}}{[Co]} + 2RS_2\bullet \rightleftharpoons \text{py-[Co]-}S_4\text{-[Co]-py} + RS_4R \qquad (12)$$

51 52

with the Co-S_2-Co or the Co-S_4-Co linkage have been prepared.[122,123] A nickel complex 53 has also been reported, although this is strictly a metal-polythioether species.[124] Compounds containing a chelating divalent S_4 chain include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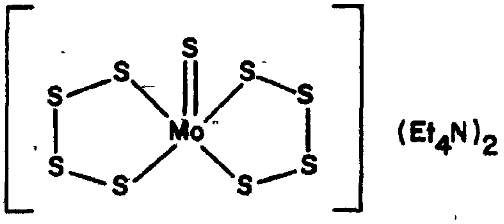
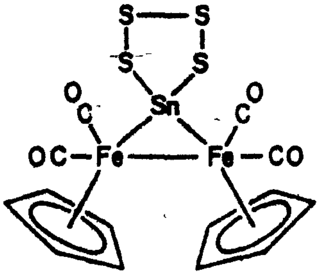

54

$(PPh_3)_2PtS_4$,[100,125-127] (dppe)MS_4 (M = Ni, Pd, Pt),[100,125] $[P(4-C_6H_4Me)_3]_2PtS_4$,[100] and $(Et_4N)_2MoS_9$ (54).[128]

Organometallic complexes are also known. Ungurenașu et al.[129] reported the synthesis of $[CpFe(CO)_2]_2$-SnS_4. Its proposed structure (55) was based on spectroscopic and molecular weight measurements. The related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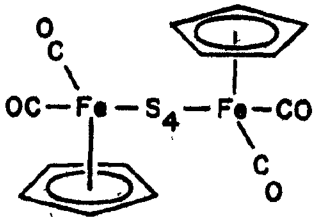
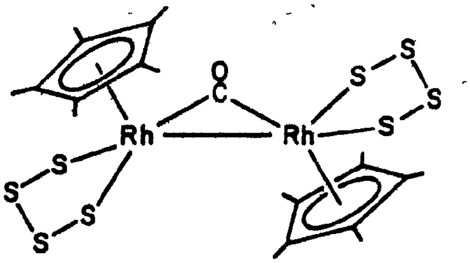

56

complex $[CpFe(CO)_2]_2(\mu-S_4)$ (56) has recently been reported and characterized crystallographically.[102] An interesting binuclear rhodium complex $[(Me_5Cp)RhS_4]_2(\mu-CO)$ (57) which contains two RhS_4 metallacycles has been reported.[130] The bis(η-cyclopentadienyl) metal compounds Cp_2MS_4 where M = Mo (58)[59,131-133] and W (59)[134-136] have been shown to have a MS_4 ring.



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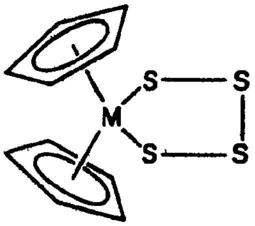
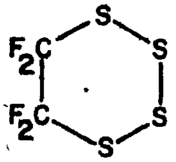


58 M = Mo
59 M = W

Organic acyclic tetrasulfides are not unknown but few have been examined crystallographically.[137] Cyclic tetrasulfides are quite scarce. Meyer[138] has reported a general route to seven- to twelve-membered rings having three to eight catenated sulfur atoms (eq. 13). The per-

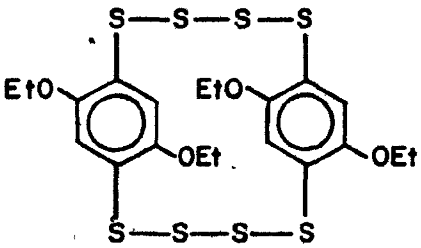
$$(CH_2)_n(SH)_2 + S_mCl_2 \longrightarrow \underset{m\,=\,1-6}{(CH_2)_nS_{m+2}} + 2HCl \qquad (13)$$

fluorinated tetrathiane (60) has been prepared. ^{19}F NMR studies showed that several conformers were present in

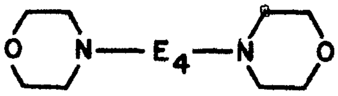


60

solution at room temperature.[139] The tetrasulfide 61 contains two S_4 bridges in a 16-membered ring[140] while 62 is a linear tetrasulfide.[137]

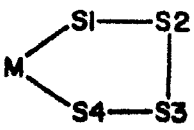


61

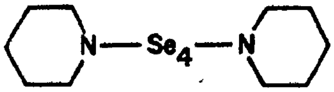


62 E = S
63 E = Se

In covalently bonded tetrasulfides a variation in bond lengths along the S_4 chain exists, although the trend differs for organic and transition metal compounds. Thus in $(Et_4N)_2MoS_9$ (54),[128] Cp_2MoS_4 (58),[133] and Cp_2WS_4 (59),[135,136] the inner bond S2-S3 is significantly shorter than the outer bonds S1-S2 and S3-S4. The opposite is true in the organic examples 61[140] and 62.[141] Longer



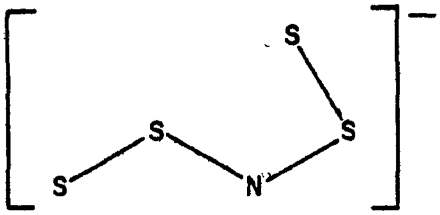
inner bonds are also found in dimorpholinotetraselenane (63) and dipiperidinotetraselenane (64).[141]



64

The S_5 Linkage

Pentasulfur is an allotrope of sulfur that is thought to have borderline stability under normal laboratory conditions.[21] Like the lower molecular weight species, it has been detected in the vapour by mass spectrometry.[75] It is also found in liquid sulfur.[76,77] Photolysis of chlorosulfanes is a route for its *in situ* preparation and spectroscopic study.[29] Its structure in any state, whether cyclic or not, is in doubt.[24] It has been suggested[24] that a cyclic structure would be highly strained but that a comparison with an isoelectronic species such as S_4N^- might provide clues as to the solid state structure for the sulfur allotrope. A similar analogy can be used for the series S_7NR to $S_4(NR)_4$ (R = H or CH_3) which are isoelectronic to S_8, and which have puckered rings similar to S_8.[142] Recently Chivers *et al.* determined the structure of two dark blue salts of the S_4N^- ion. The anion has a planar, acyclic structure with a central nitrogen atom (65).[143,144]



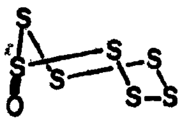
65

There has been only one reported synthesis of S_5 by Schmidt[21,145] using Cp_2MoS_4 (58), which contains a five-membered MoS_4 ring[133] (eq. 14). The product was reported

$$\underset{58}{Cp_2MoS_4} + SCl_2 \longrightarrow Cp_2MoCl_2 + S_5 \qquad (14)$$

to be liquid at room temperature but it polymerized readily, particularly in the presence of light. The oxide of this allotrope is also unstable. The cyclic sulfur oxides S_xO (x = 5 - 10) have been prepared *via* the low temperature oxidation of the corresponding sulfur allotrope,[146,147] although the route to the S_5 precursor was not specified. All of them decompose at or above room temperature, except S_5O which decomposes at above -50°C in solution.[147] A cyclic structure was proposed[147] for S_5O in keeping with the established solid-state structures of S_7O (66)[148] and S_8O (67).[149]

The chemistry of oxidized S_5 is rather limited. The radical monocation S_5^+ has been firmly identified by ESR



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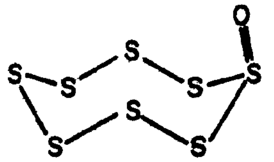
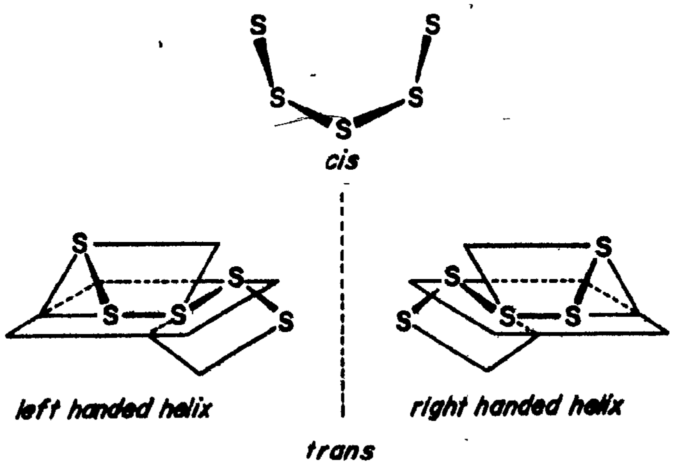
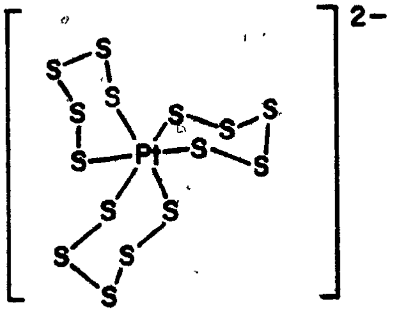


67

spectroscopy in oleum solutions.[114] The S_5^{2+} dication has not been prepared. The linear dianion is the only well characterized reduced species. Alkali metal salts of S_5^{2-} have been well characterized by vibrational spectroscopy in the solid, the melt, and in solution.[82,83] The ammonium,[150] potassium,[151] rubidium,[152] and thallium[153] salts have been studied crystallographically. For an unbranched S_5^{2-} chain two geometric isomers are possible, <u>cis</u> and <u>trans</u>, the latter form being enantiomeric. In all of the salts studied the S_5^{2-} chains adopted a <u>trans</u> form.[153]



Inorganic compounds containing an S_5 chain covalently bonded to a metal atom in a cyclic fashion are well established. Probably the oldest representative of this class is salts of the dianion $[Pt(S_5)_3]^{2-}$ (2) which were first prepared in 1903[10] but not crystallographically studied until 1969. Both $(NH_4)_2[Pt(S_5)_3]\cdot 2H_2O$[11,154] and $K_2[Pt(S_5)_3]$[155] have been examined this way. In the former complex the sulfur-sulfur bond distances were equal, with an average value of 2.049 Å.[11] The SSS bond angles ranged from 100.7° to 109.8° and the SSSS dihedral angles from 72.3° to 82.5°.[11] In comparison, there was a clear variation in sulfur-sulfur bond lengths (mean value 2.054 Å) in the dipotassium salt.[155] The SSS bond angles fell in the range 100.5° to 110.3° while the dihedral angles were not reported.[155]



2

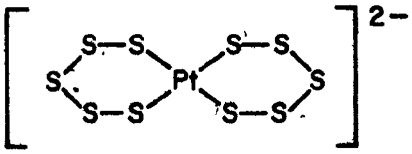
In 1978 Gillard and Wimmer[12] reported that 2 could be crystallized in a racemic or an optically active form. They isolated the anhydrous levo enantiomer using $(+)-[Ru(phen)_3]^{2+}$ as the counterion (phen = 1,10-phenanthroline). Variable temperature

^{195}Pt NMR studies on 2 have been used to determine the barrier to PtS_5 ring inversion in solution ($\Delta G^{\ddagger} = 50.5 \pm 1.3$ kJ mol^{-1}).[14]

Complex 2 was reduced with aqueous cyanide ion with complete desulfurization (eq. 15).[13] However, a partially desulfurized species could be intercepted during the course of the reaction as the tetrapropylammonium salt,

$$\underset{\underline{2}}{PtS_{15}{}^{2-}} + 17CN^- \longrightarrow Pt(CN)_4{}^{2-} + 13SCN^- + 2S^{2-} \qquad (15)$$

$[(C_3H_7)_4N]_2PtS_{10}$. On the basis of its infrared spectrum a planar PtS_4 core was assigned (68). Spontaneous reduction of 2 to 68 occurs over several hours in neutral aqueous solution but much more rapidly in alkaline solutions.[12] Other nucleophiles[156] such as sulfite, arsenite, sulfide or hydroxide ions similarly degrade 2 to 68. Treatment of 2 with excess triphenylphosphine, however, gave $(PPh_3)_2PtS_4$ (69)[100,125-127] in high yield.[156]



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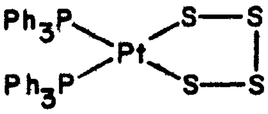
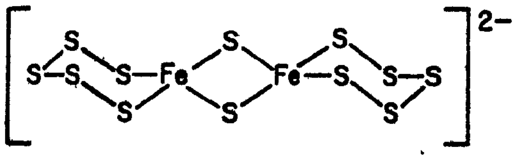


69

Other inorganic complexes which probably contain a chelating $S_5{}^{2-}$ ligand include $(NH_4)_3[M(S_5)_3]$ (M = Rh,[157] Ir[99]). The rhodium salt spontaneously desulfurized rapidly in water to give a polymeric species thought to be RhS_{10}^{-}.[157] None of these compounds have been crystallographically characterized. Other complexes which are known to contain the chelating S_5^{2-} ligand include $(\mathrm{Ph_4P})_2(\mathrm{Fe_2S_{12}})$[158] (70), $(\mathrm{Ph_4P})_2(\mathrm{FeMS_9})$[159] (M = Mo, W; 71), and $\mathrm{Os_2(S_5)(S_3CNEt_2)}$-$\mathrm{(S_2CNEt_2)_3}$[160] (72). The S_5^{2-} ligand in the last example has one terminal (metal-bonded) sulfur atom that bridges both osmium centers. The bond distances from this unique sulfur atom to each osmium atom are equal.



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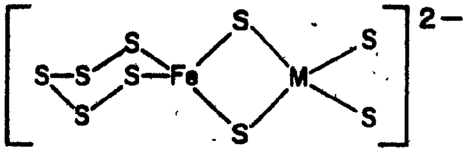
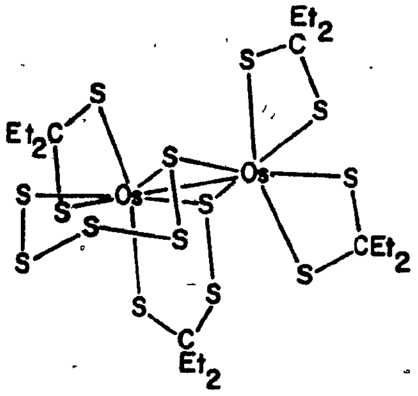
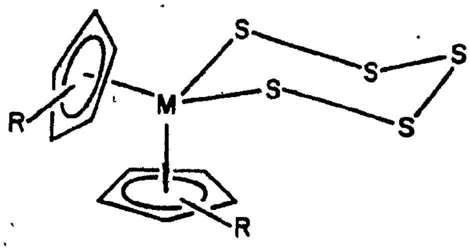


71 M=Mo,W

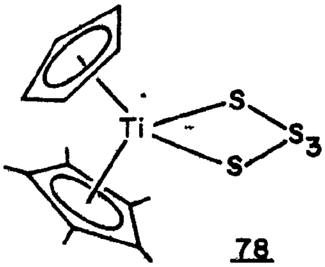


72

The first organometallic complex to contain a metal-S_5 ring was Cp_2TiS_5 (73) which was prepared in 1966.[161,162] Several preparative routes have been developed[99,161-165] and the crystal structures of two modifications have been reported.[166,167] Numerous substituted-cyclopentadienyl complexes are also known: $(MeCp)_2TiS_5$ (74),[168] $Cp(MeCp)TiS_5$,[168] and $Me_2M'(\eta\text{-}C_5H_4)_2TiS_5$ (M' = Si, Ge).[169] As part of this thesis the new compounds Cp_2MS_5 [M = Zr (75), Hf (76)],[170] $(Me_3SiCp)_2TiS_5$ (77), $(Me_5Cp)CpTiS_5$ (78), and $CH_2Cp_2TiS_5$ (79) have been prepared and characterized. The paramagnetic vanadium compound Cp_2VS_5 (80) has also been prepared[167,171] and studied by ESR spectroscopy[167,172,173] and X-ray crystallography.[167] A few mono-cyclopentadienyl metallacyclohexasulfanes are known. These include $CpLMS_5$ [M = Co, L = PMe_3



73	M=Ti	R=H
74	M=Ti	R=Me
77	M=Ti	R=$SiMe_3$
75	M=Zr	R=H
76	M=Hf	R=H
80	M=V	R=H



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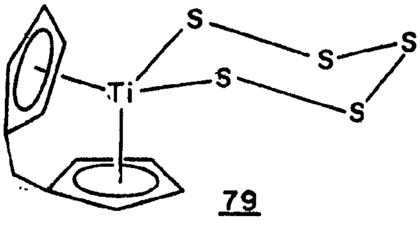
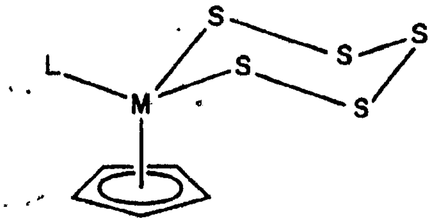


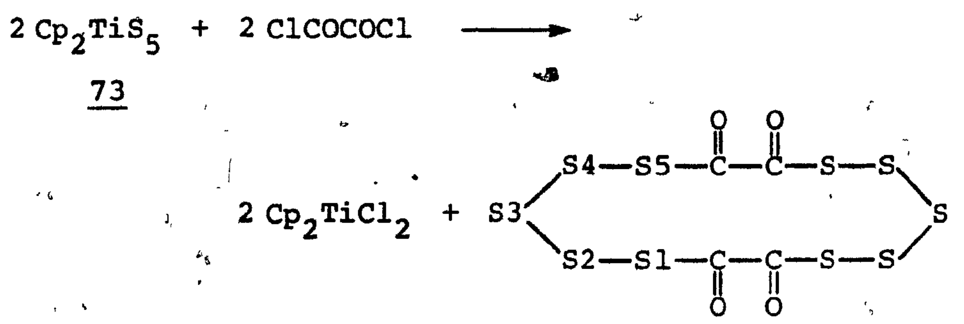
79

(<u>81</u>);[174,175] M = Rh, L = PPh_3 (<u>34</u>)[67]]. An X-ray crystal structure determination of <u>81</u> established the location of the Cp ligand in the axial position.[174]



<u>81</u> M=Co L=PMe_3
<u>34</u> M=Rh L=PPh_3

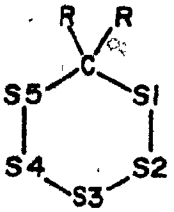
Some organic compounds with a pentasulfide linkage incorporated in a bridging or chelating fashion are known. A particularly interesting example was prepared <u>via</u> treatment of Cp_2TiS_5 (<u>73</u>), which contains a six-membered TiS_5 ring, with oxalyl chloride (eq. 16).[176] An X-ray crystallographic study confirmed the presence of the two bridging S_5 chains within the 14-membered ring. Bond length alternation was observed, with the longest sulfur-sulfur bond (S4-S5) next to the shortest sulfur-sulfur bond (S3-S4). The two terminal bonds S1-S2 and S4-S5 were equal in length. The two internal bonds S2-S3 and S3-S4 were also equal in



(16)

length but ca. 0.02 Å shorter than the terminal bonds.[176,177] The analogous reaction using Cp_2MS_4 [M = Mo (58), W (59)] might give the analogous 10-membered organosulfur ring but this reaction has not yet been reported.

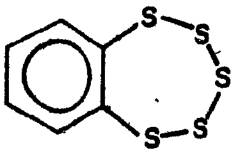
Several organic compounds which contain the S_5 chain as part of a six-membered ring have been isolated. Some have been studied crystallographically. Two such compounds are pentathiane (83) and dibenzylpentathiane (84).[178]



83 R=H
84 R=CH_2Ph

In both cases the six-membered ring was in the chair conformation and in 84 there was evidence for a flattening of the chair relative to the unsubstituted pentathiane. The two internal sulfur-sulfur bonds were significantly longer than the terminal ones. Variable-temperature ^1H NMR studies of 83 gave the value of $\Delta G^{\ddagger} >$ ca. 60 kJ mol^{-1} for chair-to-chair conversion.[179]

Benzopentathiepine (85) contains a seven-membered ring with five catenated sulfur atoms.[180] The ring adopts a chair conformation[181] similar to that found for solid S_7O (66).[148]



85

The S_6 Linkage

Cyclohexasulfur and cycloheptasulfur are the only lower allotropes besides S_8 that exhibit significant stability under normal laboratory conditions. Both are thought to maintain cyclic structures in the solid,[26,182-184] melt,[185] and gas[75] phases, although acyclic modifications may coexist in the melt and vapour.[24] Recently, quantitative separation of S_6 and S_7 from a solution of sulfur rings (S_6, S_7, S_8, S_{10}, S_{12}, S_{18}, and S_{20}) was achieved without decomposition by high pressure liquid chromatography (HPLC).[186] This analytical method was used to examine the sulfur species obtained from the thermal decomposition of unstable iodosulfanes. It was shown that all the allotropes from S_6 through S_{26} were formed.[186] Neutral S_6 has also been trapped and studied spectroscopically in low temperature matrices by quenching sulfur vapour or by the in situ photolysis of chlorosulfanes.[24]

Cyclohexasulfur was first prepared in 1891[187] via the low temperature decomposition of thiosulfate ions upon treatment with concentrated hydrochloric acid (eq. 17). A

$$6Na_2S_2O_3 + 12HCl \longrightarrow S_6 + 6SO_2 + 12NaCl + 6H_2O \qquad (17)$$

proposed mechanism for the formation of cyclic species from acyclic starting materials involves a folding-back of long sulfur chains (Scheme 1).[21] The degradation of long sulfur

Scheme 1

$$SSO_3^{2-} + S_2O_3^{2-} \rightleftharpoons S\text{-}S\text{-}SO_3^{2-} + SO_3^{2-}$$

$$S\text{-}S\text{-}SO_3^{2-} + S_2O_3^{2-} \rightleftharpoons S\text{-}S\text{-}S\text{-}SO_3^{2-} + SO_3^{2-}$$

$$\vdots$$

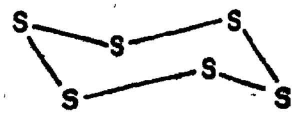
$$S_5\text{-}SO_3^{2-} + S_2O_3^{2-} \rightleftharpoons S\text{-}S\text{-}S\text{-}S\text{-}S\text{-}S\text{-}SO_3^{2-} + SO_3^{2-}$$

$$S\text{-}S\text{-}S\text{-}S\text{-}S\text{-}S\text{-}SO_3^{2-} \rightleftharpoons S_6 + SO_3^{2-}$$

chains into shorter ones is well documented for polysulfide ions.[188] More recent syntheses have used a simultaneous low-temperature addition of dilute ether solutions of H_2S_4 and S_2Cl_2 (eq. 18).[189] Alternatively, S_6 can be

$$H_2S_4 + S_2Cl_2 \longrightarrow S_6 + 2HCl \qquad (18)$$

prepared (together with S_{12} as a minor by-product) from Cp_2TiS_5 (73) and SCl_2.[190] Orange-red S_6 decomposes at 50°-60°C to give S_8[21] and is also light-sensitive (decomposing to S_8 and S_{12}).[138] An X-ray crystallographic study revealed the chair-shaped structure 86.[183] A re-



86

determination of the structure, offering significantly more precise bond angles and distances, has been recently published.[182] All sulfur-sulfur bond distances were equal and averaged 2.068(2) Å. Average SSS bond angles of 102.61(6)° and SSSS dihedral angles of 73.8(1)° were found. Although the bond distance is longer than that reported for S_8, it was not unexpected. On the basis of an electron-repulsion model[22] the smaller dihedral angle observed for S_6 (S_8, 98.5°)[191] should lead to an increase in the bond length (S_8, 2.046 Å).[191]

Although discrete cations and the monoanion of S_6 are unknown, the doubly reduced species has been extensively studied. Vibrational studies of K_2S_6 in the solid and molten states were recently reported. The crystal structure of the cesium analogue[192] revealed non-planar S_6^{2-} chains with alternating long (2.11 Å) and short (2.02 Å) sulfur-sulfur bonds, with the two terminal and one central bond comprising the shorter set. The longer bonds are associated with smaller dihedral angles.[193] It is noteworthy that a regular alternation of carbon-carbon bond lengths has been observed in the crystal structures of long aliphatic chains such as in adipic (<u>87</u>)[194] and sebacic (<u>88</u>)[195] acids and in hexamethylenediamine (<u>89</u>).[196]

$HOOC-(CH_2)_x-COOH$

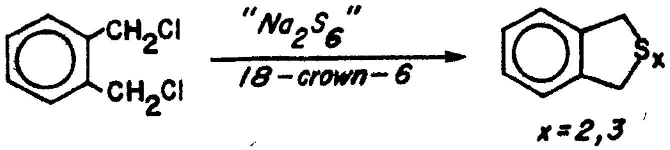
x = 4, <u>87</u>

x = 8, <u>88</u>

$H_2N-(CH_2)_6-NH_2$

<u>89</u>

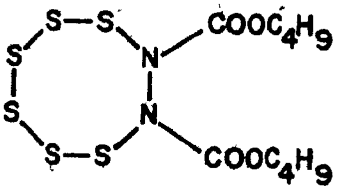
It has been suggested[28] that the S_3^- radical anion readily dimerizes to give S_6^{2-}. However, Na_2S_6 dissolved in acetonitrile, benzene, or tetrahydrofuran in the presence of dicyclohexyl 18-crown-6 gives $Na^+S_3^-$.[20] This "naked" S_3^- radical, presumably formed via disproportionation of the S_6^{2-} chain, is chemically reactive (eq. 19).[198]



(19)

A cyclic metal-S_6 geometry is unknown for transition-metal compounds. An example containing a bridging S_6 group is $(NH_4)_2PdS_{11}\cdot 2H_2O$. Like $(NH_4)_2[Pt(S_5)_3]$, this palladium complex was first reported in 1903[8,99] yet was only reinvestigated in 1977.[197] It was prepared via the treatment of an aqueous ammonium polysulfide solution with aqueous K_2PdCl_4. The analogous synthesis using aqueous ammonium polysulfide and K_2PtCl_4 gave only $(NH_4)_2[Pt(S_5)_3]$ and not $(NH_4)_2[Pt(S_5)_2]$.[13] The X-ray structure of $(NH_4)_2PdS_{11}\cdot 2H_2O$ revealed metal atoms linked by S_6 chains in a three-dimensional array.[197]

A ring containing the S_6 fragment is known in sulfur-nitrogen chemistry. The structure of $S_6N_2(COOC_4H_9)_2$ (90) consists of crown-shaped molecules having a nitrogen-nitrogen single bond and a chain of six sulfur atoms.[200]



90

Organic hexasulfides, RS_6R, are quite rare compounds. A general synthesis of acyclic dialkyl pentasulfides and hexasulfides has been reported (eq. 20).[199] An

$$2\,RSSH + S_xCl_2 \longrightarrow RS_{x+4}R + 2\,HCl \qquad (20)$$

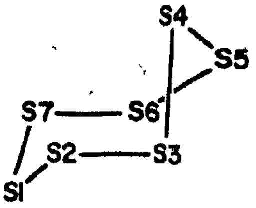
$$x = 1,2$$

interesting cyclic compound, hexathiepane (91), has been isolated from mushrooms. The ring in this seven-membered heterocycle exists in the twist form with alternating short (terminal and central) and long sulfur-sulfur bond lengths.[178]

91

The S_7 Linkage

Cycloheptasulfur was first prepared in 1968[201] as thermally- and light-sensitive yellow plates[21] or needles.[201] Although it melts reversibly[21] at 39°C, polymerization[145] occurs at ca. 45°C. Prolonged storage at room temperature or exposure to light causes decomposition to give S_8. However, it may be stored in the dark at low temperature without decomposition.[202] This allotrope is also found in liquid[185,202] and gaseous[202] sulfur where it probably maintains its solid-state cyclic structure.[24,26] At least four modifications of S_7 have been postulated on the basis of Raman spectroscopy,[202] two of which have been examined by X-ray crystallography. For one of these, only a projection of the molecule onto a plane was reported. A chair conformation having four atoms nearly coplanar was suggested.[21,184] A second modification (δ-S_7) received complete crystallographic analysis[26] and its structure was described as a derivative of S_8, since removal of one sulfur atom followed by connection of the resulting chain ends results in the observed structure (92).[26]



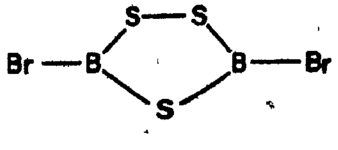
92

This connection, identified as the S5-S6 bond, is relatively long [2.181(3) Å] and was attributed to a very small (*ca.* 1°) dihedral angle about this bond. In accord with the theory on alternating sulfur-sulfur bond distances,[27,148] bonds adjacent to this long bond are the shortest in the molecule. The presence of a four-center molecular orbital was postulated on the basis of the planar arrangement of the four atoms S4-S5-S6-S7.[26,202]

There is only one preparative route to cycloheptasulfur (eq. 21).[201] The general reaction of Cp_2TiS_5 ($\underline{73}$) with chlorosulfanes containing the appropriate number of sulfur atoms is an extremely useful, and in this case the only, route to higher sulfur allotropes. S_7 has also been

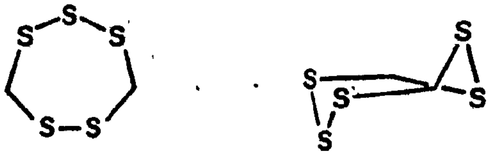
$$\underset{\underline{73}}{Cp_2TiS_5} + S_2Cl_2 \longrightarrow Cp_2TiCl_2 + S_7 \qquad (21)$$

prepared as a by-product in the synthesis of the trithiaborolane $(BrB)_2S_3$ ($\underline{93}$) from $\underline{73}$ and BBr_3.[203]



93

Replacement of one or two sulfur atoms in S_7 with methylene groups markedly improves the thermal stability of the seven-membered ring. Hexathiepane (<u>91</u>) and lenthionine (<u>94</u>) which both occur in certain species of edible mushrooms,[204] are more stable than S_7, probably because of the absence of very small dihedral angles about the sulfur-sulfur bonds[178] (i.e., none less than 70° in <u>91</u>). Both are stereochemically non-rigid in solution[178,205] and exist in the twist conformation in the crystal.[206]



<u>94</u>

The chemistry of charged S_7 ions, cationic or anionic, is limited. To date no discrete cations have been identified, nor has the singly charged anion. The heptasulfide dianion is known in alkali metal salts.

There are a few compounds containing a covalently bonded S_7 chain that have been characterized by X-ray crystallography. An inorganic example is S_7NH which, like the S_8 parent molecule, has a crown shape.[207] The elemental analyses of an organic example, heptathiepane (S_7CH_2), prepared at high dilution from $CH_2(SH)_2$[208] and S_5Cl_2 (eq. 22), did not agree with the calculated formula but a

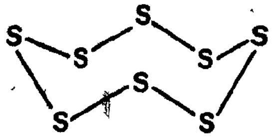
$$CH_2(SH)_2 + S_5Cl_2 \longrightarrow CH_2S_7 + 2\,HCl \qquad (22)$$

solution molecular weight determination supported a monomeric structure. It reportedly polymerized slowly at room temperature,[209] in marked contrast to the high stability of the parent molecule, S_8, which shows no tendency to polymerize in the solid state.

The S_8 Linkage

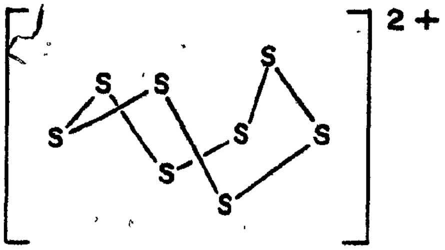
Cyclooctasulfur is the most studied allotrope of sulfur and has been characterized as three polymorphs, labelled (appropriately) α, β, and γ. Many other modifications have been suggested but none have been firmly identified.[24,138] The orthorhombic α form is the thermodynamically most stable allotrope under normal laboratory conditions.[24] When heated to 95.3°C, α-S_8 undergoes a phase transition to monoclinic β-S_8 which melts at 119.6°C.[210] The latter slowly converts to α-S_8 in the solid state.[211] The third polymorph, γ-S_8, was first described in 1890.[212] It can be crystallized as light yellow needles which decompose at room temperature.[24] Both the β and γ modifications of S_8 are metastable relative to the α-form. The crystal structures of α-,[17,191] β-,[213] and γ-[214] S_8 have been reported and show that each polymorph consists of discrete crown-shaped S_8 molecules. For α-S_8 (3) the observed molecular parameters were as follows:[191] bond distance

2.046 Å, bond angle 108.2°, dihedral angle[182] 98.5°.



3

Charged S_8 species are restricted to the paramagnetic monocation S_8^{+} and the diamagnetic ions S_8^{2+} and S_8^{2-}. The monocation is thought to be the source of paramagnetism of sulfur solutions in oleum,[110] although others have contested this view.[28] It has also been detected during the reaction of chlorine with sulfur in a NaCl--$AlCl_3$ melt.[116] The blue S_8^{2+} ion can be prepared, for example, by the oxidation of sulfur by AsF_5 or SbF_5 in liquid HF or SO_2.[215] In the solid state the sulfur cation in $S_8(AsF_6)_2$ adopts a folded eight-membered ring structure with an endo,exo conformation (95).[216] Since the neutral molecule 3 has an exo,exo conformation the structure of the dication can be viewed as that of the S_8 molecule with one end folded up.



95

The octasulfide ion S_8^{2-} has been studied in aqueous and nonaqueous media. Long-chain polysulfide ions readily degrade into smaller chains.[21] Thus solutions of Na_2S_8 in dimethylsulfoxide contain the red S_8^{2-} dianion as well as the blue S_3^- radical anion.[217] The latter species has been observed, together with S_8^{2-}, in dimethylsulfoxide solutions of Na_2S_4 and Na_2S_6 as well. The relative concentration of the S_3^- ion increased with increasing dilution.[217]

Compounds containing a covalently bonded S_8 linkage are scarce and none have been characterized by X-ray methods. There is one reported synthesis of a cyclic molecule containing methylene groups and an S_8 chain, but specific details regarding its ring size, stability, or conformation are not known.[218] The route utilized (eq. 23) has been successful for the preparation of other organic cyclopolysulfanes.[86,138]

$$(CH_2)_n(SH)_2 + S_6Cl_2 \longrightarrow \underset{\text{ring}}{(CH_2)_nS_8} + 2\,HCl \qquad (23)$$

Linkages Longer than S_8

Those polysulfur rings larger than S_8 that have been prepared to date are S_9, S_{10}, S_{11}, S_{12}, S_{18}, and S_{20}. Recently Steudel et al. reported that a mixture of sulfur allotropes S_x (x = 6, 7, 8, 10, 12, 18, 20) could be separated quantitatively (though not on a preparative scale) by high pressure liquid chromatography.[186] Analysis of the products of the thermal decomposition of S_xI_2 (x = 1, 2) or those found in the carbon disulfide-soluble portion of a sulfur melt established the presence of allotropes up to and including S_{26}.[186] Many catenated sulfur species which had previously been identified only in the gas phase by mass spectrometry[75] (up to S_{22}) have now been detected in liquid sulfur. The rings larger than S_8 are discussed collectively in the following pages.

Cycloenneasulfur, S_9, can be prepared as light- and heat-sensitive (mp > 50°C with decomposition into polymeric sulfur) yellow needles (Scheme 2). The reactivity of

<u>Scheme 2</u>

$$\underset{\underline{73}}{Cp_2TiS_5} + HCl \longrightarrow Cp_2Ti(Cl)S_5H$$

$$Cp_2Ti(Cl)S_5H + S_4Cl_2 \longrightarrow HCl + Cp_2Ti(Cl)S_9Cl$$

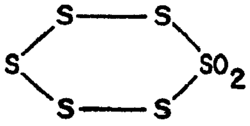
$$Cp_2Ti(Cl)S_9Cl \longrightarrow Cp_2TiCl_2 + S_9$$

the S-Cl bond in chlorosulfanes markedly falls off after S_3Cl_2. The introduction of a catalytic amount of anhydrous hydrogen chloride was sufficient to drive the reaction to completion.[219] The postulated intermediates have not been isolated. No crystal structure has been published for S_9 but the structure is predicted.[220]

Cyclodecasulfur, S_{10}, can be made according to eq. 24.[201] The expected intermediate cyclic sulfone (<u>96</u>) is

$$\underset{\underline{73}}{Cp_2TiS_5} + SO_2Cl_2 \longrightarrow Cp_2TiCl_2 + \frac{1}{2}S_{10} + SO_2 \qquad (24)$$

supposedly unstable towards SO_2 elimination and was not isolated.[21] This allotrope crystallizes as light- and heat-

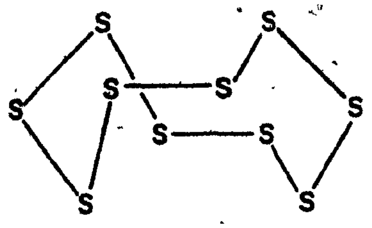


<u>96</u>

sensitive yellow plates, but storage in the dark at -40°C apparently prevents decomposition.[201] Another less convenient route is *via* the reaction of H_2S_6 with S_4Cl_2 (eq. 25).[189] Decomposition of cyclic polysulfur oxides

$$H_2S_6 + S_4Cl_2 \longrightarrow S_{10} + 2\,HCl \qquad (25)$$

such as S_6O and S_7O is also reported to give S_{10} but preparative details of these syntheses have not been given.[221] The crystal structure of S_{10} (<u>97</u>)[221] revealed a distinct alternation of bond lengths that was attributed to dihedral angles ranging from 123° to 77°. The exceptionally large value causes the bond to stretch which in turn strengthens the adjacent bonds.[22,221]



97

Cycloundecasulfur, S_{11}, has been reported but its precise structure is unknown. The synthetic route used is analogous to that employed for S_9 (eq. 26).[24] Presumably

$$\underset{\underline{73}}{(C_5H_5)_2TiS_5} + S_6Cl_2 \longrightarrow (C_5H_5)_2TiCl_2 + S_{11} \qquad (26)$$

a small amount of HCl was used to initiate the reaction.[219]

Cyclododecasulfur, S_{12} (98), was the third cyclic allotrope to be isolated after S_6 and S_8 and crystallizes as dark yellow needles. Its structure is shown below.[222,231] This thermally stable (mp 148°C) allotrope can be prepared by a wide variety of techniques:[222]

(i) from quenched sulfur melts;[190,223,224]

(ii) from the treatment of Cp_2TiS_5 with SCl_2 (plus a little S_6);[201]

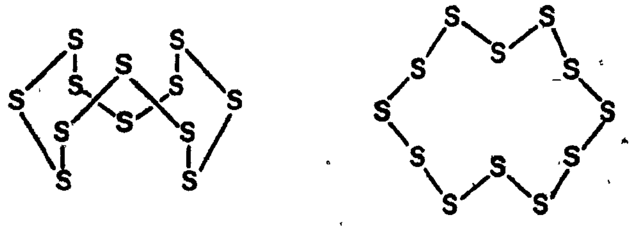
(iii) from the reaction of H_2S_4 with S_2Cl_2[225] or H_2S_8 with S_4Cl_2;[226]

(iv) from the decomposition of S_2I_2 (together with some S_6, S_8, S_{18}, and S_{20});[227]

(v) <u>via</u> ultraviolet irradiation of carbon disulfide or toluene solutions of S_8;[228,229]

(vi) <u>via</u> decomposition of a carbon disulfide solution of S_8O;[230]

(vii) <u>via</u> light-induced decomposition of saturated benzene solutions of S_6.[21]



<u>98</u>

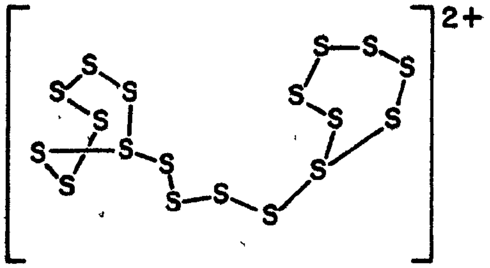
Reports[173,232] suggesting the formation of red S_{16}^{2+} by oxidation of S_8 by peroxodisulfuryl difluoride in fluorosulfuric acid (eq. 27) or by the Lewis acids AsF_5 or SbF_5 in liquid SO_2 or oleum (eq. 28) have been shown to be incorrect. In fact, the resulting cation is S_{19}^{2+}. The

$$2\,S_8 + S_2O_6F_2 \longrightarrow \text{"}S_{16}(SO_3F)_2\text{"} \qquad (27)$$

$$2\,S_8 + 3\,MF_5 \longrightarrow \text{"}S_{16}(MF_6)_2\text{"} + MF_3 \qquad (28)$$

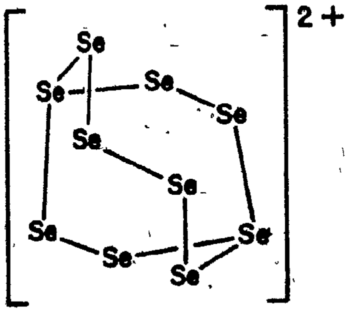
$$M = As,\ Sb$$

X-ray structure showed that it consists of two seven-membered rings connected by a five sulfur atom chain (<u>99</u>).[115] There was a wide variation in bond lengths and angles in the two different rings while the all-<u>cis</u> five-atom bridge



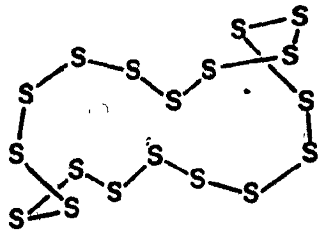
<u>99</u>

had more regular values. The bonds to the three-coordinate sulfur atom are the longest, those adjacent are the shortest, and the remaining bonds of intermediate length alternating from longer to shorter. A similar trend was observed for the Se_{10}^{2+} (<u>100</u>) cation.[233]



<u>100</u>

Cyclooctadecasulfur, S_{18} (<u>101</u>), is also quite thermally stable (mp 128°C with decomposition)[24] and is indefinitely stable in the dark.[138] It is known to exist in two crystalline modifications (α and β). The crystal structures (α,[234] β[235,236]) consist of rings having very similar bond lengths, bond angles, and dihedral angles. The α form



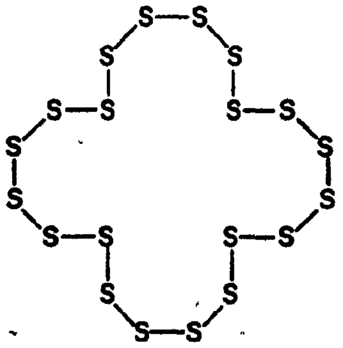
101

can be prepared in very low yield from quenched sulfur melts[237] and isolated as intensely yellow rhombic platelets. The vibrational spectra have been reported.[237] A synthesis from sulfane and chlorosulfane mixtures gave a mixture of S_{18} and S_{20}, both in low yield.[236]

The largest sulfur ring isolated in a crystalline form to date is cycloicosasulfur, S_{20} (102). It can be prepared in very low yield as the carbon disulfide solvate from quenched sulfur melts[237] (crystallizing as pale yellow rods), cocrystallizing with α-S_{18}. Although S_{20} melts at 124°C, decomposition occurs in solution at 35°C.[236] Another route to S_{20} is *via* the reaction of H_2S_{10} with $S_{10}Cl_2$ in the presence of a catalytic amount of anhydrous hydrogen chloride[236] (eq. 29). The crystal structure[236] of S_{20}, consists

$$H_2S_{10} + S_{10}Cl_2 \longrightarrow S_{20} + 2\,HCl \qquad (29)$$

of clover-shaped rings whose form may be visualized as derived from the crown-shaped S_8 molecule. If two adjacent sulfur atoms are removed from the latter then the shape of one quarter of the S_{20} ring is obtained.[193] The vibrational spectra of α-S_{18} and S_{20} have been reported.[238]



102

Overall, the chemical reactivities and thermal stabilities of the established sulfur allotropes follow the sequence shown below.[239] All of the rings decompose to S_8

← increasing thermal stability

S_8 S_{12} S_{18} S_{20} S_7 S_9 S_6 S_{10}

increasing reactivity →

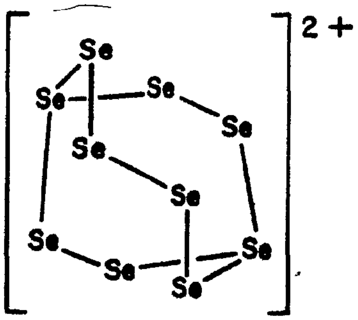
and polymeric, insoluble sulfur.[201] This conversion to the most thermodynamically stable allotrope (S_8) is thought to be a consequence of the ease of cleaving the first sulfur-sulfur bond to produce a chain diradical.[240] For S_8 the bond dissociation energy for ring opening is ca. 138 kJ mol^{-1}.[22] The varying stabilities of the smaller rings may be due to non-optimal bond and dihedral angles.[240] It has been suggested that the surprising stability of the larger sulfur rings S_{18} and S_{20} is due to their low angle strain.[241]

Selenium

Selenium has a tendency, though not as pronounced as for sulfur, to catenate. Neutral species that have been structurally characterized include paramagnetic, gaseous Se_2,[242] grey selenium,[243] Se_6,[244,245] and Se_8 [246] (three forms, α, β, and γ). In sharp contrast to sulfur, though, the Se_8 molecule is not the thermodynamically most stable allotrope of selenium. Grey selenium has this distinction. It is formally analogous to helical (polymeric) sulfur and consists of parallel infinite spiral chains of selenium atoms having a constant bond length of 2.373(5) Å and a constant bond angle of 103.1(2)°.[243] The interchain separation of 3.436(5) Å is significantly less than the van der Waals contact distance of 4.0 Å.[247] The Se_6 and Se_8 molecules are isostructural with their sulfur analogs having chair- and crown-shaped structures, respectively.

A large number of polysulfur cations have been prepared and structurally characterized. For selenium, however, only Se_4^{2+}, Se_8^{2+}, and Se_{10}^{2+} are known.[248] No selenium radical cations analogous to S_4^+ and S_8^+ have been observed spectroscopically.[249] The structures of the Se_4^{2+} [250]

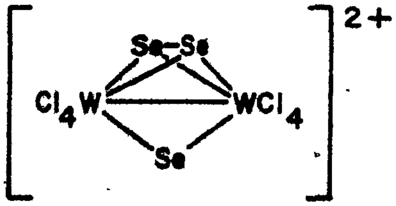
and Se_8^{2+} [251] dications are analogous to those of S_4^{2+} (<u>50</u>) and S_8^{2+} (<u>95</u>). The cyclodecaselenium dication, Se_{10}^{2+} (<u>100</u>), has no sulfur analog. It has a bicyclic structure in the crystal with unequal Se-Se bond distances.[240]



<u>100</u>

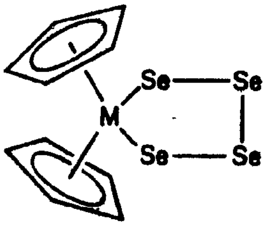
All known reduced polyselenium species are doubly-charged and may be ionic as in alkali-metal or alkaline earth salts of the form MSe_x or M_2Se_x where x = 2,[252] 3,[253,254] or 5 [152] or covalent as in organic compounds.

Although many transition metal disulfanes are known in which there is a metal-S_2-metal linkage, very few selenium examples exist. Notable examples are the cation $[W_2Cl_8(\mu\text{-}Se)(\mu\text{-}Se_2)]^{2+}$ (<u>104</u>)[255] and $[CpMn(CO)_2]_2(\mu\text{-}Se_2)$.[40] The sulfur analog of the latter is also known.[40] Transition-

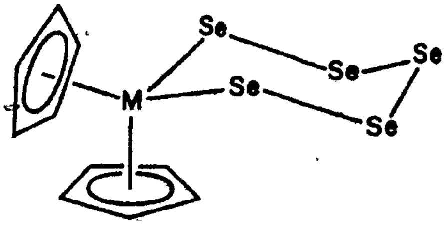


<u>104</u>

metal complexes containing longer bridging polyselenium chains are as yet unknown. A few organometallic compounds containing a chelating Se_4^{2-} and Se_5^{2-} ligand, such as Cp_2MSe_4 [M = Mo (105), W (106)][134] and $Cp_2M'Se_5$ [M' = Ti (107),[163] Zr (108), Hf (109)], are analogs to the previously discussed sulfur complexes. No metal complexes containing



105 M = Mo
106 M = W



107 M = Ti
108 M = Zr
109 M = Hf

bridging Se_x^{2-} ($x \geq 3$) ligands are known. Indeed, only a few organic examples containing chalcogen chains of this length have been isolated. Organic polyselenides up to the tetraselenides have been isolated and include t-butyl triselenide $[(Me_3C)_2CH]_2Se_3$[256] and 1,2,3-triselena[3]ferrocenophane.[257] The sulfur analog of the latter, 41, was mentioned previously.

As in the case of sulfur, metal complexes bearing the metal-Se_xR linkage, where $x \geq 2$ and R is an alkyl or aryl moiety, are uncommon. No complexes having $x \geq 3$ are known. Compounds such as $Os(\eta^1\text{-}Se_2Me)H(CO)_2(PPh_3)_2$,[56] (24) were mentioned in a preceding section.

Summary

It is clear that catenation of sulfur atoms is extensive in its allotropes and in its compounds. The few known organometallic complexes containing catenated polysulfur ligands suggest that sulfur catenation could play a more important role in organometallic chemistry. To explore this possibility several modern reagents were applied to organometallic compounds, specifically to those of titanium(IV), zirconium(IV), and hafnium(IV).

The reagents of the types $>N-S_x-N<$ (where $>N$ is an imidyl or azolyl group) and $>N-SR$ (where $>N$ is an imidyl group and R is an alkyl or aryl moiety) have been used by organic chemists in the reactions of thiols to produce polysulfides (eqs. 30 and 31).[258,261] Bis(hydrosulfido)[259] complexes such as $Cp_2Ti(SH)_2$ (<u>110</u>)[260] are

$$>N-S_x-N< \; + \; 2\,RSH \longrightarrow RS_{x+2}R \; + \; 2\,>NH \qquad (30)$$

$$>N-SR \; + \; R'SH \longrightarrow RSSR' \; + \; >NH \qquad (31)$$

organometallic analogs of organic thiols. As the pages to follow will detail <u>110</u> reacts with the above reagents to give interesting titanacyclopolysulfanes such as Cp_2TiS_5, (<u>73</u>)[103,161-173] and complexes of the types $Cp_2Ti(SSR)_2$ and $Cp_2Ti(SR)(SSSR)$.

The anhydrous lithium polychalcogenides, prepared *in situ* by the reduction of sulfur or selenium with $LiEt_3BH$ (eq. 32), have also recently been exploited by organic chemists for the synthesis of polysulfides and polyselenides from alkyl halides (eq. 33).[262,263] Extension of this

$$xE + 2\,LiEt_3BH \longrightarrow Li_2E_x + 2\,Et_3B + H_2 \qquad (32)$$

E = S, Se
x = 1, 2

$$Li_2E_x + 2RX \longrightarrow RE_xR + 2LiX \qquad (33)$$

technology to organometallic systems has led to the isolation of several new compounds of the types Cp_2ME_5 (E = S, Se) and $(Me_5Cp)_2MS_3$ (M = Ti, Zr, Hf) from the appropriate dichloro precursors.

It will be shown that these new reagents are useful for the synthesis of novel organometallic complexes containing catenated polychalcogen ligands. Several new structural types have been established for this class of compounds. The chemistry of metal polysulfur complexes is much richer than previously thought.

2. EXPERIMENTAL

Physical and Analytical Measurements

^{1}H NMR spectra were recorded on Varian T-60 and T-60A, Bruker WH-90, or a Varian XL-200 instrument. Variable temperature units calibrated with methanol and ethylene glycol gave temperatures that are considered accurate to ±0.5°C. Routine spectra were recorded at 35°C (T-60, T-60A) or 23°C (XL-200). All ^{1}H chemical shifts (δ ppm) are reported relative to internal tetramethylsilane unless otherwise noted and are considered accurate to ±0.05 ppm (T-60, T-60A) and ±0.005 ppm (WH-90, XL-200). Proton decoupled ^{13}C NMR spectra were recorded at 23°C on the Varian XL-200 with chemical shifts (δ ppm) relative to benzene (δ 128.00). The following abbreviations are used to describe ^{1}H NMR signals: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Coupling constants are given in Hertz. Deuterated chlorinated solvents were dried over type 4A molecular sieves. Other NMR solvents were used as received from Merck, Sharp and Dohme Canada Ltd. Air-sensitive samples were dissolved under nitrogen and transferred to a NMR tube which had been previously evacuated and filled with nitrogen. Samples using a $CD_2Cl_2:CFCl_3$ solvent mixture for low temperature ^{1}H NMR studies and those for high temperature studies (above 100°C) were prepared similarly and sealed in vacuo following a freeze-thaw degassing cycle.

Infrared spectra of samples prepared as KBr discs were recorded on a Perkin-Elmer 297 spectrometer. All band positions are reported relative to the 1601 cm^{-1} calibration peak of polystyrene. The following abbreviations are used to describe absorption bands: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder. Visible spectra in the 400-700 nm region were recorded on a Cary 17 instrument.

Mass spectra were recorded on a Hewlett-Packard HP 5980A [for $Cp_2Ti(Cl)SCHMe_2$, <u>114</u>, $(MeCp)_2TiS_5$, <u>74</u>, and $(Me_5Cp)_2HfS_3$, <u>49</u>], a DuPont 21-492B [for $Cp_2Hf(SH)_2$, <u>113</u>] or an LKB 9000 (for all other compounds) spectrometer operating at 70 eV and using direct sample inlet. The reported m/z value for a metal-containing species is the principal ion of the cluster.

Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana; Guelph Chemical Laboratories, Guelph, Ontario; or Galbraith Laboratories, Inc., Knoxville, Tennessee. In many instances acceptable carbon and hydrogen analyses, but somewhat low sulfur analyses, were obtained. Such discrepancies have been noted for other cyclopentadienyl metal complexes with sulfur-containing ligands.[264,265] Molecular weights were determined by Spang Microanalytical Laboratory, Eagle Harbour, Michigan.

Melting points were determined for samples sealed in air in capillary tubes on a Thomas-Hoover Melting Point

Apparatus and are uncorrected.

Materials and Methods

Reaction solvents were dried and deoxygenated by distillation under nitrogen from the appropriate desiccant: hexane over sodium-potassium alloy, toluene and tetrahydrofuran over sodium/benzophenone, and methylene chloride over phosphorus pentoxide.

Titanium trichloride (Alfa, 98+%, H_2 reduced), titanium tetrachloride (J.T. Baker, purified), zirconium tetrachloride (Alfa, reaction grade, 99.6%), and hafnium tetrachloride (Alfa) were used as received. Powdered selenium metal (99.5%) was obtained from Anachemia. The metallocene dichlorides Cp_2MCl_2 [M = Ti, Zr (Alfa); Hf (Strem)] were used as received, as was η-cyclopentadienyltitanium trichloride, $CpTiCl_3$ (Strem). The substituted metallocene dichlorides bis(η-methylcyclopentadienyl)titanium dichloride, $(MeCp)_2TiCl_2$,[266,267] bis(η-trimethylsilylcyclopentadienyl)-titanium dichloride, $(Me_3SiCp)_2TiCl_2$,[266] and 1,1'-methylenebis(η-cyclopentadienyl)titanium dichloride, $CH_2Cp_2TiCl_2$,[268] were prepared according to published procedures with minor modifications *via* the reaction of stoichiometric amounts of the lithium salts of the appropriate diene[269,270] with titanium tetrachloride in tetrahydrofuran solutions. The compound $CH_2Cp_2TiCl_2$ could not be purified by the literature methods.[268] The crude product was therefore used without further purification in all subsequent reactions. Treatment of $CpTiCl_3$ with lithium pentamethylcyclopentadienide in refluxing tetrahydrofuran (two days) gave a mixture of Cp_2TiCl_2 (major product) and (η-cyclopentadienyl)(η-pentamethylcyclopentadienyl)titanium dichloride, $Cp(Me_5Cp)TiCl_2$ (minor product). The latter compound was isolated in 3% yield by column chromatography on silica gel with CH_2Cl_2 as eluent. The literature procedure using (η-pentamethylcyclopentadienyl)-titanium trichloride, $(Me_5Cp)TiCl_3$, and sodium cyclopentadienide in a tetrahydrofuran solution gave $Cp(Me_5Cp)TiCl_2$ in 54% yield.[271] The bis(η-pentamethylcyclopentadienyl)metallocene dichlorides, $(Me_5Cp)_2MCl_2$ (M = Ti,[272,273] Zr,[274] Hf[275]), were prepared by established procedures.

The reagents 1,1'-thiobisbenzimidazole,[258] 1,1'-dithiobisbenzimidazole,[258] 1,1'-thiobisphthalimide,[276] 1,1'-dithiobisphthalimide,[276] N-2-propylthiophthalimide,[277,278] and N-phenylthiosuccinimide[277] were prepared by the literature procedures or received as gifts from Dr. D.N. Harpp (McGill University, Montreal). A sample of N-4-methylphenylthiophthalimide was supplied by Ms. J. Hartgerink.

The following liquid reagents were obtained from the indicated sources and used without additional treatment unless otherwise noted: triethylamine (Anachemia), thiols (Aldrich), pentamethylcyclopentadiene (Aldrich) [also prepared using 2-bromo-2-butene (Aldrich) by the method of Threlkel and Bercaw[279]], methyl lithium in ether (Aldrich, 1.6 M), n-butyl lithium in hexane (Aldrich, 1.6 M), and Super Hydride (Aldrich, 1 M solution of $LiEt_3BH$ in THF).

Hydrogen sulfide gas (Linde) was dried by passing it through a short column of calcium chloride prior to use. Effluent vapours were passed through three scrubbing towers containing: 1) 5 M aqueous sodium hydroxide, 2) saturated aqueous lead acetate, and 3) 5 M aqueous sodium hydroxide before venting into an efficient fume hood. Even with these precautions it was necessary to use a low gas flow.

Deactivated neutral alumina for column chromatography was prepared from activated alumina (Anachemia, 80-200 mesh) according to Coutts et al.[265] Florisil (Fisher, 60-100 mesh) and silica gel (Merck, 70-230 mesh) were used as received. Alumina (Merck, neutral type T) and silica gel (Eastman) TLC plates with fluorescent indicators were also used as received.

All glassware used in the preparation and manipulation of zirconium and hafnium complexes was dried at 120°C overnight and cooled in a nitrogen stream. Dry solvents used in these experiments were purged with nitrogen prior to use.

Unless otherwise noted, all procedures were conducted under an atmosphere of nitrogen (Linde, prepurified) using conventional round-bottomed flasks and established inert-atmosphere bench-top techniques.[280] Reactions were done in appropriately sized three-necked round-bottomed flasks containing a magnetic stirring bar and fitted with a stopcock adaptor and two stoppers unless otherwise stated. Addition of H_2S to reaction solutions was by means of a gas inlet tube. The reaction vessel and contents (and attached pressure-equalizing dropping funnel when required) were evacuated and filled with nitrogen (for at least one cycle) before adding dry solvent. Subsequent attachment of a rubber serum stopper and transferral of solutions to the dropping funnel by syringe was done under a brisk flow of nitrogen. Liquid reagents were added by syringe through the serum stopper.

Solutions of lithium polysulfides or polyselenides were prepared as follows: Super Hydride was slowly added by syringe to stirred sulfur powder (or to a stirred suspension in a small volume of THF when indicated) or grey selenium powder. The resulting exothermic and effervescent reaction was stirred for ca. 20 minutes before a solution of the metallocene dichloride was added dropwise. Following the addition the flask in which the metallocene dichloride solution was prepared, the syringe used to transfer the solution to the dropping funnel, and the dropping funnel itself were washed with ca. 10 mL of THF and the washings added to the reaction mixture.

All reactions generated compounds which were malodorous to varying degrees and consequently were conducted in a fume hood. This precaution was especially important in the syntheses of the selenium derivatives. In the preparation of the lithium polyselenide reagent from elemental selenium and Super Hydride a red solid, presumed to be elemental selenium derived from the decomposition of volatile selenium compounds, formed in the attached Tygon tubing.

In some reactions sulfur was used in excess or was a by-product and was isolated during the work-up of the experiment. Its identity was confirmed by TLC (alumina) using hexanes as eluent.

Product yields are based on the limiting reactants.

I) Metal Bis(hydrosulfides)

(A) Bis(η-cyclopentadienyl)bis(hydrosulfido)titanium(IV), $Cp_2Ti(SH)_2$, 110

A red solution of Cp_2TiCl_2 (6.04 g, 24.3 mmol) in THF (500 mL) was treated with H_2S for 10 minutes. Slow addition of Et_3N (6.90 mL, 49.6 mmol) caused the solution to darken. Hydrogen sulfide was passed through the solution for 90 more minutes. In order to remove excess H_2S, nitrogen gas was bubbled through the red-black solution for 30 minutes. Rapid filtration in air through Celite, followed by washing the filter cake with THF (4 x 10 mL) gave a malodorous red-black solution while an off-white insoluble residue remained on the fritte. The combined filtrate and washings were stripped to dryness by rotary evaporation and the malodorous brown powder (5.55 g, 93%, dec. ca. 130°C) (lit.[260] dec. 150-

160°C) was dried by pumping on it overnight. Since excessive loss of compound occurred during recrystallization, the crude product was the analytical sample and was used in all subsequent reactions.

^{1}H NMR ($CDCl_3$): δ 6.28 (s, 10H, C_5H_5), 3.38 (s, 2H, SH).

IR (KBr): 3130 (w), 3090 (m), 2960 (w), 2920 (w), 2530 (w), 1725 (w), 1438 (s), 1382 (w), 1367 (m), 1288 (m), 1263 (m), 1160 (w), 1130 (w), 1075 (w), 1025 (s, sh), 1018 (s), 930 (w), 822 (vs), 730 (w), 674 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\cdot}$, 244 (3.8); $M^{+\cdot}-2H^{\cdot}$, 242 (4.4); $M^{+\cdot}-H^{\cdot}-S^{\cdot}$, 211 (35.5); $M^{+\cdot}-2H^{\cdot}-S^{\cdot}$, 210 (45.8); $M^{+\cdot}-C_5H_5^{\cdot}$, 179 (19.7); $M^{+\cdot}-2H^{\cdot}-2S^{\cdot}$, 178 (100.0); $M^{+\cdot}-2H^{\cdot}-S^{\cdot}-C_5H_5^{\cdot}$, 145 (34.9); $M^{+\cdot}-2H^{\cdot}-2S^{\cdot}-C_5H_5^{\cdot}$, 113 (14.8); $M^{+\cdot}-2H^{\cdot}-S^{\cdot}-2C_5H_5^{\cdot}$, 80 (12.4); $H_2S^{+\cdot}$, 34 (44.2).

Visible spectrum max. (CH_2Cl_2): 476 nm (ε 3.0 x 10^3).

Anal. (%): Calcd. for $C_{10}H_{12}S_2Ti$: C, 49.18; H, 4.95; S, 26.26. Found: C, 49.97; H, 5.18; S, 23.18, 23.41.

(B) Bis(η-cyclopentadienyl)bis(hydrosulfido)zirconium(IV), $Cp_2Zr(SH)_2$, 111, and 1,3-Bis[bis(η-cyclopentadienyl)zircona(IV)]cyclotetrasulfane, $(Cp_2ZrS)_2$, 112*

A solution of Cp_2ZrCl_2 (4.38 g, 15.0 mmol) in THF (80 mL) was treated with H_2S for about 10 minutes. Slow

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*An alternative name for 112 is bis(μ-thio)bis[bis(η-cyclopentadienyl)zirconium(IV)].

addition of Et_3N (4.20 mL, 30.2 mmol) caused copious quantities of Et_3NHCl to precipitate. To assist with the stirring of the thick slurry additional solvent (50 mL) was introduced. After stirring for one hour the slurry was filtered and the filter cake was washed with 20 mL of solvent. Removal in vacuo of the volatiles from the clear yellow filtrate gave a yellow-green microcrystalline solid. This was redissolved in excess THF to give an emerald green solution which was concentrated in vacuo at ambient temperature until small crystals appeared. Storage at -20°C for five days gave large yellow-green crystals of $Cp_2Zr(SH)_2$, 111, (1.70 g). By repeating the concentration and cooling cycle on the mother liquor an additional crop of 0.26 g was isolated. Further concentration of the filtrate resulted in the formation of turquoise microcrystals of $(Cp_2ZrS)_2$, 112, which were isolated by filtration (0.08 g). Refrigeration (-20°C) of the emerald green mother liquor gave a mixture of small yellow crystals and turquoise microcrystals. These were redissolved by refluxing in their mother liquor for four hours. Cooling for 11 days at -20°C gave turquoise microcrystals (0.60 g) contaminated by a few very small yellow crystals which were easily removed by hand after filtration. The overall yield of $Cp_2Zr(SH)_2$, 111, was 1.96 g (45%). Decomposition without melting occurs at ca. 145°C.

^1H NMR ($CDCl_3$): δ 6.28 (s, 10H, C_5H_5), 1.94 (s, 2H, SH).

IR (KBr): 3160 (s), 2550 (br, vw), 1854 (vw), 1758 (w), 1660 (w), 1428 (s), 1358 (vw), 1262 (w), 1395 (vw), 1112 (w), 1051 (vw), 1015 (sh, s), 1002 (s), 920 (m), 818 (vs), 802 (vs), 721 (m), 663 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): The mass spectrum was consistent with the presence of a small amount of $(Cp_2ZrS)_2$, <u>112</u>, and possibly $(Cp_2Zr)_2OS$. However, a molecular ion was observed at m/z = 286 as well as the fragment $M^{+\bullet}-H^{\bullet}-S^{\bullet}$ (m/z = 253) and $M^{+\bullet}-2H^{\bullet}-S^{\bullet}$ (m/z = 252). The most prominent ions are listed here for completeness: 504 (14.0), 488 (4.3), 439 (34.8), 423 (14.3), 405 (8.2), 374 (13.1), 358 (4.7), 347 (1.4), 325 (2.4), 308 (3.1), 286 (13.6), 253 (100.0), 252 (100.0), 225 (8.3), 220 (10.9), 219 (10.2), 187 (55.8), 161 (11.1), 147 (5.8).

Anal. (%): Calcd. for $C_{10}H_{12}S_2Zr$: C, 41.77; H, 4.21; S, 22.30. Found: C, 42.17; H, 4.49; S, 21.72.

The overall yield of $(Cp_2ZrS)_2$, <u>112</u>, was 0.68 g (18%); decomposition occurred at 210-215°C.

^1H NMR ($CDCl_3$): δ 6.44 (s, 20H, C_5H_5).

IR (KBr): 3108 (w), 3063 (w), 1822 (br, vw), 1712 (br, w), 1442 (m), 1434 (m), 1380 (vw), 1360 (w), 1260 (vw), 1124 (w), 1061 (vw), 1016 (s), 1008 (s), 918 (w), 888 (w), 842 (m), 830 (s), 818 (sh, s), 800 (vs), 780 (vs), 730 (s), 667 (w), 644 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 504 (47.9); $M^{+\bullet}-C_5H_5^{\bullet}$, 439 (100.0); $M^{+\bullet}-C_5H_5^{\bullet}-2H^{\bullet}-S^{\bullet}$, 405 (18.8);

$M^{+\bullet}-2C_5H_5^{\bullet}$, 374 (33.7); $M^{+\bullet}-3C_5H_5^{\bullet}$, 308 (6.8); $M^{+\bullet}-2C_5H_5^{\bullet}-Zr^{\bullet}$, 283 (2.3); $M^{+\bullet}-2C_5H_5^{\bullet}-Zr^{\bullet}-S^{\bullet}$, 253 (8.1); $M^{+\bullet}-3C_5H_5^{\bullet}-Zr^{\bullet}-S^{\bullet}$, 187 (9.3); $M^{+\bullet}-4C_5H_5^{\bullet}-Zr^{\bullet}-S^{\bullet}$, 122 (0.4).

Visible spectrum max. (CH_2Cl_2): 594 nm (ε 70).

Anal. (%): Calcd. for $C_{10}H_{10}SZr$: C, 47.39; H, 3.98; S, 12.65. Found: C, 46.79; H, 4.26; S, 12.85.

(C) Reaction of $(Cp_2ZrS)_2$, 112, with H_2S in a ^1H NMR Tube

A ^1H NMR tube containing a sample of 112 was evacuated and then filled with nitrogen. Deuterochloroform was passed several times through a short column of type 4A molecular sieves and added to the tube. The resulting turquoise solution exhibited a single η^5-cyclopentadienyl resonance at δ 6.47 [relative to $\delta(CHCl_3)$ = 7.24]. Hydrogen sulfide gas was added to displace the nitrogen atmosphere in the NMR tube which was capped and shaken. The solution became yellow in colour and the peak due to 112 was replaced by four signals at δ 6.31, 6.17, 1.97, and 0.84 [all relative to $\delta(CHCl_3)$ = 7.24] within 15 minutes. The peaks at δ 6.31 and 1.97 were the same within experimental error (shifts and relative intensities) as those for an authentic sample of $Cp_2Zr(SH)_2$, 111. The signal at δ 6.17 could not be assigned but may be due to impurities formed from reaction with traces of water or oxygen. The signal at δ 0.84 is attributed to H_2S.[281] After standing for 24 hours, the signals due to

111 and H_2S were still clearly visible, with no trace of 112, but the signal at δ 6.17 was much more intense. Evaporation of the solvent and H_2S by means of a nitrogen stream gave a yellow microcrystalline solid. This sample, in fresh $CDCl_3$, exhibited resonances at δ 6.28, 6.16, and 1.94 with the signal at δ 6.16 now being the most intense signal.

Attempts to repeat this experiment on a preparative scale were unsuccessful.

(D) Attempted Synthesis of Bis(η-cyclopentadienyl)-bis(hydrosulfido)hafnium(IV), $Cp_2Hf(SH)_2$, 113

Cp_2HfCl_2 (0.5023 g, 1.323 mmol) in THF (25 mL) was treated with H_2S for two minutes. Triethylamine (0.37 mL, 2.7 mmol) was added by syringe into the colourless solution. A white precipitate formed immediately and the reaction mixture became warm. Hydrogen sulfide was bubbled through the slurry for an additional 25 minutes, and the mixture was filtered through Celite. The filtrate was reduced to dryness *in vacuo*, leaving a very malodorous white solid. This was extracted with THF (65 mL) and the resultant slurry filtered; a malodorous residue (0.117 g) was collected and discarded. The filtrate was evaporated *in vacuo* to about 10 mL volume and cooled at -20°C overnight to give after removal of the supernatant by syringe a malodorous white microcrystalline solid (0.088 g). The product decomposes at about 150°C with evolution of H_2S (the gases evolved gave a positive test with lead acetate paper).

^1H NMR ($CDCl_3$): δ 6.06 (s, 10.8H, C_5H_5), 0.58 (s, 1.0H, SH).

IR (KBr): 3100 (m), 3085 (m), 2850 (vw), 2705 (vw), 2565 (vw), 2415 (vw), 2280 (vw), 2080 (vw), 1840 (w, br), 1730 (w, br), 1630 (w, br), 1446 (m, sh), 1438 (m), 1383 (vw), 1362 (m), 1268 (w), 1238 (vw), 1128 (vw), 1071 (w), 1062 (w), 1020 (s), 1013 (s), 962 (w), 918 (w), 893 (w), 852 (s), 849 (s), 842 (s), 810 (vs), 776 (vs), 692 (vw), 668 (m) cm^{-1}.

Mass spectrum: Fragments containing more than one Hf atom were observed up to at least m/z = 600. No $M^{+\cdot}$ ion at m/z = 376 expected for $Cp_2Hf(SH)_2$ was observed.

Anal. (%): Calcd. for $C_{10}H_{12}HfS_2$: C, 32.04; H, 3.23; S, 17.11. Found: C, 23.12; H, 2.67; S, 7.52. Calcd. for $C_{10}H_{11}Hf_2S$: C, 23.09; H, 2.13; S, 6.16.

II) Metal Thiolates: $Cp_2Ti(Cl)SR$, $Cp_2Ti(SR)_2$, and $Cp_2M[S(CH_2)_3S]$ (M = Ti, Zr)

(A) Bis(η-cyclopentadienyl)chloro(2-propylthiolato)-titanium(IV), $Cp_2Ti(Cl)SCHMe_2$, 114

To a solution of Cp_2TiCl_2 (0.2467 g, 0.9908 mmol) in THF (20 mL) was added by syringe 2-propanethiol (0.20 mL, 2.1 mmol) followed by Et_3N (0.30 mL, 2.2 mmol). The solution was refluxed under nitrogen for 23 hours. After cooling, the mixture was filtered through a pad of silica gel. The filter cake was washed with ca. 50 mL of THF. The red filtrate was reduced to dryness *in vacuo* to give red, malodorous, solid $Cp_2Ti(Cl)SCHMe_2$, 114, (0.222 g, 78%), pure by ^1H NMR spectroscopy. This was dissolved in 1:1 hexanes:CH_2Cl_2 and applied to a chromatography column (deactivated alumina). Elution with 1:1 hexanes:CH_2Cl_2 gave a red solution which was collected under nitrogen. Slow evaporation of the solvent *in vacuo* gave 114 as red crystals, mp 150-152°C with decomposition.

^1H NMR ($CDCl_3$): δ 6.33 (s, 10H, C_5H_5), 4.20 (m, 1H, J = 7 Hz, CH), 1.35 (d, 6H, J = 7 Hz, CH_3).

IR (KBr): 3125 (vw), 3108 (m), 3100 (m), 3090 (m), 2965 (m), 2955 (m), 2925 (w), 2910 (w), 2860 (w), 1460 (w), 1452 (m, sh), 1444 (m), 1379 (vw), 1361 (w), 1258 (m, br), 1233 (m), 1152 (m), 1129 (vw), 1069 (vw), 1040 (w), 1029 (w, sh), 1023 (w), 1014 (m), 942 (w, br), 868 (w), 829 (w), 848 (m), 838 (m), 824 (s), 807 (vs), 717 (m, br), 652 (vw, br), 628 (vw) cm^{-1}. The absorption at 717 cm^{-1} may be due to the TiOTi moiety which is known to absorb in this region.[161]

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 288 (28.7); $M^{+\bullet}-C_3H_7^{\bullet}-S^{\bullet}$, 213 (100.0); $M^{+\bullet}-C_5H_5^{\bullet}-C_3H_6$, 181 (15.3); $M^{+\bullet}-C_3H_7^{\bullet}-S^{\bullet}-Cl^{\bullet}$, 178 (4.1); $M^{+\bullet}-C_3H_7^{\bullet}-S^{\bullet}-C_5H_5^{\bullet}$, 148 (11.8); $M^{+\bullet}-C_3H_7^{\bullet}-Cl^{\bullet}-C_5H_5^{\bullet}$, 145 (19.3); $M^{+\bullet}-C_3H_7^{\bullet}-Cl^{\bullet}-2C_5H_5^{\bullet}$, 80 (2.3); $C_3H_7^+$, 43 (27.0); $C_3H_5^+$, 41 (28.1);

$C_3H_3^+$, 39 (40.5).

Anal. (%): Calcd. for $C_{13}H_{17}ClSTi$: C, 54.09; H, 5.94; Cl, 12.28; S, 11.11. Found: C, 53.06; H, 6.12; Cl, 12.86; S, 10.44.

(B) Bis(η-cyclopentadienyl)bis(2-propylthiolato)-titanium(IV), $Cp_2Ti(SCHMe_2)_2$, 115

A solution of 2-propanethiol (2.0 mL, 2.11 mmol) in THF (50 mL) was cooled in a dry ice / acetone bath. To the cold stirred solution was added methyl lithium (1.5 mL of a 1.6 M solution in ether, 2.4 mmol). After stirring for five minutes the cold bath was removed and the reaction allowed to warm to room temperature. Stirring was continued for an additional 10 minutes. The solution was cooled by means of an ice bath and a solution of Cp_2TiCl_2 (0.2489 g, 0.9996 mmol) in THF (50 mL) was added dropwise. A reaction took place immediately and the reaction solution became purple in colour. Stirring was continued at ambient temperature for 23 hours after which the volatiles were removed *in vacuo*. The residue was dissolved in 1:1 hexanes:CH_2Cl_2 and transferred to a chromatography column (deactivated alumina). Elution with the same solvent mixture gave a purple solution of $Cp_2Ti(SCHMe_2)_2$, 115, in the first band and a red solution of $Cp_2Ti(Cl)SCHMe_2$, 114, in the second band, both of which were collected under nitrogen. The solvent was removed from each *in vacuo* or by means of evaporation in a stream of nitrogen until the onset of crystallization. Cooling at -20°C overnight gave deep purple, malodorous crystals of the dithiolate <u>115</u> (0.056 g, 17%, mp 144-146°C) and red microcrystals of the monothiolate <u>114</u> (0.014 g, 5%, mp 156-158°C with decomposition). For spectroscopic details of the latter compound, see the following experiment. The analytical sample of <u>115</u> was obtained by sublimation at 90°C (0.03 torr, 4.0 Pa).

^{1}H NMR ($CDCl_3$): δ 6.15 (s, 10H, C_5H_5), 3.65 (m, 2H, J = 6 Hz, CH), 1.30 (d, 12H, J = 6 Hz, CH_3).

IR (KBr): 3122 (w), 3108 (vw), 2970 (m), 2955 (m), 2920 (m), 2910 (m), 2858 (m), 1850 (vw, br), 1750 (vw, br), 1635 (vw, br), 1448 (m), 1440 (m, sh), 1375 (w), 1368 (w), 1359 (m), 1304 (vw), 1266 (vw), 1255 (vw), 1241 (m, sh), 1238 (m), 1153 (m), 1148 (w, sh), 1101 (vw), 1059 (m), 1042 (w, sh), 1038 (m), 1026 (s), 1013 (m), 881 (vw), 856 (m), 848 (vw), 842 (w, sh), 839 (m), 831 (vw), 823 (w), 811 (vs), 630 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 328 (14.3); $M^{+\bullet}-C_3H_7^{\bullet}$, 285 (1.4); $M^{+\bullet}-C_3H_7^{\bullet}-S^{\bullet}$, 253 (8.5); $M^{+\bullet}-C_3H_7^{\bullet}-C_3H_6$, 243 (3.0); $M^{+\bullet}-C_3H_7^{\bullet}-C_3H_6-S^{\bullet}$, 211 (4.0); $M^{+\bullet}-2C_3H_7^{\bullet}-S^{\bullet}$, 210 (3.3); $M^{+\bullet}-(C_3H_7)_2S_2$, 178 (100.0); $(C_3H_7)_2S_2^{+\bullet}$, 150 (1.1); $M^{+\bullet}-2C_3H_7^{\bullet}-S^{\bullet}-C_5H_5^{\bullet}$, 145 (23.8); $(C_3H_7)_2S^{+\bullet}$, 118 (1.5); $M^{+\bullet}-2C_3H_7^{\bullet}-2S^{\bullet}-C_5H_5^{\bullet}$, 113 (7.6); $M^{+\bullet}-2C_3H_7^{\bullet}-S^{\bullet}-2C_5H_5^{\bullet}$, 80 (4.6); $C_3H_7^+$, 43 (10.5). Metastable ions, m/z: 247.6 (m/z = 328 → m/z = 285), 118.1

(m/z = 178 → m/z = 145), 96.6 (m/z = 328 → m/z = 178), 71.7 (m/z = 178 → m/z = 113).

Anal. (%): Calcd. for $C_{16}H_{24}S_2Ti$: C, 58.52; H, 7.37; S, 19.53. Found: C, 57.88; H, 7.68; S, 17.93.

(C) Bis(η-cyclopentadienyl)chloro(2-methyl-2-propylthiolato)titanium(IV), $Cp_2Ti(Cl)SCMe_3$, 116

A solution of 2-methyl-2-propanethiol (0.24 mL, 2.13 mmol) in THF (75 mL) was cooled in a dry ice / acetone bath. Methyl lithium (1.5 mL of a 1.6 M solution in ether, 2.4 mmol) was added by syringe. The cooling bath was removed and the solution was allowed to warm to ambient temperature. Stirring was continued for five hours. A solution of Cp_2TiCl_2 (0.2495 g, 1.002 mmol) in THF (20 mL), prepared under nitrogen, was added dropwise to the Me_3CSLi solution. Immediate reaction caused the reaction solution to turn a purple colour. The solution was refluxed for 13 hours. Volatiles were removed *in vacuo* from the then deep red solution. A CH_2Cl_2 extract of the residue was filtered through a pad of deactivated alumina which was then washed with 10 mL of solvent. The deep red filtrate was evaporated *in vacuo*, then dissolved in a minimum of 1:1 hexanes:CH_2Cl_2. This solution was transferred to a chromatography column (deactivated alumina). A red solution of $Cp_2Ti(Cl)SCMe_3$, 116, was removed with 1:1 hexanes:CH_2Cl_2. Concentration and cooling at -20°C gave deep red crystals (0.028 g, 9%, mp 112-118°C).

^{1}H NMR ($CDCl_3$): δ 6.39 (s, 10H, C_5H_5), 1.60 (s, 9H, CH_3).

IR (KBr): 3095 (w, br), 2995 (vw), 2965 (w), 2935 (vw), 2890 (vw), 2860 (vw), 1469 (vw), 1447 (m, br), 1363 (w), 1259 (w), 1152 (w), 1139 (vw, br), 1106 (vw, br), 1070 (vw, br), 1036 (vw, sh), 1027 (m), 1013 (m), 868 (w, sh), 852 (m, sh), 841 (m, sh), 824 (m, sh), 811 (vs), 718 (s, br) cm^{-1}. The absorption at 718 cm^{-1} may be due to the TiOTi moiety which is known to absorb in this region.

Mass spectrum, m/z (rel. intensity): $M^{+\cdot}$, 302 (6.6); $M^{+\cdot}-Cl^{\cdot}$, 267 (0.6); $M^{+\cdot}-C_4H_8$, 246 (2.5); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}$, 213 (58.5); $M^{+\cdot}-C_4H_9^{\cdot}-Cl^{\cdot}$, 210 (64.2); $M^{+\cdot}-C_4H_9^{\cdot}-C_5H_5^{\cdot}-C_4H_8$, 181 (13.2); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}-Cl^{\cdot}$, 178 (9.0); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}-C_5H_5^{\cdot}$, 148 (34.3); $M^{+\cdot}-C_4H_9^{\cdot}-Cl^{\cdot}-C_5H_5^{\cdot}$, 145 (21.4); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}-Cl^{\cdot}-C_5H_5^{\cdot}$, 113 (3.8); $C_4H_{10}S^{+\cdot}$, 90 (32.5); $C_3H_7S^{+}$, 75 (13.1); $C_4H_9^{+}$, 57 (100.0); $C_3H_5^{+}$, 41 (72.2). Metastable ions, m/z: 116.2 (m/z = 181 → m/z = 145), 102.8 (m/z = 213 → m/z = 148), 100.6 (m/z = 210 → m/z = 145), 29.5 (m/z = 57 → m/z = 41).

Anal. (%): Calcd. for $C_{14}H_{19}ClSTi$: C, 55.55; H, 6.33; Cl, 11.71; S, 10.59. Found: C, 55.51; H, 6.41; Cl, 11.75; S, 10.37.

(D) Bis(η-cyclopentadienyl)bis(2-methyl-2-propylthiolato)titanium(IV), $Cp_2Ti(SCMe_3)_2$, 117

A solution of 2-methyl-2-propanethiol (0.70 mL, 6.2 mmol) in THF (50 mL) was cooled in an ice bath. To this was added n-butyl lithium (4.0 mL of a 1.6 M solution in hexane, 6.4 mmol). The ice bath was removed and stirring was continued for two hours. A solution of Cp_2TiCl_2 (0.2488 g; 0.9992 mmol) in THF (50 mL) was added dropwise causing the reaction solution to become purple in colour. Stirring was continued for one more hour. Filtration through activated alumina followed by washing of the filter pad with 10 mL of THF gave a purple solid. All volatiles were removed in vacuo. The residue was extracted with 2 x 20 mL of dry CH_2Cl_2, filtered through Celite, and the filter cake washed with 20 mL of solvent. The solvent was evaporated in vacuo from the combined filtrate and washings. Recrystallization of the residue from anhydrous diethyl ether gave malodorous, slightly air-sensitive purple microcrystals (0.229 g, 64%, mp 176-178°C). An analytical sample was obtained by sublimation at 75°C (0.03 torr, 4.0 Pa).

^1H NMR ($CDCl_3$): δ 6.20 (s, 10H, C_5H_5), 1.52 (s, 18H, CH_3).

IR (KBr): 3115 (vw), 2985 (vw, sh), 2965 (m), 2935 (vw, sh), 2910 (m), 2885 (w), 2850 (w), 1830 (vw, br), 1730 (vw, br), 1470 (w), 1460 (w, sh), 1450 (m), 1439 (w, sh), 1383 (w), 1365 (w, sh), 1356 (m), 1260 (w), 1208 (w), 1198 (w), 1160 (m), 1147 (m, sh), 1132 (w, sh), 1070 (vw), 1028 (m), 1016 (m), 913 (vw), 840 (m), 821 (m), 808 (vs), 787 (w, sh), 661 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\cdot}$, 356 (8.4); $M^{+\cdot}-C_4H_8$, 300 (1.0); $M^{+\cdot}-C_4H_9^{\cdot}$, 299 (3.3); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}$, 267 (3.0); $M^{+\cdot}-C_4H_9^{\cdot}-C_4H_8$, 243 (13.6); $M^{+\cdot}-C_4H_9^{\cdot}-S^{\cdot}-C_4H_8$, 211 (20.0); $M^{+\cdot}-2C_4H_9^{\cdot}-S^{\cdot}$, 210 (12.7); $M^{+\cdot}-2C_4H_9^{\cdot}-2S^{\cdot}$, 178 (100.0); $M^{+\cdot}-2C_4H_9^{\cdot}-S^{\cdot}-C_5H_5^{\cdot}$, 145 (29.2); $M^{+\cdot}-2C_4H_9^{\cdot}-2S^{\cdot}-C_5H_5^{\cdot}$, 113 (6.4); $C_4H_{10}S^{+\cdot}$, 90 (4.4); $M^{+\cdot}-2C_4H_9^{\cdot}-S^{\cdot}-2C_5H_5^{\cdot}$, 80 (3.8); $C_4H_9^+$, 57 (29.9); $C_3H_5^+$, 41 (21.6). Metastable ions, m/z: 251.1 (m/z = 356 → m/z = 299), 197.5 (m/z = 299 → m/z = 243), 166.8 (m/z = 267 → m/z = 211), 150.9 (m/z = 210 → m/z = 178), 71.7 (m/z = 178 → m/z = 113), 29.5 (m/z = 57 → m/z = 41).

Anal. (%): Calcd. for $C_{18}H_{28}S_2Ti$: C, 60.65; H, 7.92; S, 17.99. Found: C, 60.59; H, 7.83; S, 17.82.

(E) Bis(η-cyclopentadienyl)bis(phenylthiolato)titanium(IV), $Cp_2Ti(SPh)_2$, 118

This compound was prepared by the reported method of Giddings[282] from Cp_2TiCl_2 (0.1271 g, 0.5104 mmol), PhSH (0.15 mL, 1.4 mmol), and Et_3N (0.20 mL, 1.4 mmol) in refluxing toluene. Chromatography on deactivated alumina with elution with 1:1 hexanes:CH_2Cl_2 gave two bands: a purple one followed by a slower moving red band which was eluted with CH_2Cl_2. The ^1H NMR of the residue from the red fraction indicated the presence of several compounds and this fraction was not examined further. The volume of the purple eluate was reduced in vacuo until the onset of crystallization. Cooling (-20°C) overnight gave the product as a maroon microcrystalline solid (0.128 g, 63%, mp 194-196°C) (lit.[282] 199-201°C).

^1H NMR ($CDCl_3$): δ 7.3 (m, 10H, C_6H_5), 5.98 (s, 10H, C_5H_5).

IR (KBr): 3120 (w), 3065 (w), 3050 (w), 3040 (w), 2995 (vw), 2925 (vw), 2955 (vw), 1755 (vw, br), 1578 (m), 1564 (w), 1478 (m), 1463 (m), 1459 (w, sh), 1440 (w, sh), 1438 (m), 1434 (m), 1363 (w), 1302 (w), 1261 (w), 1171 (w), 1160 (vw), 1152 (vw), 1129 (w), 1083 (m), 1062 (m), 1027 (s, sh), 1022 (s), 1016 (s), 997 (w), 978 (vw), 965 (vw), 920 (w, br), 850 (m), 837 (s, sh), 827 (vs, sh), 822 (vs), 743 (vs), 698 (s), 689 (s) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 396 (7.3); $M^{+\bullet}-C_6H_5S^\bullet$, 287 (68.8); $M^{+\bullet}-C_6H_5^\bullet-S^\bullet-C_5H_5^\bullet$, 222 (9.7); $M^{+\bullet}-C_6H_5^\bullet-S^\bullet-C_5H_5^\bullet-H^\bullet$, 221 (16.0); $M^{+\bullet}-C_6H_5^\bullet-S^\bullet-C_5H_5^\bullet-H_2S$, 188 (11.7); $M^{+\bullet}-2C_6H_5S^\bullet$, 178 (100.0); $M^{+\bullet}-2C_6H_5^\bullet-S^\bullet-C_5H_5^\bullet$, 145 (6.9); $M^{+\bullet}-2C_6H_5^\bullet-2S^\bullet-C_5H_5^\bullet$, 113 (8.4); $C_6H_6S^{+\bullet}$, 110 (15.8); $C_6H_5S^+$, 109 (6.9); $M^{+\bullet}-2C_6H_5^\bullet-S^\bullet-2C_5H_5^\bullet$, 80 (5.9). Metastable ions, m/z: 208.0 (m/z = 396 → m/z = 287), 159.2 (m/z = 222 → m/z = 188), 110.4 (m/z = 287 → m/z = 178), 71.7 (m/z = 178 → m/z = 113).

Visible spectrum max. (CH_2Cl_2): 537 nm (ε 5.2 x 10^3).

Anal. (%): Calcd. for $C_{22}H_{20}S_2Ti$: C, 66.66; H, 5.09; S, 16.18. Found: C, 67.02; H, 5.02; S, 16.22.

(F) Bis(η-cyclopentadienyl)bis(4-methylphenylthiolato)titanium(IV), $Cp_2Ti(SC_6H_4Me)_2$, 119

This compound was prepared by the general method of Köpf and Schmidt[283] from Cp_2TiCl_2 (0.2496 g, 1.002 mmol), $4\text{-}MeC_6H_4SH$ (0.2491 g, 2.005 mmol) and Et_3N (0.29 mL, 2.1 mmol) in THF. The crude reaction product contained a small amount of $Cp_2Ti(Cl)(S\text{-}4\text{-}C_6H_4Me)$ (by ^1H NMR) which was removed during chromatography on alumina. The desired product 119 was eluted with 1:1 hexanes:CH_2Cl_2 as a purple band. This fraction was stripped to dryness on a rotary evaporator and recrystallized in air from CH_2Cl_2 / CH_3OH at -20°C to give lustrous purple plates (0.203 g, 48%). This was recrystallized twice from CH_2Cl_2 / hexanes mixtures to give the analytical sample as red-black crystals, mp 182-184°C (lit.[283] 198.5-199.5°C).

^1H NMR ($CDCl_3$): δ 7.25 (AB quartet, 8H, J = 8 Hz, C_6H_4), 6.03 (s, 10H, C_5H_5), 2.35 (s, 6H, CH_3).

IR (KBr): 3120 (w), 3065 (vw), 3045 (vw), 3030 (w), 3010 (vw), 2970 (vw), 2920 (w), 2860 (w), 2490 (vw), 1645 (w, br), 1590 (vw), 1555 (w, br), 1485 (s), 1440 (m, br), 1420 (vw), 1393 (w), 1365 (w), 1298 (vw), 1210 (vw), 1175 (m), 1155 (vw), 1128 (vw), 1113 (vw), 1100 (w), 1080 (m), 1065 (w), 1020 (m, sh), 1013 (s), 980 (vw, br), 960 (vw, br), 939 (vw), 918 (w), 850 (w), 818 (vs), 804 (vs), 790 (m, sh), 701 (vw), 626 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 424

(13.7); $M^{+\bullet}-C_5H_5^\bullet$, 359 (1.4); $M^{+\bullet}-C_7H_7S^\bullet$, 301 (98.4); $M^{+\bullet}-C_7H_7^\bullet-S^\bullet-C_5H_5^\bullet$, 236 (10.0); $M^{+\bullet}-C_7H_7^\bullet-S^\bullet-C_5H_5^\bullet-H^\bullet$, 235 (14.8); $M^{+\bullet}-C_7H_7^\bullet-S^\bullet-C_5H_5^\bullet-H_2S$, 202 (7.9); $M^{+\bullet}-2C_7H_7S^\bullet$, 178 (100.0); $M^{+\bullet}-2C_7H_7^\bullet-S^\bullet-C_5H_5^\bullet$, 145 (6.8); $C_7H_8S^{+\bullet}$, 124 (10.9); $C_7H_7S^+$, 123 (6.6); $M^{+\bullet}-2C_7H_7^\bullet-2S^\bullet-C_5H_5^\bullet$, 113 (6.7); $C_7H_7^+$, 91 (14.7); $M^{+\bullet}-2C_7H_7^\bullet-S^\bullet-2C_5H_5^\bullet$, 80 (4.4). Metastable ions, m/z: 213.7 (m/z = 424 → m/z = 301), 172.9 (m/z = 236 → m/z = 202), 105.3 (m/z = 301 → m/z = 178).

Anal. (%): Calcd. for $C_{24}H_{24}S_2Ti$: C, 67.91; H, 5.70; S, 15.11. Found: C, 67.78; H, 5.51; S, 15.24.

(G) Bis(η-cyclopentadienyl)titana(IV)-2,6-dithiacyclohexane, $Cp_2Ti[S(CH_2)_3S]$, 120

To a stirred THF solution (40 mL) of 1,3-propanedithiol (0.50 mL, 5.0 mmol) was added methyl lithium (5.5 mL of a 1.8 M ether solution, 9.9 mmol) slowly by syringe. An exothermic reaction occurred to give a suspension of the white dilithium salt. Stirring was continued for two hours after which all volatiles were removed *in vacuo*. A suspension of Cp_2TiCl_2 (1.233 g, 4.951 mmol) in THF (70 mL) was added dropwise to the solid dilithium salt in an exothermic reaction to give a deep purple mixture which was stirred for 2.75 hours. Removal of the solvent *in vacuo* gave a purple residue. The product may be isolated by extraction at ambient temperature with CH_2Cl_2 or, more efficiently, by using a Soxhlet apparatus. The solvent was removed from the purple extract by rotary evaporation until the onset of crystallization whereupon cooling at −20°C overnight gave the product as small, deep purple needles (0.531 g, 38%, mp 207-208°C with decomposition).

^{1}H NMR ($CDCl_3$): δ 6.11 (s, 10H, C_5H_5), 3.08 (t, 4H, J = 6.0 Hz, CH_2), 1.93 (quintet, 2H, J = 6.0 Hz, CH_2).

IR (KBr): 3120 (vw, br), 3085 (w), 3075 (w, sh), 2958 (vw), 2935 (w), 2920 (w), 2905 (w), 2815 (w), 2335 (w, br), 1845 (vw, br), 1745 (vw, br), 1640 (vw, br), 1560 (vw), 1448 (m, sh), 1438 (s), 1420 (m), 1385 (vw), 1370 (w, sh), 1365 (w), 1345 (w), 1320 (w), 1290 (w), 1265 (w), 1250 (w, sh), 1243 (w), 1233 (m), 1182 (w), 1129 (w), 1068 (w), 1152 (vw), 1020 (s), 1013 (s, sh), 1010 (m, sh), 939 (vw), 908 (vw, br), 855 (m), 848 (m), 835 (s), 829 (s), 810 (vs), 801 (vs, sh), 798 (vs, sh), 785 (s, sh), 755 (w), 728 (w, br), 673 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 284 (59.2); $M^{+\bullet}-H_2S$, 250 (1.6); $M^{+\bullet}-2H^\bullet-H_2S$, 248 (2.2); $M^{+\bullet}-C_5H_5^\bullet$, 219 (2.7); $M^{+\bullet}-C_3H_3S^\bullet$, 213 (11.5); $M^{+\bullet}-C_3H_7S^\bullet$, 209 (9.8); $M^{+\bullet}-C_5H_5^\bullet-H_2S$, 185 (10.8); $M^{+\bullet}-C_5H_5^\bullet-2H^\bullet-H_2S$, 183 (14.7); $M^{+\bullet}-C_3H_4S_2$, 180 (47.2); $M^{+\bullet}-C_3H_5S_2^\bullet$, 179 (100.0); $M^{+\bullet}-C_3H_6S_2$, 178 (24.3); $M^{+\bullet}-C_5H_5^\bullet-C_3H_6$, 177 (65.8); $M^{+\bullet}-C_3H_8S_2$, 176 (61.4); $M^{+\bullet}-C_5H_5^\bullet-C_2H_4S$, 159 (10.1); $M^{+\bullet}-C_5H_5^\bullet-C_3H_6S$, 145 (66.9); $M^{+\bullet}-C_5H_5^\bullet-C_3H_6S_2$, 113 (53.8); $C_3H_6S_2^{+\bullet}$, 106 (9.1); $M^{+\bullet}-2C_5H_5^\bullet-C_3H_6S$, 80 (25.2).

Molecular weight ($CHCl_3$): Calcd. for $C_{13}H_{16}S_2Ti$:

284.30. Found: 281.

Anal. (%): Calcd. for $C_{13}H_{16}S_2Ti$: C, 54.92; H, 5.67; S, 22.56. Found: C, 52.89; H, 5.66; S, 21.73. Calcd. for $C_{13}H_{16}S_2Ti \cdot 1/6\,CH_2Cl_2$: C, 53.02; H, 5.52; S, 21.49. Methylene chloride was observed in the ^1H NMR spectrum.

(H) Bis(η-cyclopentadienyl)zircona(IV)-2,6-dithiacyclohexane, $Cp_2Zr[S(CH_2)_3S]$, **121**

1,3-Propanedithiol (0.32 mL, 3.2 mmol) in THF (50 mL) was treated with methyl lithium (4.0 mL of a 1.6 M ether solution, 6.4 mmol) via syringe to give exothermically a white precipitate of $Li_2S_2(CH_3)_3$. The slurry was stirred for 20 minutes. To this was added dropwise Cp_2ZrCl_2 (0.8765 g, 2.998 mmol) in THF (20 mL). A bright yellow solution formed immediately and after the addition was completed the stirring was continued for another three hours at ambient temperature. Removal of the volatiles in vacuo left a bright yellow solid which was transferred to a Soxhlet apparatus in a nitrogen-filled glove-bag. Extraction under nitrogen with CH_2Cl_2 for 20.5 hours gave a lemon yellow extract which was cooled overnight at -20°C. Filtration gave the product as a bright yellow microcrystalline solid (0.522 g). The complex melts at 248-252°C with decomposition although darkening of the sample was evident at ca. 200°C.

^1H NMR ($CDCl_3$, 200 MHz): At least seven resonances were present in the Cp region at *ca.* δ 6.2 Complex sets of signals also were observed in the δ 1.2 to δ 3.4 region.

IR (KBr): 3097 (vw, br), 3065 (w), 2938 (vw), 2915 (vw), 2905 (w), 2828 (w), 1823 (vw, br), 1726 (vw, br), 1633 (vw, br), 1455 (vw), 1435 (m), 1428 (m, sh), 1420 (m), 1381 (vw), 1369 (vw, sh), 1359 (w), 1343 (w), 1326 (vw, sh), 1322 (w), 1290 (w), 1260 (vw), 1249 (w, sh), 1243 (w), 1238 (w, sh), 1228 (w), 1185 (w), 1164 (vw), 1122 (vw), 1113 (vw), 1063 (vw), 1052 (vw, sh), 1042 (vw), 1018 (s), 1012 (s, sh), 1008 (m, sh), 980 (vw), 949 (vw), 942 (vw, sh), 922 (vw), 905 (vw), 893 (vw), 846 (m), 823 (s), 806 (vs, sh), 803 (vs), 793 (vs), 757 (w), 733 (w), 705 (vw), 670 (w), 635 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $P^{+\bullet}$, 326 (99.1); $P^{+\bullet}-C_3H_6$, 284 (26.9); $P^{+\bullet}-C_2H_4S$, 266 (4.7); $P^{+\bullet}-C_3H_5S^{\bullet}$, 253 (100.0); $P^{+\bullet}-C_3H_6S$, 252 (72.4); $P^{+\bullet}-C_3H_6S_2$, 220 (59.1); $P^{+\bullet}-C_2H_4S-C_5H_5^{\bullet}$, 201 (5.3); $P^{+\bullet}-C_3H_6S-C_5H_5^{\bullet}$, 187 (76.3); $P^{+\bullet}-C_3H_6S_2-C_5H_5^{\bullet}$, 155 (5.7); $P^{+\bullet}-C_3H_6S-2C_5H_5^{\bullet}$, 122 (7.1). Metastable ions, m/z: 196.3 (m/z = 326 → m/z = 253), 138.2 (m/z = 253 → m/z = 187).

Anal. (%): Calcd. for $C_{13}H_{16}S_2Zr$: C, 47.66; H, 4.92; S, 19.57. Found: C, 44.24; H, 4.69; S, 17.12. Calcd. for $C_{13}H_{16}S_2Zr \cdot 1/2\ CH_2Cl_2$: C, 43.81; H, 4.63; S, 17.33.

III) Titanium Polysulfanes

(A) Bis(η-cyclopentadienyl)bis(2-propyldisulfano)titanium(IV), $Cp_2Ti(S_2CHMe_2)_2$, 122

A colourless solution of N-2-propylthiophthalimide (0.4437 g, 2.005 mmol) in THF (20 mL) was cooled in an ice bath. A red-brown solution of $Cp_2Ti(SH)_2$ (0.2440 g, 0.9906 mmol) in THF (15 mL) was added dropwise to the stirred Phth-$SCHMe_2$ solution. The reaction solution became purple in colour. After stirring at 0°C for one hour the solvent was removed *in vacuo* at this temperature. The dry purple residue was extracted with 25 mL of CS_2 at 0°C to remove the phthalimide by-product and filtered through Celite into an ice-cold receiving vessel. Removal of the solvent *in vacuo* left a sticky purple solid. This was extracted with several portions of hot hexanes (total volume about 125 mL). The volume of the combined warm extracts was reduced *in vacuo* to *ca.* 50 mL and cooled to ambient temperature. Refrigeration at -20°C gave the product as a malodorous purple solid (0.285 g, 73%, mp 76-78°C) which was stable to air for short periods of time. Recrystallization at 0°C from 1:1 CH_2Cl_2:hexanes gave the analytical sample.

^1H NMR ($CDCl_3$): δ 6.21 (s, 10H, C_5H_5), 3.06 (m, 2H, J = 6.7 Hz, CH), 1.28 (d, 12H, J = 6.7 Hz, CH_3).

^{13}C NMR (C_6D_6): δ 113.17 (C_5H_5), 42.31 (CH), 23.14 (CH_3).

IR (KBr): 3110 (vw, br), 3085 (w), 3075 (vw), 2975 (w, sh), 2965 (m, sh), 2957 (m), 2940 (vw), 2920 (w), 2910 (vw, sh), 2885 (vw), 2856 (w), 1455 (vw), 1440 (m, br), 1373 (w), 1361 (w, sh), 1358 (m), 1310 (vw), 1258 (vw), 1243 (w), 1231 (m), 1151 (m), 1145 (vw, sh), 1127 (vw), 1103 (vw), 1069 (vw), 1047 (m), 1021 (m), 1010 (w), 1002 (w), 918 (vw, br), 888 (vw), 856 (w), 840 (w), 832 (vw, sh), 824 (s), 815 (vs), 790 (vw, sh), 660 (w, br) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 392 (0.2); $M^{+\bullet}-S^{\bullet}$, 360 (1.1); $M^{+\bullet}-2S^{\bullet}$, 328 (0.8); $M^{+\bullet}-C_3H_7^{\bullet}-S^{\bullet}$, 317 (0.6); $M^{+\bullet}-C_3H_7^{\bullet}-2S^{\bullet}$, 285 (20.6); $M^{+\bullet}-C_3H_7^{\bullet}-3S^{\bullet}$, 253 (23.2); $M^{+\bullet}-C_3H_7^{\bullet}-2S^{\bullet}-C_3H_6$, 243 (21.3); $M^{+\bullet}-2C_3H_7^{\bullet}-2S^{\bullet}$, 242 (8.2); $C_6H_{14}S_4^{+\bullet}$, 214 (13.4); $M^{+\bullet}-2C_3H_7^{\bullet}-3S^{\bullet}$, 210 (7.9); $M^{+\bullet}-2C_3H_7^{\bullet}-S^{\bullet}-C_5H_5^{\bullet}$, 209 (12.0); $M^{+\bullet}-2C_5H_5^{\bullet}-2S^{\bullet}-H^{\bullet}$, 197 (7.4); $C_6H_{14}S_3^{+\bullet}$, 182 (7.2); $M^{+\bullet}-2C_3H_7^{\bullet}-4S^{\bullet}$, 178 (57.3); $M^{+\bullet}-2C_3H_7^{\bullet}-2S^{\bullet}-C_5H_5^{\bullet}$, 177 (32.7); $C_6H_{14}S_2^{+\bullet}$, 150 (4.9); $M^{+\bullet}-2C_3H_7^{\bullet}-3S^{\bullet}-C_5H_5^{\bullet}$, 145 (18.4); $C_6H_{14}S^{+\bullet}$, 118 (2.1); $M^{+\bullet}-2C_3H_7^{\bullet}-4S^{\bullet}-C_5H_5^{\bullet}$, 113 (11.3); $C_3H_7S_2^{+}$, 107 (25.0); $M^{+\bullet}-2C_3H_7^{+}-3S^{\bullet}-2C_5H_5^{\bullet}$, 80 (6.0); $C_3H_7S^{+}$, 75 (8.7); $C_3H_7^{+}$, 43 (100.0); $C_3H_5^{+}$, 41 (52.8); $C_3H_3^{+}$, 39 (32.6). Metastable ions, m/z: 207.2 (m/z = 285 → m/z = 243), 71.7 (m/z = 178 → m/z = 113).

Anal. (%): Calcd. for $C_{16}H_{24}S_4Ti$: C, 48.96; H, 6.16; S, 32.68. Found: C, 49.03; H, 6.05; S, 32.45.

(B) Bis(η-cyclopentadienyl)(phenylthiolato)(phenyltrisulfano)titanium(IV), $Cp_2Ti(SPh)(S_3Ph)$, 123

A solution of N-phenylthiosuccinimide (0.4148 g, 2.001 mmol) in THF (25 mL) was treated dropwise with $Cp_2Ti(SH)_2$, 110 (0.2442 g, 1.000 mmol) in THF (25 mL) at 0°C over 25 minutes. The solution turned purple. After stirring at 0°C for 30 minutes the solvent was removed *in vacuo* at this temperature leaving a dry purple solid which was extracted at 0°C with portions of CS_2 and filtered through Celite. The combined filtrates (*ca.* 90 mL) were stripped *in vacuo* to leave a sticky residue. This was dissolved in excess boiling 1:1 hexanes:CH_2Cl_2 and the solution concentrated by means of a nitrogen stream until the onset of crystallization. Cooling to ambient temperature and refrigerating at −20°C gave the product as a purple microcrystalline solid (0.307 g, 67%). The mother liquor was removed at 0°C by means of a Pasteur pipette and discarded. The analytical sample of crystallographic grade crystals was obtained by two recrystallizations from CH_2Cl_2/hexanes, mp 131-132°C with decomposition.

^1H NMR ($CDCl_3$): δ 7.2 (m, 10H, C_6H_5), 6.08 (s, 10H, C_5H_5).

IR (KBr): 3115 (w), 3060 (w), 3045 (w), 2995 (vw, br), 2920 (vw), 1947 (vw, br), 1853 (vw, br), 1759 (vw, br), 1661 (vw, br), 1583 (w, sh), 1576 (m), 1562 (vw), 1473 (s), 1462 (m), 1435 (s), 1420 (vw, sh), 1371 (vw), 1363 (w), 1323 (vw), 1297 (w), 1260 (w), 1179 (w), 1168 (vw), 1150 (w), 1128 (w), 1081 (w), 1073 (w), 1068 (w), 1062 (w), 1021 (s), 1010 (m), 996 (w), 979 (vw), 968 (vw), 924 (vw), 917 (vw), 909 (vw), 892 (vw), 856 (m), 849 (m, sh), 840 (m), 830 (s, sh), 821 (vs), 812 (vs), 748 (vs), 738 (vs), 698 (s), 690 (s), 683 (m), 610 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}-2S^{\bullet}$, 396 (7.2); $C_{10}H_{10}S_5Ti^{+\bullet}$, 338 (3.8); $M^{+\bullet}-2C_6H_5^{\bullet}$, 306 (5.1); $M^{+\bullet}-2S^{\bullet}-C_6H_5S^{\bullet}$, 287 (71.4); $M^{+\bullet}-2C_6H_5^{\bullet}-S^{\bullet}$, 274 (1.5); $C_{12}H_{10}S_3^{+\bullet}$, 250 (2.5); $M^{+\bullet}-2C_6H_5^{\bullet}-C_5H_5^{\bullet}$, 241 (19.9); $C_{12}H_{10}S_2^{+\bullet}$, 218 (32.3); $M^{+\bullet}-2C_6H_5^{\bullet}-S^{\bullet}-C_5H_5^{\bullet}$, 209 (6.5); $M^{+\bullet}-3S^{\bullet}-C_6H_5S^{\bullet}-C_6H_5^{\bullet}$, 178 (100.0); $M^{+\bullet}-2C_6H_5^{\bullet}-C_5H_5^{\bullet}-S_2$, 177 (11.8); $C_{12}H_{10}^{+}$, 154 (5.1); $M^{+\bullet}-2C_6H_5^{\bullet}-3S^{\bullet}-C_5H_5^{\bullet}$, 145 (13.3); $C_6H_5S_2^{+}$, 141 (7.1); $M^{+\bullet}-2C_6H_5^{\bullet}-4S^{\bullet}-C_5H_5^{\bullet}$, 113 (10.6); $C_6H_6S^{+\bullet}$, 110 (48.3); $C_6H_5S^{+}$, 109 (41.5). Metastable ions, m/z: 208.0 (m/z = 396 → m/z = 287), 159.4 (m/z = 274 → m/z = 209), 157.8 (m/z = 396 → m/z = 250), 130.0 (m/z = 241 → m/z = 177), 110.4 (m/z = 287 → m/z = 178), 71.7 (m/z = 178 → m/z = 113).

Visible spectrum max. (CH_2Cl_2): 534 nm (ε 5.2 x 10^3).

Anal. (%): Calcd. for $C_{22}H_{20}S_4Ti$: C, 57.37; H, 4.38; S, 27.85. Found: C, 56.59; H, 4.12; S, 27.29.

(C) Bis(η-cyclopentadienyl)(4-methylphenylthiolato)-(4-methylphenyltrisulfano)titanium(IV), $Cp_2Ti(SC_6H_4Me)(S_3C_6H_4Me)$, 124

A solution of N-4-methylphenylthiophthalimide (0.2692 g, 0.9996 mmol) in THF (20 mL) was treated at 0°C with $Cp_2Ti(SH)_2$, 110 (0.1218 g, 0.4987 mmol) in THF (30 mL) dropwise over 33 minutes to give a purple solution. Stirring at 0°C was continued for 50 minutes after the addition had been completed. Removal of the solvent *in vacuo* gave a dry purple solid. This was extracted at 0°C with CS_2 (total 10 mL) and filtered through Celite into an ice-cold receiving flask. The CS_2 was stripped at 0°C *in vacuo*. Recrystallization from hot hexanes, 1:1 hexanes:CH_2Cl_2 or diethyl ether gave the product (0.149 g, 61%, mp 108-110°C).

^1H NMR ($CDCl_3$): δ 7.57 - 7.03 (m, 8.7H, C_6H_4), 6.12 (s, 10.0H, C_5H_5), 2.35 (s, 5.1H, CH_3).

IR (KBr): 3115 (w), 3065 (vw), 3040 (vw), 3005 (vw), 2960 (vw), 2910 (vw), 2850 (vw), 1596 (vw), 1557 (vw), 1488 (s), 1462 (vw, sh), 1440 (m), 1431 (m), 1418 (vw, sh), 1395 (w), 1374 (vw), 1363 (vw), 1301 (vw), 1293 (vw), 1258 (w), 1206 (w), 1180 (w), 1173 (w), 1128 (w), 1112 (vw), 1099 (w), 1083 (w), 1078 (vw, sh), 1011 (w), 1035 (vw), 1020 (m), 1010 (s), 920 (vw), 853 (m), 838 (m, sh), 821 (vs), 818 (vs), 810 (vs), 808 (vs, sh), 701 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}-2S^\bullet$, 424 (2.1); $C_{10}H_{10}S_5Ti^{+\bullet}$, 338 (1.4); $M^{+\bullet}-C_7H_7^\bullet-3S^\bullet$, 301 (22.4);

$C_{14}H_{14}S_3^{+\bullet}$, 278 (5.9); $C_{14}H_{14}S_2^{+\bullet}$, 246 (59.8); $M^{+\bullet}-2C_7H_7^{\bullet}-C_5H_5^{\bullet}$, 241 (9.7); $M^{+\bullet}-C_7H_7^{\bullet}-H^{\bullet}-3S^{\bullet}-C_5H_5^{\bullet}$, 235 (4.8); $M^{+\bullet}-2C_7H_7^{\bullet}-S^{\bullet}-C_5H_5^{\bullet}$, 209 (3.8); $C_{14}H_{14}^{+\bullet}$, 182 (4.3); $M^{+\bullet}-2C_7H_7^{\bullet}-4S^{\bullet}$, 178 (35.2); $C_7H_7S_2^{+}$, 155 (7.7); $M^{+\bullet}-2C_7H_7^{\bullet}-3S^{\bullet}-C_5H_5^{\bullet}$, 145 (7.5); $C_7H_8S^{+\bullet}$, 124 (32.9); $C_7H_7S^{+}$, 123 (100.0); $M^{+\bullet}-2C_7H_7^{\bullet}-4S^{\bullet}-C_5H_5^{\bullet}$, 113 (5.3); $C_7H_7^{+}$, 91 (62.4).

Anal. (%): Calcd. for $C_{24}H_{24}S_4Ti$: C, 59.00; H, 4.95; S, 26.75. Found: C, 57.62; H, 4.95; S, 25.12.

IV) Cyclic Metal Polysulfanes

(A) The Reactions of $Cp_2Ti(SH)_2$, 110, with:

(i) Sulfur

In air $Cp_2Ti(SH)_2$, 110 (0.98 g, 4.0 mmol) in CH_2Cl_2 (100 mL) was added dropwise to sulfur powder (1.03 g, 4.02 mmol) in CH_2Cl_2 (100 mL). The mixture was refluxed in air (with a calcium chloride drying tube attached to the condenser) for 1.25 hours. The deep red mixture was filtered in air and the light brown insoluble was washed with 10 mL of dry CH_2Cl_2. The combined filtrates were evaporated to dryness to give a deep red slightly oily residue. Fractional crystallization from CH_2Cl_2 at -20°C gave brick-coloured needles (0.48 g, mp 117-119°C) which were mostly sulfur by TLC. Chromatography of the mother liquor on Florisil eluting with 1:1 hexane:toluene and then pure toluene gave a red band which was collected and stripped to dryness to pure Cp_2TiS_5, 73 [0.61 g, 45% based on

$Cp_2Ti(SH)_2$, mp 196-197°C] (lit.[163] mp 201-202°C).

(ii) 1,1'-Thiobisbenzimidazole

The compound 1,1'-thiobisbenzimidazole (Bz-S-Bz) (0.5451 g, 2.047 mmol) was suspended in toluene (20 mL) and treated dropwise with a suspension of $Cp_2Ti(SH)_2$, 110, (0.5000 g, 2.043 mmol) in toluene (50 mL). The reaction mixture initially assumed a purple colour which darkened as the reaction progressed. After stirring for three hours at room temperature TLC (alumina/CH_2Cl_2) indicated the absence of 110. All volatiles were removed *in vacuo*. The residue was extracted with CH_2Cl_2 (2 x 20 mL) and the extracts were filtered through Celite. The filter cake was washed with 3 x 5 mL of CH_2Cl_2. A purple residue of low solubility in CH_2Cl_2 remained on the Celite pad and was discarded. The filtrate was evaporated to dryness to give a black residue. This was dissolved in CH_2Cl_2 and chromatographed on Florisil. Toluene eluted a red band which was collected and evaporated *in vacuo* to give Cp_2TiS_5, 73 (0.147 g, 64% based on Bz-S-Bz). Elution with 1:1 toluene:CH_2Cl_2 gave a blue band (strongly overlapped by the red band due to 73). The fractions in which the blue product was most highly concentrated (TLC) was collected and reduced in volume to about 5 mL whereupon a dark solid began to precipitate. After cooling at -20°C for 11 hours a pink supernatant (containing 73 by TLC) was removed by syringe from a dark blue solid (0.0023 g, 1% based on Bz-S-Bz) which was free of 73 (TLC). The blue product was identified as 1,5-$(Cp_2TiS_3)_2$ by comparison of its colour, ^1H NMR spectrum, and electronic spectrum with that reported in the literature.[103] No molecular ion was seen in the mass spectrum (70 eV) of this minor product.

(iii) 1,1'-Dithiobisbenzimidazole

A suspension of 1,1'-dithiobisbenzimidazole (Bz-S_2-Bz) (0.63 g, 2.1 mmol) in THF (80 mL) was added dropwise over 40 minutes at 27°C to a solution of $Cp_2Ti(SH)_2$, 110 (0.50 g, 2.1 mmol). Stirring was continued for an additional 21 hours. The reaction mixture was filtered through Celite which was washed with 10 mL of solvent. The deep red filtrate was reduced in volume to *ca.* 35 mL and transferred to a chromatography column (Florisil). Elution with 4:1 hexanes:toluene (200 mL) gave a tailing red-violet band which was collected. Further elution with 1:1 hexanes:toluene followed by pure toluene gave red fractions which consisted only of Cp_2TiS_5, 73 (NMR). Upon standing the 4:1 hexanes:toluene fraction deposited a brown solid and the solvent was removed under reduced pressure. The resulting red-black solid was extracted with dry toluene (3 x 30 mL) and filtered through a small amount of Florisil leaving behind the brown solid. The solvent was removed *in vacuo*.

The major component was 73 (NMR) but a small amount of 1,5-$(Cp_2TiS_3)_2$ (ca. 4% by NMR relative to Cp_2TiS_5) was also present.[103] The yield of 73 was 0.33 g (70%) based on Bz-S_2-Bz as the limiting reagent.

(iv) 1,1'-Thiobisphthalimide

A slurry of 1,1'-thiobisphthalimide (Phth-S-Phth) (0.3265 g, 1.007 mmol) in THF (20 mL) was treated dropwise with a solution of $Cp_2Ti(SH)_2$, 110 (0.2442 g, 1.000 mmol). The initially colourless Phth-S-Phth suspension became purple and then red-black as the addition progressed. The reaction mixture was allowed to stir for 70 minutes following the addition after which the volatiles were removed in vacuo. In air, the residue was extracted with CS_2, the extracts filtered, and the solvent removed in vacuo to leave a brown residue. This was dissolved in CH_2Cl_2, filtered, and chromatographed on a silica gel column. Elution with 1:1 hexanes:CH_2Cl_2 gave a slowly moving red band, which was collected and stripped to give Cp_2TiS_5, 73 (0.043 g). Additional 73 (0.005 g) was obtained by extracting the CS_2 insoluble residue with CH_2Cl_2, filtering, rotary evaporating, and washing with hexanes. A sample for microanalysis was obtained by recrystallization from CH_2Cl_2/hexanes at -20°C, mp 194.5-195°C (lit.[163] 201-202°C). The yield was 42% based on Phth-S-Phth as the limiting reactant.

Anal. (%): Calcd. for $C_{10}H_{10}S_5Ti$: C, 35.49;

H, 2.98; S, 47.37. Found: C, 37.37; H, 3.01; S, 44.55.

(v) 1,1'-Dithiobisphthalimide

A slurry of 1,1'-dithiobisphthalimide (Phth-S_2-Phth) (0.3654 g, 1.205 mmol) in THF (25 mL) was treated dropwise over 30 minutes with a solution of $Cp_2Ti(SH)_2$, 110 (0.2500 g, 1.022 mmol) in THF (25 mL). The suspension was stirred for an additional 2.5 hours. The volatiles were removed *in vacuo* from the deep red reaction mixture. The residue was extracted with CH_2Cl_2, rapidly filtered in air, and the filtrate chromatographed on a Florisil column. Elution with CH_2Cl_2 gave a deep red fraction which was stripped by rotary evaporation to leave Cp_2TiS_5, 73 (0.151 g, 45% based on Phth-S_2-Phth as the limiting reactant). This was recrystallized from CH_2Cl_2/pentane at -20°C to give the analytical sample, mp 192-193°C (lit.[163] 201-202°C).

Anal. (%): Calcd. for $C_{10}H_{10}S_5Ti$: C, 35.48; H, 2.98; S, 47.36. Found: C, 34.98; H, 2.92; S, 46.85.

(B) Reactions of $Cp_2Zr(SH)_2$, 111, with:

(i) Sulfur

Toluene (50 mL) was added to an ice-cold solid mixture of $Cp_2Zr(SH)_2$, 111 (0.64 g, 2.2 mmol) and sulfur (0.51 g, 2.0 mmol). The mixture was stirred over four hours during which time it was allowed to warm to ambient temperature. The colour changed from pale yellow to bright yellow. The mixture was filtered, its volume reduced *in vacuo* and cooled at -20°C for several days. The first product consisted of a mixture of small orange crystals and large pale yellow crystals. These were collected by filtration and the mother liquor reduced further in volume and cooled. Subsequent products were similar mixtures of crystals. The crystals were separated manually and combined. The yellow product was sulfur by TLC. The orange crystals (0.104 g, 12%) were subsequently identified as Cp_2ZrS_5, 75 (see page 109). It decomposed without melting at *ca.* 169°C.

Anal. (%): Calcd. for $C_{10}H_{10}S_5Zr$: C, 31.46; H, 2.64; S, 42.00. Found: C, 30.21; H, 2.59; S, 42.97.

(ii) 1,1'-Dithiobisbenzimidazole

Toluene (50 mL) was added to an ice-cold vessel containing a mixture of powdered $Cp_2Zr(SH)_2$, 111 (0.58 g, 2.0 mmol) and 1,1'-dithiobisbenzimidazole ($Bz-S_2-Bz$) (0.60 g, 2.0 mmol). The ice bath was removed and the slurry was stirred for 12 hours. This was filtered and the pale yellow insoluble material was washed with solvent (2 x 5 mL). The combined lemon yellow filtrate and washings were concentrated and cooled *in vacuo* at -20°C for 10 days to give a mixture of large, well-formed golden crystals and smaller yellow crystals. The mother liquor was removed by syringe and the crystals dried first in a stream of nitrogen and finally in vacuo. The air-stable mixture of crystals was separated manually in air to give golden Cp_2ZrS_5, 75 (0.163 g, 32% based on the $Bz-S_2-Bz$) and 0.110 g of the yellow microcrystals. The ^1H NMR and infrared spectra of the latter were consistent with a mixture of benzimidazole and an unidentified Cp_2Zr-containing product, and were not further characterized. The golden crystals irreversibly became deep red between 160°C and 170°C.

For spectral data see page 109.

Anal. (%): Calcd. for $C_{10}H_{10}S_5Zr$: C, 31.46; H, 2.64; S, 42.00. Found: C, 31.65; H, 2.75; S, 39.18.

(iii) Iodine

A solution of $Cp_2Zr(SH)_2$, 111 (0.162 g, 0.563 mmol) in toluene (25 mL) was prepared. A preweighed solids addition tube containing powdered iodine (1.310 g) was attached to the reaction vessel and the iodine was slowly added until the solution maintained a red colouration. A slight precipitate was noticed at this point. The solids addition tube was removed and weighed which indicated that 0.164 g (0.646 mmol) of iodine had been added. All volatiles were removed from the reaction mixture in vacuo and the residue pumped on to leave a yellow powder (0.269 g, quantitative yield) which appeared to be pure (NMR). Recrystallization from CH_2Cl_2/pentane gave bright yellow crystals (mp 296-298°C with decomposition; lit.[284] 299-301°C) which exhibited a strong positive Beilstein Test for halogen.[285] These were subsequently identified by mass spectrometry as Cp_2ZrI_2.

^1H NMR ($CDCl_3$): δ 6.67 (s, 10H, C_5H_5).

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 474 (78.9); $M^{+\bullet}-C_5H_5^{\bullet}$, 409 (14.9); $M^{+\bullet}-I^{\bullet}$, 347 (100.0); $M^{+\bullet}-2C_5H_5^{\bullet}$, 344 (2.8); $M^{+\bullet}-C_5H_5^{\bullet}-I^{\bullet}$, 282 (13.8); $M^{+\bullet}-2I^{\bullet}$, 220 (7.1); $M^{+\bullet}-2C_5H_5^{\bullet}-I^{\bullet}$, 217 (0.4); $M^{+\bullet}-C_5H_5^{\bullet}-2I^{\bullet}$, 155 (1.1).

(C) Reactions of Group IVB Metallocene Dichlorides with Lithium Polysulfides to give:

(i) Bis(η-cyclopentadienyl)titana(IV)cyclohexasulfane, Cp_2TiS_5, 73

A yellow solution of lithium polysulfides was prepared from sulfur powder (0.4820 g, 1.879 mmol) and Super Hydride (6.0 mL of a 1M solution of $LiEt_3BH$ in THF, 6.0 mmol). A red solution of Cp_2TiCl_2 (0.7468 g, 2.999 mmol) in THF (75 mL) was added dropwise over 20 minutes to give a deep red reaction solution which was stirred at 26°C for 14 hours. The volatiles were removed *in vacuo* and the residue extracted with CH_2Cl_2 (100 mL). Filtration through Celite and removal of the solvent from the filtrate by rotary evaporation gave the product as dark red microcrystals (0.994 g, 98%). The crude product was pure by TLC and was the analytical sample, mp 196-198°C (lit.[163] 201-202°C).

^1H NMR ($CDCl_3$): δ 6.32 (s, 5H, C_5H_5), 6.03 (s, 5H, C_5H_5).

IR (KBr): 3130 (vw), 3110 (m), 3095 (w, sh), 3080 (vw), 2950 (vw), 2870 (vw), 2690 (vw), 2495 (vw), 2425 (vw), 2270 (vw), 2075 (vw), 1872 (vw, br), 1853 (vw, br), 1763 (vw, br), 1675 (w, br), 1700 (w, br), 1450 (w, sh), 1434 (s), 1419 (s, sh), 1363 (w), 1340 (vw), 1282 (w), 1265 (vw), 1210 (vw), 1154 (vw), 1128 (m), 1062 (w), 1022 (s), 1015 (s, sh), 1010 (s), 925 (w), 857 (m), 833 (s), 823 (vs), 815 (vs), 656 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 338 (24.2); $M^{+\bullet}-S^{\bullet}$, 306 (0.3); $M^{+\bullet}-S_2$, 274 (19.7); $M^{+\bullet}-3S^{\bullet}$, 242 (100.0); $M^{+\bullet}-2S_2$, 210 (51.3); $M^{+\bullet}-S_2-C_5H_5^{\bullet}$, 209 (58.8); $M^{+\bullet}-3S^{\bullet}-S_2$, 178 (77.6); $M^{+\bullet}-4S^{\bullet}-C_5H_5^{\bullet}$, 145 (39.9); $M^{+\bullet}-2S^{\bullet}-2C_5H_5^{\bullet}$, 144 (23.1); $M^{+\bullet}-5S^{\bullet}-C_5H_5^{\bullet}$, 113 (17.9); $M^{+\bullet}-4S^{\bullet}-2C_5H_5^{\bullet}$, 80 (14.8). Metastable ions, m/z: 222.1 (m/z = 338 → m/z = 274), 160.9 (m/z = 274 → m/z = 210), 130.9 (m/z = 242 → m/z = 178), 100.6 (m/z = 209 → m/z = 145), 71.7 (m/z = 178 → m/z = 113).

Visible spectrum max. (CH_2Cl_2): 491 nm (ε 1.7×10^3).

Anal. (%): Calcd. for $C_{10}H_{10}S_5Ti$: C, 35.49; H, 2.98; S, 47.37. Found: C, 35.22; H, 3.34; S, 47.27.

(ii) Bis(η-methylcyclopentadienyl)titana(IV)-cyclohexasulfane, $(MeCp)_2TiS_5$, 74

Sulfur powder (0.2910 g, 1.134 mmol) was treated with Super Hydride (3.7 mL of a 1M solution of $LiEt_3BH$

in THF, 3.7 mmol) to give a golden lithium polysulfide solution. A red solution of $(MeCp)_2TiCl_2$ (0.5014 g, 1.810 mmol) in THF (30 mL) was added dropwise over 25 minutes. Stirring was continued for two hours at ambient temperature. Removal of the volatiles in vacuo left a slightly sticky red solid which was triturated with hexane (20 mL) for 2.5 hours to give a dry red solid. The red supernatant was reduced in volume by rotary evaporation to leave a small amount of a brown oil which was not examined further. Extraction of the red solid with CH_2Cl_2 (2 x 30 mL) and filtration through Celite gave a deep red filtrate. The Celite pad was washed with CH_2Cl_2 (20 mL) leaving a white filter cake. Removal of the solvent from the combined filtrate and washings in vacuo gave a slightly sticky residue. Recrystallization from CH_2Cl_2/pentane at -20°C gave the product as two types of crystals: large irregular light red plates and small deep red rhombohedral plates (0.566 g, 85%, mp 171-172°C) (lit.[168] dec. 200°C).

^{1}H NMR (toluene-d8, 200 MHz): δ 5.62 (t, 2H, J = 2.6 Hz, C_5H_4), 5.59 (t, 2H, J = 2.6 Hz, C_5H_4), 5.45 (t, 2H, J = 2.6 Hz, C_5H_4), 5.32 (t, 2H, J = 2.6 Hz, C_5H_4), 1.97 (s, 3H, Me), 1.65 (s, 3H, Me).

IR (KBr): 3090 (m), 2975 (vw), 2950 (vw), 2915 (vw), 2890 (vw), 2850 (vw), 1494 (m), 1487 (m), 1448 (m), 1438 (m), 1410 (w), 1388 (vw), 1369 (m), 1349 (vw), 1308 (vw), 1258 (vw), 1243 (vw), 1235 (w), 1078 (w), 1065 (vw), 1048 (w), 1036 (m), 1019 (m), 976 (vw), 938 (w), 928 (m), 904 (m), 900 (m), 849 (m), 846 (m), 841 (s), 838 (s), 833 (vs), 830 (vs), 629 (vw), 608 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 366 (10.2); $M^{+\bullet}-S^{\bullet}$, 334 (6.6); $M^{+\bullet}-2S^{\bullet}$, 302 (31.0); $M^{+\bullet}-C_6H_7^{\bullet}$, 287 (5.1); $M^{+\bullet}-3S^{\bullet}$, 270 (100.0); $M^{+\bullet}-S^{\bullet}-C_6H_6$, 256 (11.1); $M^{+\bullet}-4S^{\bullet}$, 238 (17.5); $M^{+\bullet}-2S^{\bullet}-C_6H_7^{\bullet}$, 223 (54.9); $M^{+\bullet}-5S^{\bullet}$, 206 (51.8); $M^{+\bullet}-5S^{\bullet}-2H^{\bullet}$, 204 (30.9); $M^{+\bullet}-3S^{\bullet}-C_6H_6$, 192 (19.0); $M^{+\bullet}-3S^{\bullet}-C_6H_7^{\bullet}$, 191 (17.0); $M^{+\bullet}-2S^{\bullet}-C_6H_7^{\bullet}-H_2S$, 189 (16.4); $M^{+\bullet}-3S^{\bullet}-CH_3^{\bullet}-C_6H_6$, 177 (13.8); $M^{+\bullet}-4S^{\bullet}-C_6H_6$, 160 (19.6); $M^{+\bullet}-4S^{\bullet}-C_6H_7^{\bullet}$, 159 (21.6); $M^{+\bullet}-4S^{\bullet}-CH_3^{\bullet}-C_6H_6$, 145 (23.2); $M^{+\bullet}-5S^{\bullet}-C_6H_6$, 128 (9.9); $M^{+\bullet}-4S^{\bullet}-C_6H_6-H_2S$, 126 (24.5); $M^{+\bullet}-5S^{\bullet}-CH_3^{\bullet}-C_6H_6$, 113 (49.0); $M^{+\bullet}-2C_6H_7^{\bullet}-4S^{\bullet}$, 80 (75.7); $C_6H_5^{+}$, 77 (48.3).

Visible spectrum max. (CH_2Cl_2): 488 nm (ε 1.9×10^3), 434 (sh, 1.0×10^3).

Anal. (%): Calcd. for $C_{12}H_{14}S_5Ti$: C, 39.33; H, 3.85; S, 43.75. Found: C, 38.96; H, 4.10; S, 43.92.

(iii) Bis(η-trimethylsilylcyclopentadienyl)-titana(IV)cyclohexasulfane, $(Me_3SiCp)_2TiS_5$, 77

Sulfur powder (0.1593 g, 0.6210 mmol) was treated with Super Hydride (2.0 mL of a 1M solution of $LiEt_3BH$ in THF, 2.0 mmol) to give a lithium polysulfide solution. A deep red solution of $(Me_3SiCp)_2TiCl_2$ (0.3932 g, 1.000 mmol) in THF (20 mL) was added dropwise over 20 minutes and followed by stirring at ambient temperature for 3.75 hours. Volatiles were removed in vacuo to leave a malodorous oily purple residue. Extraction with CH_2Cl_2 (30 mL) and filtering through Celite gave a purple filtrate and a cream-coloured filter cake. The methylene chloride was removed in vacuo and the oily residue was recrystallized from hexanes at -20°C. Three crops of deep red crystals (0.31 g, 64%, mp 106-107°C) were isolated by repeated concentration of the mother liquor and cooling at -20°C.

^1H NMR (toluene-d8, 200 MHz): δ 6.09 (t, 2H, J = 2.4 Hz, C_5H_4), 6.04 (t, 2H, J = 2.4 Hz, C_5H_4), 5.76 (overlapping pair of triplets, 4H, J = 2.4 Hz, C_5H_4), 0.21 (s, 9H, Me), 0.08 (s, 9H, Me).

IR (KBr): 3130 (vw), 3100 (vw), 3090 (w), 2965 (w, sh), 2955 (m), 2895 (vw), 2850 (vw), 2790 (vw), 2640 (vw, br), 2310 (vw, br), 2230 (vw, br), 2090 (vw, br), 1935 (vw, br), 1870 (vw, br), 1825 (vw), 1745 (vw, br), 1655 (vw, br), 1448 (vw), 1420 (vw), 1401 (m), 1399 (m), 1372 (m), 1317 (w), 1266 (m, sh), 1260 (m), 1253 (m, sh), 1244 (s), 1197 (vw), 1173 (m), 1169 (m, sh), 1095 (vw, br), 1062 (vw), 1045 (m), 1032 (m), 1010 (vw, br), 930 (vw), 922 (w), 898 (s, sh), 895 (s), 848 (s), 835 (vs, sh), 823 (vs), 758 (m), 748 (s), 687 (w), 630 (m), 621 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}-2S^{\bullet}$, 418 (17.3); $M^{+\bullet}-3S^{\bullet}$, 386 (74.2); $M^{+\bullet}-3S^{\bullet}-CH_3^{\bullet}$, 371 (7.7);

$M^{+\bullet}-2S^{\bullet}-S_2$, 354 (26.6); $M^{+\bullet}-C_8H_{13}Si^{\bullet}$, 345 (3.6); $M^{+\bullet}-4S^{\bullet}-CH_3^{\bullet}$, 339 (6.2); $M^{+\bullet}-3S^{\bullet}-S_2$, 322 (60.0); $M^{+\bullet}-S^{\bullet}-C_8H_{13}Si^{\bullet}$, 313 (5.4); $M^{+\bullet}-2S^{\bullet}-C_8H_{13}Si^{\bullet}$, 281 (28.6); $M^{+\bullet}-2S^{\bullet}-C_8H_{13}Si^{\bullet}-CH_3^{\bullet}$, 266 (12.9); $M^{+\bullet}-3S^{\bullet}-C_8H_{13}Si^{\bullet}$, 249 (5.3); $M^{+\bullet}-3S^{\bullet}-C_8H_{13}Si^{\bullet}-CH_3^{\bullet}$, 234 (14.1); $M^{+\bullet}-3S^{\bullet}-C_8H_{13}Si^{\bullet}-2CH_3^{\bullet}$, 219 (12.5); $M^{+\bullet}-4S^{\bullet}-C_8H_{13}Si^{\bullet}-CH_3^{\bullet}$, 202 (11.0); $M^{+\bullet}-4S^{\bullet}-C_8H_{13}Si^{\bullet}-2CH_3^{\bullet}$, 187 (8.9); $M^{+\bullet}-2S^{\bullet}-C_8H_{13}Si^{\bullet}-CH_3^{\bullet}-C_2H_6SiS$, 176 (12.9); $M^{+\bullet}-4S^{\bullet}-C_8H_{13}Si^{\bullet}-3CH_3^{\bullet}$, 172 (7.7); $M^{+\bullet}-5S^{\bullet}-C_8H_{13}Si^{\bullet}-2CH_3^{\bullet}$, 155 (3.4); $M^{+\bullet}-4S^{\bullet}-C_8H_{13}Si^{\bullet}-CH_3^{\bullet}-C_2H_6Si$, 144 (6.9); $C_3H_9Si^+$, 73 (100.0). Metastable ions, m/z: 299.8 (m/z = 418 → m/z = 354), 268.6 (m/z = 386 → m/z = 322), 251.8 (m/z = 281 → m/z = 266), 205.0 (m/z = 234 → m/z = 219), 173.1 (m/z = 202 → m/z = 187), 116.5 (m/z = 266 → m/z = 176), 102.7 (m/z = 202 → m/z = 144), 94.7 (m/z = 219 → m/z = 144).

Visible spectrum max. (CH_2Cl_2): 504 nm (ε 2.0 x 10^3).

Anal. (%): Calcd. for $C_{16}H_{26}S_5Si_2Ti$: C, 39.81; H, 5.43; S, 33.21. Found: C, 39.98; H, 5.83; S, 32.64.

(iv) <u>1,1'-Methylenebis(η-cyclopentadienyl)-titana(IV)cyclohexasulfane, $CH_2Cp_2TiS_5$,</u> <u>79</u>

A yellow lithium polysulfide solution was prepared from powdered sulfur (0.1610 g, 0.6277 mmol) and Super Hydride (2.1 mL of a 1M solution of $LiEt_3BH$ in THF, 2.1 mmol). After stirring for 10 minutes THF (20 mL) was added. The vessel was cooled in an ice bath and $CH_2Cp_2TiCl_2$ (0.2608 g, 0.9992 mmol) was added. The colour slowly became red and the solution was allowed to warm to room temperature. The reaction was stirred for three days. The solvent and other volatiles were removed in vacuo to leave an orange oil which solidified upon pumping overnight. The oil was extracted with CH_2Cl_2 (3 x 20 mL) and filtered through a bed of Celite to give a red filtrate with a considerable amount of red-brown residue retained by the Celite. The filtrate was reduced to dryness in vacuo, dissolved in a minimum volume of $CHCl_3$ and applied to a silica gel column. Elution with 1:2 hexanes:CH_2Cl_2 gave an orange band which gave red $CH_2Cp_2TiS_5$, 79 (0.030 g, 9%, dec. ca. 180°C) upon evaporation to dryness. Methylene chloride eluted an orange band which gave 0.007 g of an as yet unidentified red solid, 79A.

^1H NMR (toluene-d8, 200 MHz): δ 6.51 (s, br, 2H, C_5H_4), 6.30 (s, br, 2H, C_5H_4), 4.71 (s, br, 2H, C_5H_4), 4.28 (s, br, 2H, C_5H_4), 2.53 (s, 2H, CH_2).

IR (KBr): 3115 (vw), 3105 (vw), 3085 (m), 3065 (vw), 2960 (vw), 2945 (m), 2920 (vw), 2855 (vw), 1712 (vw, br), 1640 (w, br), 1493 (vw), 1473 (m, br), 1467 (m), 1458 (w, sh), 1439 (w), 1411 (m), 1375 (w), 1270 (w), 1259 (s), 1250 (w, sh), 1240 (m), 1218 (m), 1100 (vw, br), 1067 (s), 1062 (s, sh), 1050 (w), 1044 (s), 1032 (s), 936 (m), 923 (w), 880 (w), 856 (m), 849 (w, sh), 842 (vw), 830 (m), 819 (vs), 815 (s, sh), 810 (s, sh), 802 (vs), 773 (vw), 758 (s), 727 (w), 692 (vw), 662 (s), 652 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 350 (9.6); $M^{+\bullet}-S^{\bullet}$, 318 (0.5); $M^{+\bullet}-S_2$, 286 (81.1); $M^{+\bullet}-3S^{\bullet}$, 254 (100.0); $M^{+\bullet}-2S_2$, 222 (92.2); $M^{+\bullet}-C_{11}H_{10}$, 208 (8.1); $M^{+\bullet}-5S$, 190 (60.9); $M^{+\bullet}-2S_2-H_2S$, 188 (21.2); $M^{+\bullet}-C_{11}H_{10}-S^{\bullet}$, 176 (1.4); $M^{+\bullet}-C_{11}H_{10}-2S^{\bullet}$, 144 (30.4); $M^{+\bullet}-C_{11}H_{10}-3S^{\bullet}$, 112 (6.9); $M^{+\bullet}-C_{11}H_{10}-4S^{\bullet}$, 80 (15.8). Metastable ions, m/z: 233.7 (m/z = 350 → m/z = 286), 172.3 (m/z = 286 → m/z = 222), 159.2 (m/z = 222 → m/z = 188).

Anal. (%): Calcd. for $C_{11}H_{10}S_5Ti$: C, 37.70; H, 2.89; S, 45.75. Found: C, 39.69; H, 3.13; S, 41.57. Calcd. for $C_{11}H_{10}S_5Ti\cdot\frac{1}{5}CH_2Cl_2\cdot\frac{1}{4}C_6H_{14}$: C, 39.22; H, 3.60; S, 41.22. Both methylene chloride and hexanes were seen in the ^1H NMR spectrum.

(v) (η-Cyclopentadienyl)(η-pentamethylcyclopentadienyl)titana(IV)cyclohexasulfane, $Cp(Me_5Cp)TiS_5$, 78

A yellow solution of lithium polysufides was prepared from powdered sulfur (0.0248 g, 0.0967 mmol) and Super Hydride (0.32 mL of a 1M solution of $LiEt_3BH$ in THF, 0.32 mmol). After stirring for five minutes THF (5 mL) was added. A deep red solution of $Cp(Me_5Cp)TiCl_2$ (0.0491 g, 0.154 mmol) in THF (11 mL) was added dropwise over five minutes. The reaction was stirred for 18 hours at room temperature and was clear deep orange in colour. The volatiles were removed *in vacuo* to leave an orange-red residue. This was extracted with CH_2Cl_2 (50 mL), filtered through Celite, and evaporated to dryness *in vacuo* to give the product as a dark red solid (0.058 g, 92%). The analytical sample was recrystallized from hot 1:1 hexanes:toluene to give irregular needles, mp 212.5-213°C.

^1H NMR ($CDCl_3$): δ 5.90 (s, 5H, C_5H_5), 2.05 (s, 15H, C_5Me_5).

IR (KBr): 3085 (w), 2970 (w, sh), 2950 (w, sh), 2920 (s), 2900 (w, sh), 2850 (m), 1741 (w, br), 1483 (w), 1462 (w), 1445 (w, br), 1424 (m), 1384 (m), 1374 (s), 1360 (w, sh), 1330 (w), 1260 (m), 1155 (w, br), 1092 (w), 1053 (w), 1020 (s), 1011 (s, sh), 948 (w), 915 (w), 841 (w), 822 (vs), 800 (m), 695 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity); $M^{+\bullet}$, 408 (2.5); $M^{+\bullet}-S^\bullet$, 376 (2.5); $M^{+\bullet}-2S^\bullet$, 344 (36.3); $M^{+\bullet}-3S^\bullet$, 312 (100.0); $M^{+\bullet}-4S^\bullet$, 280 (44.4); $M^{+\bullet}-2S^\bullet-C_5H_5^\bullet$, 279 (88.7); $M^{+\bullet}-C_5Me_5^\bullet$, 273 (1.8); $M^{+\bullet}-5S^\bullet$, 248 (38.2); $M^{+\bullet}-2S^\bullet-C_5H_5^\bullet-SH^\bullet$, 246 (39.8); $M^{+\bullet}-S^\bullet-C_5Me_5^\bullet$, 241 (5.4); $M^{+\bullet}-2S^\bullet-C_5Me_5^\bullet$, 209 (15.9); $M^{+\bullet}-5S^\bullet-C_5H_5^\bullet$, 183 (1.2); $M^{+\bullet}-3S^\bullet-C_5Me_5^\bullet$, 177 (8.8); $M^{+\bullet}-4S^\bullet-C_5Me_5^\bullet$, 145 (17.7); $C_5Me_5^+$, 135 (32.8); $C_5Me_3CH_2^+$, 119 (42.9); $M^{+\bullet}-5S^\bullet-C_5Me_5^\bullet$, 113 (9.7); $C_8H_9^+$, 105 (21.4); $C_7H_7^+$, 91 (19.0); $M^{+\bullet}-4S^\bullet-C_5H_5^\bullet-C_5Me_5^\bullet$, 80 (11.8). Metastable ions, m/z: 216.9 (m/z = 279 → m/z = 246), 104.9 (m/z = 135 → m/z = 119).

Visible spectrum max. (CH_2Cl_2): 476 nm (ε 1.4 x 10^3), 445 (1.4 x 10^3).

Anal. (%): Calcd. for $C_{15}H_{20}S_5Ti$: C, 44.10; H, 4.93; S, 39.24. Found: C, 44.15; H, 4.88; S, 28.85, 29.57, 35.51.

(vi) Bis(η-pentamethylcyclopentadienyl)titana(IV)cyclotetrasulfane, $(Me_5Cp)_2TiS_3$, 47

Powdered sulfur (0.1604 g, 0.6253 mmol) was treated with Super Hydride (2.0 mL of a 1M solution of $LiEt_3BH$ in THF, 2.0 mmol) to give a lithium polysulfide solution. A suspension of $(Me_5Cp)_2TiCl_2$ (0.3889 g, 0.9991 mmol) in THF (30 mL) was added dropwise over 30 minutes. After stirring at room temperature for one hour the reaction mixture was refluxed at 81-83°C (oil bath) for 10.5 hours. The volatiles were removed _in vacuo_ and the residue extracted with CH_2Cl_2 (2 x 25 mL plus 2 x 10 mL) and filtered through Celite. Removal of the solvent from the purple filtrate gave the product as a black microcrystalline solid (sole product by ^1H NMR). Recrystallization from THF/pentane at -20°C for several days produced black crystals. Repeated concentration of the mother liquors gave two more crops of crystals (0.228 g combined, 55%, mp 149-152°C). The moderate isolated yield is in part due to the high solubility of the compound. Crystals suitable for an X-ray structure determination were grown from CH_2Cl_2/pentane at -20°C.

^1H NMR ($CDCl_3$): δ 1.83 (s, 30H, C_5Me_5).

IR (KBr): 2970 (s), 2900 (vs), 2860 (s, sh), 2720 (w), 1625 (w, br), 1490 (s), 1440 (s, sh), 1430 (s), 1377 (vs), 1372 (vs), 1360 (s, sh), 1260 (w), 1155 (w, br), 1095 (vw, br), 1058 (w), 1015 (s), 808 (m) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 414 (25.2); $M^{+\bullet}-S^{\bullet}$, 382 (9.2); $M^{+\bullet}-2S^{\bullet}$, 350 (8.0); $M^{+\bullet}-2S^{\bullet}-H^{\bullet}$, 249 (11.9); $M^{+\bullet}-3S^{\bullet}$, 318 (4.4); $M^{+\bullet}-C_{10}H_{15}{}^{\bullet}$, 279 (100.0); $M^{+\bullet}-S^{\bullet}-C_{10}H_{15}{}^{\bullet}$, 247 (7.5); $M^{+\bullet}-S^{\bullet}-C_{10}H_{15}{}^{\bullet}-H^{\bullet}$, 246 (10.5); $M^{+\bullet}-2S^{\bullet}-C_{10}H_{15}{}^{\bullet}-H^{\bullet}$, 214 (14.6); $C_{20}H_{30}S_2{}^{+\bullet}$, 199 (5.6); $C_{10}H_{15}S^+$, 167 (13.3); $C_{10}H_{15}{}^+$, 135 (41.8); $C_{10}H_{14}{}^{+\bullet}$, 134 (48.8); $C_9H_{11}{}^+$, 119 (52.6); $C_8H_9{}^+$, 105 (24.9); $C_7H_7{}^+$, 91 (19.8); $C_6H_5{}^+$, 77 (10.1). Metastable ions, m/z: 105.7 (m/z = 134 → m/z = 119), 84.8 (m/z = 167 → m/z = 119), 69.6 (m/z = 119 → m/z = 91).

Visible spectrum max. (CH_2Cl_2): 504 nm (ε 5.2 x 10^2).

Molecular weight (CH_2Cl_2): Calcd. for $C_{20}H_{30}S_3Ti$: 414.55. Found: 407.

Anal. (%): Calcd. for $C_{20}H_{30}S_3Ti$: C, 57.95; H, 7.29; S, 23.20. Found: C, 57.43; H, 7.40; S, 22.83.

(vii) Bis(η-cyclopentadienyl)zircona(IV)-cyclohexasulfane, Cp_2ZrS_5, 75

Powdered sulfur (2.57 g, 10.0 mmol) was treated with Super Hydride (10.0 mL of a 1M solution of $LiEt_3BH$ in THF, 10.0 mmol) to give a deep yellow lithium polysulfide solution. Some sulfur remained unreacted. A solution of Cp_2ZrCl_2 (2.91 g, 9.95 mmol) in THF (50 mL) was added dropwise over 80 minutes. The lemon yellow solution was stirred at room temperature for 15 hours. Filtration retained 0.53 g of sulfur (by TLC) on the fritte. The solution was cooled at -20°C overnight, filtered, and the solution concentrated <u>in vacuo</u> and cooled at -20°C. In this way three additional crops of mostly sulfur were isolated. The mother liquor of the last crop was reduced to dryness <u>in vacuo</u>. The malodorous yellow residue was extracted with toluene (8 x 25 mL) and filtered to remove LiCl. The solution was evaporated to dryness <u>in vacuo</u> to give a bright yellow solid. This residue was dissolved in CH_2Cl_2 (50 mL) and cooled at -20°C overnight. A small amount of yellow crystalline sulfur was isolated by filtration. The golden solution was concentrated <u>in vacuo</u> and stored at -20°C for one day. The product Cp_2ZrS_5, <u>75</u>, was isolated as large orange crystals (0.70 g) by filtration. By concentrating the mother liquors until the onset of crystallization, cooling at -20°C, and filtering an additional 0.42 g of <u>75</u> were obtained. Similar treatment of the mother liquor gave a mixture of orange <u>75</u> crystals (0.09 g) and yellow Cp_2ZrCl_2 microcrystals (0.29 g) which were separated manually. The combined yield of <u>75</u> was 1.21 g (63% based on Super Hydride as the limiting reactant, dec. 165-170°C).

^{1}H NMR ($CDCl_3$): δ 6.20 (s, 10H, C_5H_5).

IR (KBr): 3100 (m), 3095 (m, sh), 3070 (w, sh), 1830 (vw, br), 1740 (vw, br), 1640 (vw, br), 1431 (m), 1360 (vw), 1260 (vw), 1150 (vw, br), 1123 (m), 1060 (vw), 1018 (s), 1010 (s), 914 (w), 847 (w), 840 (w), 821 (vs), 818 (vs), 803 (vs) cm^{-1}.

Mass spectrum, m/z (rel intensity): $M^{+\bullet}$, 380 (12.3); $M^{+\bullet}-S^{\bullet}$, 348 (3.3); $M^{+\bullet}-H^{\bullet}-S^{\bullet}$, 347 (8.7); $M^{+\bullet}-S_2$, 316 (100.0); $M^{+\bullet}-3S^{\bullet}$, 284 (73.0); $M^{+\bullet}-2S_2$, 252 (38.9); $M^{+\bullet}-C_5H_5{}^{\bullet}-2S^{\bullet}$, 251 (48.9); $M^{+\bullet}-3S^{\bullet}-S_2$, 220 (9.4); $M^{+\bullet}-C_5H_5{}^{\bullet}-3S^{\bullet}$, 219 (9.4); $M^{+\bullet}-C_5H_5{}^{\bullet}-2S^{\bullet}-S_2$, 187 (14.6); $M^{+\bullet}-C_5H_5{}^{\bullet}-5S^{\bullet}$, 155 (1.5). Metastable ions, m/z: 262.8 (m/z = 380 → m/z = 316), 201.0 (m/z = 316 → m/z = 252), 170.4 (m/z = 284 → m/z = 220), 139.3 (m/z = 251 → m/z = 187).

Molecular weight (CH_2Cl_2): Calcd. for $C_{10}H_{10}S_5Zr$: 381.73. Found: 375.

Anal. (%): Calcd. for $C_{10}H_{10}S_5Zr$: C, 31.46; H, 2.64; S, 42.00. Found: C, 31.46; H, 2.98; S, 41.98.

(viii) Bis(η-pentamethylcyclopentadienyl)-zircona(IV)cyclotetrasulfane, $(Me_5Cp)_2ZrS_3$, 48

A lithium polysulfide solution was prepared by treating powdered sulfur (0.1601 g, 0.6241 mmol) with Super Hydride (2.0 mL of a 1M solution of $LiEt_3BH$ in THF, 2.0 mmol). A solution of $(Me_5Cp)_2ZrCl_2$ (0.4321 g, 0.9989 mmol) in THF (20 mL) was added dropwise over 15 minutes as the reaction solution became a vivid orange colour. The reaction was stirred at ambient temperature for 1.5 hours, followed by refluxing for 19 hours. All the volatile components were removed <u>in vacuo</u> to leave a bright orange microcrystalline solid. This residue was extracted with CH_2Cl_2 (2 x 20 mL plus 2 x 10 mL) and filtered through a pad of Celite. The orange filtrate was reduced in volume <u>in vacuo</u> to <u>ca</u>. 5 mL and the flask was stored under nitrogen at -20°C for one day. Removal of the mother liquor by a Pasteur pipette gave 0.246 g of deep orange crystals, mp 182-185°C. The mother liquor was evaporated to dryness <u>in vacuo</u>. The residue was extracted with hexanes (50 mL), filtered through Celite, concentrated in a nitrogen stream until the onset of crystallization, and stored at -20°C. Filtration gave 0.101 g of orange microcrystals for a combined yield of 0.347 g (76%).

^1H NMR ($CDCl_3$): δ 1.87 (s, 30H, C_5Me_5).

IR (KBr): 2970 (s), 2930 (s, sh), 2895 (vs), 2850 (s, sh), 2710 (w), 1626 (w, br), 1485 (s), 1442 (s, sh), 1422 (s), 1402 (m, sh), 1375 (vs), 1361 (s, sh), 1259 (w), 1158 (w), 1096 (w, br), 1059 (w), 1017 (s), 949 (w, br), 802 (m) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 456 (92.5); $M^{+\bullet}-S^{\bullet}$, 424 (3.3); $M^{+\bullet}-2S^{\bullet}$, 392 (22.6); $M^{+\bullet}-2S^{\bullet}-CH_3^{\bullet}$, 377 (6.9); $M^{+\bullet}-2S^{\bullet}-H_2S$, 358 (5.1); $M^{+\bullet}-3H_2S$, 354 (3.4); $M^{+\bullet}-2S^{\bullet}-CH_3^{\bullet}-H_2S$, 343 (4.4); $M^{+\bullet}-C_{10}H_{14}^{+\bullet}$, 322 (100.0); $M^{+\bullet}-C_{10}H_{15}^{\bullet}$, 321 (84.4); $M^{+\bullet}-S^{\bullet}-C_{10}H_{15}^{\bullet}$, 289 (20.6); $M^{+\bullet}-C_{10}H_{14}-H_2S$, 288 (27.9); $M^{+\bullet}-2S-C_{10}H_{15}^{\bullet}$, 257

(10.0); $M^{+\cdot}-C_{10}H_{14}^{+\cdot}-2H_2S$, 254 (16.2); $C_{10}H_{15}^{+}$, 135 (21.1); $C_{10}H_{14}^{+\cdot}$, 134 (54.4); $C_{10}H_{13}^{+}$, 133 (43.7); $C_9H_{11}^{+}$, 119 (62.4); $C_8H_9^{+}$, 105 (25.3); $C_7H_7^{+}$, 91 (26.2); $C_6H_5^{+}$, 77 (14.1). Metastable ions, m/z: 257.6 (m/z = 322 → m/z = 288), 69.6 (m/z = 119 → m/z = 91).

Molecular weight (CH_2Cl_2): Calcd. for $C_{20}H_{30}S_3Zr$: 457.87. Found: 439.

Anal. (%): Calcd. for $C_{20}H_{30}S_3Zr$: C, 52.46; H, 6.60; S, 21.01. Found: C, 52.18; H, 6.78; S, 21.04.

(ix) Bis(η-cyclopentadienyl)hafna(IV)cyclohexasulfane, Cp_2HfS_5, 76

Sulfur powder (0.2117 g, 0.8253 mmol) was suspended in THF (10 mL) and treated with Super Hydride (2.7 mL of a 1M solution of $LiEt_3BH$ in THF, 2.7 mmol). A solution of Cp_2HfCl_2 (0.5004 g, 1.318 mmol) in THF (20 mL) was added dropwise over 20 minutes to give a lemon-yellow reaction solution. After stirring at ambient temperature for 17 hours the ^1H NMR spectrum of an aliquot of the reaction solution indicated that no Cp_2HfCl_2 was present. All the volatile components were removed *in vacuo*. The lemon-yellow residue was extracted with CH_2Cl_2 (20 mL) and filtered to give a cloudy yellow filtrate. Reduction of the volume *in vacuo* to *ca*. 10-15 mL, followed by storage at -20°C for three days gave the product as small yellow crystals (0.165 g). The mother liquor was decanted, filtered, reduced in volume *in* vacúo, and stored at -20°C for two weeks. A second crop of very large crystals (0.162 g) was isolated. Thus the yield of Cp_2HfS_5, 76, after two crops was 0.327 g (53%, dec. 150-155°C).

^1H NMR ($CDCl_3$): δ 6.18 (10H, s), minor impurity δ 6.23.

IR (KBr): 3105 (w), 3095 (m, sh), 3080 (w, sh), 2275 (vw), 2080 (vw), 1840 (w, br), 1740 (w, br), 1645 (w, br), 1431 (m), 1362 (w), 1261 (vw), 1148 (vw), 1123 (m), 1060 (w), 1018 (s), 1011 (s), 942 (vw), 918 (w), 850 (m), 845 (m), 823 (vs), 808 (vs), 662 (w) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 470 (10.8); $M^{+\bullet}-S^\bullet$, 438 (2.4); $M^{+\bullet}-S_2$, 406 (99.6); $M^{+\bullet}-C_5H_5^\bullet$, 405 (54.0); $M^{+\bullet}-3S^\bullet$, 374 (87.6); $M^{+\bullet}-S^\bullet-C_5H_5^\bullet$, 373 (50.7); $M^{+\bullet}-4S^\bullet$, 342 (61.7); $M^{+\bullet}-2S^\bullet-C_5H_5^\bullet$, 341 (100.0); $M^{+\bullet}-3S^\bullet-C_5H_5^\bullet$, 309 (19.5); $M^{+\bullet}-4S^\bullet-C_5H_5^\bullet$, 277 (25.6). Metastable ions, m/z: 350.7 (m/z = 470 → m/z = 406), 349.0 (m/z = 470 → m/z = 405). Other clusters having principal ions m/z = 682, 617, 583, and 552 may be attributed to $(Cp_2HfS)_2$ present as a minor impurity: $M^{+\bullet}$, 682 (7.2); $M^{+\bullet}-C_5H_5^\bullet$, 617 (10.7); $M^{+\bullet}-2C_5H_5^\bullet$, 552 (2.2); $M^{+\bullet}-C_5H_5^\bullet-H_2S$, 583 (2.9).

Anal. (%): Calcd. for $C_{10}H_{10}HfS_5$: C, 25.61; H, 2.15; S, 34.18. Found: C, 22.37, 24.93; H, 2.56, 2.42; S, 34.23, 33.27.

(x) Bis(η-pentamethylcyclopentadienyl)hafna(IV)-cyclotetrasulfane, $(Me_5Cp)_2HfS_3$, 49

Powdered sulfur (0.0311 g, 0.121 mmol) was treated with Super Hydride (0.65 mL of a 1M solution of $LiEt_3BH$ in THF, 0.65 mmol) to give a yellow lithium polysulfide solution. A solution of $(Me_5Cp)_2HfCl_2$ (0.1652 g, 0.3178 mmol) in THF (50 mL) was added dropwise over 10 minutes. The golden reaction solution was refluxed for four hours at 80-90°C (oil bath). All the volatile components were removed *in vacuo*. The residue was extracted with CH_2Cl_2 and the solution filtered through Celite and evaporated to dryness *in vacuo* to give a slightly sticky orange solid. This solid was washed with hexanes (20 mL) and recrystallized from CH_2Cl_2 at -20°C for seven months. Removing the mother liquor by Pasteur pipette gave the product as an orange solid (0.015 g, 9%, mp 169-173°C).

^1H NMR ($CDCl_3$): δ 1.92 (s, 30H, C_5Me_5).

IR (KBr): 2965 (s), 2940 (s, sh), 2900 (vs), 2855 (s), 2720 (vw), 2490 (vw), 1705 (vw, br), 1489 (w), 1438 (m, br), 1378 (vs), 1362 (m, sh), 1261 (m), 1090 (m), 1018 (s), 798 (m), 700 (w), 667 (vw) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 546 (100.0); $M^{+\bullet}-S^{\bullet}$, 514 (1.0); $M^{+\bullet}-H_2S$, 512 (2.1); $M^{+\bullet}-2S^{\bullet}$, 482 (25.3); $M^{+\bullet}-S^{\bullet}-H_2S$, 480 (27.3); $M^{+\bullet}-2S^{\bullet}-CH_3^{\bullet}$, 467 (12.5); $M^{+\bullet}-S^{\bullet}-CH_3^{\bullet}-H_2S$, 465 (15.8); $M^{+\bullet}-S^{\bullet}-CH_3^{\bullet}-2H_2S$, 431 (2.4); $M^{+\bullet}-C_{10}H_{15}^{\bullet}$, 411 (61.0); $M^{+\bullet}-S^{\bullet}-C_{10}H_{15}^{\bullet}$, 379 (5.7);

$M^{+\bullet}-S^{\bullet}-C_{10}H_{15}^{\bullet}-H^{\bullet}$, 378 (20.2); $M^{+\bullet}-2S^{\bullet}-C_{10}H_{15}^{\bullet}$, 347 (3.8); $C_{10}H_{15}^{+}$, 135 (8.0); $C_{10}H_{14}^{+\bullet}$, 134 (22.5); $C_{10}H_{13}^{+}$, 133 (11.3); $C_9H_{11}^{+}$, 119 (17.2); $C_8H_9^{+}$, 105 (8.9); $C_7H_7^{+}$, 91 (12.5); $C_6H_5^{+}$, 77 (8.4).

Anal. (%): Calcd. for $C_{20}H_{30}HfS_3$: C, 44.07; H, 5.55; S, 17.65. Found: C, 42.77; H, 5.83; S, 13.88.

V) Cyclic Metal Polyselenanes

Reactions of Metallocene Dichlorides with Lithium Polyselenides to give:

(i) Bis(η-cyclopentadienyl)titana(IV)cyclohexaselenane, Cp_2TiSe_5, 107

Powdered grey selenium (1.1821 g, 14.97 mmol) was treated with Super Hydride (6.0 mL of a 1M solution of $LiEt_3BH$ in THF, 6.0 mmol) to give a brown solution of lithium polyselenides. A suspension of Cp_2TiCl_2 (0.7458 g, 2.995 mmol) in THF (50 mL) was added dropwise. The colour of the reaction mixture became purple. The reaction mixture was stirred at ambient temperature for 4.75 hours. Removal of the volatiles in vacuo gave a black residue which was extracted with CH_2Cl_2 (6 x 50 mL plus 2 x 100 mL) and filtered through Celite. The purple filtrate was concentrated in vacuo to ca. 50 mL and stored at -20°C overnight. The product Cp_2TiSe_5, 107, as air-stable purple crystals was collected by filtration from successive concentration of the mother liquors (1.227 g, 72%). The product foamed without melting at 209-211°C (lit.[163] mp 211°C).

^{1}H NMR ($CDCl_3$): δ 6.34 (s, 5H, C_5H_5), 5.92 (s, 5H, C_5H_5).

IR (KBr): 3100 (m), 3080 (m), 1858 (w, br), 1758 (w, br), 1644 (w, br), 1434 (s), 1366 (w), 1359 (w), 1262 (vw), 1123 (w), 1068 (w), 1053 (w), 1018 (s), 1009 (s), 980 (vw), 960 (vw), 930 (w), 909 (w), 852 (m, sh), 842 (s, sh), 831 (s, sh), 821 (vs) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 574 (2.4); $M^{+\bullet}-C_5H_5^{\bullet}$, 509 (0.2); $M^{+\bullet}-Se^{\bullet}$, 494 (0.1); $Se_6^{+\bullet}$, 476 (1.8); $M^{+\bullet}-C_5H_5^{\bullet}-Se^{\bullet}$, 431 (0.1); $M^{+\bullet}-Se_2$, 416 (20.4); $Se_5^{+\bullet}$, 396 (2.4); $M^{+\bullet}-C_5H_5^{\bullet}-2Se^{\bullet}$, 351 (10.0); $M^{+\bullet}-3Se^{\bullet}$, 338 (11.9); $Se_4^{+\bullet}$, 318 (1.1); $M^{+\bullet}-2C_5H_5^{\bullet}-2Se^{\bullet}$, 286 (1.8); $M^{+\bullet}-C_5H_5^{\bullet}-3Se^{\bullet}$, 273 (6.7); $M^{+\bullet}-2Se_2$, 258 (33.9); $Se_3^{+\bullet}$, 238 (2.4); $M^{+\bullet}-2C_5H_5^{\bullet}-3Se^{\bullet}$, 208 (4.0); $M^{+\bullet}-C_5H_5^{\bullet}-4Se^{\bullet}$, 193 (21.3); $M^{+\bullet}-Se^{\bullet}-2Se_2$, 178 (100.0); $Se_2^{+\bullet}$, 160 (25.4); $M^{+\bullet}-2C_5H_5^{\bullet}-4Se^{\bullet}$, 128 (10.5); $M^{+\bullet}-C_5H_5^{\bullet}-Se^{\bullet}-2Se_2$, 113 (36.8); Se^+, 80 (9.3). Metastable ions, m/z: 301.5 (m/z = 574 → m/z = 416), 160.0 (m/z = 416 → m/z = 258), 122.8 (m/z = 258 → m/z = 178), 71.7 (m/z = 178 → m/z = 113).

Anal. (%): Calcd. for $C_{10}H_{10}Se_5Ti$: C, 20.97; H, 1.76. Found: C, 21.13; H, 1.77.

(ii) Bis(η-cyclopentadienyl)zircona(IV)cyclohexaselenane, Cp_2ZrSe_5, 108

Powdered grey selenium (1.977 g, 25.04 mmol) was treated with Super Hydride (10.0 mL of a 1M solution of $LiEt_3BH$ in THF, 10.0 mmol) to give a deep red solution of lithium polyselenides. A solution of Cp_2ZrCl_2 (1.461 g, 4.998 mmol) in THF (20 mL) was added dropwise over 15 minutes. There was no obvious colour change. After stirring at ambient temperature for 3 hours the ^1H NMR spectrum of an aliquot of the reaction solution indicated an absence of Cp_2ZrCl_2. A small amount of black precipitate was present in the red-brown reaction solution. All the volatile components were removed *in vacuo*. The resulting foam was extracted with CH_2Cl_2 (20 mL) and the solution was filtered through Celite/Florisil (*ca*. 5:1 by volume). This was repeated until the extracts were pale yellow, leaving a brown residue on the filter pad. Evaporation of the solvent *in vacuo* from the combined filtrates gave the product as a brick-red microcrystalline solid (1.545 g, 50 %). The analytical sample was recrystallized from CH_2Cl_2 at -20°C in an aluminum-foil wrapped vessel and was obtained as orange flakes which decomposed without melting at 135-140°C.

^1H NMR ($CDCl_3$): δ 6.15 (s, 10H, C_5H_5).

IR (KBr): 3090 (m), 3075 (m), 1825 (w, br), 1735 (w, br), 1635 (w, br), 1428 (m), 1383 (vw), 1358 (w), 1257 (w), 1119 (m), 1054 (w), 1012 (s), 1005 (s), 908 (w), 838 (w), 815 (vs), 801 (vs), 718 (m) cm^{-1}.

Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 618 (1.5); $M^{+\bullet}-C_5H_5^{\bullet}$, 553 (1.4); $M^{+\bullet}-Se^{\bullet}$, 535 (0.5); $M^{+\bullet}-2C_5H_5^{\bullet}$, 488 (0.4); $M^{+\bullet}-C_5H_5^{\bullet}-Se^{\bullet}$, 476 (8.3); $M^{+\bullet}-2Se^{\bullet}$, 460 (84.5); $M^{+\bullet}-2C_5H_5^{\bullet}-Se^{\bullet}$, 412 (0.8); $M^{+\bullet}-C_5H_5^{\bullet}-2Se^{\bullet}$, 395 (22.5); $M^{+\bullet}-3Se^{\bullet}$, 380 (9.8); $M^{+\bullet}-2C_5H_5^{\bullet}-2Se^{\bullet}$, 330 (6.2); $M^{+\bullet}-C_5H_5^{\bullet}-3Se^{\bullet}$, 315 (20.4); $M^{+\bullet}-4Se^{\bullet}$, 300 (100.0); $M^{+\bullet}-2C_5H_5^{\bullet}-3Se^{\bullet}$, 250 (6.9); $M^{+\bullet}-C_5H_5^{\bullet}-4Se^{\bullet}$, 235 (50.0); $M^{+\bullet}-5Se^{\bullet}$, 220 (17.6); $M^{+\bullet}-2C_5H_5^{\bullet}-4Se^{\bullet}$, 170 (7.6); $Se_2^{+\bullet}$, 160 (29.1); Se^{+}, 80 (15.6).

Anal. (%): Calcd. for $C_{10}H_{10}Se_5Zr$: C, ~~19.49;~~ H, 1.64. Found: C, 19.47; H, 1.66.

(iii) Bis(η-cyclopentadienyl)hafna(IV)cyclohexaselenane, Cp_2HfSe_5, 109

Powdered grey selenium (0.3925 g, 4.971 mmol) was suspended in THF (20 mL) and treated with Super Hydride (2.0 mL of a 1M solution of $LiEt_3BH$ in THF, 2.0 mmol). The reaction flask was wrapped with aluminum foil. A solution of Cp_2HfCl_2 (0.3711 g, 0.9776 mmol) in THF (20 mL) was added dropwise over 30 minutes and stirring was continued for 5.5 hours. The amber coloured reaction mixtured contained a little black precipitate. The volatile components were removed *in vacuo*, the residue was extracted with CH_2Cl_2 (2 x 30 mL), and the solution was filtered through Celite. The reaction flask, filter Schlenk, and receiving flask were wrapped in aluminum foil at all times. The orange filtrate was concentrated in vacuo until the onset of crystallization and stored overnight at -20°C. The orange supernatant was removed by syringe from the product, an orange microcrystalline solid (0.355 g, 52%, dec. 130°C). Efforts to obtain a second crop of product by concentration and cooling of the mother liquor resulted in codeposition of orange and brown solids which were discarded.

^{1}H NMR ($CDCl_3$): δ 6.08 (s, 10H, C_5H_5).

IR (KBr): 3095 (w), 3070 (w), 1830 (vw, br), 1745 (vw, br), 1630 (vw, br), 1433 (m), 1420 (w, sh), 1362 (w), 1260 (w), 1122 (m), 1057 (w), 1018 (s), 1013 (s, sh), 1004 (s), 960 (vw), 930 (vw), 915 (w), 902 (w), 890 (vw), 851 (m), 842 (m), 824 (vs), 811 (vs), 764 (m) cm^{-1}.

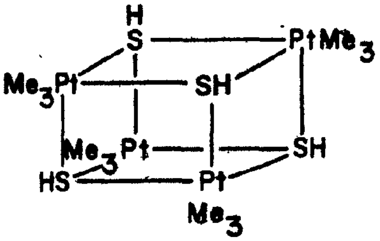
Mass spectrum, m/z (rel. intensity): $M^{+\bullet}$, 704 (1.9); $M^{+\bullet}-2Se^{\bullet}$, 546 (67.9); $M^{+\bullet}-C_5H_5^{\bullet}-2Se^{\bullet}$, 481 (20.2); $M^{+\bullet}-3Se^{\bullet}$, 468 (11.0); $M^{+\bullet}-C_5H_5^{\bullet}-2Se^{\bullet}$, 416 (2.9); $M^{+\bullet}-C_5H_5^{\bullet}-3Se^{\bullet}$, 403 (25.9); $M^{+\bullet}-4Se^{\bullet}$, 388 (100.0); $M^{+\bullet}-2C_5H_5^{\bullet}-3Se^{\bullet}$, 336 (6.2); $M^{+\bullet}-C_5H_5^{\bullet}-4Se^{\bullet}$, 323 (22.2); $M^{+\bullet}-5Se^{\bullet}$, 307 (5.3); $M^{+\bullet}-2C_5H_5^{\bullet}-4Se^{\bullet}$, 258 (4.2); $Se_3^{+\bullet}$, 238 (8.7); $Se_2^{+\bullet}$, 160 (51.3); Se^{+}, 80 (37.7).

Anal. (%): Calcd. for $C_{10}H_{10}HfSe_5$: C, 17.07; H, 1.43. Found: C, 17.14; H, 1.51.

3. THE SYNTHESIS OF $(\eta-C_5H_5)_2M(SH)_2$ (M = Ti, Zr, Hf)

Introduction

Organic thiols are important precursors to catenated sulfur compounds of the type RS_xR where $x > 1$.[258] Thus, transition metal complexes containing the hydrosulfide ligand could be equally important precursors to catenated sulfur derivatives of the types MS_xR and MS_xM. Monohydrosulfido complexes are quite numerous. Like the sulfur atom, the HS^- group can bond to metal centers in a variety of ways. It can occur terminally bonded to a metal as in $(H_2O)_5CrSH^{2+}$,[286,287] as a singly-bridging ligand as in $[W(CO)_5]_2(\mu-SH)^-$,[281,288-290] or as a triply-bridging group as in $(Me_3PtSH)_4$ (125).[291] Bis(hydrosulfido) complexes are relatively rare. A summary of the transition metal hydrosulfides according to group is presented in the following pages.



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The Titanium Group

Prior to this research only one hydrosulfido derivative of the group IVB metals was known, namely the complex $Cp_2Ti(SH)_2$ (110) reported by Köpf and Schmidt.[260] It was originally prepared by the treatment of Cp_2TiCl_2 in anhydrous ether with H_2S in the presence of a stoichiometric amount of Et_3N (eq. 34). However, this preparation has been found here to be unsatisfactory (*vide infra*). The related complex $(MeCp)_2Ti(SH)_2$ has been recently reported.[292] It was synthesized according to the route developed by McCall and Shaver[170] for 110: treating a THF solution of Cp_2TiCl_2 and Et_3N with H_2S.

$$Cp_2TiCl_2 + 2H_2S + 2Et_3N \longrightarrow \underset{\underline{110}}{Cp_2Ti(SH)_2} + 2Et_3NHCl \qquad (34)$$

The Chromium Group

The ion $(H_2O)_5CrSH^{2+}$ has been isolated in the solid state as the sulfate salt. It was prepared by the treatment of the aqueous Cr^{2+} ion with sodium polysulfide (as oxidant) and perchloric acid.[286,287] Other sulfur-containing oxidizing agents such as lead or silver sulfide can be used but give lower yields.[286]

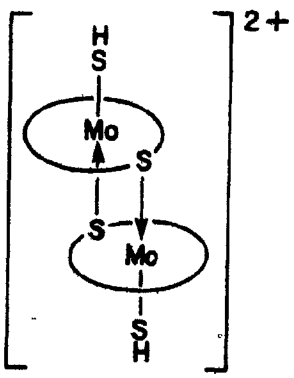
The macrocyclic polythiaether 1,5,9,13-tetrathiacyclohexadecane (16-ane[S_4]) has been used as a ligand in the preparation of molybdenum(II) bis(hydrosulfido) and molybdenum(IV) hydrosulfido complexes (eq. 35).[293,294]

$$[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_2)_2 \; + \; 16\text{-ane}[S_4] \longrightarrow$$

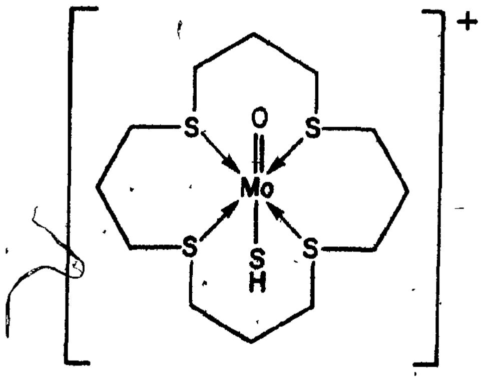
$$\underset{\underline{126}}{[Mo^{II}_2(SH)_2(16\text{-ane}[S_4])_2](CF_3SO_3)_2 \cdot 2H_2O} \; + \qquad (35)$$

$$\underset{\underline{127}}{Mo^{IV}O(SH)(16\text{-ane}[S_4])]CF_3SO_3} \; + \; \text{other products}$$

The X-ray structures of <u>126</u> and <u>127</u> are shown below where S Mo represents Mo(16-ane[S₄]).



<u>126</u>



<u>127</u>

The metal carbonyl anions $M(CO)_5EH^-$ (M = Cr, Mo, W; E = S, Se, Te) have been prepared <u>via</u> the reaction of $M(CO)_5THF$ (generated by irradiation of a THF solution of the hexacarbonyl) with an alkali metal chalcogenide $M_2'E$ (M' = Li, Na) in the presence of a protic solvent such as methanol or ethanol. The dimeric ions $[M(CO)_5]_2(\mu\text{-EH})^-$ formed as minor by-products (eq. 36).[288] In addition, irradiation of

$$2M(CO)_6 + M_2{}'E \xrightarrow[-2CO]{h\nu} [M(CO)_5EH]M' + [M(CO)_5]_2(\mu\text{-}EH)M' \qquad (36)$$

a THF/EtOH solution of $Mo(CO)_6$ and Li_2S gave the doubly-bridged anion $[Mo(CO)_4(\mu\text{-}SH)]_2^{2-}$ as the major product.[288] The monomers $M(CO)_5EH^-$ react with $M(CO)_5THF$ to give the anions $[M(CO)_5]_2(\mu\text{-}EH)^-$. Treatment of $Cr(CO)_5Cl^-$ with alkali metal chalcogenides gave $Cr(CO)_5EH^-$. The anions were conveniently isolated as tetraphenylarsonium (TPA^+) or bis-(triphenylphosphine)iminium (PPN^+) salts.

The preparation of $M(CO)_5SH^-$ (M = Cr, Mo, W) and $[W(CO)_5]_2(\mu\text{-}SH)^-$ and their isolation as the PPN^+ and Et_4N^+ salts, respectively, has also been reported by Gingerich and Angelici.[281] The monomers were prepared by reacting the hexacarbonyl with [PPN]SH prepared in situ (eq. 37). The

$$M(CO)_6 + [PPN]SH \longrightarrow [PPN][M(CO)_5SH] + CO \qquad (37)$$

attempted protonation of $W(CO)_5SH^-$ with a non-coordinating acid gave $[W(CO)_5]_2(\mu\text{-}SH)^-$ and H_2S (eq. 38) in an ^1H NMR

$$2\,W(CO)_5SH^- + CF_3SO_3H \longrightarrow [W(CO)_5]_2(\mu\text{-}SH)^- + H_2S + CF_3SO_3^- \qquad (38)$$

tube experiment.[281] The thermal reaction of the hexacarbonyl with sodium hydrosulfide in THF/EtOH gave only the binuclear species (eq. 39). Treatment with aqueous Et_4NBr gave the

$$2W(CO)_6 + NaSH \xrightarrow{\Delta} Na[W(CO)_5]_2(\mu\text{-SH}) \qquad (39)$$

corresponding salt which could be deprotonated by NaH to give $Na[Et_4N][W(CO)_5]_2(\mu\text{-S})$.

The reactivity of the $W(CO)_5SH^-$ and $[W(CO)_5]_2(\mu\text{-S})^{2-}$ anions was also explored.[281] For example, reaction of the former with acetic anhydride gave the thioacetate complex $W(CO)_5[MeC(=O)S]^-$ while with acetyl chloride $W(CO)_5Cl^-$ was obtained. Reaction of the dimer with electrophiles El-Cl (where El = Me_3Sn or Ph_2P, for example) gave sulfur-bridged species (eq. 40). Interestingly, the reaction of $(PPh_3)_2PdCl_2$

$$[W(CO)_5]_2(\mu\text{-S})^{2-} + \text{El-Cl} \longrightarrow [W(CO)_5]_2(\mu\text{-SEl})^- + Cl^- \qquad (40)$$

with $[W(CO)_5]_2(\mu\text{-S})^{2-}$ in a 1:2 stoichiometry gave only $W(CO)_5(PPh_3)$ and $W(CO)_5Cl^-$ and no new cluster compounds. The fate of the palladium was not specified.

Cooper et al.[289] used a photochemical route in the synthesis of $[Na(18\text{-crown-}6)][M(CO)_5SH]$ and $[Na(18\text{-crown-}6)][M_2(CO)_{10}(\mu\text{-SH})]$ (M = Cr, Mo, W). Irradiation of $M(CO)_6$ (M = Cr, Mo, W), $Na_2S{\cdot}9H_2O$, and 18-crown-6 in ethanol gave the mononuclear anions exclusively (eq. 41). When M = Cr or W the dinuclear species, along with a small amount of

$$\mathrm{M(CO)_6} + \mathrm{Na_2S\cdot 9H_2O} + \text{18-crown-6} \xrightarrow{h\nu} [\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{M(CO)_5SH}] \qquad \mathrm{M = Cr, Mo, W} \tag{41}$$

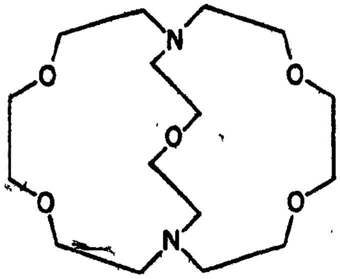
the mononuclear compound, could be prepared by varying the stoichiometry (eq. 42). However, replacement of $Na_2S\cdot 9H_2O$

$$2\mathrm{M(CO)_6} + \mathrm{Na_2S\cdot 9H_2O} + \text{18-crown-6} \xrightarrow{h\nu} [\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{M_2(CO)_{10}(\mu\text{-}SH)}] \qquad \mathrm{M = Cr, W} \tag{42}$$

by $NaSH\cdot H_2O$ gave purer products and a decrease in the irradiation time.[289] The syntheses of the dimolybdenum compound and all of the mixed-metal complexes were accomplished by virtue of the high reactivity of $[M(CO)_5(SH)]^-$ towards $M(CO)_5THF$ (eq. 43). The stabilizing effect of the Na(18-crown-6)$^+$ cation enabled the direct synthesis of $[M(CO)_5]_2(\mu\text{-}SH)^-$ (M = Cr, Mo) and greatly improved the solid state

$$\mathrm{M(CO)_5THF} + [\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{M'(CO)_5SH}] \longrightarrow [\mathrm{Na(18\text{-}crown\text{-}6)}][\mathrm{MM'(CO)_{10}(\mu\text{-}SH)}] \qquad \mathrm{M, M' = Cr, Mo, W} \tag{43}$$

stabilities of the dinuclear as well as the mononuclear species.[281] The reaction of $M(CO)_6$ (M = Cr, Mo, W) with cryptand-solubilized NaSH in CH_3CN solutions gave the analogous [Na(kryptofix-221)][$M(CO)_5SH$] derivatives where kryptofix-221 is 128.[290] The X-ray crystal structures of



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[Na(18-crown-6)][$W(CO)_5SH$], [Na(kryptofix-221)][$Cr(CO)_5SH$], and [Na(18-crown-6)][$W_2(CO)_{10}(\mu\text{-}SH)$] have been reported.[290]

Displacement of C_7H_8 from (η^4-C_7H_8)$M(CO)_3$ (M = Cr, Mo, W) by L=2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), or ethylenediamine (en) in the presence of NaSH gave [$M(CO)_3L(SH)$]$^-$ (eq. 44). Addition of Ni(phen)$_3Cl_2$ or PPh_4Cl to the reaction solution gave the Ni(phen)$_3^{2+}$ and PPh_4^+ salts, respectively.[295]

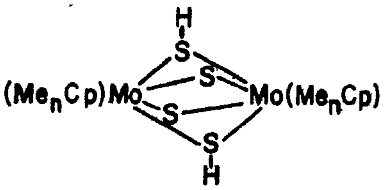
$$C_7H_8M(CO)_3 + L + NaSH \longrightarrow [M(CO)_3L(SH)]Na + C_7H_8 \qquad (44)$$

The cyclopentadienyl complexes $CpW(CO)_3SH$ (129),[296] [$(C_5H_{5-n}Me_n)Mo(\mu\text{-}S)(\mu\text{-}SH)$]$_2$ (n = 0, 1, 5) (130)[297] and $Cp_2M(SH)_2$ [M = Mo (131), W (132)][298] have been reported. Complex 129 was prepared via sulfur abstraction from propylene episulfide by $CpW(CO)_3H$ (eq. 45).[296] However, this was found not to be a preparatively useful reaction for

129

(45)

large amounts of 129.[264] A better route to 129 is *via* treatment of $CpW(CO)_3I$ with a three-fold excess of NaSH in THF.[264] The dimers 130 were prepared by H_2 reduction of the sulfido-molybdenum precursors $[(Me_nCp)MoS_x]_y$ (n = 0, 1, 5; x and y indeterminate), $[(MeCp)MoS_2]_2$, $[(Me_5Cp)MoS_5]_2$, and $[(Me_5Cp)MoS_2]_2$.[297,299] The complexes 130 all catalyze the



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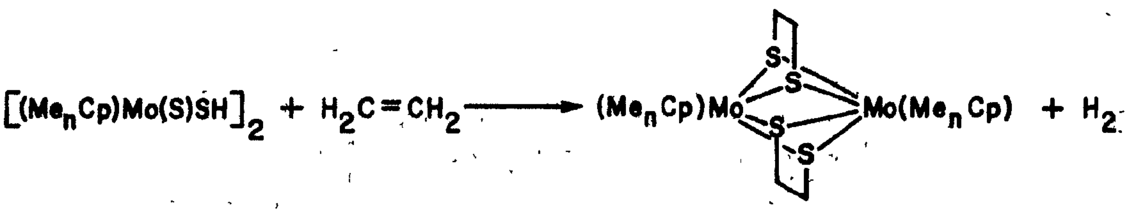
reduction of elemental sulfur to H_2S at low temperature and low hydrogen pressures. They react with ethylene or acetylene to give ethanedithiolato- (133) and ethenedithiolato-bridged (134) complexes, respectively (eqs. 46 and 47).[297]



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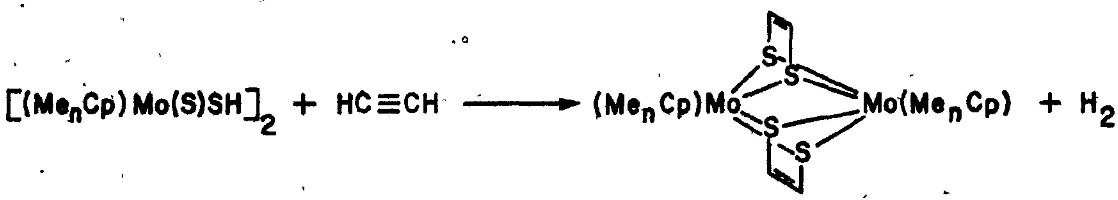
133



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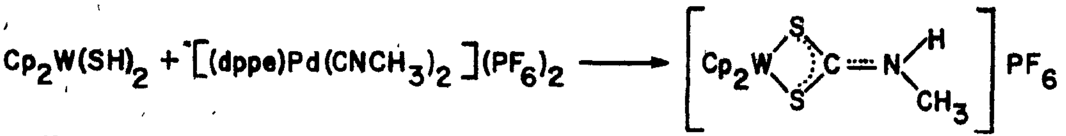
(47)

$$Cp_2MCl_2 \;+\; \text{excess NaSH} \;\longrightarrow\; Cp_2M(SH)_2 \;+\; 2\,NaCl \qquad (48)$$

131 M = Mo

132 M = W



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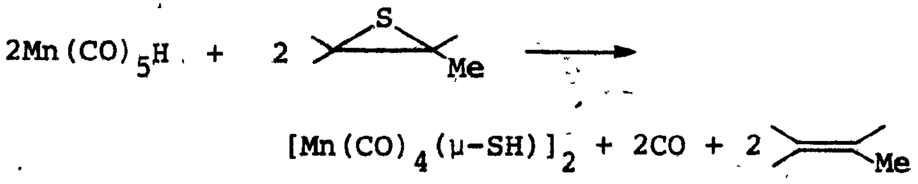
(49)

Complexes containing two hydrosulfide ligands bonded to the same metal atom are quite rare. Although $Cp_2Mo(SH)_2$ (131) and $Cp_2W(SH)_2$ (132) have been known since 1967, their reactivity has only been explored recently. They were prepared by treating the dichlorides with NaSH (eq. 48).[298] Rauchfuss and Ruffing[300] treated 132 with MeNC "activated" via coordination to palladium to obtain the N-methyldithiocarbamate derivative 135 (eq. 49).

The Manganese Group

Several interesting hydrosulfido complexes of manganese(I) and rhenium(I) have been isolated. The hydride $Mn(CO)_5H$ reportedly reacts smoothly with propylene episulfide to give the dimer $[Mn(CO)_4(\mu\text{-}SH)]_2$ (<u>136</u>) (eq. 50).[301] The complex $Mn(CO)_5SH$ (<u>137</u>) was proposed



<u>136</u>

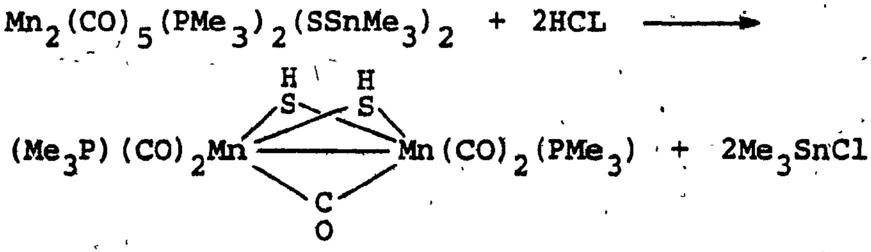
(50)

as an intermediate but was not isolated. Küllmer and Vahrenkamp[302] prepared <u>137</u> but noted that it is quite unstable in solution, reverting to <u>136</u>. Complexes <u>136</u> and $[Mn(CO)_3(\mu_3\text{-}SH)]_4$ and their rhenium analogues were prepared by treatment of $[M(CO)_4(\mu\text{-}SSnMe_3)]_2$ or $[M(CO)_3(\mu_3\text{-}SSnMe_3)]_4$ (M = Mn, Re) with hydrogen chloride. Conversion of the tetramer into the dimer, and the dimer into the monomer occurred in solution under a pressure of carbon monoxide (eqs. 51 and 52). The reaction of $[M(CO)_3(PMe_3)(\mu\text{-}SSnMe_3)]_2$

$$\underset{(M = Mn, Re)}{[M(CO)_3SH]_4} \xrightarrow[CCl_4]{130\ atm\ CO} \underset{\underline{136}}{[M(CO)_4(\mu\text{-}SH)]_2} \qquad (51)$$

$$\underset{\underline{136}}{[Mn(CO)_4(\mu\text{-}SH)]_2} \xrightarrow[CCl_4]{200\ atm\ CO} \underset{\underline{137}}{Mn(CO)_5SH} \qquad (52)$$

(M = Mn, Re) with HCl similarly gave $[M(CO)_3(PMe_3)(\mu\text{-}SH)]_2$.[303] Direct treatment of $[M(CO)_4(\mu\text{-}SH)]_2$ with PMe_3 gave the mononuclear species mer-trans-$Mn(CO)_3(PMe_3)_2SH$ and fac-$Re(CO)_3(PMe_3)_2SH$.[303] The mer-trans rhenium isomer was isolated from the reaction of $[Re(CO)_3(PMe_3)SH]_2$ with PMe_3 under more vigorous conditions or by recrystallization of the fac isomer at room temperature. These bis(phosphine) complexes react with the hexacarbonyls $M'(CO)_6$ (M' = Cr, Mo, W) to give the SH-bridged mixed-metal dimers of the type $(Me_3P)_2(CO)_3M\text{-}SH\text{-}M'(CO)_5$ as mer-trans and fac isomers.[304] Complex 138 containing two SH-bridges was prepared from $Mn_2(CO)_5(PMe_3)_2(SSnMe_3)_2$ and HCl (eq. 53).[303]

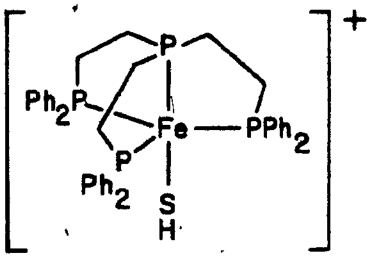


(53)

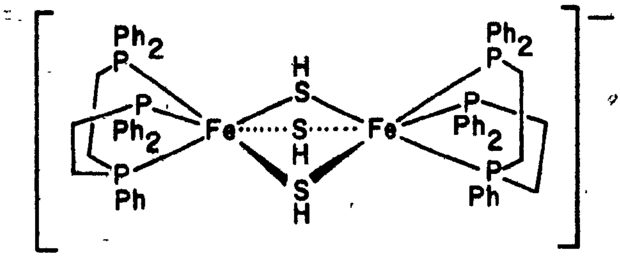
138

The Iron Group

To date no hydrosulfido complexes of ruthenium and osmium have been reported. The single iron complex containing a single SH group, namely $[Fe(SH)pp_3]BPh_4$ (139, where pp_3 = tris[(2-diphenylphosphinoethyl)phosphine]) was prepared via the reaction of $[Fe(H_2O)_6](BF_4)_2$ with H_2S in the presence of pp_3.[305] The X-ray crystal structure of the BPh_4 salt revealed a five-coördinate trigonal bipyramidal arrangement of the ligands.[305] The analogous reaction of $[Fe(H_2O)_6]X_2$ ($X = ClO_4$ or BF_4) with H_2S in the presence of ppp (bis[2-(diphenylphosphino)ethyl]phenylphosphine) gave a dimeric anion with three bridging SH groups, $[Fe_2(\mu\text{-}SH)_3(ppp)_2]^-$, (<u>140</u>). Its X-ray structure has been determined.[306]

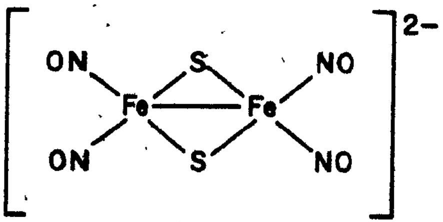


<u>139</u>



<u>140</u>

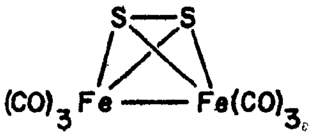
A dimeric iron(I) species of particular interest is $[Fe(NO)_2(\mu\text{-}SH)]_2$ (<u>141</u>). Although salts of the deprotonated species <u>1</u> were first made in 1858,[307] little attention was paid to the system until recently. The disodium salt of <u>1</u>,



<u>1</u>

known as "Roussin's red salt", can be transformed in low yield into the neutral doubly-SH-bridged compound <u>141</u> by treatment with acetic acid, trifluoroacetic acid, or tetrafluoroboric acid.[8] The dimeric complex $Fe_2(CO)_6(\mu\text{-}S_2)$ (<u>142</u>)

was first reported in 1958[308] and its X-ray structure reported in 1965.[309] Cleavage of the sulfur-sulfur bond

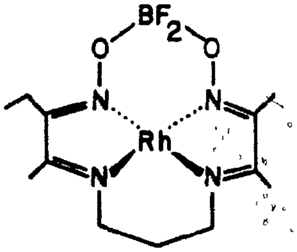


142

with $LiEt_3BH$ followed by protonation with CF_3COOH at low temperature gave the very air-sensitive complex $[Fe(CO)_3(\mu\text{-}SH)]_2$ in situ as a mixture of isomers.[310,311]

The Cobalt Group

The complex $[Co(SH)L]BPh_4$ (L = np_3 = tris(2-diphenylphosphinoethyl)amine or pp_3] was prepared[305] from $Co(H_2O)_6(BF_4)_2$, L, and H_2S followed by the addition of $NaBPh_4$. The interesting rhodium(III) species RhL'(H)(SH) was prepared via oxidative addition of H_2S to the highly reactive RhL' precursor 143.[312] It is stable in the solid state but in solution reductively eliminates H_2S to form the starting material.[312] The bis(hydrosulfido) complex



143

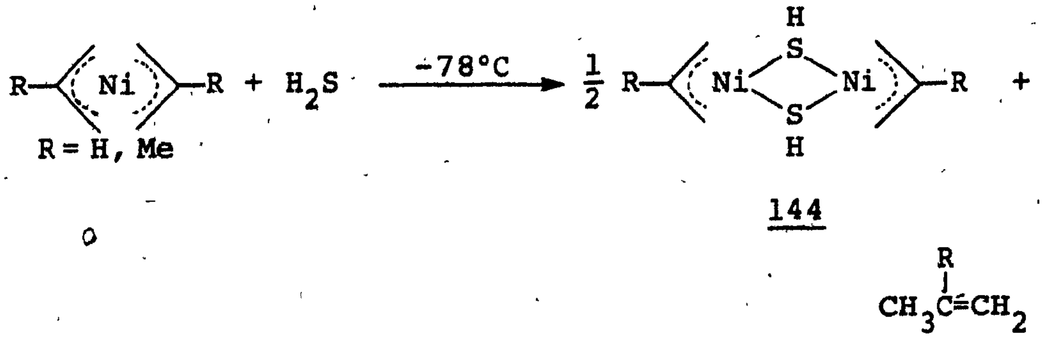
$RhL'(SH)_2$ was prepared via the hydrolysis of $RhL'(SGeEt_3')_2$. Although a macrocyclic ligand such as L' has a stabilizing influence on metal-SH bonds,[312] it is not necessary for the isolation of rhodium(III) hydrosulfido compounds. The complex $RhClH(SH)(PPh_3)_2$ was isolated from the reaction of $RhCl(PPh_3)_3$ and H_2S.[313] The complex $Rh(SH)(CO)(PPh_3)_2$ was prepared from $Rh(OCO_2H)(CO)(PPh_3)_2$ and H_2S [314] or alternatively via treatment of $RhH(CO)(PPh_3)_3$ with carbonyl sulfide (eq. 54).[315] The iridium complex $IrClH(SH)(PPh_3)_2$

$$RhH(CO)(PPh_3)_3 + COS \longrightarrow Rh(SH)(CO)(PPh_3)_2 + CO + PPh_3 \quad (54)$$

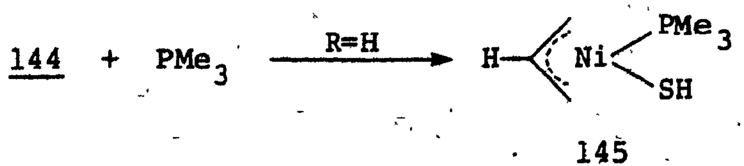
was made by oxidative addition of H_2S to trans-$IrCl(CO)(PPh_3)_2$.[313]

The Nickel Group

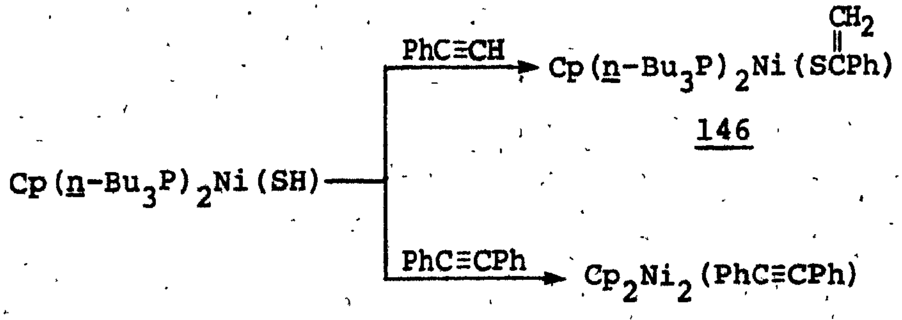
Numerous hydrosulfido complexes are known for nickel, platinum, and palladium. The cations $[Ni(SH)L]^+$ were prepared by bubbling H_2S through a solution containing $[Ni(H_2O)_6]^{2+}$ and L where L is a stabilizing poly(tertiary phosphine) ligand.[305,316] The bis(hydrosulfido) complex $(dppe)Ni(SH)_2$, where dppe = 1,2-bis(diphenylphosphino)ethane, was obtained from the reaction of NaSH with $(dppe)NiCl_2$.[127,317,318] Isomeric dimers of the type 144 were prepared from $(\eta\text{-allyl})_2Ni$ or $(\eta\text{-2-methylallyl})_2Ni$ and H_2S at low temperature (eq. 55); however, the products decomposed above 20°C into nickel sulfide and propene or isobutene.[319] Treatment with trimethylphosphine cleaved the dimer to give the monomer 145. The latter was found to be stereochemically non-rigid in solution above -100°C (eq. 56).[319] The



144 (55)



145 (56)



$$Cp(\underline{n}\text{-}Bu_3P)_2Ni(SH) \xrightarrow{PhC\equiv CH} Cp(\underline{n}\text{-}Bu_3P)_2Ni(S\overset{\overset{CH_2}{\|}}{C}Ph) \qquad (57)$$

146

$$Cp(\underline{n}\text{-}Bu_3P)_2Ni(SH) \xrightarrow{PhC\equiv CPh} Cp_2Ni_2(PhC\equiv CPh) \qquad (58)$$

147

η-cyclopentadienyl complex $Cp(\underline{n}\text{-}Bu_3P)_2Ni(SH)$ was prepared from NaSH and $Cp(\underline{n}\text{-}Bu_3P)_2NiCl$.[320] Phenylacetylene inserts into the S-H bond to give 146 (eq. 57).[321] Diphenylacetylene gave the dimer 147 with loss of hydrosulfide and phosphine ligands (eq. 58).[321]

For platinum, the complex cis-$(PPh_3)_2Pt(SH)_2$ (148) has been the subject of several reports.[126,127,318,322-324] Several[127,318,322,323] of these syntheses were not reproducible.[325] A proven route[325] is a modification of Briant's procedure[324] wherein $(PPh_3)_2PtO_2$ was treated with H_2S with THF as the solvent instead of $CHCl_3$ (eq. 59). The X-ray crystal structure of 148 confirmed the cis monomeric

$$(PPh_3)_2PtO_2 + H_2S \longrightarrow \underset{\underline{148}}{\underline{cis}\text{-}(PPh_3)_2Pt(SH)_2} + H_2O_2 \qquad (59)$$

formulation.[324] The reactions of trans-$(PEt_3)_2PtCl_2$ and trans-$(PEt_3)_2PtHCl$ with excess NaSH gave trans-$(PEt_3)_2Pt(SH)_2$ and trans-$(PEt_3)_2PtH(SH)$, respectively.[326] Treatment of trans-$(PEt_3)_2PtHI$ with H_2S gave trans-$(PEt_3)_2PtI(SH)$ which was identified spectroscopically.[326] The analogous complexes trans-$(PPh_3)_2PtH(SH)$[327-328] and trans-$[P(CH_2Ph)_3]_2PtH(SH)$ [329] have also been reported. The complex trans-$\{[(PEt_3)_2PtH]_2(\mu\text{-}SH)\}BF_4$ is a rare example of a monobridged bis-platinum(IV) species.[330] It was prepared by the treatment of a mixture of trans-$(PEt_3)_2PtHCl$ and trans-$(PEt_3)_2PtH(SH)$ with $AgBF_4$. The cubane-like complex $(Me_3PtSH)_4$ (125) contains triply-bridging SH groups.[291]

Two palladium hydrosulfido complexes have been reported. The palladium analog to 148, $(PPh_3)_2Pd(SH)_2$, was prepared <u>via</u> the treatment of $Pd(PPh_3)_2(N_3)_2$ [126] or $Pd(PPh_3)_4$ [331] with H_2S. The complex $(dppe)_2Pd$ reacted with H_2S to give $(dppe)Pd(SH)_2$.[331] This compound was also prepared from $(dppe)PdCl_2$ and H_2S in the presence of Et_3N,[122,323] or by treatment of the dichloride with NaSH.[318]

Results

The complex $Cp_2Ti(SH)_2$ (110) was prepared by the treatment of a red THF solution of Cp_2TiCl_2 with H_2S in the presence of a stoichiometric amount of Et_3N. The rapid reaction (eq. 34) occurred with an immediate precipitation of Et_3NHCl and a colour change to red-black. The cream-coloured Et_3NHCl was easily removed by filtration. Evaporation of the filtrate *in vacuo* gave brown malodorous 110 in nearly quantitative yield.[170] Incomplete dissolution of the Cp_2TiCl_2 prior to the addition of H_2S gave a crude product which contained large amounts of cyclopentadienyltitanium containing impurities (detected in the ^1H NMR spectrum) which were difficult to remove. Recrystallization of 110 resulted in excessive loss of compound. Since crude 110 was pure by ^1H NMR it was used in all subsequent

$$Cp_2TiCl_2 + 2Et_3N + 2H_2S \longrightarrow \underset{\underline{110}}{Cp_2Ti(SH)_2} + 2Et_3NHCl \qquad (34)$$

experiments. This compound can be manipulated freely in air as a solid and in solution at room temperature. However, Köpf and Schmidt[260] noted a thermal decomposition to give polycrystalline oligomers having Ti-S-Ti bonds when 110 was boiled in benzene. When 110 was stored in air at room temperature for several months partial decomposition occurred. However, 110 could be recovered by extraction of the mixture in air with CH_2Cl_2. A sample of 110 stored in a closed air-filled vessel at -20°C showed no evidence of decomposition after one year.

The method successfully used to prepare $Cp_2Ti(SH)_2$ (110) was extended to the zirconium and hafnium system. Treatment of a THF solution of Cp_2ZrCl_2 and Et_3N with H_2S gave primarily $Cp_2Zr(SH)_2$ (111) as malodorous yellow crystals which could be handled briefly in air in the solid state. Prolonged contact with air caused a white layer to form on their surface. Decomposition appeared to occur even when 111 was stored under nitrogen for several months at -20°C. Although the crystals were unchanged in colour they were insoluble in common organic solvents. A freshly prepared solution of 111 was bright yellow. However, after standing at room temperature for 15 minutes the solution was green in colour. This colour change did not occur when the solution was saturated with H_2S.

The crude reaction mixture in the preparation of 111 was filtered and the initially yellow filtrate was concentrated in vacuo. Even when this evaporation was conducted at 0°C the filtrate slowly became emerald green in colour. The first product isolated was large and bright yellow crystals of 111. Further evaporation gave additional product, the final sample of which was turquoise microcrystalline 112. The spectral and microanalytical data (Experimental section) for the turquoise product 112 are consistent with a dimeric formulation, $(Cp_2ZrS)_2$. Treatment of Cp_2HfCl_2 with H_2S in the presence of Et_3N in THF gave a white product 113 whose characterization is discussed below.

When a THF solution of $(Me_5Cp)_2TiCl_2$ and a stoichiometric amount of Et_3N was treated with H_2S at room temperature, no reaction occurred. The unreacted dichloro complex was recovered.

The ^1H NMR spectra ($CDCl_3$) of the complexes $Cp_2M(SH)_2$ (M = Ti, Zr) each consisted of two singlets. For the titanium complex 110 these appeared at δ 6.28 (10H, C_5H_5) and δ 3.38 (2H, SH). The zirconium complex 111 displayed a η-C_5H_5 signal also at δ 6.28 (10H) and an SH signal to higher field, at δ 1.94 (2H). The spectrum of turquoise 112 in $CDCl_3$ showed only a single sharp peak at δ 6.44 for the η-C_5H_5 protons consistent with the absence of SH ligands. The product 113 from the attempted synthesis of $Cp_2Hf(SH)_2$ showed two signals in its ^1H NMR spectrum ($CDCl_3$) at δ 6.06 (s, 10.8H, C_5H_5) and δ 0.58

(s, 1.0H, SH).

A turquoise solution of 112 in $CDCl_3$, prepared under nitrogen, was treated with H_2S. A rapid colour change to yellow occurred. The ^1H NMR signal at δ 6.44 for 112 was replaced by signals at δ 6.28 (s, 10H) and δ 1.94 (s, 2H) consistent with the formation of 111. Under the H_2S atmosphere no signal due to 112 was evident after 24 hours.

The solid-state infrared spectra of 110-113 were dominated by absorption bands due to vibrations of the η-C_5H_5 rings. The precursor dichlorides Cp_2MCl_2 (M = Ti, Zr, Hf) show five characteristic bands[332] at ca. 3100 (medium, CH stretch), 1440 (medium, CC stretch), 1130 (weak, CC stretch), 1020 (medium, CH deformation in plane), and 820 cm^{-1} (very strong, CH deformation out of plane). Complexes 110-113 displayed bands in these regions also and resembled the dichlorides in their intensities and locations. The hydrosulfido complexes 110, 111, and 113 additionally showed weak features near 2500 cm^{-1}. No absorption was observed in this region for 112. The SH stretching band of mercaptans and thiophenols occurs at 2590 to 2540 cm^{-1} and is weak in the infrared.[333] Thus, weak bands at 2530 (broad), 2550 (broad), and 2565 cm^{-1} (sharp) in the spectra of 110, 111, and 113 are tentatively assigned to the SH stretching vibration in these compouds. No strong resolved bands were observed below 750 cm^{-1} for the hydrosulfido complexes. A strong, broad absorption was present at 730 cm^{-1} for 112, though.

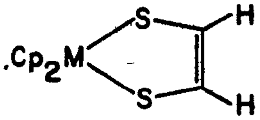
The electron-impact mass spectra (70 eV) of 110, 111, and 112 displayed molecular ion peaks and support their formulation as $Cp_2Ti(SH)_2$, $Cp_2Zr(SH)_2$, and $(Cp_2ZrS)_2$, respectively. Köpf and Schmidt[260] did a molecular weight determination of 110 in $CHCl_3$ which confirmed the monomeric formulation. The zirconium analog 111 is assumed to be monomeric. Due to decomposition a solution molecular weight determination of 112 was not possible. On the basis of its mass spectrum a dimeric structure is proposed for 112, although other oligomeric structures cannot be ruled out completely. The mass spectrum of the hafnium complex 113 did not show a molecular ion corresponding to $Cp_2Hf(SH)_2$. The observed fragmentation pattern included some peaks having isotope patterns consistent with the presence of more than one hafnium atom but these were not interpreted further. The 20 eV mass spectrum of 113 displayed peaks corresponding to H_2S_n (n = 1-6). The complex discoloured lead acetate paper when the paper was exposed to the vapours above a sample melted in air.

The microanalytical results for 110-112 were consistent with their formulations. The results for 113 were as follows: Calcd. for $Cp_2Hf(SH)_2$: C, 32.04; H, 3.23; S, 17.11. Found: C, 23.12; H, 2.67; S, 7.52. The structure of 113 was not assigned.

A few reactions of 110 and 111 were explored. Those reactions with elemental sulfur, sulfur-transfer reagents, and "blocked" sulfur-transfer reagents are detailed in subsequent chapters. Complex 110 was unreactive towards stoichiometric amounts of Me_2SiCl_2 and Et_3N in THF at room temperature. At 50°C and in the presence of two-fold excesses of Me_2SiCl_2 and Et_3N, 110 was converted into Cp_2TiCl_2 in 80% yield. The reaction of stoichiometric amounts of Me_2SnCl_2, Et_3N, and 110 in a THF solution at room temperature gave a complex mixture of very air-sensitive products which was not investigated further. Treatment of 110 with one equivalent of $(Me_3Si)_2NH$ or two equivalents of Me_3SiCl/Et_3N also gave a mixture of products (detected by ^1H NMR) which was not investigated further. Treatment of 110 with $PhPCl_2$ and Et_3N at room temperature gave Cp_2TiCl_2 as the only soluble metal-containing product. Compound 110 was unreactive towards CH_2I_2 and Et_3N at room temperature, and decomposition occurred upon refluxing in THF. However, $Cp_2Zr(SH)_2$ (111) reacted with an equimolar amount of Me_2SiCl_2 in the presence of Et_3N in THF at room temperature. The main product was a very air-sensitive lemon-yellow solid which was sublimed at 75°C and 0.015 torr (2.0 Pa) onto a water-cooled probe. Its mass spectrum showed an intense peak for $Cp_2ZrS_2SiMe^+$ but also peaks at higher m/z values which had an isotope pattern consistent with the presence of two Zr atoms. The compound was not examined further. Complex <u>111</u> reacted with iodine to give Cp_2ZrI_2 as the only isolated metal-containing product. Hydrogen sulfide gas was detected in the vapours above the solution. The reaction of Cp_2ZrS_5 (<u>75</u>) with iodine in a ^1H NMR tube in $CDCl_3$ gave Cp_2ZrI_2 (detected by NMR) and sulfur (detected by TLC).

Discussion

The literature method[260] for the synthesis of $Cp_2Ti(SH)_2$ (<u>110</u>) involves the treatment of Cp_2TiCl_2 with H_2S in the presence of Et_3N in anhydrous ether. Subsequent extraction with water was the reported method whereby the Et_3NHCl by-product was removed. Recrystallization gave <u>110</u> as brown-black crystals. The synthesis of <u>110</u> by this literature procedure was not reproducible by the author when the water extraction was performed. Ralea <u>et al.</u>[105] had cautioned against the isolation of <u>110</u> due to attendant decomposition. Instead, they prepared an acetone solution of <u>110</u> <u>via</u> the addition of H_2S to stoichiometric amounts of Cp_2TiCl_2 and pyridine. This solution was purged with a nitrogen stream to expel unreacted H_2S and used immediately in subsequent reactions. The <u>in situ</u> synthesis of <u>110</u> was inconvenient from a preparative standpoint. An improved, reproducible synthesis of <u>110</u> is the treatment of a THF solution of Cp_2TiCl_2 with Et_3N and H_2S. Simple filtration of the reaction mixture in air removed the Et_3NHCl and evaporation of the solvent from the filtrate gave 110 in nearly quantitative yield. This synthetic method has recently been applied independently to prepare the related complex $(MeCp)_2Ti(SH)_2$ which is easier to isolate in a crystalline form.[292] The ^1H NMR ($CDCl_3$) chemical shifts of the Cp and SH protons of 110, δ 6.28 and δ 3.38, respectively, compare favourably with the reported values of δ 6.34 and δ 3.44 in the same solvent.[260] The signal due to the hydrosulfide ligands of $(MeCp)_2Ti(SH)_2$ is a singlet at δ 3.09.[292] The replacement of hydrogen atoms of a cyclopentadienyl ligand with methyl groups increases the electron density at the metal center.[334] The chemical shift of the hydrosulfide ligand appears to be sensitive to the electron density at the metal. The SH resonance in the ^1H NMR spectrum of $Cp_2Zr(SH)_2$ (111) in $CDCl_3$ occurs at δ 1.94, significantly upfield from the corresponding signal for 110 at δ 3.38. A similar shift to higher field of the SH resonance was observed for the complexes (dppe)-M'$(SH)_2$ when Ni (δ 1.67), a first row metal, was replaced by Pd (δ 1.56)[127] and in complexes of the type 149 where M = Ti and Zr.[335-336] The olefinic protons in the zirconium complex occur at δ 7.11 vs. δ 7.43 for the titanium complex. This was explained as being due to the poorer π-accepting ability of zirconium(IV).[335] In the bis(hydrosulfido)



149

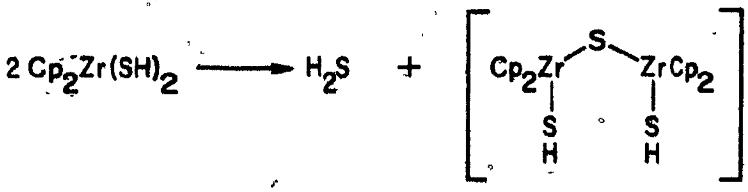
complexes 110 and 111 a degree of pπ(S)-dπ(metal) bonding cannot be excluded. Thiolate ligands are thought to behave as π-acceptors in complexes of the type Cp_2MX_2 (X = SR).[337]

The complex $Cp_2Ti(SH)_2$ (110) was the only organometallic product isolated from the reaction of Cp_2TiCl_2 with Et_3N and H_2S in THF. However, the analogous reaction with Cp_2ZrCl_2 gave two products which have been formulated (vide supra) as $Cp_2Zr(SH)_2$ (111) and $(Cp_2ZrS)_2$ (112). A ^1H NMR experiment demonstrated that 112 could be converted into 111 in $CDCl_3$ solution in the presence of H_2S. Moreover, under an atmosphere of H_2S a solution of 111 does not revert into 112. Thus under the reaction conditions for the synthesis of 111 it is likely that no 112 forms. Only during evaporation of the $Cp_2Zr(SH)_2$ solution, when the solution is degassed, does the yellow colour characteristic of 111 change to the emerald green of 112. Speculation on possible mechanisms of formation of the dimer 112 from 111 lead to at least two possibilities. Intramolecular elimination of H_2S from 111 could generate an intermediate such as $Cp_2Zr{=}S$ (150, eq. 60). Dimerization of 150 could give 112 (eq. 61). A second mechanism involves

$$\underset{\underline{111}}{Cp_2Zr(SH)_2} \longrightarrow H_2S + \underset{\underline{150}}{[Cp_2Zr{=}S]} \qquad (60)$$

$$2\ \underline{150} \longrightarrow \underset{\underline{112}}{(Cp_2ZrS)_2} \qquad (61)$$

intermolecular elimination of H_2S to give an intermediate such as 151 (eq. 62). Subsequent ring-closure via elimination of a second H_2S molecule could give 112 (eq. 63). At



(62)

111

151

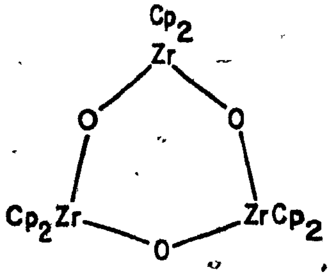
$$\underline{151} \longrightarrow H_2S + \underset{\underline{112}}{(Cp_2ZrS)_2} \qquad (63)$$

this time it is not known if either or both of the mechanisms are operative.

Dimer 112 is a rare example of a sulfur-bridged organozirconium complex. Multinuclear selenium- and oxygen-bridged species have been isolated, though. Gautheron et al.[338] prepared the complexes $[(RCp)_2M(\mu\text{-}Se)]_2$ where M = Zr, Hf and R = t-Bu and H. The oxygen analog of 150 has been suggested[339] as a possible precursor to $(Cp_2ZrO)_3$ (152) (eq. 64). Neither 150 nor $Cp_2Zr{=}O$ have been isolated, however. The oxygen-bridged trimer 152 was prepared according to eq. 64. The structure of the toluene solvated

$$Cp_2Zr(CO)_2 + CO_2 \longrightarrow \tfrac{1}{3}\underset{\textbf{152}}{(Cp_2ZrO)_3} + 3CO \qquad (64)$$

complex consists of a nearly planar six-membered Zr_3O_3 ring with short Zr–O bonds.[339] A single sharp peak at



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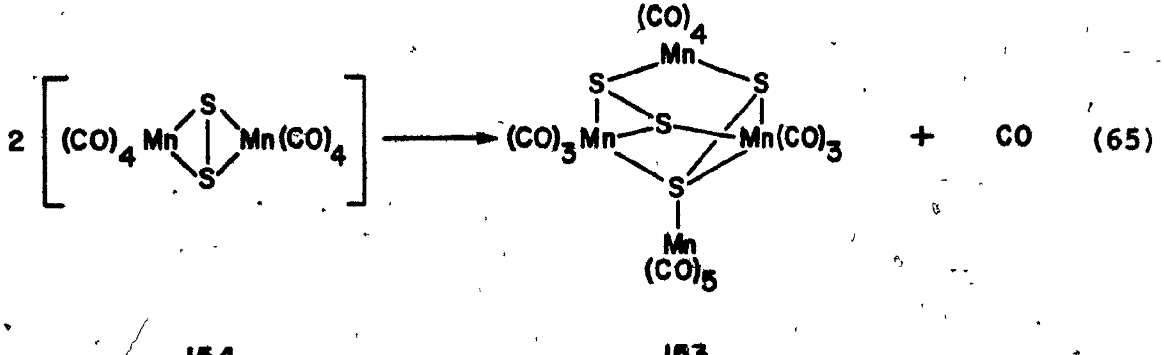
δ 6.25 was seen in its ^1H NMR spectrum ($CDCl_3$). The infrared spectra of the hydrosulfido complexes 110, 111, and 113 and the dimer 112 displayed infrared absorption bands characteristic of the η-C_5H_5 ligand.[332] The infrared spectrum of 152 displayed an intense, broad absorption band from 760 to 790 cm^{-1}. An intense band in this region is characteristic of an M–O–M linkage (M = Ti, Zr, Hf) and may be due to the asymmetric M-O-M stretching vibration.[161,339] It is reasonable to expect a Zr-S-Zr stretching mode to occur at lower frequency than the corresponding Zr-O-Zr band. Complex 112 showed a strong, broad band at 730 cm^{-1} which may be tentatively assigned as a Zr-S-Zr stretch.

One route to organic disulfides is via iodine oxidation of thiols in polar media.[340] Although this has been successful with some hydrosulfido complexes, others give unexpected products. For example, Ramasami et al.[42] found that oxidation of the $CrSH^{2+}$ ion in aqueous perchloric acid gave the μ-disulfido chromium(III) ion CrS_2Cr^{4+}. However, Küllmer et al.[341] found that $[Mn(CO)_4(\mu\text{-}SH)]_2$ (135) was unreactive towards common oxidizing agents such as H_2O_2, I_2, azobisisobutyronitrile, or dimethyl sulfoxide.[342] The oxidation of $[Mn(CO)_4]_2(\mu\text{-}SSnMe_3)$ with iodine gave the interesting tetranuclear complex $Mn_4S_4(CO)_{15}$ (153). This was proposed to be formed via dimerization of the μ-disulfido intermediate $[Mn(CO)_4]_2(\mu\text{-}S_2)$ (154) accompanied by rearrangement of the CO ligands (eq. 65).[341]



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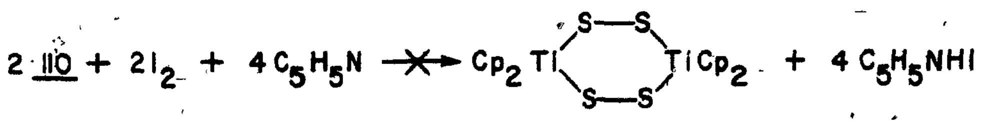
154 153

An early study suggested that treatment of $Cp_2Ti(SH)_2$ (110) with iodine in the presence of pyridine gave the titanium(III) complex $[CpTi(\mu\text{-}S_2)]_2$.[105] A more careful study,[106] however, showed that the soluble metal-containing products were Cp_2TiI_2 and Cp_2TiS_5 (73). The dimer 155 expected from the oxidation of 110 with iodine (eq. 66) was not observed.[106] Some sulfur was liberated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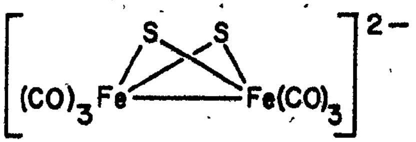
as H_2S.[106] The similar oxidation of $Cp_2Zr(SH)_2$ (111) with iodine reported here led to Cp_2ZrI_2 (^1H NMR) and sulfur (TLC). The products of a few exploratory reactions of $Cp_2Ti(SH)_2$ (110) and $Cp_2Zr(SH)_2$ (111) with Me_2SiCl_2, Me_2SnCl_2, Me_3SiCl, $(Me_3Si)_2NH$, and $PhPCl_2$ could not be identified. Other hydrosulfido organometallic compounds have been successfully reacted with the reagents, however. For example, Seyferth et al.[9,343] found that salts of $[Fe(NO)_2(\mu\text{-}S)]_2^{2-}$ (1) and $[Fe(CO)_3(\mu\text{-}S)]_2^{2-}$ (156) (which can be viewed as the deprotonated known[8,310,311] bis(hydrosulfido) derivatives) reacted under mild conditions to give complexes such as $[Fe(NO)_2(\mu\text{-}SSnMe_3)]_2$ and $Fe_2(CO)_6(\mu\text{-}S_2MMe_2)$ (157, M = Si, Sn). It is interesting to note that 156 and Me_3SnCl failed to give stable products.[9]



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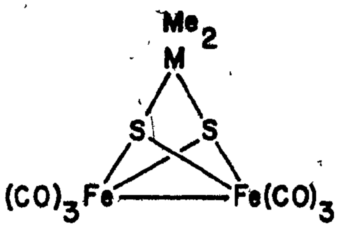

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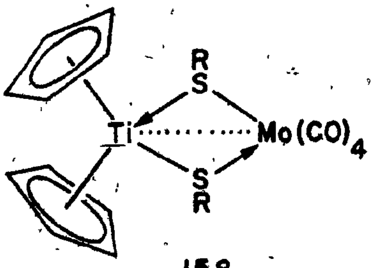
In the reaction of 110 in THF at 50°C with two-fold excesses of Me_2SiCl_2 and Et_3N, Cp_2TiCl_2 was the isolated product. No cyclosilthianes such as $(Me_2SiS)_2$ and $(Me_2SiS)_3$ were detected in the ^1H NMR spectrum of the crude reaction products.[344] Dimethyldichlorosilane reacts with H_2S in the presence of Et_3N to form the stable cyclosilthianes $(Me_2SiS)_2$ and $(Me_2SiS)_3$.[345,346] The fate of the SH groups in the above reaction of Me_2SiCl_2 and Et_3N with 110 is not known.

4. THE SYNTHESIS OF BIS(η-CYCLOPENTADIENYL)TITANIUM(IV) THIOLATES

Introduction

One of the objects of this research was to prepare new compounds containing catenated sulfur ligands of the type S_xR where $x > 1$. Consequently, it was necessary to prepare the analogous complexes with $x = 1$ (i.e., thiolate complexes) for comparison.

Metal thiolates can be defined as those compounds having a metal-sulfur-carbon linkage. This rather broad category, however, can be subdivided. Transition metal complexes in which there formally is a dative bond from a sulfur ligand to the metal (e.g., 158)[347,348] will not be discussed here. Transition metal complexes of 1,1-dithioacids in which the XCS_2^- ligand is present, where X may be a group such as NR_2 (to give dithiocarbamate complexes) or OR (to give xanthate complexes) (159), are well-known and have been thoroughly reviewed[349,350] and will not be discussed. This



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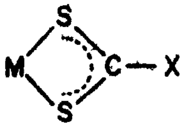
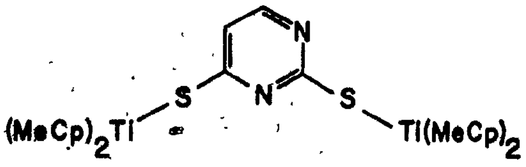


159

section will review the complexes of titanium, zirconium, and hafnium containing the η-cyclopentadienyl group and simple thiolate ligands. Such compounds are relatively common for titanium, but are scarce for zirconium and virtually unknown for hafnium.[351] They are most common for the +4 oxidation state of the metals, although several titanium(III) thiolates have been isolated. For example, multinuclear titanium(III) complexes with bridging ligands such as the dianion of 2,4-dithiopyrimidine (160) and the trianion of trithiocyanuric acid (161) have been isolated.[352] Substituted-η-cyclopentadienyltitanium(III) complexes with chelating dithiolate ligands have also been synthesized. Treatment of $(R'Cp)TiCl_2$ (R' = $CHMe_2$, CHMePh) with the sodium salt of toluene-3,4-dithiol gave the complexes 162. The reaction of these compounds with CCl_4 in refluxing THF gave the titanium(IV) derivatives of the type 163 (eq. 67).[353]



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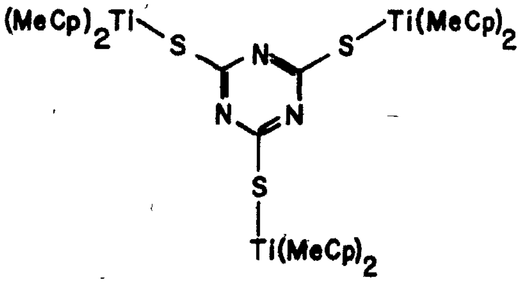

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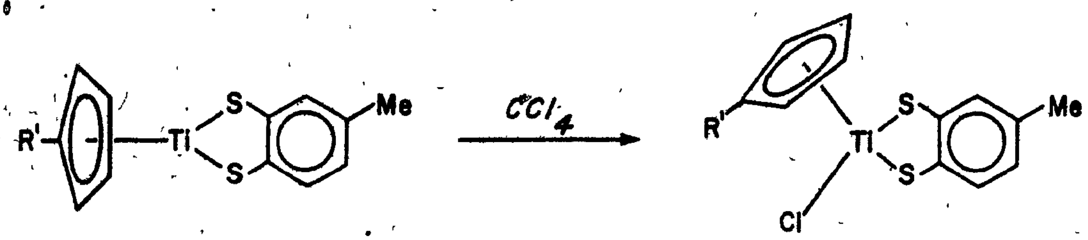

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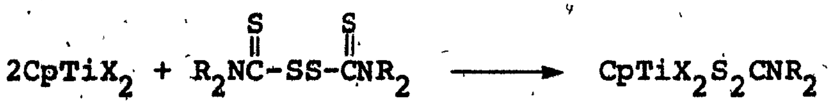
162 163

Coutts et al. have studied the reactions of the titanium(III) compounds $CpTiX_2$ (X = Cl, Br)^{354} and Cp_2TiCl^{265} with disulfides (eqs. 68 and 70) and thiuram disulfides (eq. 69). In each case cleavage of the sulfur-sulfur bond occurred with oxidation of the metal to the +4 state.

$$2CpTiCl_2 + RSSR \longrightarrow 2CpTiCl_2SR \qquad (68)$$

R = Me, Et, Ph



$$2CpTiX_2 + R_2N\overset{\overset{\displaystyle S}{\|}}{C}-SS-\overset{\overset{\displaystyle S}{\|}}{C}NR_2 \longrightarrow CpTiX_2S_2CNR_2 \qquad (69)$$

R = Me, Et

$$2Cp_2TiCl + RSSR \longrightarrow 2Cp_2Ti(Cl)SR \qquad (70)$$

R = Me, Et, CH_2Ph, Ph

$$CpTiCl_3 + nPhSH + nEt_3N \longrightarrow$$

$$CpTi(Cl)_{3-n}(SPh)_n + nEt_3NHCl \qquad (71)$$

n = 1,3

Depending on the stoichiometry, the reaction between $CpTiCl_3$ and thiophenol in the presence of Et_3N gave $CpTiCl_2(SPh)$ or $CpTi(SPh)_3$ (eq. 71).[355] Both products are air- and thermally-sensitive compounds. Decomposition of $CpTi(SPh)_3$ in air gave PhSSPh and a yellow compound of low solubility thought to be $[CpTi(SPh)O]_n$ (n not specified).[355]

Bis(η-cyclopentadienyl) complexes of titanium(IV) have been prepared by various routes and include mono- and bis(thiolato) derivatives of the types $Cp_2Ti(X)SR$ (X = halide) and $Cp_2Ti(SR)_2$, respectively. In the generally high-yield syntheses of the complexes $Cp_2Ti(Cl)SR$ from organic disulfides and Cp_2TiCl (eq. 70), the compounds $Cp_2Ti(SR)_2$ were usually observed as by-products.[265] A much better preparative route is <u>via</u> the reaction of Cp_2TiCl_2 with NaSR (1:2 molar ratio) which gave quantitative yields of $Cp_2Ti(SR)_2$ for R = Me, Et, CH_2Ph, Ph (eq. 72).[265,282] The complexes where R = Me and Ph were also obtained from the reaction of Cp_2TiCl_2 with Me_3SiSR with elimination of volatile Me_3SiCl (eq. 73).[356] Köpf and Block[357] found that treatment of "titanocene" with the organic disulfides RSSR (R = Me, Ph) also gave the bis(thiolato) complexes, but in low yields. Perhaps the most used route is the treatment of Cp_2TiCl_2 with the thiol in the presence of a base such as Et_3N as an HCl scavenger (eq. 74).[282,283,358]

$$Cp_2TiCl_2 + 2NaSR \longrightarrow Cp_2Ti(SR)_2 + 2NaCl \qquad (72)$$

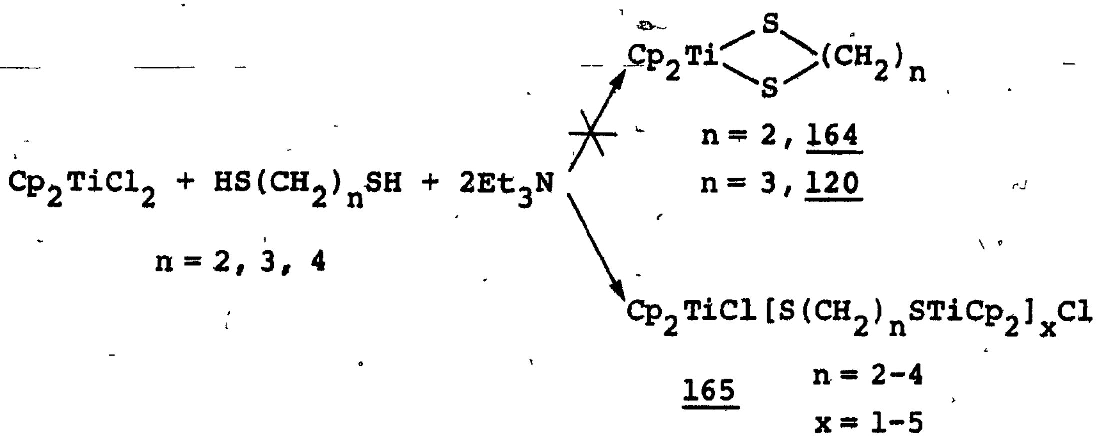
$$Cp_2TiCl_2 + 2Me_3SiSR \longrightarrow Cp_2Ti(SR)_2 + 2Me_3SiCl \qquad (73)$$

$$Cp_2TiCl_2 + 2RSH + 2Et_3N \longrightarrow Cp_2Ti(SR)_2 + 2Et_3NHCl \qquad (74)$$

R = Me, Et, n-Pr, CH_2Ph, $(CH_2)_2Ph$,
Ph, $4\text{-}C_6H_4Me$, $4\text{-}C_6H_4Cl$

Chaudhari and Stone[359] prepared $Cp_2Ti(SMe)_2$ via treatment of the σ-phenyl derivative $Cp_2Ti(Cl)(C_6F_5)$ with excess NaSMe. The bis(η-methylcyclopentadienyl) analogs $(MeCp)_2Ti(SR)_2$ where R = Me, Et, n-Pr, i-Pr, sec-Bu have recently been prepared via the base/thiol route.[360]

A number of bis(η-cyclopentadienyl)titanium(IV) complexes with chelating dithiolato ligands have been reported. They were prepared via the base/dithiol or the disodium dithiolate routes. Köpf and Schmidt[361] explored the reactions of Cp_2TiCl_2 with an equimolar amount of $HS(CH_2)_nSH$ (n = 2, 3, 4) and the stoichiometric amount of Et_3N in refluxing toluene, conditions previously successful[282,283] for the synthesis of many $Cp_2Ti(SR)_2$ (R = alkyl, aryl) derivatives. Although the latter were well-defined monomeric complexes, the alkane dithiols gave only violet-red air-sensitive chlorine-containing oligomers. The desired five-, six-, or seven-membered titanadithiacycloalkanes (e.g., 120 and 164) were not obtained (eq. 75). Microanalytical results were consistent with the formation of oligomers 165. However, their low solubilities



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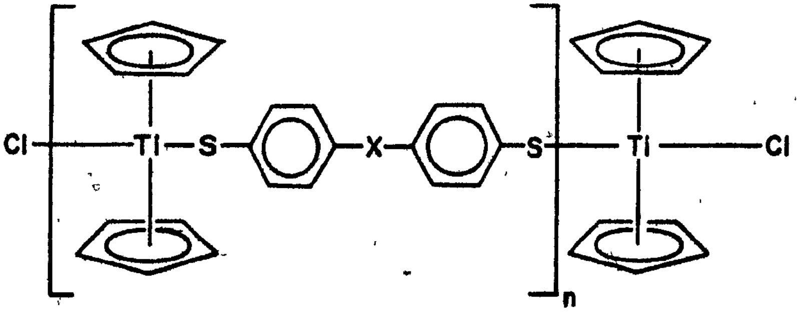
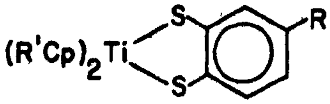
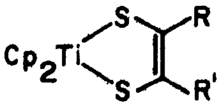
precluded molecular weight determinations. Similar observations were made by Sergeev _et_ _al_.[362] in the syntheses of polyarylene bis(cyclopentadienyl)titanium sulfides 166 from Cp_2TiCl_2 and aromatic dithiols. In this case infrared, microanalytical, as well as molecular weight determinations established the polymeric nature and the presence of chlorine end-groups. Others have reported the synthesis of $Cp_2Ti[S(CH_2)_2S]$ (164) as a monomer from Cp_2TiCl_2 and $HS(CH_2)_2SH$ in the presence of ammonia[358] or from $Na_2S_2(CH_2)_2$.[359]



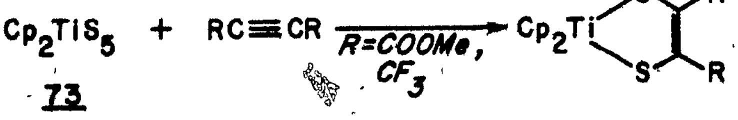
166
X = O,S,SO_2
n = 2-14

Complexes of this type will be discussed further in the Results and Discussion sections of this chapter. The reaction of Cp_2TiCl_2 with toluene-3,4-dithiol and triethylamine[361] or ammonia,[358] or with the sodium salt of the dithiol[359] gave $Cp_2Ti(S_2C_6H_3CH_3)$ (<u>167</u>, R' = H, R = Me) which was shown to be monomeric by a solution molecular weight determination.[358,361] The benzene-1,2-dithiolato complex $Cp_2Ti(S_2C_6H_4)$ (<u>167</u>, R = R' = H), prepared in a similar manner, was also monomeric.[361]


<u>167</u>


<u>168</u>

A number of air-stable cyclic ethylenedithiolato complexes, <u>168</u> (R = R' = H,[335,336] CN,[359,361,363] R = Ph, R' = H[335]), have been isolated. All have been prepared <u>via</u> the reaction of the sodium salts of the appropriate dithiol with Cp_2TiCl_2. These were also monomeric. Thus, both aryl- and alkenyl-1,2-dithiols seem to give monomeric complexes. Additional derivatives (R = R' = COOMe, CF_3) have recently been made in a rather novel way from Cp_2TiS_5 and the appropriate electrophilic acetylene (eq. 76).[364] The MeCp analog of the methylcarboxylate derivative was prepared <u>via</u> cleavage of the dimer



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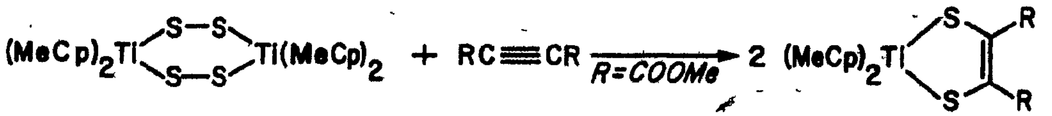
1,4-[(MeCp)$_2$Ti(μ-S$_2$)]$_2$ (169) with dimethylacetylenedicarboxylate (eq. 77).[292]



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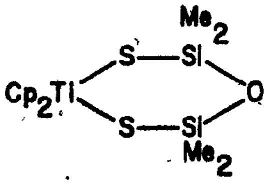
The complex Cp$_2$Ti(SH)$_2$ (110) reacted with dichlorotetramethyldisiloxane, dichlorohexamethyltrisiloxane, and dichlorooctamethyltetrasiloxane in the presence of Et$_3$N to give the cyclic species 170-172, respectively. These were monomeric according to solution molecular weight determinations.[365]



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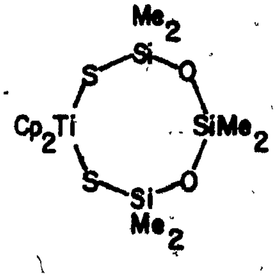

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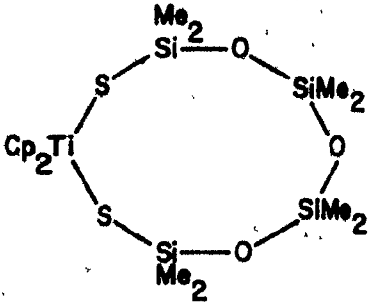
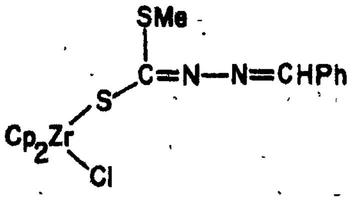


172

Thiolato complexes of zirconium(IV) and hafnium(IV) are much scarcer than for titanium. Organozirconium xanthate or Schiff base derivatives which have been isolated include CpZr(S$_2$COMe)$_3$[366] and Cp$_2$Ti(TSB)Cl (173, where TSBH is S-methyldithiocarbazate).[367] The only derivatives



173

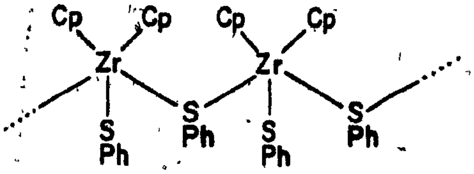
containing simple alkylthiolato ligands are $Cp_2M(SCMe_3)_2$ where M = Zr and Hf. These sublimable yellow compounds were obtained in high yield via treatment of the bis(dimethylamido) precursors $Cp_2M(NMe_2)_2$ with the thiol (eq. 78).[368] There seems to be no reason why this route could not be applied to the synthesis of many other examples. The mono(thiolato) derivatives $Cp_2Zr(Cl)SR$ have been prepared in situ via the reaction of Schwartz's reagent, $Cp_2Zr(Cl)H$, with thioketones $R_2C{=}S$ where R = alkyl or aryl (eq. 79). Subsequent cleavage of the Zr-S bond with electrophiles such as bromine gave a variety of organosulfur compounds (eq. 80).[369] The only bis(thiolato) complexes of aromatic thiols are $Cp_2Zr(SPh)_2$[370,371] and the cyclic derivatives $Cp_2Zr(S_2C_6H_4)$[371] and $Cp_2Zr(3,4\text{-}S_2C_6H_3Me)$,[371]

$$Cp_2M(NMe_2)_2 + 2Me_3CSH \longrightarrow Cp_2M(SCMe_3)_2 + 2Me_2NH \qquad (78)$$

$$Cp_2Zr(H)Cl + R_2C{=}S \longrightarrow [R_2CHSZr(Cl)Cp_2] \qquad (79)$$

$$[R_2CHSZr(Cl)Cp_2] + Br_2 \longrightarrow R_2CHSBr + Cp_2ZrBrCl \qquad (80)$$

all of which are extremely sensitive to air and water. Even under nitrogen or *in vacuo* these bis(thiolato) complexes decompose into polymers of the types 174 and 175.[371] The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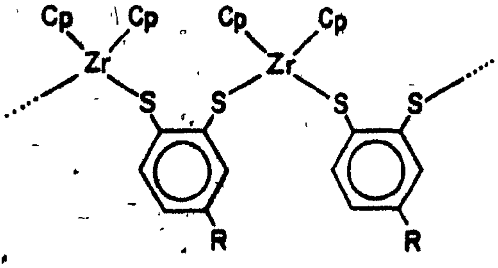

175 R=H,Me

bis(thiolato) complexes were prepared by treating Cp_2ZrCl_2 with the thiol or dithiol in the presence of triethylamine.[371] The thiophenolato derivative can also be isolated *via* free-radical cleavage of the Zr-C bonds in $Cp_2Zr(CH_2Ph)_2$ (eq. 81).[370]

$$Cp_2Zr(CH_2Ph)_2 + 2PhSH \longrightarrow Cp_2Zr(SPh)_2 + 2PhCH_3 \qquad (81)$$

The treatment of Cp_2ZrCl_2 with disodium ethylenedithiolate[335,336] or disodium maleonitriledithiolate[371] gave the zirconium analogs to 168.

Results

The complexes $Cp_2Ti(SR)_2$ where R = CH_2Ph (176), $CHMe_2$ (115), CMe_3 (117), Ph (118), and 4-C_6H_4Me (119) have been prepared. The complexes where R = CH_2Ph, Ph, and 4-C_6H_4Me have been reported elsewhere.[265,282,283,356-358] In the treatment of Cp_2TiCl_2 with thiols RSH in the presence of Et_3N or with alkali metal salts of thiols there are two possible products, namely the mono- and bis(thiolato) complexes $Cp_2Ti(Cl)SR$ and $Cp_2Ti(SR)_2$, respectively. The use of Cp_2TiCl_2 and RSH/Et_3N or RS^- in a 1:2 stoichiometry generally leads to a mixture of the two products. The relative proportions of these products depends on the R group and on the reaction solvent. In the synthesis of $Cp_2Ti(SCH_2Ph)_2$ (176) from the stoichiometric amounts of Cp_2TiCl_2, $PhCH_2SH$, and Et_3N (1:2:2) in refluxing toluene (2 hours) the crude organometallic product consisted of mostly 176 with a little $Cp_2Ti(Cl)SCH_2Ph$ present.[265] The Cp signals in the ^1H NMR spectrum for these compounds appeared at δ 6.20 and δ 6.37, respectively. The mono(thiolato) derivative was present in ca. 6% yield as determined by NMR. Only the CH_2 signal at δ 4.23 for 176 was detected (Table 1). The isolated yield of 176 was 63%. Under the same conditions Me_2CHSH was slow to react. After three hours in refluxing toluene the yield of $Cp_2Ti(Cl)SCHMe_2$ (114) was ca. 17% as determined by NMR. None of the bis(thiolato) complex 115 was detected. However, refluxing in THF for 23 hours increased the yield of 114 to

TABLE 1

The ^{1}H NMR Spectra of Thiolato Complexes of Titanium[a,b]

Compound	C_5H_5	Ph	$(CH)_x$	CH_3
$Cp_2Ti(Cl)SCH_2Ph$	6.37 (6.29)[c]	7.16	4.63	
$Cp_2Ti(SCH_2Ph)_2$	6.20		4.23	
$Cp_2Ti(Cl)SCHMe_2$	6.33		4.20[d]	1.35[d]
$Cp_2Ti(SCHMe_2)_2$	6.15		3.65[e]	1.30[e]
$Cp_2Ti(Cl)SCMe_3$	6.39			1.60
$Cp_2Ti(SCMe_3)_2$	6.20			1.52
$Cp_2Ti(Cl)SPh$	6.21[c]	7.32[c]		
$Cp_2Ti(SPh)_2$	5.98	7.3		
$Cp_2Ti(Cl)(S\text{-}4\text{-}C_6H_4Me)$	6.27	f		2.32
$Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)_2$	6.02	7.25[g]		2.35
$Cp_2Ti[S(CH_2)_3S]$[h]	6.11		1.93[i] 3.08[i]	

[a] Spectra were recorded at 60 MHz in $CDCl_3$ unless noted otherwise. Chemical shifts are in units of δ ppm.

[b] All data are from this work except where indicated.

[c] Reference 265.

[d] J(H-H) = 7 Hz.

[e] J(H-H) = 6 Hz.

[f] Not observed.

[g] J(H-H) = 8 Hz.

[h] The spectrum was recorded at 200 MHz.

[i] J(H-H) = 6.3 Hz.

ca. 78%. Treatment of Cp_2TiCl_2 with Me_2CHSLi (1:2 stoichiometry) for 23 hours in THF at room temperature gave a mixture of Cp_2TiCl_2 (ca. 49% as determined by NMR), 114 (ca. 18%), and $Cp_2Ti(SCHMe_2)_2$, (115, ca. 32%). The complexes 114 and 115 were separated by column chromatography. The isolated yields of 114 and 115 were 5% and 17%, respectively. The two products are readily distinguishable by the positions and relative intensities of the Cp and CH signals in their ^1H NMR spectra. These appear at δ 6.33 and δ 4.20 for 114 and δ 6.15 and δ 3.65 for 115. The methyl doublets for 114 and 115 occur at δ 1.35 and δ 1.30, respectively (Table 1). The reaction between Cp_2TiCl_2, Me_3CSH, and Et_3N (in a 1:2:2 stoichiometry) was sluggish in refluxing THF. After two days the yields of $Cp_2Ti(Cl)SCMe_3$ (116) and $Cp_2Ti(SCMe_3)_2$ (117) were ca. 15% and ca. 9%, respectively, as determined by NMR. When Cp_2TiCl_2 was treated with Me_3CSLi (in a 1:2 stoichiometry) in THF at room temperature both 116 and 117 were detected by TLC. Refluxing this solution for 13 hours caused 117 to decompose (its characteristic purple TLC spot was not present). The ^1H NMR spectrum of the crude reaction products showed that approximately equal amounts of Cp_2TiCl_2 and 116 were present. No 117 was evident, although five equally intense closely spaced signals at δ 6.27 to δ 6.20 may correspond to some of its decomposition products. Column chromatography removed these decomposition products together with the Cp_2TiCl_2 to give 116 in 9% yield. The low yield of 116 can be partially attributed to its decomposition on the deactivated alumina, evident by the colour change from red to yellow of the trailing edge of the band. The bis(thiolato) complex 117 was formed quantitatively, as shown by ^{1}H NMR, when Cp_2TiCl_2 was treated with a three-fold excess of Me_3CSLi in THF for one hour at room temperature (isolated yield 64%). No monothiolato compound 116 was detected in the crude reaction mixture. Like the zirconium and hafnium analogs[368] 117 can be sublimed. The ^{1}H NMR signals due to the Cp and Me groups of 116 are slightly downfield (δ 6.39 and δ 1.60, respectively) from those for 117 (δ 6.20 and δ 1.52), as expected[265] (Table 1). The synthetic routes used to prepare $Cp_2Ti(SPh)_2$ (118)[282] and $Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)_2$ (119)[283] were those reported in the literature. Thus Cp_2TiCl_2, RSH, and Et_3N (1:2:2 stoichiometry) reacted in refluxing toluene for R = Ph to give 118 (63% yield) and at room temperature in toluene for R = $S\text{-}4\text{-}C_6H_4Me$ to give 119 (48% yield). The crude reaction product in the synthesis of 118 showed two Cp signals in its NMR spectrum: a major one at δ 5.98 and a minor one (ca. 10% as intense) at δ 6.20. These values agree with the reported shifts[265] for 118 and $Cp_2Ti(Cl)SPh$ (Table 1); however, pure $Cp_2Ti(Cl)SPh$ could not be isolated by chromatography. The crude reaction product in the synthesis of 119 gave a minor red spot and a major faster-moving purple spot upon TLC analysis. These colours and relative positions are typical of the mono(thiolato) (red) and bis(thiolato) (purple) derivatives. Two Cp signals were seen in the NMR spectrum at δ 6.02 (major) and δ 6.27 (minor, ca. 30% as intense). A poorly resolved shoulder at δ 2.32 was present on the broad signal due to the Me group at δ 2.37. Column chromatography led to decomposition of the red product and only 119 was isolated. The ^{1}H NMR spectrum of 119 consisted of an AB quartet centered at δ 7.25, a sharp singlet due to the Cp ligand at δ 6.03, and a broad singlet due to the Me group at δ 2.35 having relative intensities consistent with the formulation as 119 (Table 1).

The synthesis of $Cp_2Ti[S(CH_2)_2S]$ (164) according to the method of Sen and Kantak[358] was repeated but using CH_2Cl_2 instead of $CHCl_3$ as solvent. When a solution of Cp_2TiCl_2 was treated with 1,2-ethanedithiol (1:1 stoichiometry) and anhydrous ammonia in CH_2Cl_2 the product was a light-sensitive malodorous purple solid which decomposed at ca. 125°C. The sample gave a negative Beilstein Test[285] consistent with the absence of chloro ligands. The infrared spectrum resembled that published by Sen and Kantak[358] and was as follows (KBr disc, cm^{-1}): 3090 (w, br), 2915 (w, br), 1435 (s, br), 1365 (w), 1255 (s, br), 1195 (w), 1175 (m), 1128 (w), 1065 (w), 1025 (s), 1015 (s), 915 (w), 843 (s, sh), 810 (vs), 727 (w), 692 (w). The NMR spectrum ($CDCl_3$, 200 MHz) of the solid consisted of five lines of unequal intensity in the Cp region, the most prominent at δ 6.14 and δ 6.12. A poorly resolved signal centered at δ 3.23 was also present. The relative ratio of Cp to CH_2 signals was ca. 10:4. The CH_2 signal for 1,2-ethanedithiol in $CDCl_3$

appears as a multiplet at δ 1.69.[372] The mass spectrum showed peaks for the ion $Cp_2TiS_2C_2H_4^{+\cdot}$ (at m/z = 270) and fragment ions as well as low intensity peaks (ca. 2% of the base peak which corresponded to the $Cp_2Ti^{+\cdot}$ ion) up to at least 400 mass units. These spectral data are consistent with a mixture of species of the type $(Cp_2TiSCH_2CH_2S)_x$ where x is unknown. The microanalytical data is as follows: Calcd. for $C_{12}H_{14}S_2Ti$: C, 53.33; H, 5.22; S, 23.73; Found: C, 47.56; H, 5.12; S, 22.56; Calcd. for $C_{12}H_{14}S_2Ti\cdot\frac{1}{4}CH_2Cl_2$: C, 50.47; H, 5.01; S, 22.00. CH_2Cl_2 was observed in the ^1H NMR spectrum. When Cp_2TiCl_2 was treated with a stoichiometric amount of the dilithium salt of 1,2-ethanedithiol in THF (a procedure analogous to that of Chaudhari and Stone[359]) at room temperature for eight hours, the reaction mixture changed in colour from purple to deep red. Chromatography on Florisil with toluene/ether (1:1) as eluent gave the product as a purple solid. The ^1H NMR spectrum ($CDCl_3$) consisted of broad singlets at δ 6.08 (10.0H), δ 2.93 (4.2H), and δ 1.27 (1.6H). Only one spot was present on a TLC plate in a variety of solvents. The product was not examined further.

Attempts to prepare $Cp_2Zr[S(CH_2)_2S]$ were unsuccessful. A yellow product was obtained via the dithiol/ammonia route and via the lithium dithiolate route. The ^1H NMR spectrum ($CDCl_3$) of the product from the lithium thiolate route consisted of a singlet at δ 6.23 (10.0H) and broad unresolved multiplets at δ 3.33 (2.1H) and δ 2.77 (3.3H). Although an intense peak at m/z = 312 corresponding to the $Cp_2ZrS_2C_2H_4^{+\cdot}$ ion was observed in the mass spectrum, additional ion clusters were observed up to m/z = 520. The product from the dithiol/ammonia route showed additional NMR signals at δ 6.00 and δ 3.02. The infrared spectra of the products from each route were identical and similar to the titanium complex <u>164</u> isolated from the dithiol/ammonia route. Microanalytical data for the product from both routes were similar; the results for the product from the lithium thiolate route and from the dithiol/ammonia route (in parentheses) are as follows: Found: C, 31.36 (26.10); H, 3.85 (3.52); S, 16.67 (16.47). These results are not in agreement with the values calculated for the formula $Cp_2Zr[S(CH_2)_2S]$: C, 45.96; H, 4.50; S, 20.45. The product was not examined further.

Dropwise addition of a suspension of Cp_2TiCl_2 in THF onto solid lithium 1,3-propanedithiolate at room temperature gave $Cp_2Ti[S(CH_2)_3S]$ (<u>120</u>). The ^1H NMR spectrum of <u>120</u> consisted of a sharp singlet at δ 6.11 (Cp), a triplet at δ 3.08 (terminal CH_2 protons) and a quintet at δ 1.93 (central CH_2 protons) (Table 1). The solid-state infrared spectrum of <u>120</u> displayed bands typical of an η-C_5H_5 ligand.[332] A noteworthy feature of the spectrum was a series of regularly spaced weak bands between 1365 and 1265 cm^{-1}. This band progression can be attributed to CH_2 wagging vibrations and are characteristic of straight chain aliphatic compounds.[373] The mass spectrum of <u>120</u> contained a molecular ion peak at m/z = 284.

A solution molecular weight determination gave a value of 281 which compares favourably with the theoretical value of 284. When a CH_2Cl_2 solution of Cp_2TiCl_2 was treated dropwise concurrently with CH_2Cl_2 solutions of 1,3-propanedithiol and triethylamine at room temperature for 2.5 hours followed by reflux for 2 hours the initial red colour of the solution became dark green. A deep violet product was isolated which consisted of two cyclopentadienyl-containing complexes as determined by ^1H NMR. The singlets in the Cp region appeared at δ 6.23 and δ 6.11 in the relative ratio of 10.0 to 6.6, respectively. Poorly resolved multiplets were present in the region δ 3.6 to δ 1.2. The singlet at δ 6.11 and multiplets at δ 3.08 and δ 1.93 were assigned to <u>120</u>. The other signals may be due to oligomers.[361] Attempts to purify the compounds by recrystallization or by chromatography were unsuccessful. The reaction between Cp_2TiCl_2 and 1,3-propanedithiol in the presence of ammonia in CH_2Cl_2 at room temperature gave mostly <u>120</u> as shown by NMR. However, unidentified impurities in the region δ 6.30 to δ 6.12 could not be removed by recrystallization or by chromatography due to decomposition.

When Cp_2ZrCl_2 in THF was added dropwise to a suspension of $Li_2[S(CH_2)_3S]$ at room temperature, the mixture immediately became bright yellow in colour. A bright yellow microcrystalline solid <u>121</u> was isolated which gave a negative Beilstein Test for halide.[285] The infrared spectrum of <u>121</u> was identical to that of <u>120</u> except for minor shifts in band positions. However, the ^{1}H NMR spectrum of <u>121</u> was much more complex than that for <u>120</u>. Seven signals in the Cp region were observed from δ 6.35 to δ 6.18 with the most intense located at δ 6.21. A complex set of overlapping triplets occurred in the region δ 3.35 to δ 2.50 and a complex multiplet was present between δ 2.15 and δ 1.80. The intensities of the Cp, terminal CH_2 (<u>ca</u>. δ 3), and central CH_2 (<u>ca</u>. δ 2) signals were in the ratio 10.0:5.0:2.8. In the mass spectrum of <u>121</u> an intense peak (99.1% of the base peak for the Cp_2ZrSH^+ ion) corresponding to the ion $Cp_2ZrS_2(CH_2)_3^{+\cdot}$ was observed at m/z = 326. Several peaks of low abundance (< 1%) were observed up to at least m/z = 530. Metastable ion peaks (m*) were seen for the transitions indicated in eqs. 82 and 83.

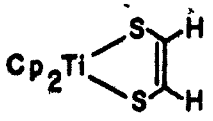
$$Cp_2ZrS_2(CH_2)_3^{+\cdot} \xrightarrow{m^*} Cp_2ZrSH^+ + C_3H_5S^\cdot \qquad (82)$$

$$Cp_2ZrSH^+ \xrightarrow{m^*} CpZrS^+ + C_5H_6 \qquad (83)$$

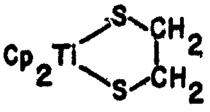
Discussion

The yields of the mono- and bis(thiolato) complexes were sharply dependent on the reaction conditions and thiolate group. For example, the yield of $Cp_2Ti(Cl)SCHMe_2$ (<u>114</u>) increased from <u>ca</u>. 17% in refluxing toluene to <u>ca</u>. 78% in refluxing THF when Cp_2TiCl_2 was treated with Me_2CHSH and Et_3N. The bis(thiolato) derivative, $Cp_2Ti(SCHMe_2)_2$ (<u>115</u>), was obtained only <u>via</u> the treatment of Cp_2TiCl_2 with $LiSCHMe_2$ in THF. The treatment of Cp_2TiCl_2 with stoichiometric amounts of Me_3CSH/Et_3N or $LiSCMe_3$ in THF gave mixtures of the mono- and bis(thiolato) products. However, if a large excess of $LiSCMe_3$ was used, $Cp_2Ti(SCMe_3)_2$ (117) was formed quantitatively. Only small amounts of the mono(thiolato) product $Cp_2Ti(Cl)SR$ (R = CH_2Ph, Ph, 4-C_6H_4Me) were formed in the synthesis of the $Cp_2Ti(SR)_2$ complex via treatment of Cp_2TiCl_2 with stoichiometric amounts of RSH and Et_3N in toluene. A marked dependence of the yield of the $Cp_2Ti(Cl)SR$ on the solvent and R group was noted by others in the reaction of Cp_2TiCl with R_2S_2.[265] In that case, when R = CH_2Ph and Ph more of the Cp_2TiCl_2 and $Cp_2Ti(SR)_2$ complexes were obtained relative to the $Cp_2Ti(Cl)SR$ derivative when the solvent was changed from benzene to THF. When R = Me and Et this strong solvent dependence was not observed. The observation and isolation in certain cases of both $Cp_2Ti(Cl)SR$ and $Cp_2Ti(SR)_2$ in the reaction of stoichiometric amounts of Cp_2TiCl_2 with RSH/Et_3N or LiSR is consistent with stepwise replacement of chloride ligands by thiolate ligands. Partial disproportionation of the $Cp_2Ti(Cl)SR$ complexes into Cp_2TiCl_2 and $Cp_2Ti(SR)_2$ under the reaction conditions cannot be excluded. This has been noted[265] for $Cp_2Ti(Cl)(SCH_2Ph)$ in $CDCl_3$ but in this solvent the complexes $Cp_2Ti(Cl)SR$ (R = Me, Et, Ph) did not disproportionate.[265]

Cyclic compounds of the type $Cp_2M[S(CH_2)_nS]$ (n = 1-3) are of particular interest insofar as the methylene group has the same number of valence electrons as a sulfur atom in the metallacyclopolysulfanes Cp_2MS_{n+2} some of which are discussed in Chapter 6. For the Group IVB metals sulfur chains of this type had hitherto been incorporated as chelating ligands only in the complex Cp_2TiS_5 (73).[99,161-167] Analogs containing a four-membered TiS_3 or a five-membered TiS_4 ring have been reported;[105] however, others have been unable to duplicate their syntheses via the treatment of Cp_2TiCl_2 with Na_2S_3 and Na_2S_4, respectively, isolating only 73 instead.[164] The complex $Cp_2Ti[S(CH_2)_2S]$ (164) has been reported.[358,359] Likewise, the complexes $Cp_2M[S(CH)_2S]$ (149; M = Ti, Zr, Mo, W) containing five-membered MS_2C_2 rings have been isolated.[335,336]



149

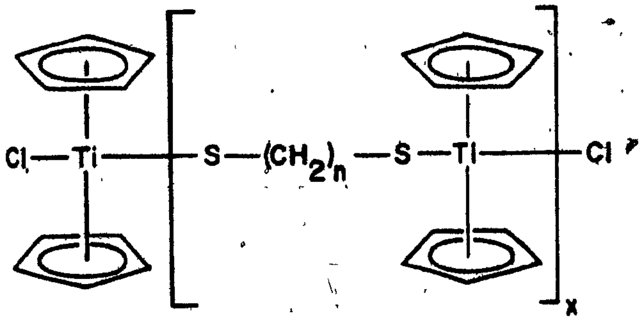


164

As noted in the introduction Chaudhari and Stone[359] reported that Cp_2TiCl_2 and $Na_2S_2(CH_2)_2$ reacted in refluxing THF to give $Cp_2Ti[S(CH_2)_2S]$ (164) as red crystals which decomposed at 50°C. Despite the absence of solution molecular weight data a monomeric cyclic structure was proposed. Sen and Kantak[358] have also reported this compound, preparing it via reaction of Cp_2TiCl_2 with $(CH_2)_2(SH)_2$ in the presence of NH_3. Their product was a violet solid which decomposed at 140°C. Total elemental analysis agreed with the formulation

$Cp_2Ti[S(CH_2)_2S]$. An apparent molecular ion peak was observed in its mass spectrum; however, solution molecular weight data was not reported. The infrared spectrum of 164 as reported by the two groups differ. In particular, Chaudhari and Stone[359] reported bands at 1220 (s) and 765 (vs) which were not mentioned by Sen and Kantak[358] although a strong band at ca. 1270 cm^{-1} was present in the latter's sample. Monomeric complexes of the type $Cp_2Ti(SR)_2$ (R = alkyl) do not absorb strongly below 800 cm^{-1} [283] while 1,2-ethanedithiol absorbs at 766 (m), 693 (vs, br), and 666 (w) cm^{-1} in the region.[374] The complex $Cp_2Ti[S(CH_2)_3S]$ (120) displayed a very strong absorption at ca. 810 cm^{-1} and weak bands at 755, 728, and 673 cm^{-1}. However, strong bands in this region are characteristic of the Ti-O-Ti linkage. The complex $(Cp_2TiCl)_2O$ absorbs strongly at 795 and 720 cm^{-1}, and $(CpTiCl_2)_2O$ absorbs strongly at 760 cm^{-1}.[375]

When the synthesis of 164 according to the method of Sen and Kantak[358] was repeated as described earlier the product was a purple solid which decomposed at ca 125°C. Its infrared spectrum was similar to that reported by those authors. The complex ^1H NMR spectrum displayed five signals due to Cp groups which is consistent with the presence of several components. The microanalytical data cannot distinguish between $\{Cp_2Ti[S(CH_2)_2S]\}_x$ where x = 1, 2, 3 ... A similar product was isolated from the attempted synthesis of $Cp_2Zr[S(CH_2)_2S]$. It seems reasonable to doubt the reports[358,359] of monomeric 164. Indeed, Köpf and Schmidt[361] reported that under the same conditions used to prepare complexes of the type $Cp_2Ti(SR)_2$, Cp_2TiCl_2 reacted with alkane dithiols $(CH_2)_n(SH)_2$ (n = 2-4) in the presence of Et_3N to give light-sensitive violet-red oligomers 165 which decompose at *ca.* 200°C. No prominent infrared bands below 800 cm^{-1} were noted. Their low solubilities precluded molecular weight determinations and the recording of ^1H NMR spectra.

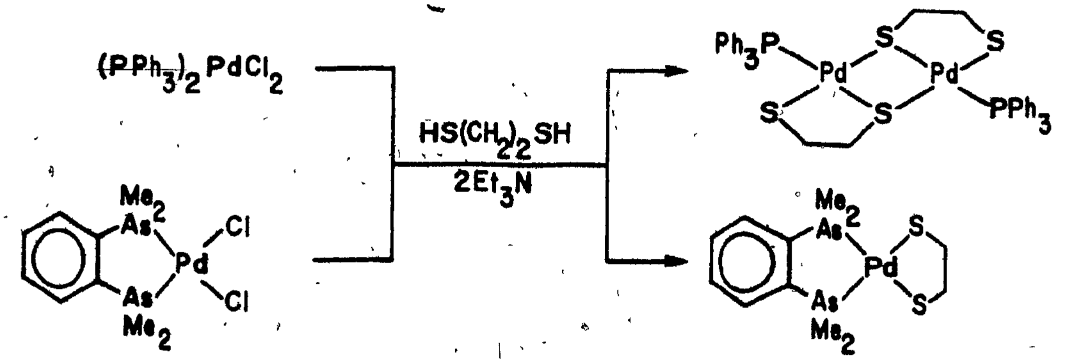


165
n = 2-4
x = 1-5

The formation of oligomeric complexes from other transition-metal halides and thiols or dithiols is well known. For example, *trans*-$(PhCN)_2PdCl_2$ reacted with sodium dithiolates to give complexes which were assumed to be polymeric having sulfur bridges (eq. 84).[376] The value of x could not be determined because of the insolubility of the products. However, treatment of $(PPh_3)_2PdCl_2$ with 1,2-ethanedithiol in the presence of triethylamine gave the dimeric species 177 (eq. 85).[377] The presence of a chelating ligand such as diars [*o*-phenylenebis(dimethylarsine)] gave monomeric 178 (eq. 86).[377]

$$\underline{\text{trans}}\text{-(PhCN)}_2\text{PdCl}_2 + \text{Na}_2[\text{S(CH}_2)_n\text{S]} \longrightarrow \{\text{Pd[S(CH}_2)_n\text{S]}\}_x \qquad (84)$$

$$n = 2, 3$$



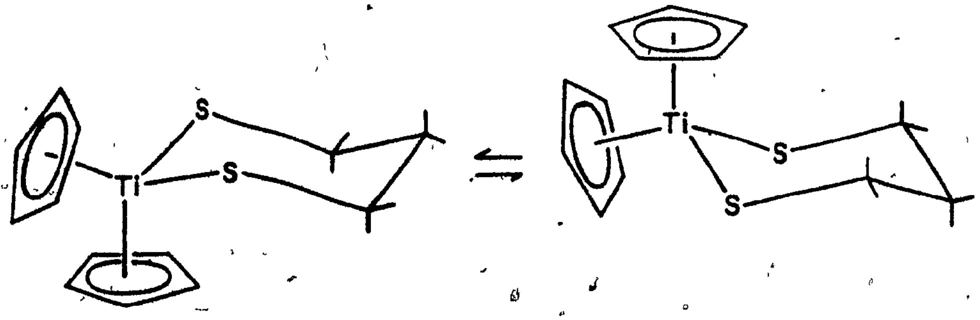
177 (85)

+ 2 Et$_3$NHCl

178 (86)

Treatment of cis-(PPh$_3$)$_2$PtCl$_2$ with 1,3-propanedithiol in the presence of Et$_3$N gave (PPh$_3$)$_2$Pt[S(CH$_2$)$_3$S] containing a six-membered PtS$_2$C$_3$ ring. It was assumed to be monomeric.[378] This compound displayed two methylene resonances in its ^{1}H NMR spectrum (CDCl$_3$). The central CH$_2$ signal appeared as a slightly broadened quintet at δ 2.00 [J(H-H) = 7 Hz] while the terminal CH$_2$ protons appeared as two overlapping triplets at δ 2.94 and δ 2.86 [J(H-H) = 7 Hz, J(P-H) = 60 Hz]. This spectrum is consistent with the presence of a rigid cyclohexane-like six-membered PtS$_2$C$_3$ ring having axial and equatorial methylene protons (see Chapter 7 for a further discussion). It should be noted that the ^1H NMR data is also consistent with one or more species of the type $[(PPh_3)_2PtS(CH_2)_3S]_x$. No solution molecular weight data was reported.

The complex $Cp_2Ti[S(CH_2)_3S]$ (<u>120</u>) was obtained <u>via</u> treatment of Cp_2TiCl_2 with $Li_2S_2(CH_2)_3$ and was shown to be monomeric in solution. The chemical shifts of the methylene signals in the ^1H NMR spectrum of <u>120</u> were similar to those of $(PPh_3)_2Pt[S(CH_2)_3S]$ and other platinum complexes containing the $-S(CH_2)_3S-$ ligand.[378] The terminal CH_2 protons of <u>120</u> appeared as a triplet at δ 3.08 [J(H-H) = 6.3 Hz] and the central CH_2 protons as a quintet at δ 1.93 [J(H-H) = 6.3 Hz]. A single sharp Cp signal appeared at δ 6.11 (Table 1). This spectrum is consistent with a six-membered TiS_2C_3 ring that is rapidly flipping on the NMR time scale. In this way the axial



<u>120</u>

and equatorial positions interconvert and become magnetically equivalent. The variable-temperature ^1H NMR study of <u>120</u> is discussed in Chapter 7.

The analogous reaction to give exclusively monomeric $Cp_2Zr[S(CH_2)_3S]$ (<u>121</u>) was unsuccessful. Although the infrared spectrum of 121 was very similar to that of 120, its ^1H NMR and mass spectra were complex and were more consistent with the presence of oligomers, perhaps containing the monomer as a component.

5. THE SYNTHESIS OF BIS(η-CYCLOPENTADIENYL)TITANIUM(IV) POLYSULFANES

Introduction

Mono- and disulfides of the type $>N-S_x-N<$, where $>N$ is an imidyl or azolyl group were developed as sulfur-transfer reagents to organic substrates. The related "blocked" reagents $>NS_xR$, where $>N$ = phthalimidyl (Phth) or succinimidyl (Succ), R = alkyl or aryl and x = 1, 2, or 3 were developed for the transfer of -SR, -SSR, or -SSSR groups to organic thiols R'SH (eq. 87). The reactivity of these thioimides has been

$$>NS_xR + R'SH \longrightarrow R'SS_xR + >NH \tag{87}$$

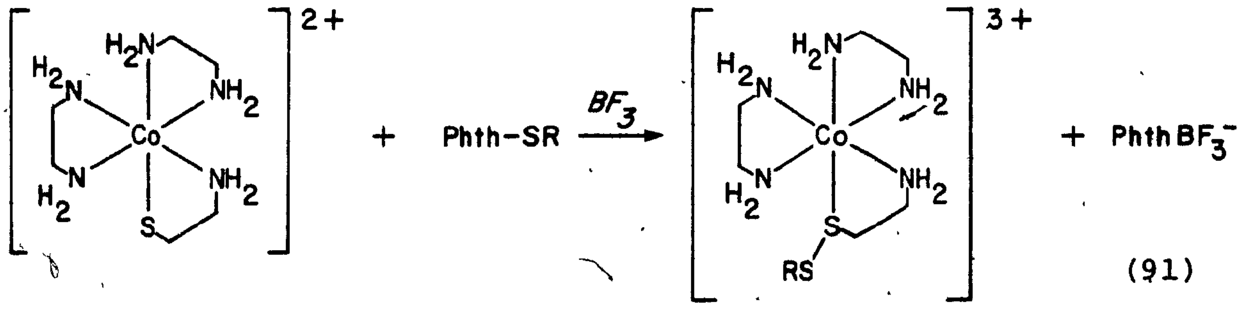
$$RSH + Cl_2 \longrightarrow RSCl + HCl \tag{88}$$

$$RSCl + >NH + Et_3N \longrightarrow >NSR + Et_3NHCl \tag{89}$$

$$Phth\text{-}SCH_2Ph + PhCH_2SSH \longrightarrow (PhCH_2)_2S_3 + PhthH \tag{90}$$

reviewed elsewhere.[261] Most of the studies[379] have used N-alkylthio- or N-arylthiophthalimide reagents probably due to their ease of synthesis from thiols or disulfides _via_ treatment of the sulfenyl chlorides RSCl (eq. 88) with phthalimide (eq. 89).[277,278] With reagents of the type Phth-SR (where Phth = phthalimidyl) symmetrical or unsymmetrical disulfides have been prepared in high yields from the thiols (eq. 87 where x = 1).[380-382] Organic hydrodisulfides (RSSH) have been used to prepare trisulfides.[381] Benzylhydrodisulfide reacted with Phth-SCH_2Ph to give the symmetrical trisulfide in nearly quantitative yield (eq. 90).[381] An obvious alternative route to unsymmetrical trisulfides is via the treatment of the reagents Phth-SSR[383] with a thiol (eq. 87 where x = 2).[384]

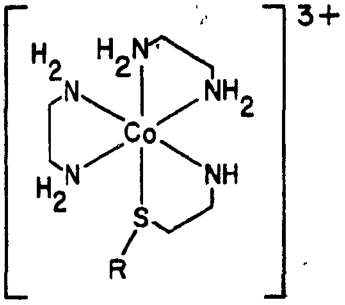
Very few studies have examined the reactivity of these transfer reagents towards transition metal complexes. Nosco et al.[278] found that Phth-SR (R = Me, Et, Me_2CH, Me_3C, Ph) reacted with the thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ (179) to give complexes with a coordinated disulfide group (eq. 91). The crystal structure of the perchlorate salt of the ethylthio cation (R = Et) established the presence of a coordinated disulfide.[278] In this reaction Ph-SR was a source of RS^+. The proposed mechanism for the formation of 180



179 180 (91)

involved nucleophilic attack by the coordinated sulfur on Phth-SR displacing the $Phth^-$ anion which forms the BF_3 adduct.[278]

The sulfur atom of 179 has also been alkylated with alkyl halides to give complexes 181 containing a coordinated thioether.[385]



181

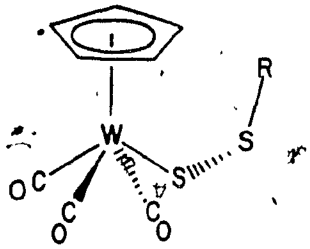
Lopez[386] investigated the reactions of N-(benzyldithio)phthalimide and N-(t-butyldithio)phthalimide (Phth-SSR) with $Fe_2(CO)_9$. When R = $PhCH_2$, the major products were $Fe_3(CO)_9S_2$ (12% yield) and $[Fe(CO)_3SCH_2Ph]_2$ (35% yield). The complexes $[Fe(CO)_3SPhth]_2$ and $Fe_2(CO)_6S_2$ were obtained in trace amounts. However, when R = t-butyl the main isolated product was t-butyldisulfide (23% yield). Only trace amounts of the dimer $[Fe(CO)_3SCMe_3]_2$, $Fe_2(CO)_6(SPhth)(SCMe_3)$, and $Fe_2(CO)_6S_2$ were isolated.

Hartgerink's study[264] of the reactivities of the reagents >N-SR where >N = Succ, Phth and R = CH_2Ph, $4\text{-}C_6H_4Me$ towards the tungsten complexes $W(CO)_5SH^-$ and $CpW(CO)_3SH$ (128) showed that these reagents were reactive towards organometallic hydrosulfides. With $W(CO)_5SH^-$ only the simple thiolate anion $W(CO)_5SR^-$ was isolated although there was ^1H NMR evidence suggesting formation of the desired disulfano product (eq. 92).

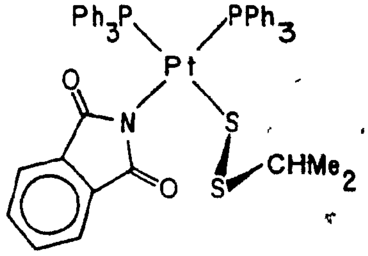
$$\mathrm{W(CO)_5SH^- + {>}N\text{-}S\text{-}4\text{-}C_6H_4Me \longrightarrow}$$
$$\mathrm{{>}N = Phth,\ Succ}$$
$$\mathrm{W(CO)_5(S\text{-}4\text{-}C_6H_4Me)^- + {>}NH} \qquad (92)$$

$$\mathrm{\underset{\underline{128}}{CpW(CO)_3SH} + Phth\text{-}SR \longrightarrow \underset{\underline{182}}{CpW(CO)_3(S_2R)} +}$$
$$\mathrm{\underset{\underline{183}}{CpW(CO)_3SR} + PhthH} \qquad (93)$$

Incorporation of a η-cyclopentadienyl moiety seemed to increase the stability of the disulfano products. Thus Phth-SR (R = CH_2Ph, 4-C_6H_4Me) reacted with $CpW(CO)_3SH$ to give $CpW(CO)_3(S_2R)$ (182) along with $CpW(CO)_3SR$ (183) as a minor by-product (5% yield) (eq. 93). The organometallic disulfanes 182 were isolated as air-stable crystalline solids. The crystal structure[387] of $CpW(CO)_3(S_2\text{-}4\text{-}C_6H_4Me)$ (182) showed a sulfur-sulfur bond distance of 2.053(4) Å with a dihedral angle of 63.1° about this bond. The analogous reactions of 128 with Phth-S_2R (R=CH_2Ph, 4-C_6H_4Me) gave $CpW(CO)_3(S_2R)$ (182) as a minor product and a major component which was formulated as $CpW(CO)_3(S_3R)$ (184) on the basis of ^1H NMR spectroscopy. Pure samples of the latter could not be obtained, however.[264] Complexes 182 and 184 decomposed in solution to give thiolates $CpW(CO)_3(SR)$ (183).[264] Complexes 182 were desulfurized by PPh_3 to give 183.[264]



182



185

Lai[325] has shown that the compounds Phth-S_xR where R = CH_2Ph, n-Pr, i-Pr, 4-C_6H_4Me and x = 1 or 2 are also reactive towards low valent metal complexes which do not contain the SH group. Thus, $(PPh_3)_2Pt(C_2H_4)$ reacted with these reagents to give the complexes cis-$(PPh_3)_2Pt(S_xR)(Phth)$ as air-stable products in high yields via oxidative-addition of the S-N bond (eq. 94). The crystal structure of

$$(PPh_3)_2Pt(C_2H_4) + Phth\text{-}S_xR \longrightarrow \text{cis-}(PPh_3)_2Pt(S_xR)(Phth) \qquad (94)$$

cis-$(PPh_3)_2Pt(S_2CHMe_2)(Phth)$ (185) confirmed the presence of the Pt-S-S-C linkage.[387] A sulfur-sulfur bond distance of 2.037(4) Å and a dihedral angle of 89.5° about this bond were found.

It was of great interest to study the reactions of the reagents >NS_xR with the bis(hydrosulfido) complex $Cp_2Ti(SH)_2$ (110). New complexes of the type $Cp_2Ti(S_{x+1}R)_2$ would be expected.

Results

The reactivity of the transfer reagents >N-SR towards $Cp_2Ti(SH)_2$ (<u>110</u>) was strongly dependent on the nature of the R group attached to the sulfur. The reaction between <u>110</u> and Phth-SCH_2Ph gave a complex mixture of Cp-containing products as shown by ^1H NMR. A complex mixture also resulted when the reaction was done at ambient temperature or at -78°C while no reaction occurred at -90°C. The bis(thiolato) complex $Cp_2Ti(SCH_2Ph)_2$ (<u>176</u>, Chapter 4) was present in at most only trace amounts as shown by TLC. The ^1H NMR spectrum was consistent with the presence of a mixture of polysulfides of the type $(PhCH_2)_2S_x$ (x = 2, 3, 4).[388,389] Attempts at separating the products by column chromatography on silica gel or deactivated alumina or by fractional crystallization were unsuccessful. In sharp contrast to this, the bis(thiolato) complex <u>176</u> is easily prepared by the literature methods (Chapter 4).

A rapid reaction occurred between <u>110</u> and Phth-$SCHMe_2$ at 0°C. Only one product was detected by TLC. The complex $Cp_2Ti(S_2CHMe_2)_2$ (<u>122</u>) along with a small amount of unreacted Phth-$SCHMe_2$ was isolated. The ^1H NMR spectrum (Table 2) of <u>122</u> showed only one Cp resonance. The CH proton was observed as a septet and the CH_3 protons appeared as a doublet. In benzene-d_6 a simple set of signals were observed for the three types of protons. The proton decoupled ^{13}C NMR spectrum of <u>122</u> in benzene-d_6 consisted of three sharp lines

TABLE 2

The ^1H NMR Spectra of the Complexes $Cp_2Ti(S_2CHMe_2)_2$ (122), $Cp_2Ti(SR)(S_3R)$ [R = Ph (123), 4-C_6H_4Me (124)], Their Bis(thiolato) Analogs, and Isopropyl Polysulfides [a]

Compound	Cp	Ph	CH		CH_3	
$Cp_2Ti(SCHMe_2)_2$	6.15		3.65^b		1.30^b	
$Cp_2Ti(S_2CHMe_2)_2{}^c$	6.21		3.06^d		1.28^d	
	5.85^e		$3.21^{e,f}$		$1.35^{e,f}$	
$Cp_2Ti(SPh)_2$	5.98	7.3				
$Cp_2Ti(SPh)(S_3Ph)$	6.08	7.2				
$Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)_2$	6.07	7.37^g 7.50^g			2.33	
$Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)\text{-}(S_3\text{-}4\text{-}C_6H_4Me)$	6.12	$7.42^{g,h}$ $7.57^{g,h}$			2.33	
$(Me_2CH)_2S^{c,e}$			2.76	6.8	1.14	6.8
$(Me_2CH)_2S_2{}^{c,e}$			2.76	6.8	1.14	6.8
$(Me_2CH)_2S_3{}^{c,e}$			3.00	6.8	1.16	6.8
$(Me_2CH)_2S_4{}^{c,e,i}$			3.01	6.8	1.13	6.8

Footnotes to Table 2

[a] In $CDCl_3$ at 60 MHz except where noted otherwise. Chemical shifts in units of δ ppm.

[b] J(H-H) = 6 Hz.

[c] Spectrum recorded at 200 MHz.

[d] J(H-H) = 7 Hz.

[e] In C_6D_6.

[f] J(H-H) = 6.7 Hz.

[g] Low field half of AB quartet.

[h] High field half of AB quartet not observable (see text).

[i] Tentatively assigned from the ^1H NMR spectrum of the crude reaction product from the reaction of $Bz-S_2-Bz$ with Me_2CHSH (see text).

at δ_c 113.17, δ_c 42.31, and δ_c 23.14 downfield from tetramethylsilane corresponding to the Cp, CH, and CH_3 carbon atoms, respectively. The ^1H and ^{13}C NMR spectra are, then, consistent with the symmetrical formulation $Cp_2Ti(S_2CHMe_2)_2$. The solid-state infrared spectrum of 122 is quite similar to that of the bis(thiolato) complex 115 being dominated by bands characteristic of the Cp ligand.[332] (see Chapter 4). It is interesting to note that the C-H stretching bands for the Cp ligands in 122 are *ca.* 35 cm^{-1} to lower frequency of those for 115. A very weak molecular ion peak ($M^{+\cdot}$, m/z = 328, 0.2%) was seen in the mass spectrum of 122. The highest mass fragment showing appreciable stability, as implied by a significant abundance (21%), corresponded to the ion $Cp_2TiS_2CHMe_2^+$ (m/z = 285). The appearance of the ion $CHMe_2^+$ as the base peak is consistent with facile S-C bond cleavage under the conditions of the experiment. In comparison, this ion appeared in only 11% relative abundance in the spectrum of $Cp_2Ti(SCHMe_2)_2$ (115). Peaks corresponding to polysulfide ions $(Me_2CH)_2S_x^{+\cdot}$ were observed in the spectrum of both 115 (x = 1 and 2) and 122 (x = 1-4).

When $Cp_2Ti(SH)_2$ (110) and Phth-$SCMe_3$ were reacted in a 1:2 stoichiometry at 0°C, no immediate reaction occurred. After stirring for 37 hours at 0° to 10°C no 110 remained as shown by TLC and ^1H NMR, but significant amounts of Phth-$SCMe_3$ were present. Examination of the solution by TLC indicated that a major purple product and a minor blue product were present. The ^{1}H NMR spectrum of the crude product was consistent with the presence of several Cp-containing compounds. An unidentified signal due to a CMe_3 group appeared slightly upfield from that of Phth-$SCMe_3$. Fractional crystallization failed to separate the organometallic components; however, about 35% of unreacted Phth-$SCMe_3$ was recovered. When <u>110</u> was treated with Phth-$SCMe_3$ in a 1:1 stoichiometry at 0°C and stirred for 17 hours at room temperature the reaction mixture consisted of essentially starting materials as shown by ^{1}H NMR and TLC. After refluxing for three days no <u>110</u> was present. Filtration removed a small amount of a red insoluble product whose solid-state infrared spectrum was similar to that of $(Cp_2ZrS)_2$ (<u>112</u>). The CS_2 extract of the crude product contained mostly Phth-$SCMe_3$ contaminated with a small amount of phthalimide. A complex set of weak signals in the region δ 6.4 to δ 6.2 may correspond to Cp protons from unknown compounds. Köpf[260] has previously noted that <u>110</u> eliminates H_2S in refluxing benzene to form oligomers having Ti-S-Ti bonds.

The reaction of <u>110</u> with Succ-SPh at 0°C was rapid. The ^{1}H NMR spectrum of the crude product gave three peaks in the Cp region at δ 6.33, δ 6.20, and δ 6.07 in the ratio 1:3:11, respectively. Recrystallization gave the major product <u>123</u> as air-stable small purple crystals suitable for X-ray crystallography. The complex decomposes in solution above 0°C. The ^{1}H NMR spectrum of <u>123</u> is given in Table 2. The solid-state infrared spectrum of <u>123</u> (Fig. 3) is very similar to that of $Cp_2Ti(SPh)_2$ (<u>118</u>, Fig. 4). The most notable difference is the presence of a sharp band at 743 cm^{-1} for <u>118</u> while for <u>123</u> two equally intense sharp bands at 748 and 738 cm^{-1} are observed. Monosubstituted phenyl rings typically display strong infrared bands at 780 to 730 cm^{-1} which correspond to a C-H bending vibration.[373] The position of this band is quite sensitive to the nature of the substituent. Thus the presence of two bands is consistent with the unsymmetrical structure of <u>123</u> (Fig. 5) determined by X-ray methods by Dr. P. Bird of Concordia University, Montreal, details of which are presented later. Complex <u>123</u> did not show a molecular ion peak in its mass spectrum (70 eV). The heaviest ion corresponded to the ion $Cp_2TiS_2Ph_2^{+\bullet}$ (m/z = 396). The mass spectrum indicated the presence of a small amount of Cp_2TiS_5 (<u>73</u>). However, this was not detected in the ^1H NMR spectrum of <u>123</u> and may therefore result from decomposition in the spectrometer.

Compounds <u>110</u> and Phth-S-4-C_6H_4Me reacted immediately at 0°C in THF. The CS_2 extract of the crude reaction product consisted of two major products, a purple one (<u>124</u>) and a colourless one as shown by TLC. No elemental sulfur or 4-methylphenyl disulfide was detected by TLC. The ^1H NMR spectrum of recrystallized <u>124</u> is given in Table 2. Unidentified peaks appeared at δ 7.07 (broad multiplet) and δ 6.17 (broad singlet). The peak at δ 7.07 is thought to obscure the high-field portion of the AB quartet expected

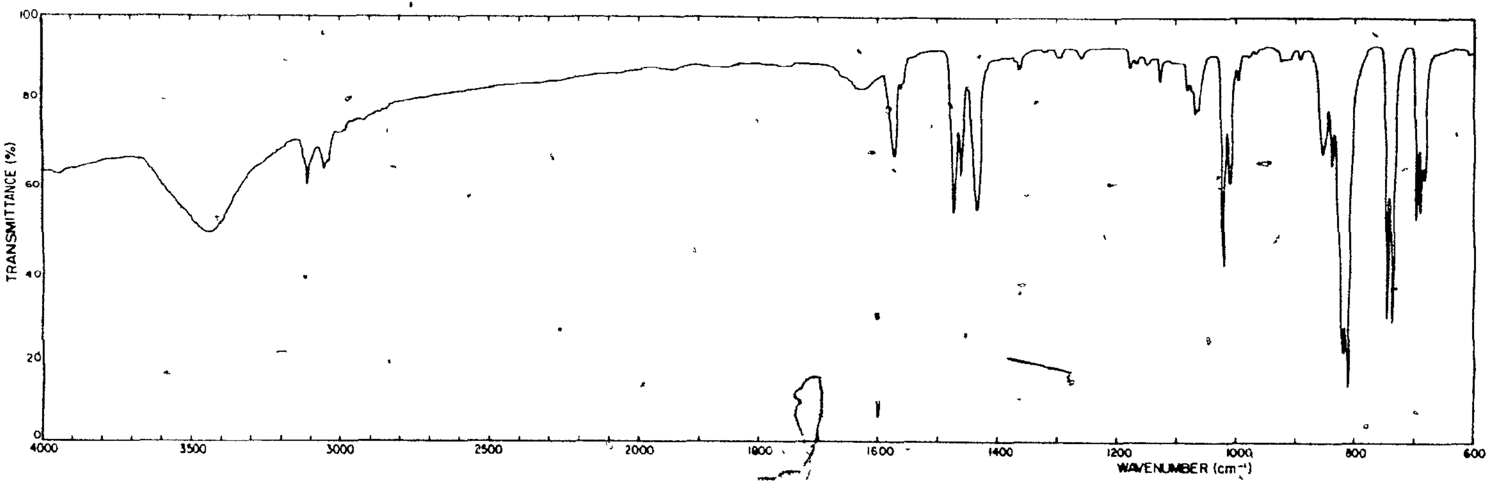


Figure 3. Infrared spectrum of $Cp_2Ti(SPh)(S_3Ph)$ (123).

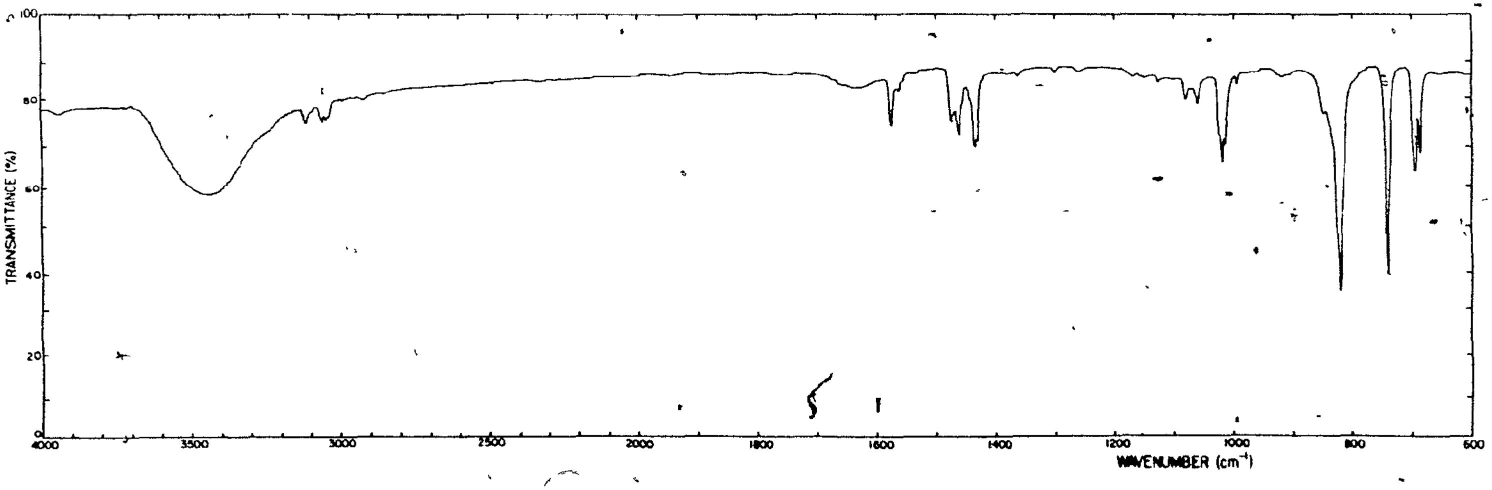
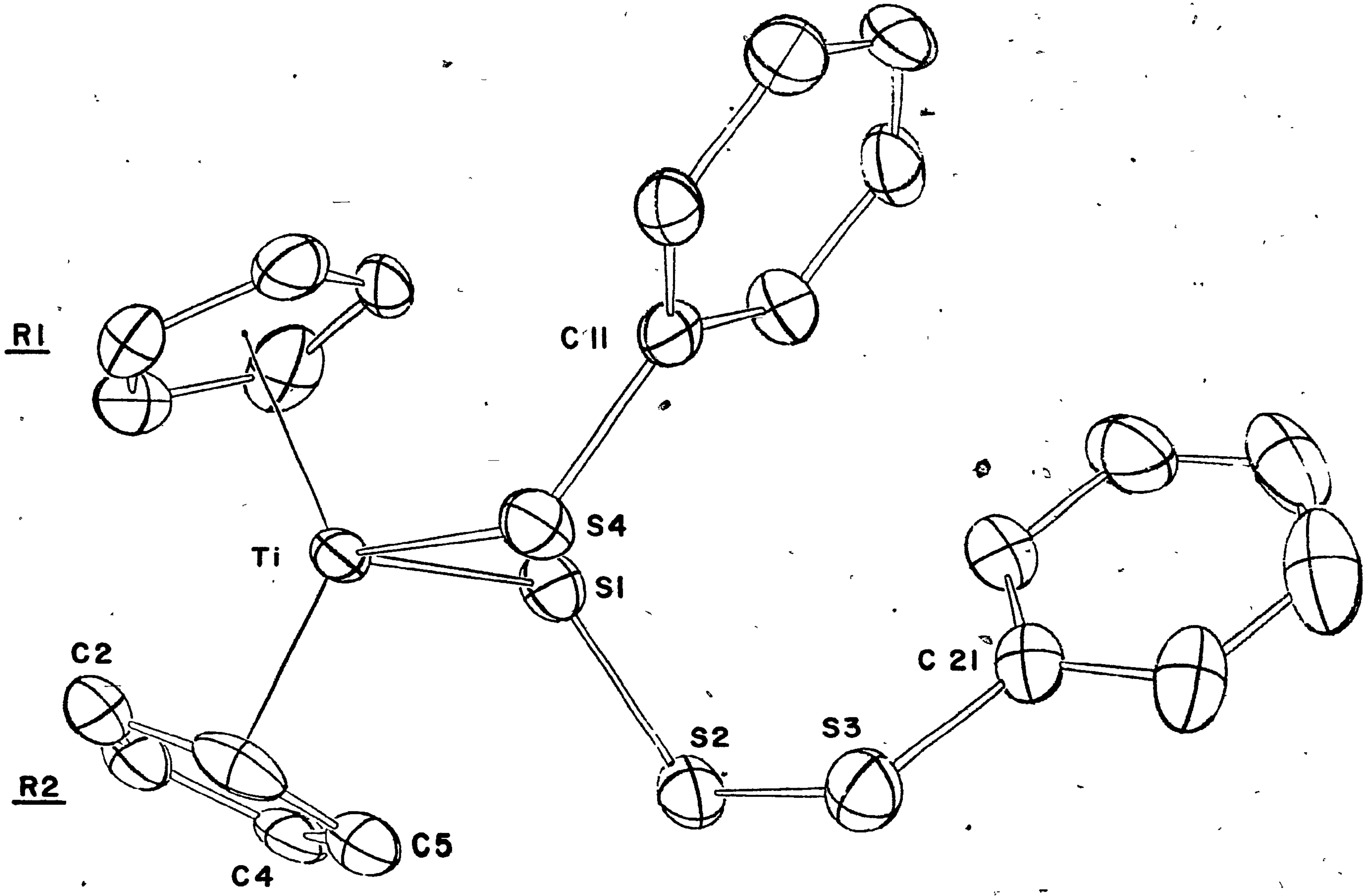


Figure 4. Infrared spectrum of $Cp_2Ti(SPh)_2$ (118).

Figure 5. Perspective drawing of $Cp_2Ti(SPh)(S_3Ph)$ (123).


C11
R1
S4
Ti
S1
C2
C21
S2
S3
R2
C5
C4

for 124. The impurities could not be removed completely by additional recrystallizations. No $Cp_2Ti(S\text{-}4\text{-}C_6H_4Me)_2$ (119) was observed among the crude reaction products. The solid-state infrared spectra of 119 and 124 were quite similar. Overlapping of cyclopentadienyl and aryl ring C-H bending bands at ca. 800 cm^{-1} precluded an examination for splitting of the bands due to the latter as had been done for $Cp_2Ti(S_xPh)_2$ (x = 1, 3) above. The most intense peaks in the electron-impact mass spectrum of 124 can be attributed to the ions R^+, RS^+, and $RS_2R^{+\cdot}$ where $R = C_7H_7$. The most intense metal-containing fragment corresponded to $Cp_2Ti^{+\cdot}$ (m/z = 178, 35.2%). No molecular ion peak was observed; the highest mass fragment observed corresponded to the ion $Cp_2TiS_2R_2^{+\cdot}$ (m/z = 424). Peaks due to the ions $Cp_2TiS_5^{+\cdot}$ and $RS_xR^{+\cdot}$ (x = 0-4) were also detected. It is not known if these compounds formed during analysis or if they were present as trace impurities in 124. The presence of minor impurities may account for the slightly low carbon and sulfur microanalyses obtained for 124. On the basis of the established structure of 123 a similar unsymmetrical structure is proposed for 124.

An attempted synthesis of $Cp_2Ti(S_3\text{-}4\text{-}C_6H_4Me)_2$ via treatment of $Cp_2Ti(SH)_2$ (110) with $Phth\text{-}S_2\text{-}4\text{-}C_6H_4Me$ was unsuccessful. The reaction, carried out in THF at -78°C, slowly became purple in colour. The rate of colour change was qualitatively slower than that for the reaction of 110 with $Phth\text{-}S\text{-}4\text{-}C_6H_4Me$. Once 110 had been consumed, as shown by TLC, the reaction solution was warmed to 0°C and the solvent removed <u>in vacuo</u>. The crude reaction products did not contain any <u>119</u> or <u>124</u> as shown by ^{1}H NMR. This spectrum displayed the following signals: several broad peaks were present in region δ 7.8 to δ 6.8 (C_6H_4), singlets of approximately equal intensity at δ 6.20, δ 6.18, and δ 6.03 (Cp) and a broad unsymmetrical singlet at δ 2.33 (CH_3). A poorly resolved multiplet at δ 7.07 matched an impurity peak found in the spectrum of <u>124</u> but remains unidentified. The product mixture could not be separated by fractional crystallization. Column chromatography eluted only a mixture of 4-methylphenyl polysulfides identified by ^{1}H NMR, Cp_2TiS_5 (<u>73</u>) identified by ^{1}H NMR and TLC, and sulfur identified by melting point and TLC.

The polysulfano complexes $Cp_2Ti(SCHMe_2)_2$ (<u>122</u>) and $Cp_2Ti(SR)(S_3R)$ [R = Ph (<u>123</u>), 4-C_6H_4Me (<u>124</u>)] were more heat- and air-sensitive than their bis(dithiolato) analogs $Cp_2Ti(SR)_2$ [R = $CHMe_2$ (<u>115</u>), Ph (<u>118</u>), 4-C_6H_4Me (<u>119</u>)]. For example, <u>122</u> could be handled in air briefly but prolonged exposure caused decomposition to an orange sticky solid. The melting points of the two types of complexes differed with the bis(thiolato) complex always having the much higher value as follows: R = $CHMe_2$, 144-146°C (<u>115</u>) and 76-78°C (<u>122</u>); R = Ph, 194-196°C (<u>118</u>) and 131-132°C (<u>123</u>); R = 4-C_6H_4Me, 198.5-199.5°C (<u>119</u>) and 108-110°C (<u>124</u>). The complexes <u>122</u>, <u>123</u>, and <u>124</u> decompose above 0°C in polar and aromatic solvents whereas their analogs <u>115</u>, <u>118</u>, and <u>119</u> are stable at this temperature.

The decomposition of 122 and 123 in solution under nitrogen at room temperature was examined. A deep purple solution of 122 in C_6D_6 was allowed to stand under nitrogen for several days. A yellow product precipitated during this time. Filtration in air gave a pale yellow solution the ^1H NMR spectrum of which was consistent with the presence of a mixture of isopropyl polysulfides (Table 2). Peaks attributed to the tetrasulfide dominated the spectrum. A weak signal due to Cp protons appeared at δ 6.29 but its source is unknown. The major soluble decomposition product of 122 is tentatively identified as $(Me_2CH)_2S_4$. Pure isopropyl tetrasulfide was not available. However, reaction of 2-methylpropylthiol with N,N'-dithiobisbenzimidazole in refluxing benzene for 20.5 hours under nitrogen gave a crude product consisting of a mixture of polysulfides as shown by the ^1H NMR and mass spectra. Decomposition occurred upon recrystallization; however, the major ^1H NMR signals of the crude product are tentatively assigned to the tetrasulfide (Table 2).

A solution of 123 in CH_2Cl_2/hexanes was allowed to decompose at room temperature under nitrogen and the products were analyzed by TLC and ^1H NMR. The following were identified: Cp_2TiS_5 (73), PhS_xPh (x not established), traces of $Cp_2Ti(SPh)_2$ (118), and an unidentified brown-yellow residue. The ^1H NMR spectrum of a $CDCl_3$ solution of this residue consisted of a broad signal from δ 7 to δ 6. No phenyl signals were present below δ 7. The solid-state infrared spectrum showed broad bands at ca. 3110 (w), 1445 (m), 1010 (m), 850 (s), and 790 (vs) cm^{-1} characteristic of the η-C_5H_5 ring[332] in addition to a broad band which extended from 710 to 610 cm^{-1} and centered at 650 cm^{-1}. Complexes containing a Ti-O-Ti linkage typically display very strong absorption bands in the region 800 to 700 cm^{-1}.[375] The analogous Ti-S-Ti group should absorb at a lower frequency.

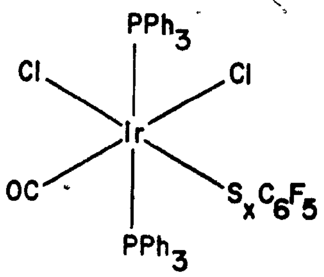
The thermal decomposition of $Cp_2Ti(SCH_2Ph)_2$ (176) contrasts with the decomposition of the titanapolysulfane complexes reported above. When a solution of 176 in THF was heated at ca. 40°C under a nitrogen atmosphere for seven days a small amount of a red insoluble product formed. The ^1H NMR spectrum ($CDCl_3$) of the soluble portion identified the presence of mostly 176 and a trace of $(PhCH_2)_2S_2$. The ratio of the areas of the CH_2 peaks of 176 (δ 4.22) to that of $(PhCH_2)_2S_2$ (δ 3.58) was five to one. The solvent was evaporated and replaced with chloroform. The solution was refluxed under nitrogen for one week until none of 176 was present as indicated by TLC. The red solution was removed by syringe from a mixture of yellow and red insoluble solids. These solids displayed broad infrared absorption bands consistent with the presence of Cp and CH_2Ph groups. A strong, positive Beilstein Test[285] implied the incorporation of chloride in the insoluble solids. The $CHCl_3$-soluble fraction contained Cp_2TiCl_2 (traces), $PhCH_2SH$, and $(PhCH_2)_2S_2$ as shown by ^1H NMR. At most only traces of $(PhCH_2)_2S_x$ (x = 1, 3, 4, 5,...) were present. Workup by column chromatography on silica gel gave $(PhCH_2)_2S_2$ in 11% of the theoretical maximum which was identified by melting point, TLC, and ^1H NMR.

Discussion

The complex $Cp_2Ti(SH)_2$ (110) reacted with "blocked" sulfur-transfer reagents of the type >N-SR to give either a symmetrical product $Cp_2Ti(S_2R)_2$ or an unsymmetrical one $Cp_2Ti(SR)(S_3R)$ depending on R. Thus 110 and Phth-$SCHMe_2$ reacted to give $Cp_2Ti(S_2CHMe_2)_2$ (122) while 110 and >N-SR gave $Cp_2Ti(SR)(S_3R)$ where R = C_6H_5 (123) and 4-C_6H_4Me (124). Complex 110 also reacted with Phth-S_2-4-C_6H_4Me but several products formed which could not be separated.

The ^1H NMR chemical shift of protons on carbon atoms adjacent to the terminal sulfur atoms in a sulfur chain of an organic polysulfide is particularly sensitive to the length of the chain. For example, in the molecules Me_2S_x,[388] $(PhCH_2)_2S_x$,[388,389] and $(Me_2CH)_2S_x$ (Table 2) these signals shift to lower field with increasing chain length, although the difference in chemical shift of consecutive members of the series diminishes as x increases. The methyl signals of $(Me_2CH)_2S_x$ and $(Me_3C)_2S_x$[388] are less sensitive to chain length. Thus the unsymmetrical isomer of 122, $Cp_2Ti(SCHMe_2)(S_3CHMe_2)$, should have two clearly resolved signals for each of the methine and methyl groups while the symmetrical species should have only one set of signals. The two possible isomers of 122 should be distinguishable by ^{13}C NMR as well. The proton decoupled ^{13}C NMR spectrum of <u>122</u> showed three lines for the Cp, CH, and CH_3 carbon atoms at δ_C 113.17, δ_C 42.31, and δ_C 23.14, respectively. For organic sulfides of the type R_2CHSR the ^{13}C NMR chemical shift for the methine proton is found between 55 and 65 ppm.[390] The compound $(Me_2CH)_2S_2$ displays signals at 41.14 ppm corresponding to the CH protons and at 22.60 ppm due to the CH_3 protons.[391] The ^1H and ^{13}C NMR spectra of <u>122</u> are consistent with a symmetrical structure.

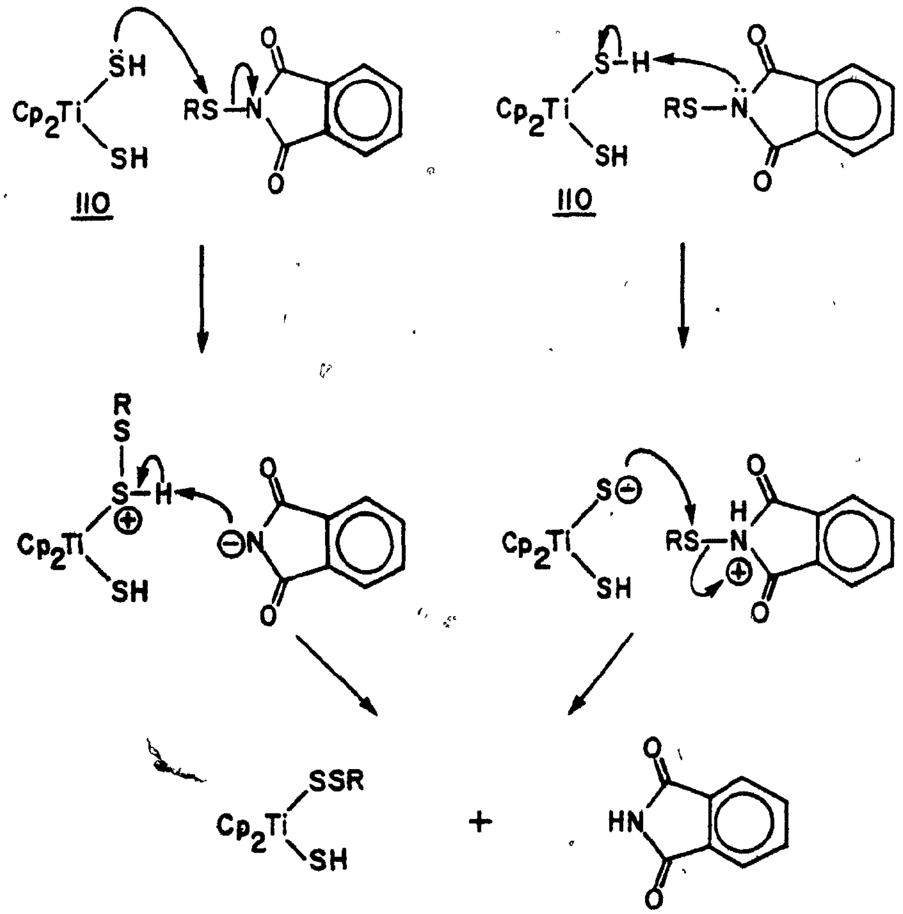
The pair of iridium(III) complexes <u>trans</u>-$IrCl_2(S_xC_6F_5)(CO)(PPh_3)_2$ (<u>186</u>, x = 1, 2) has been reported. The thiolato complex (x = 1) displayed bands in the infrared spectrum at 2065 cm^{-1} corresponding to a CO stretch and at 315 and 305 cm^{-1} for the Ir-Cl stretch.[392] The corresponding bands for the disulfano complex (x = 2) appeared at 2052, 314, and 275 cm^{-1}.[393] These data indicate an increase of electron density at the iridium as the SC_6F_5 ligand is replaced by the $S_2C_6F_5$ group.



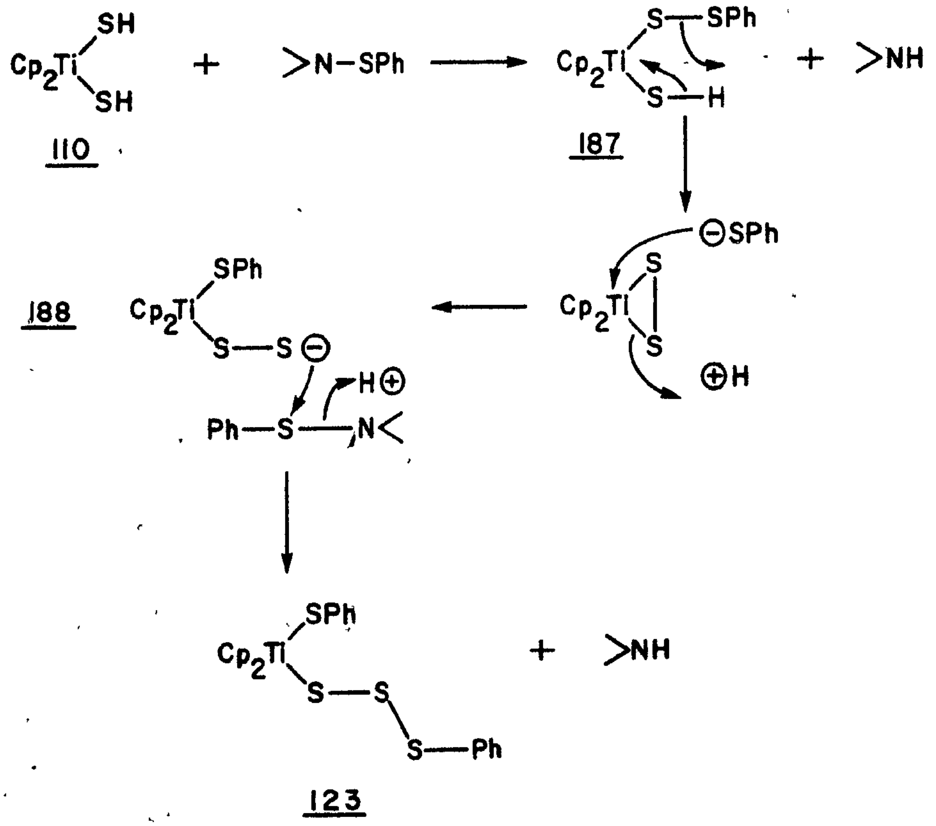
<u>186</u>

A plausible mechanism[258,264] for the reaction of $Cp_2Ti(SH)_2$ (110) with the transfer reagents Phth-SR to give symmetrical products involves stepwise replacement of metal-coordinated hydrosulfido protons with SR groups (Scheme 3). Scheme 4 outlines an alternative, but less likely, mechanism whereby the initial step is protonation of the transfer reagent. It is not known if either or both mechanisms are operating in this particular system.

Scheme 3 Scheme 4



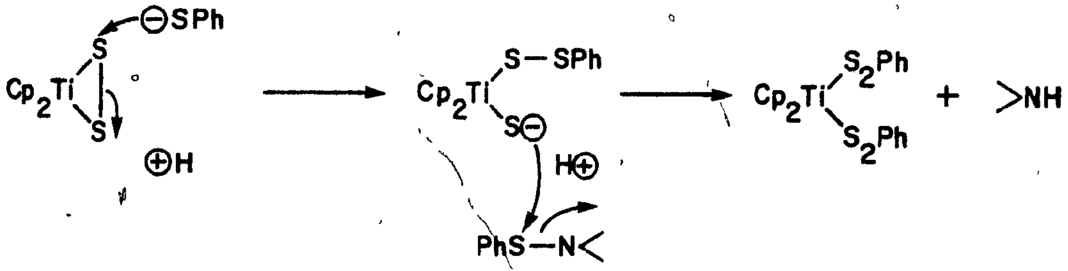
X-ray crystallography revealed that 123 was the unsymmetrical complex $Cp_2Ti(SPh)(S_3Ph)$. This is the first metal trisulfane complex of the type MSSSR (see the end of this chapter for details of the structure). Since 122 appears to be symmetrical a comment on the mechanistic implications is appropriate. Scheme 5 indicates how the "half-substituted"



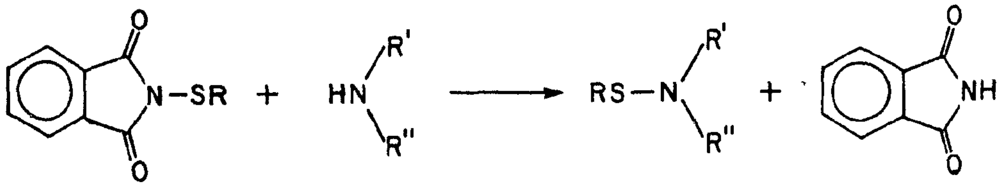
Scheme 5

species <u>187</u> could intramolecularly eliminate thiophenol to give the side-on bonded disulfane complex Cp_2TiS_2. There are many transition metal complexes that contain a η^2-S_2 ligand and include the very similar compound Cp_2MoS_2 (<u>20</u>).[59] Nucleophilic attack by the thiophenolate anion could generate the unsymmetrical anion <u>188</u> which would attack a second molecule of >NSPh to give <u>123</u>. This mechanism accounts for the formation of an unsymmetrical product but the proposed intermediate Cp_2TiS_2 could also be present during the formation of symmetrical species. The crucial step is attack by RS^- on Cp_2TiS_2. Attack at the metal leads to <u>123</u>; however, attack at the sulfur could lead to the symmetrical product $Cp_2Ti(S_2Ph)_2$ (Scheme 6). Such mechanisms, it should be noted, are speculative at present.

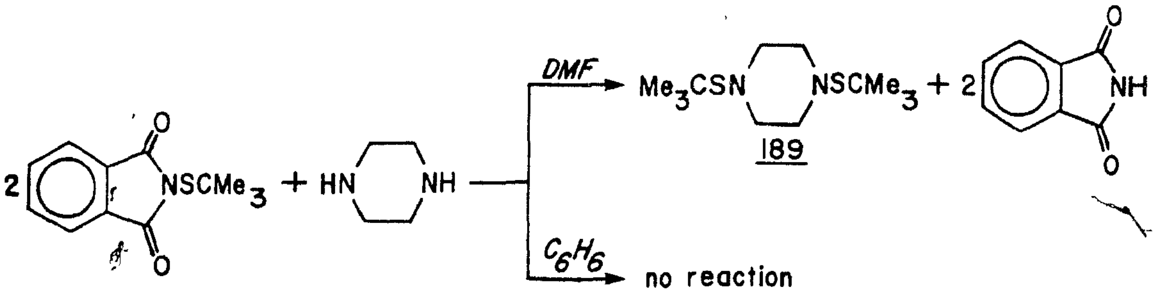
<u>Scheme 6</u>



The failure to isolate complexes from the reaction of <u>110</u> with Phth-$SCMe_3$ is consistent with the reduced reactivity of Phth-$SCMe_3$ relative to other N-alkylthiophthalimides as noted by others.[394,395] A general route to sulfenamides RSNR'R" is *via* treatment of alkyl or aryl thiophthalimides with most alkyl, cyclic or bifunctional amines (eq. 95).[394,395] The reactions generally take place at room temperature or at reflux in benzene to give the products in high yield. However, Phth-SCMe$_3$ and piperazine failed to react in boiling benzene (21 hours). In the higher boiling solvent N,N-dimethylformamide (DMF) the desired product 189 was isolated in only 22% yield (eq. 96).[395] The low reactivity of Phth-SCMe$_3$ was ascribed to the steric bulk of the *t*-butyl group which was felt to hinder nucleophilic attack by the piperazine nitrogen atom on the phthalimidyl sulfur atom.[395] Steric hindrance may also account for the reduced reactivity of Cp$_2$Ti(SH)$_2$ (110) with Phth-SCMe$_3$. It is interesting to note, however, that a two sulfur chain either reduces the steric demands

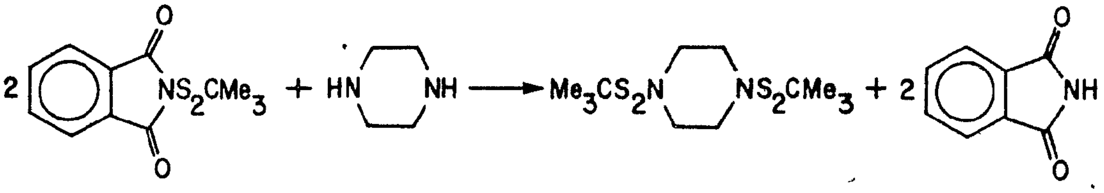


(95)



(96)

or weakens the N-S bonds since Phth-S_2CMe_3 reacted with piperazine to give the expected product in 87% yield (eq. 97).[396]



(97)

The studies on the decomposition of complexes of the type $Cp_2Ti(S_xR)_2$ (x = 1, 2) indicate that under the appropriate conditions they may behave as sources of organic polysulfides RS_yR (y = 2, 3, 4,...) with the compound where y = 2x predominating. It has been reported that solid $Cp_2V(SPh)_2$ heated <u>in vacuo</u> at <u>ca</u>. 100°C evolves the disulfide Ph_2S_2. The fate of the vanadium was not reported.[397]

The X-Ray Crystal Structure of $Cp_2Ti(SPh)(S_3Ph)$ (123, Fig. 5)

The crystal structure of 123 was solved by N. Ansari and Dr. P. Bird of Concordia University, Montreal. The numbering scheme for the atoms of $Cp_2Ti(SPh)_2$ (118)[397] and 123 are shown in Figs. 6 and 7, respectively. Table 3 lists important molecular parameters for 118[397] and 123. Both 118 and 123 have the familiar "bent sandwich" structure with a distorted tetrahedral arrangement of the ligands about the metal. Replacement of one SPh group in 118 by a SSSPh moiety causes minor changes in the bond lengths and angles in the

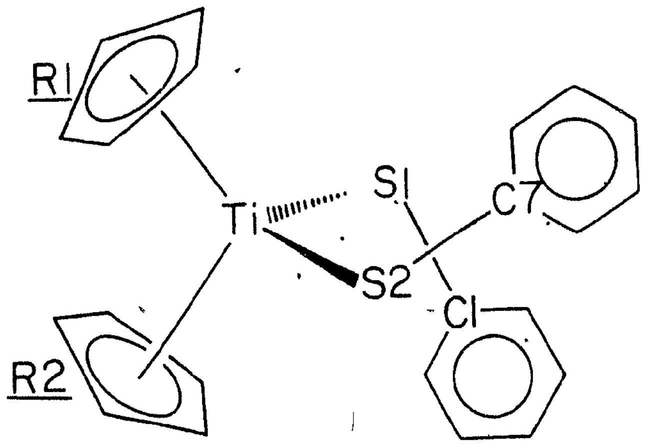


Figure 6. Atom labels for $Cp_2Ti(SPh)_2$ (118).

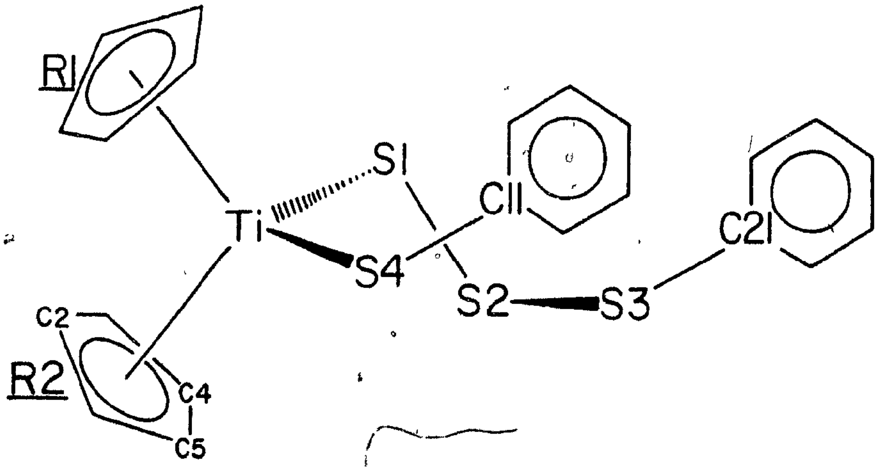


Figure 7. Atom labels for $Cp_2Ti(SPh)(S_3Ph)$ (123).

TABLE 3

Selected Bond Distances, Non-bonding Distances, Bond Angles, and Dihedral Angles for $Cp_2Ti(SPh)_2$ (118)[397] and $Cp_2Ti(SPh)(S_3Ph)$ (123)

Bond Distances (Å)

118		123	
Ti-S1	2.395(8)	Ti-S1	2.439(3)
Ti-S2	2.424(8)	Ti-S4	2.381(3)
avg.	2.410	avg.	2.410
Ti-R1	2.067		2.036
Ti-R2	2.072		2.049
avg.	2.070	avg.	2.043
		S1-S2	2.053(3)
		S2-S3	2.011(3)
S1-C1	1.78	S3-C21	1.755(7)
S2-C7	1.77	S4-C11	1.759(6)

Bond Angles (°)

118		123	
S1-Ti-S2	99.3(3)	S1-Ti-S4	98.3(1)
R1-Ti-R2	132.4		132.55(4)
Ti-S2-C7	112.9	Ti-S4-C11	114.5(2)
Ti-S1-C1	115.4	Ti-S1-S2	115.5(1)
S1-Ti-R1	101.8		99.34(5)
S1-Ti-R2	108.7		109.64(5)
S2-Ti-R1	108.3	S4-Ti-R1	110.88(6)
S2-Ti-R2	101.9	S4-Ti-R2	101.36(4)
		S1-S2-S3	109.3(1)
		S2-S3-C21	106.8(3)

Non-Bonding Distances (Å)

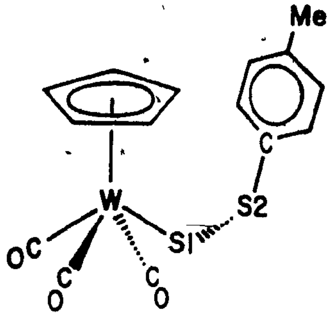
118		123	
S1···S2	3.673	S1···S4	3.646(1)

Dihedral Angles (°)

TiS1S2/S1S2S3	70.44(8)
S1S2S3/S2S3C21	78.98(8)

immediate coordination sphere of the metal atom. The average Ti-Cp distance in 123 and in 118 is similar. The unique Ti-SPh distance is significantly shorter in 123 [2.381(3) Å] than in 118 [2.410(3) Å]. The difference in the Ti-S bond lengths observed in 123 is probably not entirely due to its unsymmetrical structure since similar asymmetry was observed in 118 and in $Cp_2V(SPh)_2$.[397] Whereas the R1-Ti-R2 angles are nearly identical (123, 132.6°; 118, 132.4°) there is a greater difference in the S-Ti-S angles [123, 98.3(1)°; 118, 99.3(3)°]. There is a distinct tilting of ring R2 for 123 that is not observed for 118. The longest and shortest Ti-C bond distances in the molecule are found to R2: Ti-C2 = 2.346(7) Å, Ti-C4 = 2.385(6) Å, and Ti-C5 = 2.374(7) Å. Molecular models suggest that a steric interaction between a lone pair on S2 and the C4-H and C5-H bonds may be a cause of this distortion.

The most unusual and important feature of 123 is the S_3 chain. Very few inorganic complexes containing a $M\text{-}S_xR$ linkage where $x \geq 2$ have been studied crystallographically. Two examples are $CpW(CO)_3(S_2\text{-}4\text{-}C_6H_4Me)$ (182)[387] and cis-$(Ph_3P)_2Pt(Phth)(S_2CHMe_2)$ (185).[387] Complex 123 is the first complex bearing a $M\text{-}S_3R$ linkage to be isolated and characterized crystallographically. Some useful comparisons can be made with the structures of the dimers $[CpFe(CO)_2]_2(\mu\text{-}S_3)$ (44)[102] and $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46)[103] which contain bridging S_3 chains and with the organic trisulfides perchloro-



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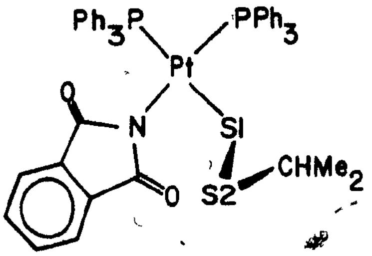

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dimethyltrisulfide (190)[398] and 3,3'-trithiobis(2,4-pentanedione) (191)[399] (Table 4).

$Cl_3C-S_3-CCl_3$

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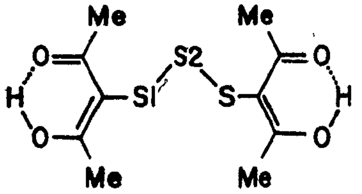

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The average S-S bond lengths in 44 and 46 are longer than the average found for 123. The marked difference in the two S-S bond distances in 123 (Table 3) was not observed for 44 or 46 or the organic trisulfides. The variation in complex 123 is presumably a consequence of the different substituents terminating the S_3 chain. It is interesting to note that the S1-S2 bond length in 182 [2.053(4) Å] is identical to the S1-S2 bond length in 123. Similarly, the S2-C distance in 182 [1.756(9) Å] is the same as the S3-C21 distance in 123 [1.755(7) Å]. It is somewhat

TABLE 4

Comparisons of Average Bond Distances (Å), Bond Angles (°), and Dihedral Angles (°) of 123 with Those of Other Compounds Containing a Non-Chelating Trisulfide Linkage

	S-S	SSS	XS-SS [a]
123	2.032	109.3	70.4
44 [b]	2.042	111.43	77.5
46 [c]	2.056	109.07	64.6
190 [d]	2.035	106.0	e
191 [f]	2.060	108.0	73.6

[a] X stands for Ti, Fe, or C terminating the S_3 chain.

[b] Ref. 102.

[c] Ref. 103.

[d] Ref. 398.

[e] Not reported.

[f] Ref. 399.

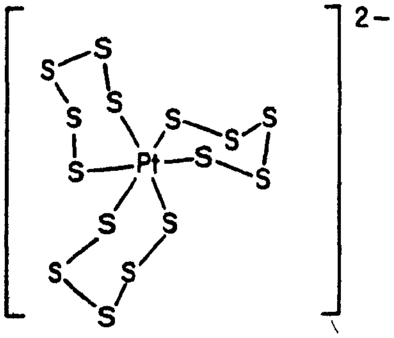
surprising that the S2-S3 distance is much shorter than the S1-S2 distance in 123 which implies it might be stronger. For polysulfides having more than two sulfur atoms helical (polymeric) sulfur should probably be used as the reference compound for the bond length, bond angle, and dihedral angle.[24] In this species the values are 2.066 Å, 106°, and 85.3°, respectively.[25] The dihedral angle about the S1-S2 and S2-S3 bonds in 123 are similar at 78.98(8)° and 70.44(8)°, respectively. Smaller SSS bond angles and SS-SS dihedral angles tend to lengthen S-S bonds.[22] However, the angle of 109.3(1)° in 123 is similar to those found in the organometallic complexes 44 [111.43(9)°] and 46 [109.07(6)°] and the organic trisulfides 190 (106.0°) and 191 (108.0°). Thus the shortening of the S2-S3 bond relative to the S1-S2 bond in 123 remains unexplained. The similarity in SSS bond angles also extends to the dihedral angles XS-SS (X = S or metal atom): 123, 70.4°; 44, 77.5°; 46, 62.7° and 66.6°; and 191, 73.6°.

6. THE SYNTHESIS OF METALLACYCLOPOLY-SULFANES AND -SELENANES

Introduction

Relatively few inorganic complexes are known which incorporate rings of the type MS_x or MSe_x where $x > 2$. Prior to this work only complexes of the type Cp_2TiE_5 where E = S (73) and Se (107) had been firmly characterized for the Group IVB metals. The complexes Cp_2TiS_3 and Cp_2TiS_4 have been reported[105] but others[164] were unable to duplicate their synthesis. The structure of Cp_2TiS_5 (73) consists of a chair-shaped six-membered TiS_5 ring.[166,167] Complexes of other metals containing MS_x rings were cited in the General Introduction according to the length of the polysulfur chain. These complexes are reiterated briefly below according to transition metal group.

Group VB species are restricted to the paramagnetic complexes Cp_2VS_5 (80)[167,171] and Cp_2VSe_5.[171] An X-ray crystallographic study[167] of the former revealed a chair-like VS_5 ring analogous to that found for Cp_2TiS_5.[166,167] For Group VIB the species Cp_2MS_4 where M = Mo (58) and W (59) and their selenium analogs 105 and 106, respectively, have been reported. The salt $(Et_4N)_2[MoS(S_4)_2]$ (54) is also known.[128] The X-ray crystal structures of 54,[128] 58,[133] and 59 [136] revealed nonplanar MS_4 rings. For the iron group the species $[FeS_5(\mu\text{-}S)]_2$ (<u>70</u>),[158] $[FeS_5(\mu\text{-}S)_2\text{-}MS_2]^{2-}$ (<u>71</u>) where M = Mo, W, and $Os_2S_5(S_3CNEt_2)(S_2CNEt_2)_3$ (<u>72</u>)[160] are known. A RhS_4 four-membered ring is thought to be present in $[(Me_5Cp)RhS_4]_2(\mu\text{-}CO)$ (<u>57</u>)[130] but MS_5 rings are found in the complexes $CpRh(PPh_3)S_5$ (<u>34</u>)[67] and $CpCo(PMe_3)S_5$ (<u>81</u>).[174] The X-ray crystal structure of <u>81</u> revealed a CoS_5 ring in a chair conformation with the Cp ligand in the axial position.[174] The species $(NH_4)_3[M(S_5)_3]$ where M = Rh[157] and Ir[99] have been reported but are not crystallographically characterized. Both five-membered MS_4 and six-membered MS_5 rings are known for the nickel group metals. For Ni(II) and Pd(II) only complexes with the chelating phosphine 1,2-bis(diphenylphosphino)ethane, dppe, have been reported, namely $(dppe)NiS_4$[100] and $(dppe)PdS_4$.[125] For Pt(II), complexes with simple or chelating phosphines are known: L_2PtS_4 where L = PPh_3,[100,125-127] $P(4\text{-}C_6H_4Me)_3$[100] or L_2 = dppe.[100,125] Salts of the ion $Pt(S_5)_3^{2-}$ (<u>2</u>) have been prepared[10,13] and characterized by X-ray crystallography[11,12] and variable temperature ^{195}Pt NMR.[14] Two PtS_5



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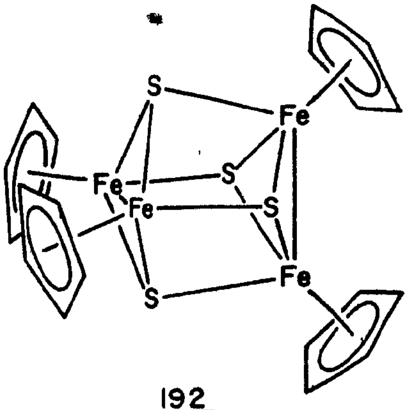
rings are thought to be present in salts of the $Pt(S_5)_2^{2-}$ ion (68).[12]

Reactions with Sulfur-Transfer Reagents

Reactions of organometallic compounds with elemental sulfur have sometimes produced new and unexpected products. Abstraction of two sulfur atoms from cyclooctasulfur is well known. Numerous examples exist, and a typical reaction is the formal oxidative addition of S_2 to $[Ir(dppe)_2Cl]$ to give $[Ir(dppe)_2S_2]Cl$ (12).[50,51] Several examples of reactions of cyclopentadienyl metal complexes with elemental sulfur have been reported. Schunn *et al.*[400] treated $[CpFe(CO)_2]_2$ and $CpV(CO)_4$ with S_8 to give $(CpFeS)_4$ (192) and $(Cp_2V_2S_5)_n$ (n not established), respectively. The structure of the MeCp analog, $(MeCp)_2V_2S_5$ (193), as revealed by X-ray crystallography is shown below.[401] McAlister *et al.*[102] found that under



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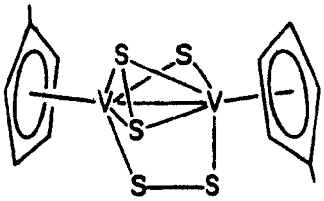

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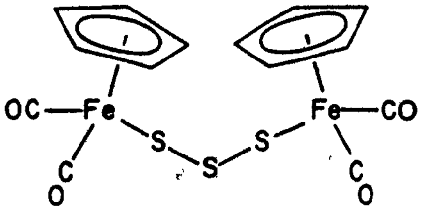
milder conditions $[CpFe(CO)_2]_2$ reacted with S_8 to give $[CpFe(CO)_2]_2(\mu\text{-}S_3)$ (<u>44</u>). They suggested that this compound was a probable intermediate in the formation of <u>192</u> under more vigorous conditions. Irradiation of solutions of sulfur and $[(RCp)Fe(CO)_2]_2$ (R = H, Me) has given several products depending on the reaction conditions. The products include $[(RCp)Fe(CO)_2]_2S_5$, $[(RCp)FeS_2]_2$, and $(RCp)_2Fe_2(CO)(S_2)_2$ (<u>194</u>).[102,121] The oily nature of the first compound has prevented a crystal structure determination. The complex $[(MeCp)Mo(CO)_3]_2$ reacted with sulfur to give $[(MeCp)MoS(\mu\text{-}S)]_2$ (<u>195</u>) in very low yield whose structure was revealed by X-ray crystallography.[299] Similarly, $(Me_5Cp)Mo(CO)_3H$ gave the analogous complex $[(Me_5Cp)MoS(\mu\text{-}S)]_2$ in addition to $[(Me_5Cp)MoS_5]_2$ (<u>196</u>).[299] In toluene



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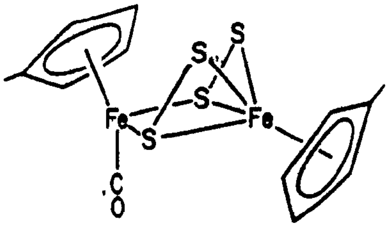

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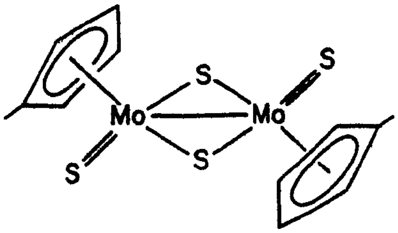

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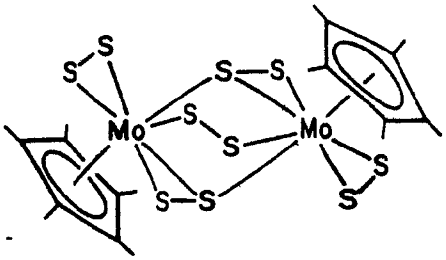

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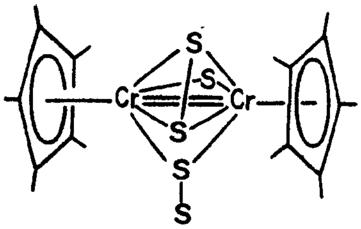
at 45°C, $[(Me_5Cp)Cr(CO)_2]_2$ reacted with sulfur to give $(Me_5Cp)_2Cr_2S_5$ (7) as the only isolable product. This complex contains three kinds of sulfur ligands including the novel η^1-(μ-S,S) ligand.[39] The molybdenum and tungsten



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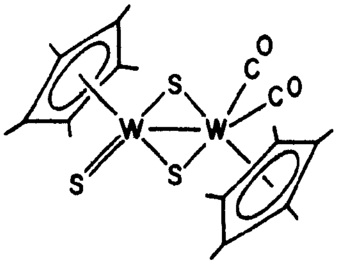
analogs $[(Me_5Cp)M(CO)_2]_2$ (M = Mo, W), however, reacted with sulfur under the same conditions to give isomeric complexes of the type $(Me_5Cp)_2M_2S_4$ and $(Me_5Cp)_2W_2(CO)_2$-$(\mu\text{-}S)_2S$ (197).[402] The X-ray structures of 197 and $(Me_5Cp)_2Mo_2(\mu\text{-}S_2)(\mu\text{-}S)_2$ (198) were determined.



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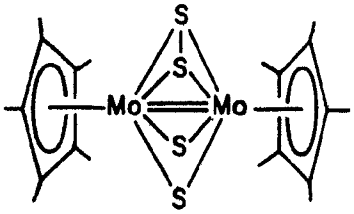

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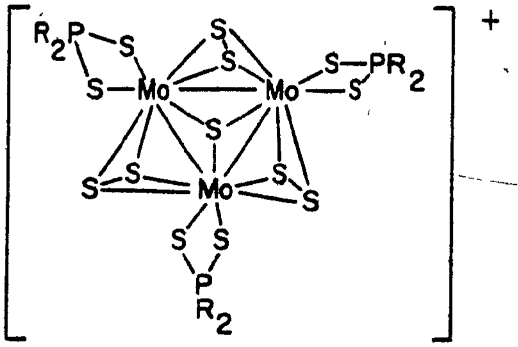
There are a few examples where sulfur appears to provide four or even five sulfur atom chains. For example, the dihydrides Cp_2MH_2 (M = Mo, W) react with sulfur to give Cp_2MS_4 and H_2S as the products.[132] Similarly, the complexes ML_4 (M = Pt, L = PPh_3 or L_2 = dppe;

M = Pd, L_2 = dppe) oxidatively add sulfur to give the species L_2MS_4 and H_2S.[125] Transfer of five sulfur atoms from S_8 occurred under photolysis[165] with Cp_2TiR_2 (R = Me, CH_2Ph) or thermally[167] with $Cp_2Ti(CO)_2$ to give Cp_2TiS_5 (<u>73</u>). The complexes $CpRh(PPh_3)_2$[67] or CpCo(CO)-(PMe_3)[174] react with elemental sulfur to give $CpRh(PPh_3)S_5$ (<u>34</u>) and $CpCo(PMe_3)S_5$ (<u>81</u>), respectively, which were mentioned previously.

The synthesis and reactivity of compounds capable of selectively transferring one or more sulfur atoms to appropriate substrates is an area of continuing interest to both inorganic and organic chemists. Elemental sulfur may be considered as a sulfur-transfer reagent, but it tends to donate sulfur atoms in an unpredictable way (<u>vide supra</u>). Modern reagents often are more predictable. For example, Keck <u>et al</u>.[403] examined the reactivity of bis(diorganothiophosphoryl)disulfanes $[R_2P(S)]_2S_2$ towards various inorganic complexes. In these cases the disulfane is reduced to the chelating dithiophosphinate ion $R_2PS_2^-$ while the metal center is oxidized. For example, the reaction of $Ni(CO)_4$ with $[Et_2P(S)]_2S_2$ gave $(Et_2PS_2)_2Ni$.[404] The disulfanes $[R_2P(S)]_2S_2$ have also been used in the synthesis of clusters such as $[Mo_3S_7(R_2PS_2)_3]^+[R_2PS_2]^-$ (<u>199</u>) and $[WS(R_2PS_2)]_2(\mu\text{-}S)_2$ (<u>200</u>) from $Mo(CO)_6$ and $W(CO)_6$, respectively.[403] In each case the reagents $[R_2P(S)]_2S_2$



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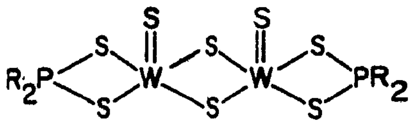

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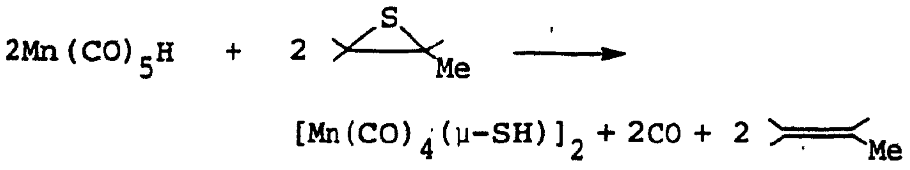
oxidized M(O) to M(IV) (M = Mo, W) as well as acted as monosulfur-transfer agents, losing sulfur to form the monosulfane $[R_2P(S)]_2S$.[403]

Episulfides have been useful for the synthesis of some complexes. Beck et al.[301] found that $Mn(CO)_5H$ reacted with propylene sulfide to give the dimeric SH-bridged complex $[Mn(CO)_4(\mu\text{-SH})]_2$ (136) (eq. 50). Formation



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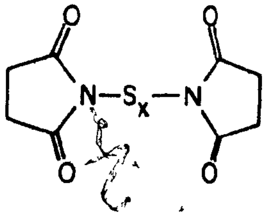
of 136 is consistent with the transfer of a single sulfur atom via insertion into the Mn-H bond.[301] The analogous reaction of $CpW(CO)_3H$ with the same episulfide gave monomeric $CpW(CO)_3SH$[296] although the degree of success of this reaction appears to be sensitive to the experimental conditions.[264]

Another class of organic sulfur-transfer reagents is those derived from imides or azoles. Several sulfur-transfer reagents of the type $>N-S_x-N<$ where $>N$ is succinimidyl (Succ, 201),[258,277] benzimidazolyl (Bz, 202),[258] phthalimidyl (Phth, 203),[276-278] and x = 1 or 2 have been prepared. These reagents are reactive towards compounds



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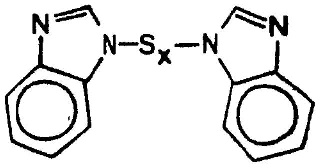

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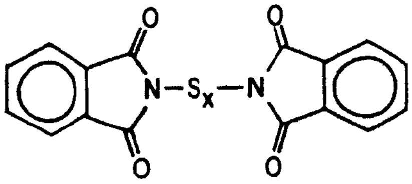

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of the type RXH where X = O, S, NR, or NH.[258] In many cases the reagents $>N-S_x-N<$ selectively transfer one (x = 1) or two (x = 2) sulfur atoms to a substrate. The general reaction with thiols is depicted in eq. 30. For

$$\underset{}{2RSH} + \underset{x=1,2}{>N-S_x-N<} \longrightarrow RS_{x+2}R + 2>NH \qquad (30)$$

example, the reagents $Bz-S_x-Bz$ (x = 1, 2) react with $PhCH_2SH$ to give the trisulfide $(PhCH_2)_2S_3$ and the tetrasulfide $(PhCH_2)_2S_4$ in near quantitative yield when x = 1 and 2, respectively.[258] The application of these organic sulfur-transfer reagents towards the complexes $Cp_2M(SH)_2$ [M = Ti (<u>110</u>), Zr (<u>111</u>)] are described in this chapter.

Alkali metal salts of the type $M_2'E_x$ (E = S, Se; x = 4, 5) are inorganic sulfur-transfer reagents of some utility. They have been used to prepare complexes such as Cp_2TiE_5 [E = S (<u>73</u>),[99,161-165] Se (<u>107</u>)[163]], Cp_2ME_4 [M = Mo, E = S (<u>58</u>),[59,131-133] Se (<u>105</u>);[134] M = W, E = S (<u>59</u>),[134-136] Se (<u>106</u>)[134]], salts of the dianions $M(S_5)_3^{2-}$ [M = Pt (<u>2</u>),[10-14] Rh,[157] Ir[99]], and the species L_2MS_4 [M = Pt, L = PPh_3; M = Ni, Pd, L_2 = dppe][100] from the appropriate dichloro precursors. Recently Gladysz <u>et al</u>. found that anhydrous solutions of Li_2E_x could be prepared <u>in situ via</u> reduction of sulfur[262] or selenium[263] with $LiEt_3BH$ (eq. 32). Subsequent reaction with alkali halides RX gave mono- and disulfides[262] and selenides[263] in high yield (eq. 33). The hydride reagent can also be

$$2LiEt_3BH + xE \longrightarrow Li_2E_x + 2Et_3B + H_2 \qquad (32)$$

$$E = S, Se$$
$$x = 1, 2$$

$$Li_2E_x + 2RX \longrightarrow RE_xR + 2LiX \qquad (33)$$

used to cleave organic disulfides, RSSR (R = $PhCH_2$, Me) to form lithium mercaptides RS^-Li^+ <u>in situ</u> (eq. 98). Subsequent treatment with electrophiles R'X (R' = alkyl, acyl, alkenyl) gave the unsymmetrical sulfides, RSR' (eq. 99).[262] McAlister et al.[102] prepared the poly-

$$RS\text{-}SR + 2LiEt_3BH \longrightarrow 2RS^-Li^+ + 2Et_3B + H_2 \qquad (98)$$

$$2RS^-Li^+ + 2R'X \longrightarrow 2RSR' + 2LiX \qquad (99)$$

sulfur-bridged dimers $[CpFe(CO)_2]_2(\mu\text{-}S_x)$ (x = 1-4) via reaction of Li_2S_x prepared in situ with $CpFe(CO)_2Br$. A study of the reactivity of reagents of this type towards the substrates Cp_2MCl_2, $(Me_5Cp)_2MCl_2$ (M = Ti, Zr, Hf), $(Me_5Cp)CpTiCl_2$, $(RCp)_2TiCl_2$ (R = Me, $SiMe_3$), and CH_2Cp_2-$TiCl_2$ to give complexes containing MS_5 and MS_3 rings is described in this chapter.

Results

(A) Synthetic Aspects

The reactions of the complexes $Cp_2M(SH)_2$ [M = Ti (110), Zr (111)], Cp_2MCl_2, $(Me_5Cp)_2MCl_2$ (M = Ti, Zr, Hf), $(Me_5Cp)CpTiCl_2$, $(RCp)_2TiCl_2$ (R = Me, $SiMe_3$), and $CH_2Cp_2TiCl_2$ with various sulfur-transfer reagents are summarized in Table 5. An authentic sample of Cp_2TiS_5 (73) was prepared according to a literature procedure using Cp_2TiCl_2 and excess $(NH_4)_2S_5$.[163] The complex Cp_2TiSe_5 (107) was first prepared via treatment of Cp_2TiCl_2 with Na_2Se_5.[163] Samples of these compounds

TABLE 5

Preparations and Yields of Metallacyclopolysulfanes and -selenanes

Reagents		Solvent	Time (hrs)[a]	Yield of $(RCp)_2ME_5$ (%)[b]
$Cp_2Ti(SH)_2$ [c]	S_8	CH_2Cl_2	1.25[d]	45[e]
	Bz-S-Bz	toluene	0.25[f]	47
		toluene	3	64[g]
		toluene	22[h]	33[i]
	Bz-S_2-Bz	THF	21	70
	Phth-S-Phth	THF	1.2	42
	Phth-S_2-Phth	THF	2.5	45
Cp_2TiCl_2	$(NH_4)_2S_5$	acetone	2	57[e]
	Li_2S_2	THF	23	trace
	Li_2S_5	THF	14	98
	Li_2Se_5	THF	4.75	72
$(MeCp)_2TiCl_2$	Li_2S_5	THF	2	85
$(Me_3SiCp)_2TiCl_2$	Li_2S_5	THF	3.75	64
$CH_2Cp_2TiCl_2$	Li_2S_5	THF	48	3
		THF	72[j]	9
		THF	1[d]	trace
$(Me_5Cp)CpTiCl_2$	Li_2S_5	THF	18	92
$(Me_5Cp)_2TiCl_2$	Li_2S_5	THF	1	no reaction
		THF	10.5[d]	55[k,l]
$Cp_2Zr(SH)_2$ [a]	S_8	toluene	4	12[j]
	Bz-S_2-Bz	toluene	12	32
		toluene	24	18[m]

TABLE 5 - continued

Reagents		Solvent	Time (hrs)[a]	Yield of $(RCp)_2ME_5$ (%)[b]
	Phth-S_2-Phth	THF	22	6
Cp_2ZrCl_2	Li_2S_5	THF	19	26
	Li_2S_{16}	THF	15	63
	Li_2Se_5	THF	3	50
$(Me_5Cp)_2ZrCl_2$	Li_2S_5	THF	19[d]	76[l]
Cp_2HfCl_2	Li_2S_5	THF	17	53
	Li_2Se_5	THF	5.5	52
$(Me_5Cp)_2HfCl_2$	Li_2S_3	THF	4[d]	9[l]

[a] The reactions were done at room temperature for the indicated time unless specified otherwise.

[b] Based on the limiting reagent; E = S, Se.

[c] The stoichiometry of $Cp_2M(SH)_2$ to the sulfur-transfer reagent was 1:1 unless noted otherwise.

[d] The reaction was done at reflux.

[e] Prepared according to ref. 163.

[f] The reaction was done at 0°C.

[g] The complex $[Cp_2Ti(\mu\text{-}S_3)]_2$ was isolated in ca. 1% yield.

[h] The reaction was done at 48°C.

[i] The yield of $[Cp_2Ti(\mu\text{-}S_3)]_2$ was estimated at ca. 4% by ^1H NMR.

[j] The reaction was started at 0°C and allowed to warm to room temperature.

[k] The yield of the crude product was much higher. The reduced yield is thought to be due to the high solubility of this complex in organic solvents.

[l] The product was $(Me_5Cp)_2MS_3$.

[m] The stoichiometry of $Cp_2Zr(SH)_2$ to Bz-S_2-Bz was 1:1.5.

prepared by the routes indicated in the Table had colours, melting points, and spectral data (^{1}H NMR, infrared) in agreement with the published data.[163] The complexes were further characterized by mass spectrometry and elemental analysis. Several of the reactions cited in the Table merit further comment. The reaction of $Cp_2Ti(SH)_2$ (110) with Bz-S-Bz gave 73 as the major product. An additional, intensely blue, product, identified as $[Cp_2Ti(\mu\text{-}S_3)]_2$ (45) by comparison of its colour, ^{1}H NMR, and electronic spectra with published data,[103] was also isolated but in much lower yield (ca. 1% from the room temperature reaction). Several less intense peaks in the region δ 6.0 to δ 6.8 in the ^{1}H NMR spectrum of the crude product corresponding to as yet unidentified products were also observed. The reaction of $Cp_2Zr(SH)_2$ (111) with $Bz\text{-}S_2\text{-}Bz$ in a 1:1.5 stoichiometry and with $Phth\text{-}S_2\text{-}Phth$ in a 1:1 stoichiometry gave Cp_2ZrS_5 (75) in 18% and 6% yields, respectively. Sulfur, as well as benzimidazole and phthalimide, were additionally isolated and identified by TLC and mass spectral analysis. The yields of 75 are much lower than the yields of 73 from the corresponding reactions of $Cp_2Ti(SH)_2$ (110). A much better yield of 73 was obtained via the treatment of Cp_2TiCl_2 with Li_2S_5. The reaction of the complexes Cp_2MCl_2 with Li_2S_5 is a general route to the species Cp_2MS_5, and is the only route at present to the complex where M = Hf. The reactions with other lithium polysulfides gave variable results as indicated in the Table. When a red solution of Cp_2TiCl_2 was added to an equimolar amount of Li_2S_2 the reaction mixture became brown in colour. After 23 hours the ^1H NMR spectrum of the slightly soluble brown crude product consisted of a complex set of signals corresponding to Cp protons in the range δ 6.6 to δ 5.9 and a complex pattern for aliphatic protons in the range δ 2.0 to δ 0.5. The infrared spectrum contained bands in the region 2980 cm^{-1} to 2840 cm^{-1} indicative of aliphatic C-H stretching vibrations in addition to broad bands at 3100, 1440, 1100, 1015, and 800 cm^{-1} typical of the Cp ligand.[332] A small amount of 73 was detected by TLC. A Beilstein Test for halide[285] was negative. The products were not examined further. If a large excess of sulfur was used to prepare a Li_2S_x solution, the subsequent reaction with Cp_2TiCl_2 was much cleaner. Thus when Cp_2TiCl_2 reacted with a solution of Li_2S_x where x was formally 16 in the stoichiometry 1:0.5, the reaction became deep red in colour. After stirring for 31.5 hours the ^1H NMR spectrum of the crude product showed that only 73 was present in addition to the unreacted Cp_2TiCl_2. Unreacted sulfur was detected by TLC analysis.

The turquoise complex $(Cp_2ZrS)_2$ (112) was obtained as a by-product in the synthesis of $Cp_2Zr(SH)_2$ (111) (Chapter 3). Therefore an attempt was made to prepare 112 *via* treatment of Cp_2ZrCl_2 with Li_2S generated in situ. When a 2.5 molar excess of Li_2S was used the reaction solution became a golden colour. Complex 75 appeared to be the major product as determined by ^1H NMR although it could not be isolated from the oily crude product. The golden colour is consistent with the absence of significant amounts of 112.

High thermal stabilities of the solid complexes Cp_2MS_5 are reflected by the melting point of Cp_2TiS_5 (73) at 196-198°C and decomposition points of ca. 165-170°C for Cp_2ZrS_5 (75) and 150-155°C for Cp_2HfS_5 (76). All three complexes are air-stable in the solid state. However, the air-sensitivity of solutions of 75 and 76 contrasts with the air-stability of solutions of the titanium analog 73. The close similarity of the infrared spectrum and mass spectral fragmentation pattern of 73, 75, and 76 (vide infra), microanalytical, and solution molecular weight determinations (for 75) supported their formulations as metallacyclohexasulfanes. The structures of 73,[166,167] 75,[405] and 76[405] established by X-ray crystallography consist of a six-membered MS_5 ring in a chair conformation (see Chapter 7).

The complexes $(RCp)_2TiCl_2$ (R = Me, $SiMe_3$) and $(Me_5Cp)CpTiCl_2$ reacted with Li_2S_5 which was prepared in situ to give the corresponding products having six-membered TiS_5 rings in good yield. The reaction of $CH_2Cp_2TiCl_2$ with Li_2S_5 was studied under several conditions. The best yield of the red complex $CH_2Cp_2TiS_5$ (79) was 9%, achieved by starting the reaction at 0°C and allowing the reaction to warm to room temperature. Stirring was continued for three days. A very small amount of a red complex 79A was also isolated. The yield of 79 was lower (3%) when the reactants were allowed to stir at room temperature for two days. When a mixture of $CH_2Cp_2TiCl_2$ and Li_2S_5 was refluxed for one hour only a trace of 79 was detected by TLC. As the heating was continued for an additional six hours another complex, 79A, as detected by TLC, decreased in concentration relative to a non-mobile brown spot. Sulfur was also detected. Neither 79 nor 79A could be isolated by chromatography. Complex 79A was too involatile to be characterized by mass spectrometry. Insufficient sample precluded elemental analyses. The compound did, however, show a positive sodium fusion test for sulfur. Its ^1H NMR spectrum ($CDCl_3$) consisted of two very broad overlapping peaks of unequal intensity extending from δ 6.6 to δ 5.4, a sharp singlet at δ 5.29 (possibly due to CH_2Cl_2) and several very broad unresolved signals in the region δ 4.0 to δ 0.6. The starting material $CH_2Cp_2TiCl_2$ was prepared according to the literature procedure[268] but could not be purified by the reported conditions because of decomposition. Hence an impurity in this reagent cannot be excluded as a precursor to 79A.

The reagents Cp_2MCl_2 (M = Ti, Zr, Hf) reacted with Li_2Se_5, prepared in situ, to give the species Cp_2MSe_5 [M = Ti (107), Zr (108), Hf (109)] in moderate yields. Complex 107 could be recrystallized as purple crystals and 108 as orange flakes. The orange hafnium species 109 decomposed somewhat if the crude product was recrystallized. Recrystallization of 109 from THF at room temperature and in subdued light led to the formation of a small amount of an unidentified black solid. Refrigeration at -20°C gave small ruby red rhombohedral crystals which decomposed at 40-45°C. THF was detected in the ^1H NMR spectrum of this compound. The solubility of these crystals decreased after prolonged storage at -20°C in vacuo possibly due to decomposition. The titanium complex 107 is monomeric in solution[163] and 108 and 109 are assumed to be similarly monomeric.

The complexes $(Me_5Cp)_2MS_3$ [M = Ti (47), Zr (48), Hf (49)] were prepared via treatment of the metallocene dichlorides with Li_2S_5 (M = Ti, Zr) and Li_2S_3 (M = Hf). They were characterized by their spectra (^1H NMR, infrared, mass), microanalyses, and for 47 and 48 by solution molecular weight determinations. These complexes are high-melting (47, 149-152°C; 48, 182-185°C; 49, 169-173°C) and are air-stable as solids and in solution. The latter behaviour is in contrast to the air-sensitivity of solutions of Cp_2ZrS_5 (75) and Cp_2HfS_5 (76). The X-ray crystal structure of <u>47</u>[104] was determined by Dr. P. Bird of Concordia University, Montreal and is described in Chapter 7. The hafnium complex $(Me_5Cp)_2HfS_3$ (<u>49</u>) was more difficult to isolate than its titanium and zirconium congeners. When a solution of $(Me_5Cp)_2HfCl_2$ and Li_2S_3 was refluxed for four hours, several products were detected by ^1H NMR. Recrystallization gave the major product, <u>49</u>, as a bright orange solid in 9% yield. The use of milder conditions did not improve the yield of <u>49</u>. The reaction between $(Me_5Cp)_2HfCl_2$ and an equimolar amount of Li_2S_3 at ambient temperature was still incomplete after one day. After refluxing for 2.5 hours no $(Me_5Cp)_2HfCl_2$ remained by ^1H NMR. The NMR ($CDCl_3$) spectrum of the crude product consisted of a major singlet at δ 1.92 due to <u>49</u> in addition to at least two other signals about half as intense at slightly higher field. Efforts to separate these products by recrystallization failed. Sulfur was detected by TLC. Stirring equimolar quantities of $(Me_5Cp)_2HfCl_2$ and Li_2S_5 for 1.5 hours followed by refluxing for 3.25 hours resulted in an orange solution. The crude product was isolated as a golden solid whose ^1H NMR spectrum consisted of the singlet at δ 1.92 due to <u>49</u> along with minor singlets at slightly higher and lower field. Complex <u>49</u> could not be isolated free of sulfur, however. Attempted purification by column chromatography (Florisil) led to decomposition.

Since Li_2S_5 solutions were used predominantly for the synthesis of the metallacyclopolysulfanes cited in Table 5 the polysulfide species S_x^{2-} present in solution were of interest. That the Li_2S_5 solutions did not, in fact, only contain the pentasulfide species was suggested by a control reaction with an organic substrate. A Li_2S_5 solution was treated dropwise with a THF solution of $PhCH_2Cl$. After stirring for four hours at room temperature the volatile components were removed in vacuo. The ^1H NMR spectrum of the oily residue was consistent with a mixture of benzyl polysulfides, $(PhCH_2)_2S_x$ (x = 2-5). The CH_2 signals were easily distinguished for various x and are diagnostic for x since a progressive downfield shift of the signal with increasing sulfur content occurs.[388,389] For a CCl_4 solution these signals were found (literature values[389] in parentheses) at δ 3.51 (x = 2, δ 3.51), δ 3.95 (x = 3, δ 3.94), δ 4.07 (x = 4, δ 4.04), and δ 4.12 (x = 5, δ 4.14). The relative amounts of the $(PhCH_2)S_x$ species was established by integration to be 2.6:1.4:1.0:4.6 for x = 2:3:4:5. Thus the pentasulfide was 48% of the product mixture.

(B) ^1H NMR Spectra

The ^1H NMR spectra of the complexes described above are collected in Table 7 (Chapter 7). The room temperature (20° to 30°C) spectra are summarized below. The chemical shifts found for Cp_2TiS_5 (73) and Cp_2TiSe_5 (107)

agreed with the published data.[163,406] Of special note is the presence of two equally intense singlets which correspond to protons of Cp groups located in axial and equatorial positions (see Chapter 7 for a further discussion). The isoleptic zirconium and hafnium complexes each gave only a single peak. The titanium complexes containing singly-substituted Cp rings, namely $(MeCp)_2TiS_5$ (74), $(Me_3SiCp)_2$-TiS_5 (77), and $CH_2Cp_2TiS_5$ (79), showed two sets of peaks corresponding to protons of axially and equatorially C_5H_4 rings and for 74 and 77 two peaks each for the protons of the substituent Me and $SiMe_3$, respectively. Those complexes containing the Me_5Cp ligand showed only a single peak for $(Me_5Cp)_2MS_3$ [M = Ti (47), Zr (48), Hf (49)] and $(Me_5Cp)CpTiS_5$ (78); the latter compound additionally gave a singlet for the protons of the Cp group. The variable temperature ^1H NMR spectra of the complexes listed in Table 7 (Chapter 7) are discussed in Chapter 7.

(C) Infrared Spectra

The metallacyclopolysulfanes and metallacyclohexaselenanes containing the η-C_5H_5 ligand had infrared spectra dominated by bands characteristic of this group[332] and resembled the spectra of their dichloro precursors. Thus the spectra of the complexes Cp_2MS_5 and Cp_2MSe_5 (M = Ti, Zr, Hf) were similar. The complex $(MeCp)_2TiS_5$ (74) is distinguished from Cp_2TiS_5 (73) by the appearance of new bands at ca. 1490 (m) cm^{-1} probably due to a CH_3 deformation mode[407] and very weak bands in the 3000 to 2850 cm^{-1} region due to aliphatic CH stretching modes. The spectrum of $(Me_3SiCp)_2TiS_5$ (77) is marked in particular by bands at 1244 (s), 1173 (m), 895 (s), and 748 (s) cm^{-1}. The most characteristic absorption for the Si-Me grouping is an intense band in the region 1240 to 1280 cm^{-1} due to the symmetric CH_3 deformation.[408] In addition two intense bands near 845 and 760 cm^{-1} are typical of the $-SiMe_3$ group in inorganic complexes and correspond to the $-CH_3$ rocking and Si-C stretching vibrations.[408] The spectra of $CH_2Cp_2TiS_5$ (79) and the by-product 79A were quite different. Generally, the bands for 79 were sharp whereas those for 79A were broad and poorly resolved. The most significant differences occurred with the intensities of bands in the regions 3120 to 2850 cm^{-1} and 775 to 650 cm^{-1}. For 79, three sharp peaks at 3085 (m), 2945 (m), and 2855 (vw) cm^{-1} were present, while for 79A four broad peaks occurred at 3110 (w), 2950 (m), 2925 (m), and 2850 (w) cm^{-1}. Those bands above 3000 cm^{-1} are due to C-H stretching modes in the C_5H_4 rings. Those at ca. 2945 cm^{-1} are likely due to asymmetric C-H stretching modes and those at ca. 2850 cm^{-1} due to symmetric C-H stretching modes of the $-CH_2-$ moiety.[409] Strong sharp bands at 758 and 662 cm^{-1} for 79 were seen whereas only very weak broad absorptions at 730 and 668 cm^{-1} were observed for 79A. Strong bands at 760 and 658 cm^{-1} are observed for $CH_2Cp_2TiCl_2$.[268] The infrared spectrum of $(Me_5Cp)CpTiS_5$ (78) exhibited bands expected for the η-C_5H_5[332] and η-Me_5Cp[410] ligand, in particular strong bands at 1374 and 1020 cm^{-1}. Like the series Cp_2MS_5, the complexes $(Me_5Cp)_2MS_3$ (M = Ti, Zr, Hf) displayed very similar infrared spectra. Six main bands appeared at (approximately) 2900 (vs), 1485 (s), 1430 (s), 1375 (vs), 1015 (s), and 800 (m) cm^{-1}. An intense band at 1380 to 1370 cm^{-1} and weaker ones at ca. 1440 and 1020 cm^{-1} are characteristic of η-Me_5Cp transition metal complexes.[410]

(D) Mass Spectra

(i) The Metallacyclohexasulfanes Cp_2MS_5 (M = Ti, Zr, Hf), $(RCp)_2TiS_5$ (R = Me, $SiMe_3$), $CH_2Cp_2TiS_5$, and $(Me_5Cp)CpTiS_5$

The listing of peaks with their relative abundances from the electron impact (70 eV) spectra of the title complexes is given in the Experimental section. Molecular ions ($M^{+\cdot}$) were observed for all of the title compounds except $(Me_3SiCp)_2TiS_5$ (77). For the complexes Cp_2MS_5 [M = Ti (73), Zr (75), Hf (76)] the peaks corresponding to the $M^{+\cdot}$ and the $Cp_2MS_4{}^{+\cdot}$ ions were weak. The series of ions Cp_nMS_m (n = 2, m = 0-5; n = 1, m = 0-3) were observed for M = Ti and Zr. The six naturally occurring hafnium isotopes prevented resolution of many of the ion clusters in these series. For Cp_2HfS_5 (75) additional low intensity (≤ ca. 10%) peaks were observed at m/z values greater than that for the molecular ion. Each of the ion clusters had peak patterns consistent with more than one hafnium atom being present. The clusters can be tentatively identified as fragment ions derived from the molecular ion $(Cp_2HfS)_2^{+\bullet}$, observed at m/z = 682 (7.2%), via loss of one or two $C_5H_5^{\bullet}$ radicals. Peaks corresponding to metastable ions, m*, consistent with this postulate were not observed, however. In both the titanium and zirconium compounds metastable ion peaks were observed for the transitions $Cp_2MS_5^{+\bullet} \rightarrow Cp_2MS_3^{+\bullet}$, $Cp_2MS_3^{+\bullet} \rightarrow Cp_2MS^{+\bullet}$, $Cp_2MS_2^{+} \rightarrow Cp_2M^{+}$, and $CpMS_3^{+\bullet} \rightarrow CpMS^{+\bullet}$; in the hafnium analog the transition $Cp_2HfS_5^{+\bullet} \rightarrow Cp_2HfS_3^{+\bullet}$ was similarly established (Table 6). This corresponds to loss of S_2. The intensity of the molecular ion $M^{+\bullet}$ relative to that of the fragment ion $M^{+\bullet}-S_2$ followed the order Ti ≫ Zr > Hf. With respect to loss of S_2 from the molecular ion, the stability of the $M^{+\bullet}$ ions may also follow this order.[411] Metastable ion peaks in the spectra of $(Me_3SiCp)_2TiS_5$ (77) and $CH_2Cp_2TiS_5$ (79) also indicated losses of neutral S_2. Thus for 77, losses of S_2 from the fragments $(Me_3SiCp)_2TiS_3^{+\bullet}$ and $(Me_3SiCp)_2TiS_2^{+}$ was observed. The absence of a molecular ion peak precluded observation of a metastable peak corresponding to the loss $M^{+\bullet}-S_2$. However, this was observed for 79. For this complex peaks corresponding to the complete series of ions

TABLE 6

Metastable Peaks, m*, Observed for Losses of S_2 and Se_2 [a]

Compound	Transition	m/z → m/z			m*		
		Cp_2TiS_5	Cp_2ZrS_5	Cp_2HfS_5	Cp_2TiS_5	Cp_2ZrS_5	Cp_2HfS_5
Cp_2MS_5	$Cp_2MS_5^{+\bullet} \rightarrow Cp_2MS_3^{+\bullet}$	338 → 274	380 → 316	470 → 406	222.1	262.8	350.7
	$Cp_2MS_3^{+\bullet} \rightarrow Cp_2MS^{+\bullet}$	274 → 210	316 → 252	406 → 342	160.9	201.0	b
	$Cp_2MS_2^{+} \rightarrow Cp_2M^{+}$	242 → 178	284 → 220	374 → 310	130.9	170.4	b
	$CpMS_3^{+} \rightarrow CpMS^{+}$	209 → 145	251 → 187	341 → 277	100.6	139.3	b

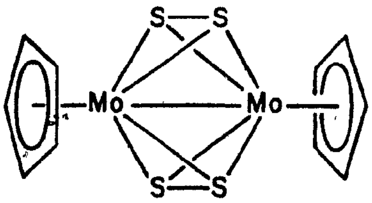
Compound	Transition	m/z → m/z	m*
$(Me_3SiCp)_2TiS_5$	$(Me_3SiCp)_2TiS_3^{+\bullet} \rightarrow (Me_3SiCp)_2TiS^{+\bullet}$	418 → 354	299.8
	$(Me_3SiCp)_2TiS_2^{+} \rightarrow (Me_3SiCp)_2Ti^{+}$	386 → 322	268.6
$CH_2Cp_2TiS_5$	$CH_2Cp_2TiS_5^{+\bullet} \rightarrow CH_2Cp_2TiS_3^{+\bullet}$	350 → 286	233.7
	$CH_2Cp_2TiS_3^{+\bullet} \rightarrow CH_2Cp_2TiS^{+\bullet}$	286 → 222	172.3
Cp_2TiSe_5	$Cp_2TiSe_5^{+\bullet} \rightarrow Cp_2TiSe_3^{+\bullet}$	574 → 416	301.5
	$Cp_2TiSe_3^{+\bullet} \rightarrow Cp_2TiSe^{+\bullet}$	416 → 258	160.0

[a] From electron impact (70 eV) mass spectra.

[b] Not observed.

$CH_2Cp_2TiS_n$ and TiS_n (n = 0-5) were observed although the peaks for n = 4 were of low intensity. In the mass spectrum of $Cp(Me_5Cp)TiS_5$ (<u>78</u>) peaks corresponding to the series of ions $Cp(Me_5Cp)TiS_n$ and $CpTiS_n$ (n = 0-5) were observed, although the peaks for n = 4, 5 were less than 3% of the base peak which corresponded to $Cp(Me_5Cp)TiS_2^+$. In the series $(Me_5Cp)TiS_n$ (n = 0-5) only the peak for the n = 3 ion was clearly distinguishable from the overlapping cluster of peaks due to $Cp(Me_5Cp)TiS_n$ ions. The peak for n = 3 was the most abundant ion after the base peak, at 88.7%. Interestingly, metastable peaks corresponding to losses of S_2 molecules were not observed.

Thus the observation of metastable ion peaks is consistent with a stepwise elimination of S_2 from the molecular ion (Table 6). This has also been observed in the mass spectrum of Cp_2MoS_4 (<u>58</u>) where the transitions $Cp_2MoS_4^{+\bullet} \rightarrow Cp_2MoS_2^{+\bullet}$ and $Cp_2MoS_2^{+\bullet} \rightarrow Cp_2Mo^{+\bullet}$ were observed.[412] Beck <u>et al</u>.[296] reported the appearance of a metastable peak for the fragmentation $Cp_2Mo_2S_4^{+\bullet} \rightarrow Cp_2Mo_2S_2^{+\bullet} + S_2$ in the mass spectrum of <u>204</u>. The stability



<u>204</u>

of the S_2 molecule[24] may account for its elimination as a neutral fragment.

(ii) The Metallacyclotetrasulfanes $(Me_5Cp)_2MS_3$ (M = Ti, Zr, Hf)

Molecular ion peaks were observed in the mass spectra of the complexes $(Me_5Cp)_2MS_3$ [M = Ti (47), Zr (48), Hf (49)]. The intensity of the molecular ion relative to that of the ion $M^{+\bullet}$-S_2 followed the order Ti < Zr < Hf, which is opposite to that observed for the analogs Cp_2MS_5. Metastable ion peaks confirming the loss of neutral S_2 as observed for the compounds Cp_2MS_5 were not observed for 47 and 48, however. The mass spectrum of 49 was not examined for metastable peaks. In the hafnium complex 49 the molecular ion peak was also the base peak. Although the intensities of the molecular ion peaks for Cp_2TiS_5 (73) and $(Me_5Cp)_2TiS_3$ (47) were very similar (24.2% and 25.2%, respectively) this was not true for the zirconium and hafnium analogs. The molecular ion peaks for the ions $(Me_5Cp)_2MS_3^{+\bullet}$ (M = Zr, Hf) were much more intense relative to those for the ions $Cp_2MS_5^{+\bullet}$ (92.5% *vs*. 6.3% for M = Zr, 100.0% *vs*. 10.8% for M = Hf).

(iii) The Metallacyclohexaselenanes Cp_2MSe_5 (M = Ti, Zr, Hf)

The title metallacyclohexaselenanes showed weak molecular ion peaks in their electron impact (70 eV) mass spectra having abundances 2.4% (Ti), 1.5% (Zr), and 1.9% (Hf). The $Cp_2MSe_4^{+}$ fragment ion peaks were either very weak (Ti, Zr) or not observed (Hf). Most of the other fragment ions were observed. Overall, the mass spectra of Cp_2ZrSe_5 (108) and Cp_2HfSe_5 (109) are very similar. In each case the two most intense peaks correspond to the ions $Cp_2MSe^{+\cdot}$ which were the base peaks and $Cp_2MSe_3^{+\cdot}$ (M = Zr, Hf). In the compounds Cp_2MS_5 (M = Zr, Hf) the ions $Cp_2MS_3^{+\cdot}$ and $CpMS_3^{+}$ were the most abundant. However, for Cp_2TiSe_5 (107) the ion Cp_2Ti^{+} gave the base peak. In the spectrum of Cp_2TiS_5 (73) the base peak corresponded to the ion $Cp_2TiS_3^{+\cdot}$, but the peak for the ion Cp_2Ti^{+} was quite intense nevertheless (77.6%). Metastable ion peaks were observed with certainty only for 107. Just as loss of S_2 was observed for the sulfur analog 73, peaks corresponding to metastable ions for the loss of neutral Se_2 were observed for 107 (Table 6).

(E) Desulfurization Reactions of Metallacyclopolysulfanes

The complex Cp_2TiS_5 (73) reacted with PPh_3 to give a small amount of a blue complex 45 in addition to mostly unreacted 73 as determined by ^1H NMR. Complex 45 was later identified as $[Cp_2Ti(\mu\text{-}S_3)]_2$ by comparison of its ^1H NMR spectrum and properties to that reported by Rauchfuss *et al.*[103] Under similar conditions Cp_2ZrS_5 (75) was found to rapidly desulfurize in the presence of triphenylphosphine in THF solution at room temperature but the products obtained absorbed strongly in the infrared in the region 800 to 700 cm^{-1} consistent with the presence of Zr-O-Zr bridges.[161,339] When one equivalent of PPh_3 was used $SPPh_3$ was isolated in 34% yield.

Rauchfuss *et al.* found that Cp_2TiE_5 where E = S (73) and Se (107) act as chalcogen-transfer reagents toward $[Ir(dppe)_2]Cl$ to give $[Ir(dppe)_2E_2]Cl$ (eq. 100).[292]

$$Cp_2TiE_5 + [Ir(dppe)_2]Cl \longrightarrow [Ir(dppe)_2E_2]Cl \qquad (100)$$

73 E = S
107 E = Se

12 E = S
13 E = Se

However, when $(MeCp)_2TiS_5$ (74) was treated with $[Ir(dppe)_2]Cl$ the complex $[(MeCp)_2Ti(\mu\text{-}S_2)]_2$ (169) was isolated.[292] Desulfurization of 74 with $P(n\text{-}Bu)_3$ in refluxing CH_2Cl_2 gave red 169 in 28% yield (eq. 101).[292] In sharp contrast,

$$2(MeCp)_2TiS_5 + 6PBu_3 \longrightarrow [(MeCp)_2Ti(\mu\text{-}S_2)]_2 + 6SPBu_3 \qquad (101)$$

74

169

Cp_2TiS_5 (73) and $(MeCp)_2TiS_5$ (74) reacted with PPh_3 under similar conditions to give the blue complexes $[Cp_2Ti(\mu\text{-}S_3)]_2$ (45) and $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46), respectively (eq. 102).[103] Complex 46 has been characterized crystallographically.[103]

$$2(RC_5H_4)_2TiS_5 + 4PPh_3 \longrightarrow \underset{\substack{\underline{45}\ (R = H)\\ \underline{46}\ (R = Me)}}{[(RCp)_2Ti(\mu\text{-}S_3)]_2} + 4SPPh_3 \qquad (102)$$

In a ^1H NMR tube experiment, no reaction seemed to occur between $(Me_5Cp)_2TiS_3$ (47) and two molar equivalents of PPh_3 in $CDCl_3$ at room temperature. After heating at 50°C for one hour signals due to $SPPh_3$, PPh_3, 47 (at δ 1.83) and a new singlet at δ 1.93 were present. A shoulder at δ 1.97 and minor peaks at δ 2.07 and δ 1.87 were just discernable. Heating for two additional hours caused the peaks at δ 2.07, δ 1.97, δ 1.93, and δ 1.87 to double in intensity relative to the peak for 47. Triphenylphosphine was still present. After 19 hours a complex set of signals in the region δ 2.2 to δ 1.7 was present. Chromatography (Florisil) failed to separate the reaction products. The zirconium complex $(Me_5Cp)_2ZrS_3$ (48) qualitatively appeared to be desulfurized by PPh_3 faster than 47. In this case a complex mixture of products was detected by ^1H NMR. These desulfurization reactions were not repeated on a preparative scale.

Discussion

(A) The Reactions of $Cp_2M(SH)_2$ (M = Ti, Zr) with Sulfur and with Reagents of the Type $>N-S_x-N<$

The complexes $Cp_2Ti(SH)_2$ (110), $Cp_2Mo(SH)_2$ (130), and $(PPh_3)_2Pt(SH)_2$ are known to react with elemental sulfur. The number of sulfur atoms incorporated into the organometallic framework varies, however. In the titanium case Cp_2TiS_5 (73) is the product.[163] For molybdenum and platinum, Cp_2MoS_4 (58)[59] and $(PPh_3)_2PtS_4$ (69)[127] were isolated. Hydrogen sulfide was evolved as a by-product. Extension of this reaction to $Cp_2Zr(SH)_2$ (111) gave the new complex Cp_2ZrS_5 (75) in low yield. Samuel and Giannotti[165] reported that 73 could be prepared in good yield *via* photolysis of Cp_2TiR_2 (R = CH_3, CH_2Ph) in the presence of elemental sulfur. When R = CH_2Ph the hexasulfide $(PhCH_2)_2S_6$ was isolated as an organic product. The analogous reaction of Cp_2ZrMe_2 gave a yellow product which desulfurized during recrystallization or sublimation. The reported ^1H NMR spectrum is consistent with the absence of methyl groups in the product displaying only a single peak at δ 6.38 corresponding to Cp protons.[165] This chemical shift does not agree with that found here for 75 (δ 6.20) and so the identity of the photolysis product remains in doubt.

Elemental sulfur also has been reported to react with the dihydrides Cp_2MH_2 (M = Mo, W) to give Cp_2MS_4 and H_2S as the reaction products (eq. 103). Two mechanisms

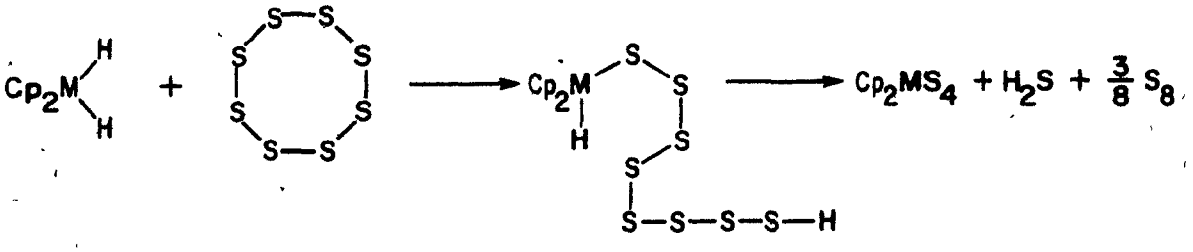
$$Cp_2MH_2 + \tfrac{5}{8}S_8 \longrightarrow \underset{\begin{array}{l}\underline{58}\ M = Mo\\ \underline{59}\ M = W\end{array}}{Cp_2MS_4} + H_2S \qquad (103)$$

were proposed:[132] 1) insertion of atomic sulfur into the M–H bond to give known $Cp_2M(SH)_2$ which could then continue to react with sulfur to form Cp_2MS_4 with H_2S elimination[59] (Scheme 7); 2) nucleophilic attack by the dihydride to open the S_8 ring and form a hydrido, polysulfano intermediate <u>205</u>. Cyclization with expulsion of excess sulfur and H_2S could give Cp_2MS_4 (Scheme 8). The latter mechanism

Scheme 7

$$Cp_2MH_2 + \tfrac{1}{4}S_8 \longrightarrow Cp_2M(SH)_2 \xrightarrow{\frac{3}{8}S_8} Cp_2MS_4 + H_2S$$

Scheme 8



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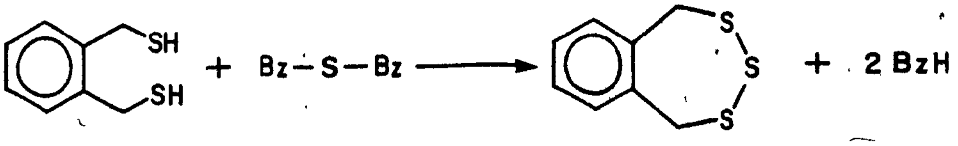
can also be invoked to explain the isolation of Cp_2TiS_5 (<u>73</u>) and Cp_2ZrS_5 (<u>75</u>) from the bis(hydrosulfido) precursors 110 and 111, respectively.

The formation of a smaller MS_x ring in the Cp_2MS_x complexes when M = Mo or W has been attributed to a repulsive interaction between the two paired metal d electrons and the electrons in the M-S bonds.[132] An ESR study of the paramagnetic Cp_2VS_5 (80) demonstrated that the unpaired electron is located in a molecular orbital whose main component is in the MS_2 plane but with only a small amount of electron density located within the S-M-S bond angle.[173] Increasing electronic repulsions as the number of d electrons increase compresses the SMS angle with the result that there may be less strain in a five-membered ring than in the corresponding six-membered ring.[132] Thus the X-ray crystal structures revealed that the S-M-S bond angle decreased from 94.59(4)° to 89.3(1)° to 88.2(2)° for the series Cp_2TiS_5 (73),[166] Cp_2VS_5 (80),[167] and Cp_2MoS_4 (58),[133] respectively, as the number of d electrons increased from 0 to 2, respectively. Comparing only second row complexes, the change in this angle is even greater since the angle for Cp_2ZrS_5 (75)[405] is 97.77(3)° (see Table 9, Chapter 7).

The reactivity of imide and azole sulfur-transfer reagents towards organic substrates bearing an SH ligand varies. For example, the dithiophthalimide and -succinimide reagents (Phth-S_2-Phth and Succ-S_2-Succ, respectively) reacted with two equivalents of benzyl mercaptan to give mixtures of the polysulfides $(PhCH_2)_2S_x$ where x = 1-4. On the other hand the azole reagents $>N-S_x-N<$ [$>N$ = imidazole, benzimidazole (Bz), 1,2,4-triazole, and 1,2,3-benzotriazole] were more selective and gave the appropriate tri- and tetrasulfides when x = 1 or 2, respectively (eq. 104).[258] In contrast, azole

$$2PhCH_2SH + >N-S_x-N< \longrightarrow (PhCH_2)_2S_{x+2} + 2>NH \qquad (104)$$

sulfur-transfer reagents reacted with the dithiols $HS(CH_2)_nSH$ (n = 2-8) to give oligomeric products.[258,413] Yet α,α'-dimercapto-o-xylene reacted with Bz-S-Bz to give the monomeric cyclic trisulfide 2,3,4-benzotrithiepin (206) in high yield (eq. 105).[413]



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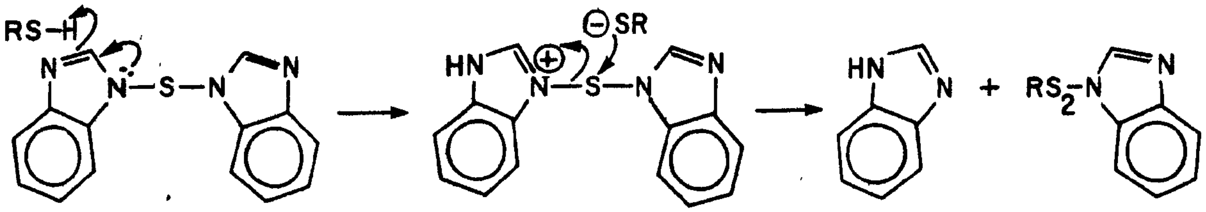
(105)

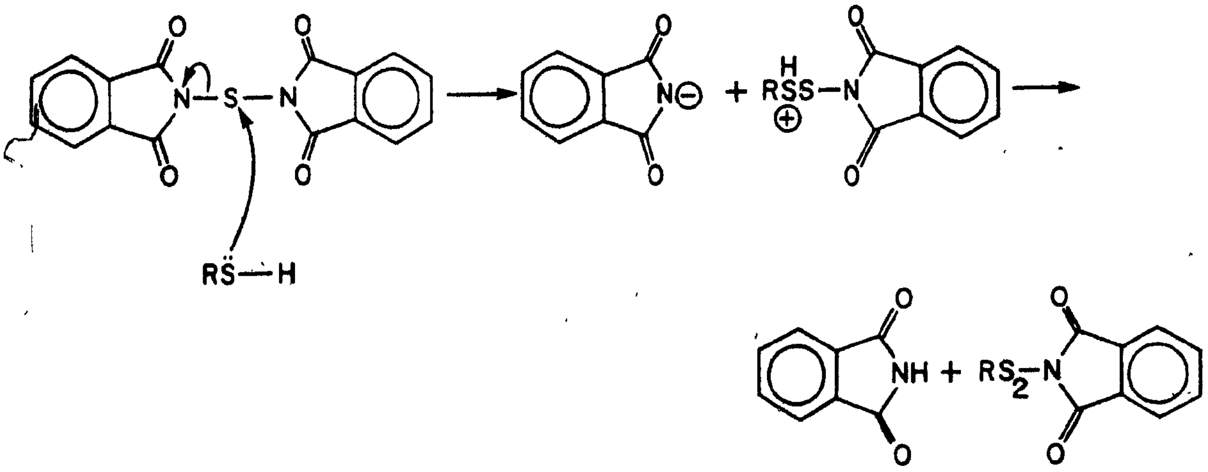
Complexes of the type $Cp_2M(SH)_2$ may be regarded as organometallic analogs of dithiols. Thus it was thought that treatment of $Cp_2M(SH)_2$ with a reagent such as $>N-S-N<$ might give the species Cp_2MS_3 while treatment with $>N-S_2-N<$ could give Cp_2MS_4. With the phthalimidyl and benzimidazolyl reagents, $Cp_2Ti(SH)_2$ (110) and $Cp_2Zr(SH)_2$ (111)

gave the complexes Cp_2MS_5, however. With 110 an additional product, $[Cp_2Ti(\mu\text{-}S_3)]_2$ (45), was isolated. One can assume that a mechanism similar to that proposed for the reactions of organic thiols RSH with the reagents >N-S_x-N< is operative. For these reactions the proposed mechanism involves an initial protonation of the nitrogen when >N is an azolyl group (Scheme 9) but an initial nucleophilic displacement of the imide anion when >N is an imidyl group (Scheme 10).[258]

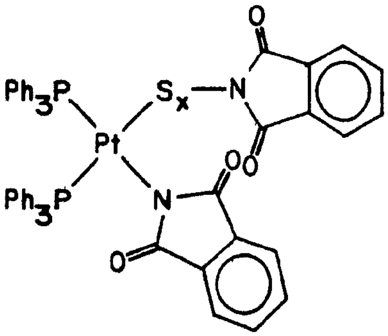
Scheme 9



Scheme 10

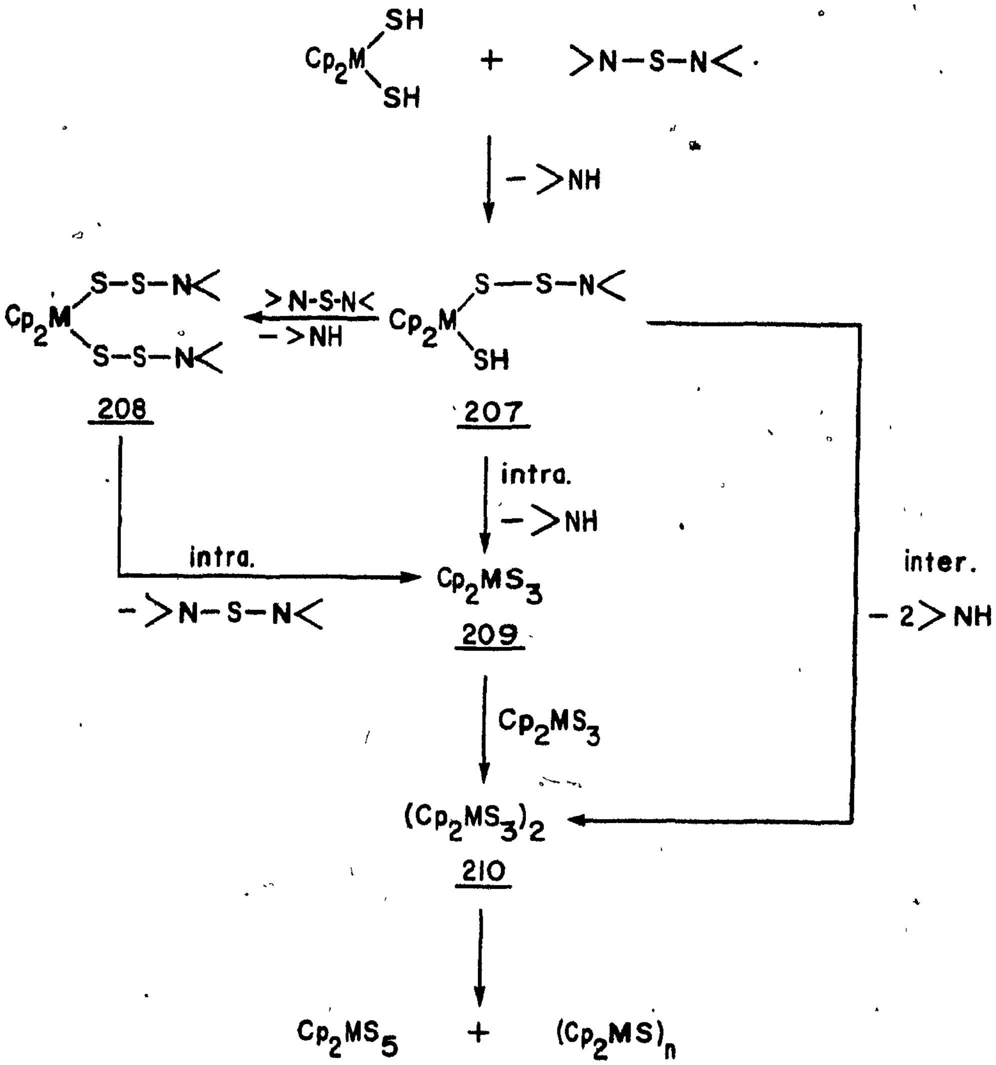


Repeating the steps would give the product RS_3R. A possible partial mechanism for the reaction of $Cp_2M(SH)_2$ with >N-S-N< is shown in Scheme 11. Initial displacement of the >NH gives rise to 207 which can react in one of three ways. Intramolecular elimination of >NH, or reaction with another molecule of >N-S-N< to give 208 followed by intramolecular elimination of >N-S-N<, gives the intermediate 209. Dimerization of 209 to 210 followed by elimination of oligomeric $(Cp_2MS)_n$ could then give Cp_2MS_5 as the final product. The mechanism whereby this dimerization-elimination is achieved is not readily apparent. Alternatively, intermolecular elimination of >NH from two molecules of 207 could give dimer 210. It is impossible to estimate at this time how accurately Scheme 14 depicts the reaction. Compounds of the type 207, 208, or 209 have not been isolated. However, Lai[325] has prepared the complexes cis-$(PPh_3)_2Pt(Phth)(S_xPhth)$ (210A) where x = 1 or 2 which contain a $Pt-S_x-N<$ linkage.



210A

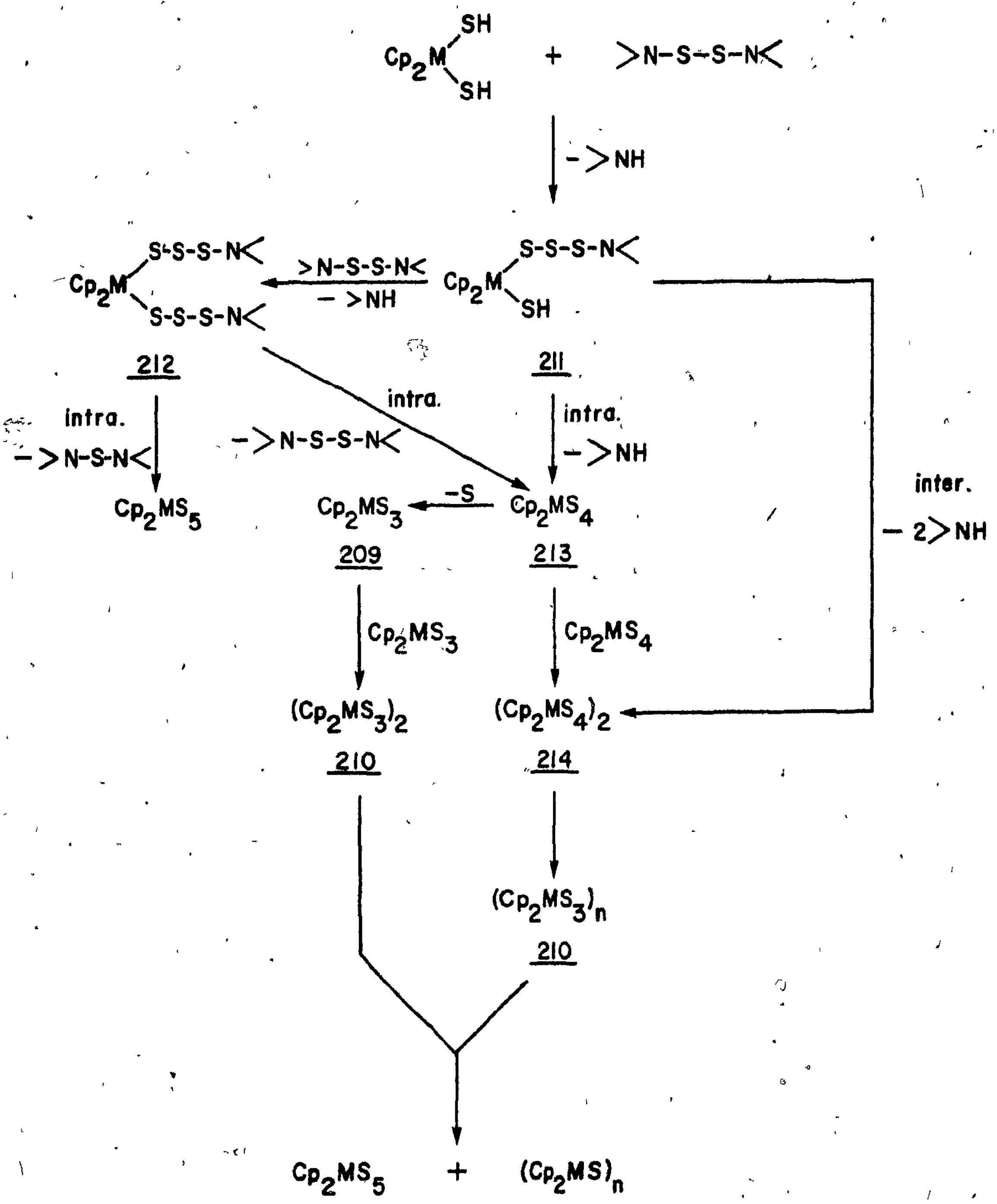
Scheme 11


Cp2M(SH)2
>N-S-N<
- >NH
>N-S-N<
- >NH
208
207
intra.
- >NH
intra.
- >N-S-N<
Cp2MS3
209
inter.
- 2>NH
Cp2MS3
(Cp2MS3)2
210
Cp2MS5
(Cp2MS)n

The complex $(Me_5Cp)_2TiS_3$ (47)[104] is an example of an analog to 209. The complex $[Cp_2Ti(\mu\text{-}S_3)]_2$ (45) analogous to 210 has been isolated by Rauchfuss *et al.*[103] *via* desulfurization of Cp_2TiS_5 (73) and was detected by ^1H NMR in the reactions of 110 with $>N\text{-}S_x\text{-}N<$ when $>N$ = benzimidazolyl and x = 1 or 2, and isolated in low yield for the case where x = 1. The X-ray crystal structure of $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ consists of a cradle-shaped eight-membered Ti_2S_6 ring.[103] Dimer 45 was found by this author to be unstable in $CDCl_3$ solution and to chromatography on Florisil, reverting partly to 73. The tendency of 45 to give 73 and an insoluble residue upon heating in benzene was also noted by Rauchfuss.[103] A potential product of the reaction of $Cp_2M(SH)_2$ with $>N\text{-}S\text{-}N<$ is the symmetrically substituted complex $Cp_2M(S_2N<)_2$ (208) but none was isolated during the workup of the reaction. There is no literature precedent for this sort of complex but the compound $Cp_2Ti(S_2R)_2$ where R = $CHMe_2$ (122) is reported here (Chapter 5).

An analogous mechanism can be derived for the reaction of $Cp_2M(SH)_2$ with the disulfur-transfer reagents $>N\text{-}S_2\text{-}N<$ (Scheme 12). The number of potential reaction pathways that could account for the formation of the products 73 and 45 is greater than for the reaction with the monosulfur-transfer reagents $>N\text{-}S\text{-}N<$. Most of the intermediates shown (i.e., 209, 211-214) have not been

Scheme 12


Cp2M(SH)2
+
>N-S-S-N<
- >NH
>N-S-S-N<
- >NH
Cp2M(S-S-S-N<)2
212
Cp2M(S-S-S-N<)(SH)
211
intra.
- >N-S-N<
Cp2MS5
intra.
- >N-S-S-N<
intra.
- >NH
-S
Cp2MS3
209
Cp2MS4
213
inter.
- 2>NH
Cp2MS3
Cp2MS4
(Cp2MS3)2
210
(Cp2MS4)2
214
(Cp2MS3)n
210
Cp2MS5
+
(Cp2MS)n

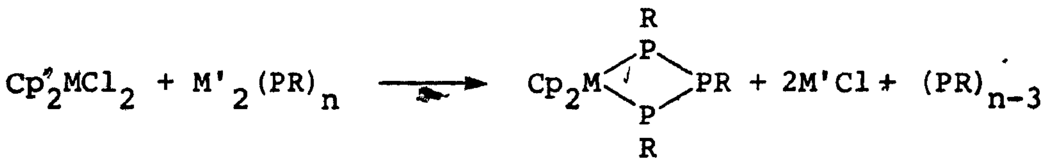
isolated. A key intermediate Cp_2MS_4 (213) although unknown for M = Ti, has been prepared and characterized by X-ray crystallography for M = Mo [133] and W.[136] Furthermore, Cp_2MoS_4 (58) and Cp_2WS_4 (59) have been isolated from the reactions of $Cp_2M(SH)_2$ (M = Mo, W) with >N-S-N< (>N = phthalimidyl).[412] Desulfurization of intermediate 213 to give the trisulfane 209 may occur. Loss of sulfur is common and has been established for alkyl polysulfides such as Me_2S_4.[414] Thermal decomposition of Me_2S_4 at 80°C *in vacuo* in the absence of light gave Me_2S_x (x = 3, 4, 5, 6). Intramolecular elimination of >N-S-N< from intermediate 212 could lead directly to Cp_2MS_5. At the present time these mechanisms are speculative. A better understanding of the mechanism(s) will require additional efforts to synthesize the many potential intermediates.

The isolation of less abundant intermediates in the synthesis of Cp_2ZrS_5 (75) from $Cp_2Zr(SH)_2$ (111) and >N-S_x-N< poses greater experimental difficulties. Solutions of 75 are extremely air-sensitive. In spite of rigorous precautions, crystalline reaction products often showed absorption bands in the infrared characteristic of the Zr-O-Zr linkage.[161,339] Extreme sensitivity to air or moisture is a feature of other zirconium complexes of the type $Cp_2Zr(SR)_2$.[371,415] The inability to isolate new complexes of the type $[Cp_2Zr(\mu\text{-}S_y)]_2$ analogous to 210 might be due in part to the sensitivity of 75 towards air.

However, the complexes $(Me_5Cp)_2ZrS_3$ (48) and $(Me_5Cp)_2HfS_3$ (49) which are analogs to 209 have been prepared as air-stable compounds.

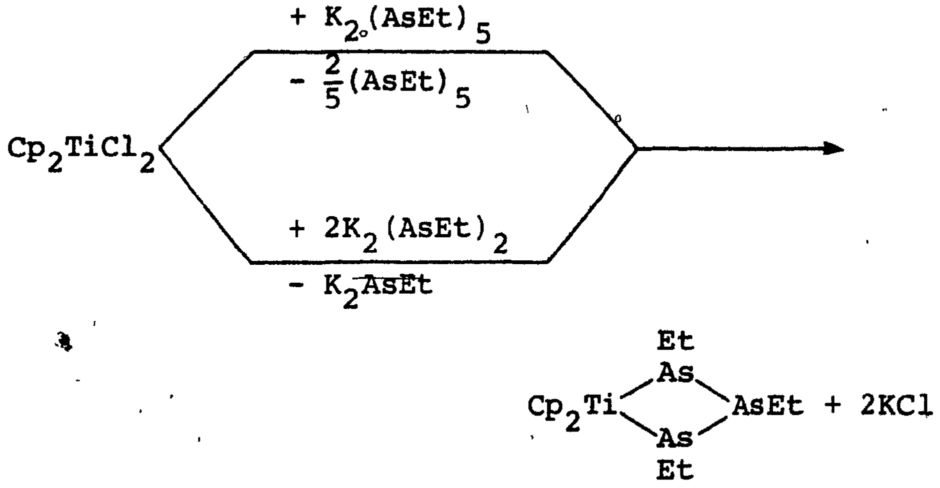
(B) The Reactions of Metallocene Dichlorides with Li_2S_x and Li_2Se_x

The metallocene dichlorides $(RCp)_2MCl_2$ (R = H, M = Ti, Zr, Hf; R = Me, $SiMe_3$, M = Ti), $CH_2Cp_2TiCl_2$, and $(Me_5Cp)CpTiCl_2$ reacted with lithium polysulfide solutions to give products containing the six-membered MS_5 ring. Likewise, the complexes Cp_2MCl_2 (M = Ti, Zr, Hf) reacted with Li_2Se_5 solutions to give the species Cp_2MSe_5. The complexes $(Me_5Cp)_2MCl_2$ gave products having a four-membered MS_3 ring. It is important to note that regardless of the conditions or polysulfur anion used only these products were isolated. For example, under similar reaction conditions Cp_2TiCl_2 and $(Me_5Cp)_2TiCl_2$ react with Li_2S_5 solutions to give Cp_2TiS_5 (73) and $(Me_5Cp)_2TiS_3$ (47), respectively. Köpf has noted a similar selectivity in the reactions of Cp_2TiCl_2 with sodium polysulfides Na_2S_x (x = 2–7)[164] and in the treatment of $Cp_2Ti(SH)_2$ (110) with sulfenyl chlorides S_xCl_2 (x = 1-3) in the presence of pyridine,[106] giving only Cp_2TiS_5 (73).. It should be pointed out, however, that the high selectivity with respect to the ME_x ring size shown in the above complexes is not always the case when E is changed from sulfur or selenium to some other atom or group. Thus, the complexes $(RCp)_2MCl_2$ (M = Ti, Zr, Hf) react with alkali metal polymethylene, polysilane, polyphosphine, and polyarsine salts to give metallacycles of different sizes. For example, Cp_2TiCl_2 reacts with $Li_2(CH_2)_x$ (x = 3-5) to give the corresponding complexes $Cp_2Ti(CH_2)_x$ which decompose in solution below room temperature.[416,417] Permethylation of the cyclopentadienyl rings does not improve the thermal stabilities. Solutions of $(Me_5Cp)_2Ti(CH_2)_4$ are stable at -40°C but decompose slowly at 0°C.[417] Bercaw *et al.*[418] have prepared the thermally stable zirconacyclopentane complex $(Me_5Cp)_2Zr(CH_2)_4$ by oxidative addition of ethylene to the zirconium(II) complex $[(Me_5Cp)_2ZrN_2]_2N_2$. The analogous complex $Cp_2Zr(CH_2)_4$ has been prepared *in situ* and decomposes in solution below room temperature.[417] The complex Cp_2TiCl_2 reacts with $Li_2(SiPh_2)_4$ to give $Cp_2Ti(SiPh_2)_4$ which contains a five-membered $TiSi_4$ ring.[419] Several metallacyclopolyphosphines of the type $Cp_2M(PR)_3$ (M = Ti, Zr, Hf; R = Me, Et, *t*-Bu, Ph; M' = Li, Na, K; n = 2-5) have been prepared according to eq. 106.[420,421]



(106)

The ^{31}P NMR spectra of several of the $M_2'(PR)_n$ reagents were consistent with a single species being present in solution.[421] Regardless of the chain length only the triphosphonato-P^1,P^3 derivatives $Cp_2M(PR)_3$ were isolated. The complexes are stereochemically non-rigid in solution and have bent MP_3 rings (see Chapter 7). Köpf and Görges[422] found a similar reactivity of Cp_2TiCl_2 towards dipotassium poly(organoarsanes), $K_2(AsEt)_x$. The only isolated product was $Cp_2Ti(AsEt)_3$ whether x = 2 or 5 (eq. 107). A cyclic molecule containing a four-membered $TiAs_3$ ring was proposed.



(107)

The constitution of the lithium polysulfide solutions used to obtain the metallacyclopolysulfanes reported here is important with respect to the MS_x ring size "selected" by these complexes. Gladysz et al.[262] have noted that the reactions of alkylating agents with Li_2S and Li_2S_2 prepared in situ gave only the organic sulfides and disulfides, respectively. Analogous reactions with the similarly prepared Li_2Se and Li_2Se_2 reagents gave the selenides and diselenides, respectively.[263] The products from the reaction of a Li_2S_3 solution with Ph_2CHBr or $PhCH_2Br$ were consistent with disproportionation of Li_2S_3 to Li_2S_x (x = 2-5) prior to reaction.[262] A similar disproportionation may occur for Li_2S_5 in solution. Although polysulfides $(PhCH_2)_2S_x$ where $x > 5$ were not observed in the control reaction with $PhCH_2Cl$ traces cannot be ruled out. Long chain polysulfides are known to be thermally sensitive; a low pressure distillation of Ph_2S_4 or Ph_2S_5 gave only Ph_2S_2 in the distillate.[423] Thus desulfurization of Li_2S_5 or disproportionation of this reagent into species containing longer and shorter sulfur chains cannot be excluded. The factors governing the ME_x ring size (E = S, Se) "selected" by metallocene dichlorides in their reactions with the above lithium polysulfides are not well understood. It would appear that the nature of the metal and its ligands is more important than the type of sulfur-transfer reagent used. The complexes Cp_2MCl_2 and $(Me_5Cp)_2MCl_2$ seem predisposed to form only MS_5 and MS_3 rings, respectively, for M = Ti, Zr, and Hf.

7. VARIABLE TEMPERATURE ^{1}H NMR STUDIES

Introduction

Dynamic nuclear magnetic resonance spectroscopy (DNMR) can often be used to study conformational changes having activation energies of ca. 25 to 105 kJ mol^{-1}.[424] The simplest case involves the coalescence of two equally intense singlets, corresponding to two conformers of equal populations, into a single line as the exchange rate between conformers increases with temperature. That temperature at which the minimum between the two coalescing signals has just disappeared is defined as the coalescence temperature, T_c.[424] If the separation between the two signals in the low-temperature limiting spectrum is Δ(Hz), then the rate constant k_c for the exchange at the coalescence temperature T_c is given by eq. 108. When k_c and T_c (in degrees Kelvin) are substituted into the Eyring equation (eq. 109) and the values inserted for the gas constant R (8.3143 J K^{-1} mol^{-1}), the Boltzmann constant k (13.8062 x 10^{-24} J K^{-1}), and Planck's constant h (662.6196 x 10^{-36} Js), the free energy of activation for the process at the coalescence temperature, $\Delta G^{\ddagger}$, is given by eq. 110. To obtain accurate values for $\Delta G^{\ddagger}$,

$$k_c = \frac{\pi\Delta}{\sqrt{2}} \qquad (108)$$

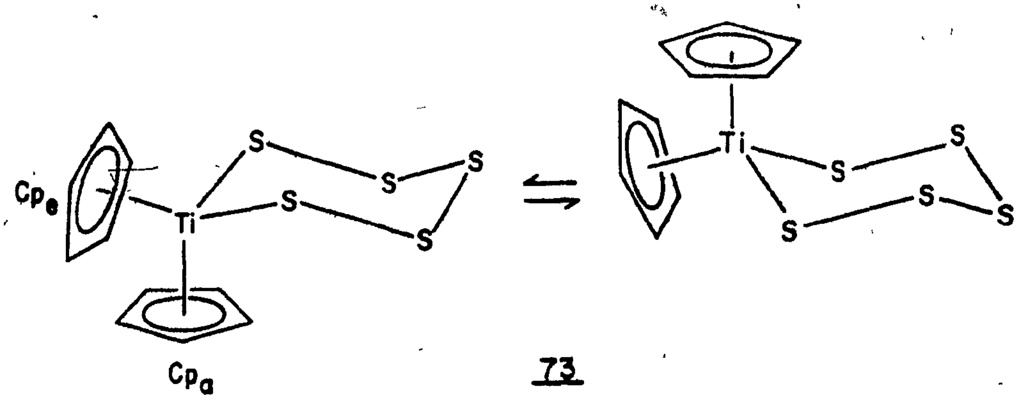
$$k_c = \frac{kT_c}{h}\exp\left(-\frac{\Delta G^{\ddagger}}{RT_c}\right) \qquad (109)$$

$$\Delta G^{\ddagger}(\mathrm{kJ\,mol^{-1}}) = (8.3143 \times 10^{-3})\,T_c\,(23.7599 + \ln T_c - \ln k_c) \quad (110)$$

$\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$, a complete line-shape and statistical analysis is required. Rate constants k' are determined at various temperatures by computer fitting observed spectra with calculated spectra. A linear plot of ln(k'/T) versus 1/T gives a line whose slope is $-\Delta H^{\ddagger}/R$. The value of $\Delta G^{\ddagger}$ is obtained from eq. 109. To determine the activation energy for the process, E_a, an Arrhenius plot of ln k' versus 1/T is prepared. The slope of the straight line is then $-E_a/R$.

A value of $\Delta G^{\ddagger}$ determined by the coalescence temperature method is usually within ±0.8 kJ mol^{-1} of the value found by line-shape analysis.[425] Equations 108, 109, and 110 can also be applied to the coalescence of mutually uncoupled first-order multiplets. In this case T_c is regarded as the temperature of maximum broadening of the signals.[425] An estimate of $\Delta G^{\ddagger}$ in this case is typically within ±4.2 kJ mol^{-1} of the line-shape value.[425]

The variable temperature ^{1}H NMR spectrum of Cp_2TiS_5 (73) has been studied by Köpf et al.[163] and by Abel et al.[406] The low-temperature limiting spectrum at 30°C in toluene-d_8 solution consisted of two sharp equally intense singlets separated by 0.10 ppm. As the solution was warmed the two singlets coalesced (T_c = 88.0°C) and sharpened into a single line.[406] These spectral changes are consistent with a ring-flipping process. The solid-state structure of <u>73</u> consists of a chair-shaped six-membered TiS_5 ring. This renders the axial and equatorial Cp ligands (Cp_a and Cp_e, respectively) magnetically inequivalent. Consequently, separate single lines are observed for the protons of each type of ring. Based on the numerous studies[426] on cyclohexanes and pentamethylene heterocycles of the type $(CH_2)_5X$, Abel <u>et al</u>.[406] suggested that the upfield signal should be assigned to Cp_a. Upon warming, the rate of TiS_5 ring flipping increases. In the fast limit a time-averaged single resonance, midway between the slow limit singlets, is observed for the Cp protons. Abel's lineshape analysis[406] over the temperature range 30° to 120°C gave the following activation



<u>73</u>

parameters: $E_a = 69.1 \pm 2.3$ kJ mol^{-1}, $\Delta G^{\ddagger}_{298} = 76.3 \pm 4.2$ kJ mol^{-1}, $\Delta H^{\ddagger}_{298} = 66.2 \pm 2.3$ kJ mol^{-1}, and $\Delta S^{\ddagger}_{298} = -33.9 \pm 6.4$ J K^{-1} mol^{-1}. Substituting a slow limit value[406] of Δ = 10.0 Hz at 30°C and a coalescence temperature[406] of 88.0°C (361.2 K) into equations 108 and 110 leads to an estimate of

$\Delta G^{\ddagger}$ = 79.7 kJ mol^{-1} at the coalescence temperature. It was of interest therefore to study the variable temperature ^{1}H NMR spectra of the new metallacyclopolysulfanes prepared here. Thus the complexes Cp_2ME_5 where M = Zr, Hf and E = S, Se, and $(Me_5Cp)_2MS_3$ where M = Ti, Zr, Hf were investigated.

Results

The ^{1}H DNMR experiments reported here were conducted on a Varian XL-200 spectrometer except for those studies of the complexes Cp_2MS_5 (M = Zr, Hf) which were done on a Bruker WH-90. Probe temperatures were read from the instrument's meter which had previously been calibrated with methanol and ethylene glycol. These temperatures are considered accurate to ±0.5 K. The reported coalescence temperatures were estimated visually from the recorded spectra and are thought to be within ±3 K of their true values. This was taken into account in the estimation of error limits for the calculated $\Delta G^{\ddagger}$ values.

(A) Metallacyclohexasulfanes and $Cp_2Ti[S(CH_2)_3S]$

Unlike the room temperature ^{1}H NMR spectrum of Cp_2TiS_5 (73), the corresponding spectra for the zirconium and hafnium analogs consisted of only one sharp singlet. Cooling the samples, though, resulted in a collapse of the signal and eventual sharpening into two singlets of equal intensity (Table 7). The calculated $\Delta G^{\ddagger}$ values were 48.6 ± 0.6 kJ mol^{-1} for Cp_2ZrS_5 (75) and 58.0 ± 0.7 kJ mol^{-1} for Cp_2HfS_5 (76) (Table 7).

The ^1H NMR spectrum of $(MeCp)_2TiS_5$ (74) consisted of two singlets of equal intensity corresponding to the methyl protons and four triplets (of which two overlapped) due to the C_5H_4 protons (Table 7, Fig. 8). The separation of the signals was found to be greatest in toluene-d_8. Decoupling experiments established that the two outer triplets were coupled as were the two inner triplets. To estimate $\Delta G^{\ddagger}$ it was necessary to monitor the coalescence of resolved signals corresponding to axially and equatorially oriented protons. Thus, two sets of signals fitted this criterion, namely the two higher field triplets and the methyl singlets. The latter were monitored because of the ease of establishing the coalescence temperature of two singlets compared with that of two coalescing triplets. A value of 75.6 ± 0.6 kJ mol^{-1} was calculated for $\Delta G^{\ddagger}$ (Table 7).

The ^1H NMR spectrum of $(Me_3SiCp)_2TiS_5$ (77) also consisted of four triplets (of which two overlapped) for the C_5H_4 protons in addition to two singlets of equal intensity for the Me protons (Table 7, Fig. 9). Decoupling experiments showed that the outer pair of triplets were coupled as were the inner pair. Coalescence of the methyl singlets was followed and a value of 78.5 ± 0.7 kJ mol^{-1}

TABLE 7

^1H NMR Spectra and Barriers to Ring Reversal of Metallacyclopolysulfanes and -selanes[a]

Compound	Solvent	Temp.	C_5H_5	C_5H_4	CH_3	Δ[b]	T_c[c]	$\Delta G^\ddagger$[c]
Cp_2TiS_5	Toluene-d_8	35	5.57[d]			10.0	88.0	79.7[d]
			5.67[d]					
	CD_2Cl_2	35	6.08[e]			16.2		
			6.35[e]					
$[(MeCp)_2Ti(\mu\text{-}S_2)]_2$	$CDCl_3$	f		5.98	1.84	223.2[f]	f	f
				6.07	2.46			
				6.33				
				6.54				
$[Cp_2Ti(\mu\text{-}S_3)]_2$	$CDCl_3$	35	6.18[e]					
	CS_2	35	6.02[e]					
		15	(6.03)[g]					g
Cp_2ZrS_5	CD_2Cl_2	-89	6.25			13.7[h]	-46	48.6 ± 0.6
			6.40					
		28	6.36					
Cp_2HfS_5	CD_2Cl_2	-51	6.29			4.0[h]	-16	58.0 ± 0.7
			6.25					
		26	6.29					

TABLE 7 - cont'd

Compound	Solvent	Temp.	C_5H_5	C_5H_4	CH_3	Δ^b	T_c^c	$\Delta G^{\ddagger c}$
$(MeCp)_2TiS_5$	Toluene-d_8	19		5.32^i	1.65	64.1	94.8	75.6 ± 0.6^j
				5.45^i	1.97			
				5.59^i				
				5.62^i				
$(Me_3SiCp)_2TiS_5$	Toluene-d_8	20		5.75^k	0.08	31.6^l	∿97	78.2 ± 0.6^m
				5.77^k	0.21	27.2^n		78.7 ± 0.7^m
				6.04^k				avg. 78.5 ± 0.7
				6.09^k		5.8^l	∿94	82.7 ± 0.7^o
						9.7^n		81.2 ± 0.7^o
								avg. 82.0 ± 0.7
$CH_2Cp_2TiS_5$ ^{p}	Toluene-d_8	-7		4.22^q		79.5	51.5	67.9 ± 0.7^r
				4.61^q		48.0	41.4	65.0 ± 0.7^s
				6.26^q				avg. 66.5 ± 0.7
				6.50^q				
$Me_2SiCp_2TiS_5$	CS_2	35	5.57^e		0.77			t
			6.20^e					
			7.07^e					
$Me_2GeCp_2TiS_5$	CS_2	35	5.53^e		0.93			t
			6.17^e					
			6.97^e					

TABLE 7 - cont'd

Compound	Solvent	Temp.	C_5H_5	C_5H_4	CH_3	Δ^b	T_c c	$\Delta G^\ddagger$ c
$(Me_5Cp)CpTiS_5$	Toluene-d_8	21	5.62		1.64			u
	CD_2Cl_2	21	5.92		2.02			
$Pt(S_5)_3{}^{2-}$	CD_3OD							50.5 ± 1.3[v]
Cp_2TiSe_5	Toluene-d_8	21	5.06			32.9	>90	>76.5
			5.22					
	CD_2Cl_2	35	5.92[e]					
			6.34[e]					
Cp_2ZrSe_5	CD_2Cl_2	-74	6.36			45.9	-29.4	49.9 ± 0.7
			6.59					
		20	6.23					
Cp_2HfSe_5	CD_2Cl_2	-29	6.16			23.9	17.8	61.6 ±0.7
			6.28					
		21	6.19					
$Cp_2Ti[S(CH_2)_3S]$[w]	CD_2Cl_2	21	6.09			~4[x]	<-120	<34

TABLE 7 - cont'd

Compound	Solvent	Temp.	C_5H_5	C_5H_4	CH_3	Δ^b	T_c [c]	$\Delta G^{\ddagger}$ [c]
$(Me_5Cp)_2TiS_3$	$CD_2Cl_2/CFCl_3$ (1:1)	-90			$\sim$1.76	11-17^y	-80 to -85	40.6 ± 0.9
					$\sim$1.83 (sh)			
	$CDCl_3$	35			1.83^e			
$(Me_5Cp)_2ZrS_3$	$CD_2Cl_2/CFCl_3$ (1:1)	-100			1.80	15.6^z	-87.2	39.3 ± 0.7
					1.88			
	$CDCl_3$	35			1.87^e			
$(Me_5Cp)_2HfS_3$	$CD_2Cl_2/CFCl_3$ (1:1)	-80			1.87	$\sim$14^A	<-130	<30
	$CDCl_3$	35			1.92^e			

[a] All data is from this work except where indicated. Spectra were recorded at 200 MHz unless indicated otherwise. Chemical shifts are in units of δ ppm. All temperatures are in degrees Celsius.

[b] Δ(Hz) is the separation of axially- and equatorially-oriented groups.

[c] $\Delta G^{\ddagger}$ (kJ mol^{-1}) was calculated at the coalescence temperature, T_c (°C). The error limits reflect an experimental uncertainty of ±3°C in the estimation of T_c.

[d] The chemical shifts are from a study done at 100 MHz by ref. 406. The $\Delta G^{\ddagger}$ was calculated using data reported in this reference.

[e] The spectrum was recorded at 60 MHz.

[f] The spectrum was recorded at 360 MHz by ref. 292. The probe temperature was not reported. A variable temperature study was not done.

[g] The spectrum was recorded at 220 MHz by ref. 103. The $\Delta G^{\ddagger}$ was not measured.

[h] The variable temperature NMR study was done at 90 MHz.

[i] $J(H-H) = 2.6$ Hz.

[j] $\Delta G^{\ddagger}$ calculated from the coalescence of singlets due to the methyl groups.

[k] $J(H-H) = 2.4$ Hz.

[l] The value of Δ corresponds to that observed at -51.0°C.

[m] $\Delta G^{\ddagger}$ calculated from the coalescence of singlets due to the trimethylsilyl groups.

[n] The value of Δ corresponds to that observed at 19.3°C.

[o] $\Delta G^{\ddagger}$ calculated from the coalescence of the triplets at δ 6.04 and δ 6.09.

[p] $\delta(CH_2) = 2.43$ at -7.1°C. The spectrum at 90°C consisted of a triplet at δ 6.42 [$J(H-H) = 2.3$ Hz], an unresolved peak at δ 4.64, and a sharp singlet at δ 2.69.

[q] $J(H-H) = 2.5$ Hz.

[r] $\Delta G^{\ddagger}$ calculated from the coalescence of the high-field pair of triplets at δ 4.22 and δ 4.61.

[s] $\Delta G^{\ddagger}$ calculated from the coalescence of the low-field pair of triplets at δ 6.26 and δ 6.50.

[t] The spectrum was reported by ref. 169. The compound gave a temperature dependent ^{1}H NMR spectrum but no $\Delta G^{\ddagger}$ value was reported.

[u] No line-shape changes were observed from -101°C to 124°C.

[v] From a ^{195}Pt NMR study conducted by ref. 14.

[w] $\delta(CH_2) = 1.82$ and 3.06 each having $J(H-H) = 6.3$ Hz.

[x] Half-height width of the singlet corresponding to the Cp protons at -120°C.

[y] Estimated from the -90°C spectrum.

[z] At -105°C.

[A] Half-height width of the signal corresponding to the methyl protons at -130°C.

<u>Figure 8</u>. Partial ^1H NMR spectrum of $(MeCp)_2TiS_5$ (<u>74</u>) in toluene-d_8.

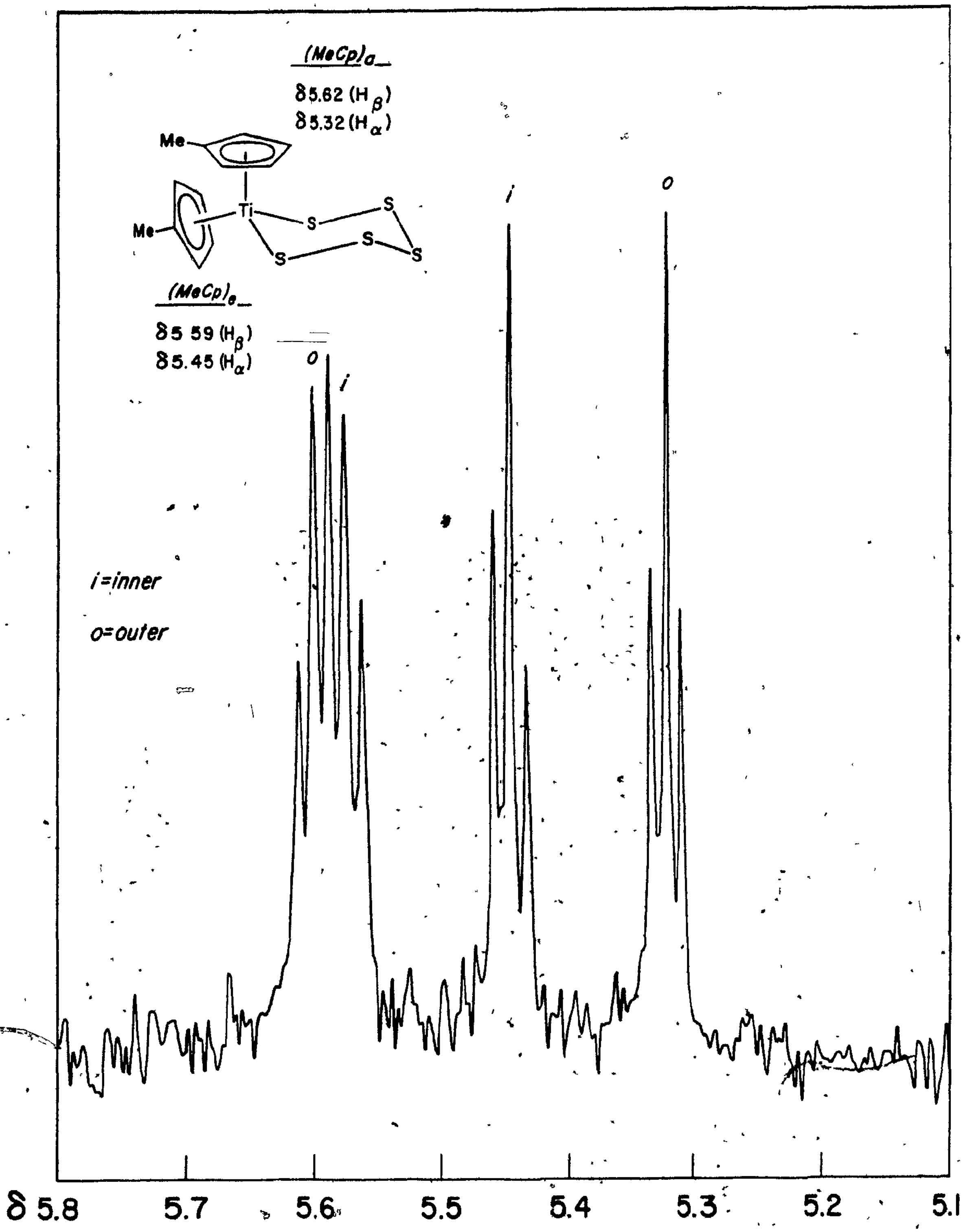
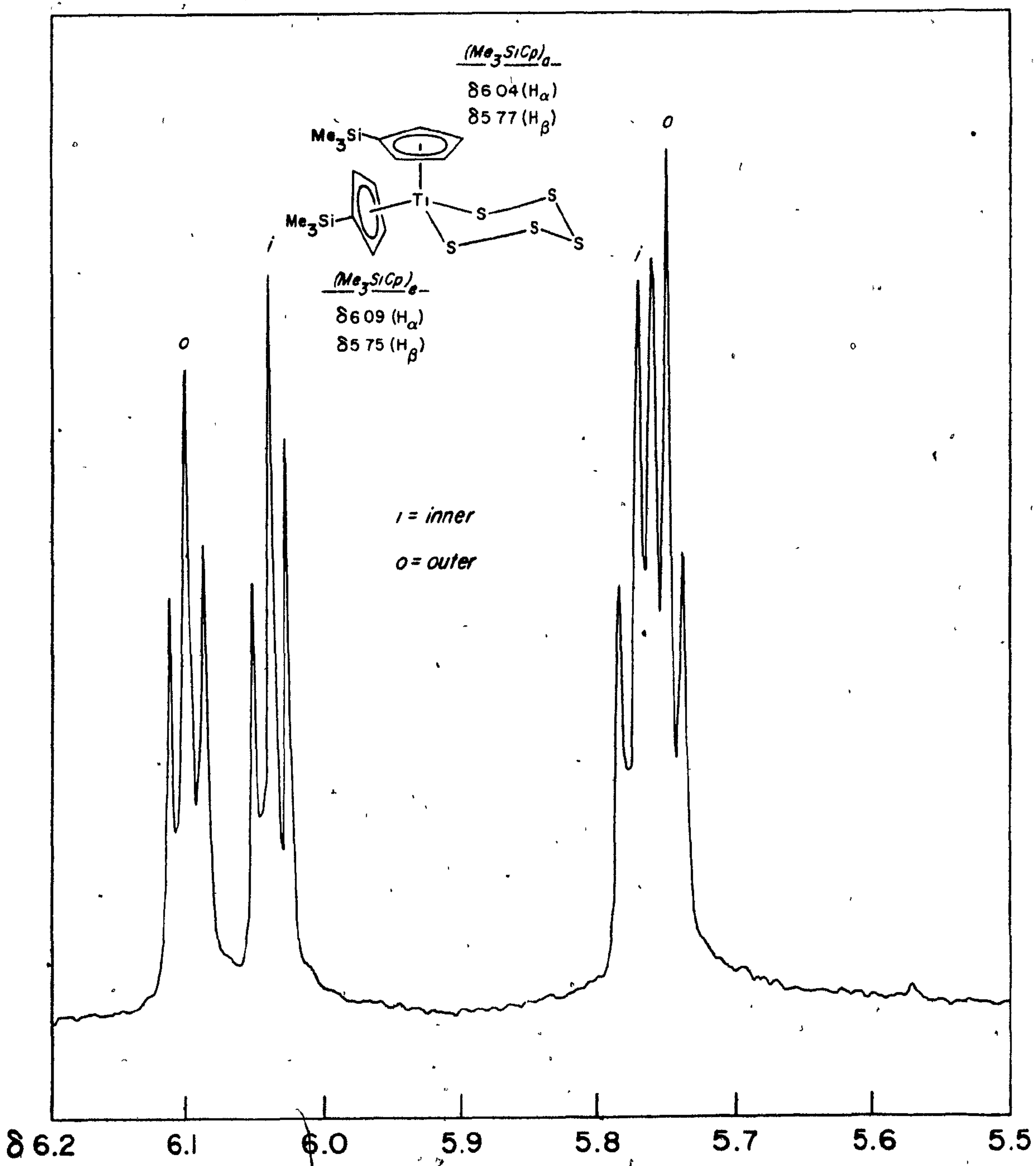

(MeCp)a
δ5.62 (Hβ)
δ5.32 (Hα)
Me
Me
Ti
S
S
S
S
S
(MeCp)e
δ5.59 (Hβ)
δ5.45 (Hα)
o
i
i
o
i=inner
o=outer
δ 5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1

Figure 9. Partial ^{1}H NMR spectrum of $(Me_3SiCp)_2TiS_5$ (77) in toluene-d_8.

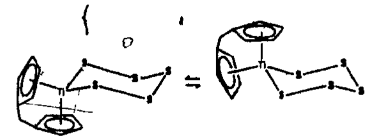

(Me$_3$SiCp)$_a$
δ6.04 (H$_\alpha$)
δ5.77 (H$_\beta$)
Me$_3$Si
Ti
S
Me$_3$Si
(Me$_3$SiCp)$_e$
δ6.09 (H$_\alpha$)
δ5.75 (H$_\beta$)
o
i
i
o
i = inner
o = outer
δ 6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5

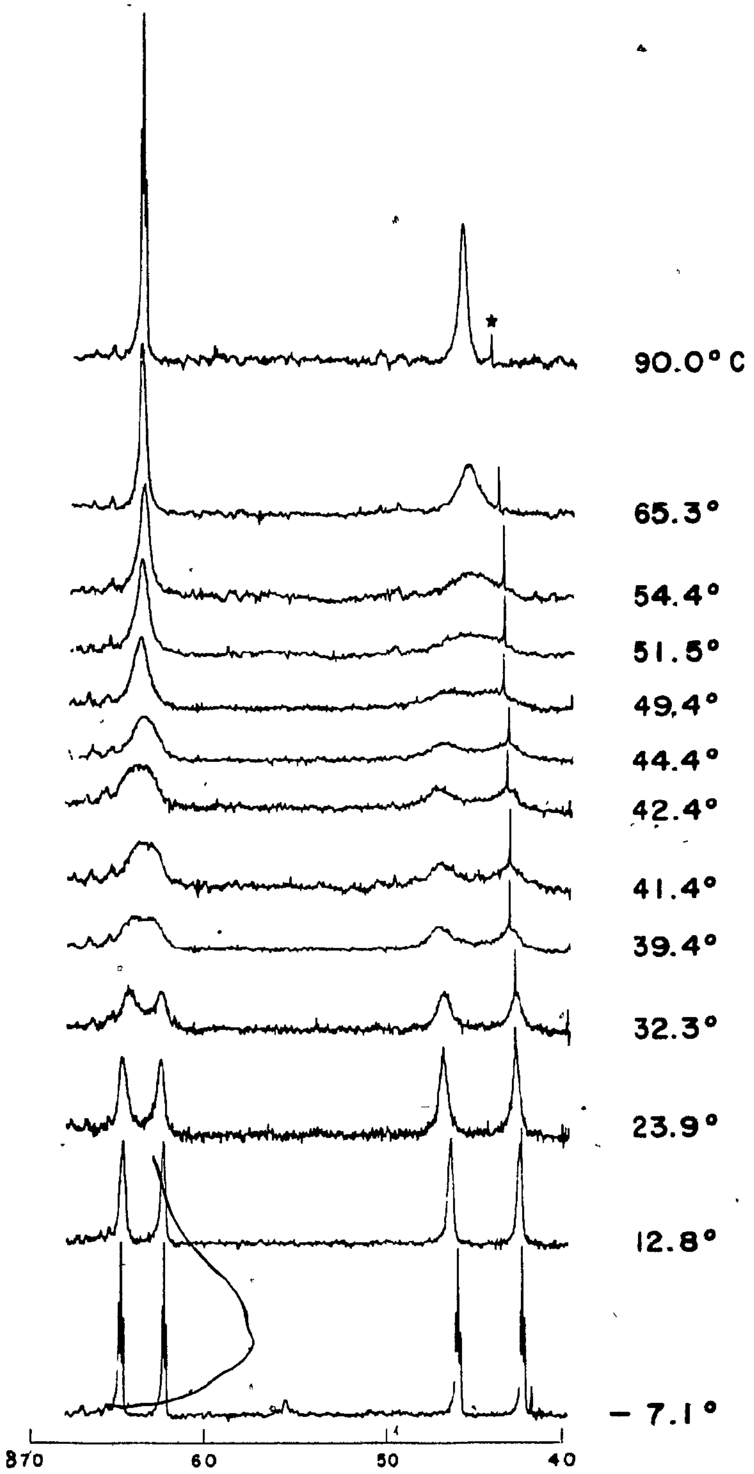
was calculated. The pair of triplets at δ 6.04 and δ 6.09 was monitored as a check on this value and gave $\Delta G^{\ddagger}$ = 82.0 ± 0.7 kJ mol^{-1}. The values for $\Delta G^{\ddagger}$ calculated using data from the 19.3°C spectrum were not significantly different from those calculated using data from the -51.0°C spectrum (Table 7). The estimate of $\Delta G^{\ddagger}$ from the coalescing triplets is higher than that determined from the coalescing singlets and is probably less accurate.[425]

Abel et al.[406] reported a temperature variation in the chemical shifts of the signals of Cp_2TiS_5 (73) in toluene-d_8. From 25° to 45°C the two singlets moved apart by 0.075 Hz/°C. A similar temperature sensitivity was found for $(MeCp)_2TiS_5$ (74) and $(Me_3SiCp)_2TiS_5$ (77) in this solvent. For 74, increasing the temperature from 19° to 50°C caused the triplets at δ 5.32 and δ 5.45 to move closer by ca. 0.16 Hz/°C. For 77, in the range from 0° to 55°C the triplets at δ 6.04 and δ 6.09 moved steadily apart by ca. 0.09 Hz/°C. The singlets due to the methyl protons for 74 and 75 moved closer by ca. 0.06 Hz/°C over the indicated temperature ranges. The origin of these variations in separation is not known.

The methylene-bridged complex $CH_2Cp_2TiS_5$ (79) was studied over the temperature range -7.1° to 90°C. The slow-limiting spectrum at -7.1°C consisted of four sharp triplets due to the C_5H_4 protons and a sharp singlet due to the CH_2 bridge protons (Fig. 10, Table 7). As the

Figure 10. Variable temperature ^{1}H NMR spectra of $CH_2Cp_2TiS_5$ (79) in toluene-d_8.





*CH_2Cl_2 trapped in the crystal lattice.

sample temperature was raised the two low-field and the two high-field pairs of triplets coalesced. At higher temperatures the broad signals sharpened. Thus, two estimates of $\Delta G^{\ddagger}$ were possible. The data from the low-field pair gives $\Delta G^{\ddagger} = 65.0 \pm 0.7$ kJ mol^{-1} and the high-field pair gives $\Delta G^{\ddagger} = 67.9 \pm 0.7$ kJ mol^{-1}. The average value for $\Delta G^{\ddagger}$ is 66.5 ± 0.7 kJ mol^{-1} (Table 7).

The DNMR study of $(Me_5Cp)CpTiS_5$ (78) was interesting. In CD_2Cl_2 and toluene-d_8 no changes occurred in the spectrum over the temperature range -101° to 124°C save for a slight broadening of the signals at the lowest temperatures (Table 7).

A similar lack of line-shape changes was observed for $Cp_2Ti[S(CH_2)_3S]$ (120). The room temperature spectrum consisted of a sharp singlet due to the Cp protons, a triplet due to the terminal CH_2 protons, and a quintet due to the central CH_2 protons (Table 7). The Cp singlet remained sharp down to -120°C but the CH_2 triplet and quintet were poorly resolved below -60°C. At -120°C the half-height width of the Cp signal was ca. 4 Hz. Assuming that the axial and equatorial Cp groups would be distinguishable in the conformationally rigid molecule one must conclude that TiS_2C_3 ring reversal is fast at -120°C. Thus assuming $T_c < -120$°C and $\Delta = 4$ Hz, $\Delta G^{\ddagger}$ can be estimated to be less than 34 kJ mol^{-1} (Table 7).

(B) Metallacyclohexaselenanes

Like its sulfur analog 73, Cp_2TiSe_5 (107) had a room temperature spectrum consisting of two equally intense singlets (Table 7). Variable temperature NMR studies were hampered by decomposition at elevated temperatures. By 90°C in toluene-d_8 some broadening of the signals was evident. The complex decomposes at lower temperatures in DMSO-d_6 and DMF. If T_c is estimated to be greater than 90°C then $\Delta G^{\ddagger}$ must be greater than 76.5 kJ mol^{-1} (Table 7).

The DNMR studies were done for Cp_2ZrSe_5 (108) and Cp_2HfSe_5 (109). At 20°C the Cp protons of 108 appear as a sharp singlet while the singlet for 109 is somewhat broadened. At lower temperatures two equally intense signals were observed. Minor unidentified broad signals in the spectrum of 108 at δ 6.19 and δ 6.29 sharpened with decreasing temperature. A slight asymmetry at the base of the peak for 109 resolved into two minor peaks of unequal intensity at δ 6.34 and δ 6.37 at -29°C. The origin of these peaks is unknown. The calculated values of $\Delta G^{\ddagger}$ are 49.9 ± 0.7 kJ mol^{-1} for 108 and 61.6 ± 0.7 kJ mol^{-1} for 109 (Table 7).

(C) Metallacyclotetrasulfanes

The complexes $(Me_5Cp)_2MS_3$ [M = Ti (47), Zr (48), Hf (49)] exhibit a sharp singlet for the methyl groups at room temperature (Table 7). For the titanium and zirconium complexes the peak broadened as the temperature was lowered. At about -80°C the signal appeared as a symmetrical broad singlet. Below this temperature the signal became unsymmetrical (Fig. 11). Between -85° and -110°C the spectrum consists of two overlapping singlets of unequal intensity. Further cooling caused the overlapping signals to broaden and become less intense. However, by -120°C the peaks appeared to be sharpening. At very low temperature (-130°C) several broad peaks appear in the spectrum of 47. A value of $\Delta G^{\ddagger} = 40.6 \pm 0.9$ kJ mol^{-1} was calculated for 47 (Table 7). The spectra of $(Me_5Cp)_2ZrS_3$ (48) (Fig. 12) were better resolved than those of 47. At -100°C two singlets were present (Table 7). The signal at lower field became more intense below the coalescence temperature. At -125°C the higher field signal was barely resolved as a shoulder of the lower field peak. The spectrum had not sharpened appreciably by -130°C. The $\Delta G^{\ddagger}$ was calculated to be 39.3 ± 0.7 kJ mol^{-1} (Table 7).

The spectrum of $(Me_5Cp)_2HfS_3$ (49) in the range -110° to -130°C showed a broad singlet with a half-height width of 10 Hz at -110°C and about 14 Hz at -130°C. Assuming a coalescence temperature of < -130°C and a value of $\Delta < 14$ Hz, $\Delta G^{\ddagger}$ is estimated to be less than 30 kJ mol^{-1} (Table 7).

Figure 11. Variable temperature ^1H NMR spectra of $(Me_5Cp)_2TiS_3$ (47) in $CD_2Cl_2/CFCl_3$ (1:1).

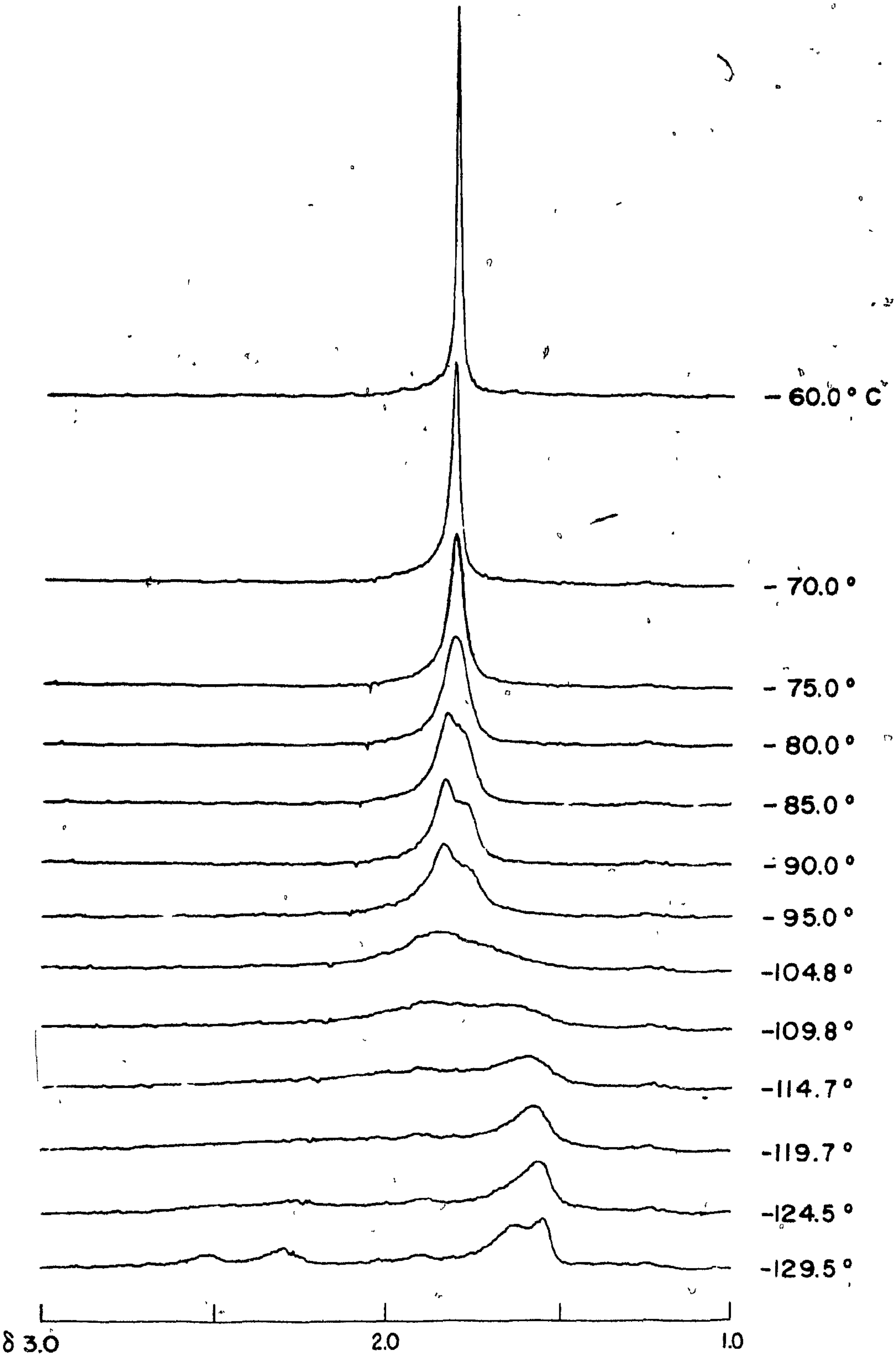
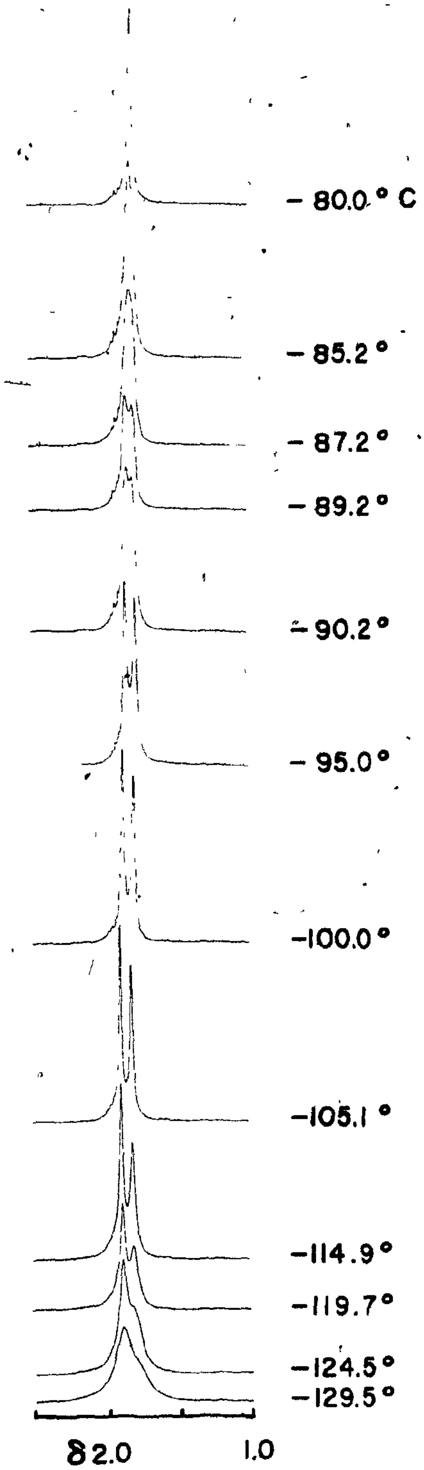

-60.0 ° C
-70.0 °
-75.0 °
-80.0 °
-85.0 °
-90.0 °
-95.0 °
-104.8 °
-109.8 °
-114.7 °
-119.7 °
-124.5 °
-129.5 °
δ 3.0
2.0
1.0

Figure 12. Variable temperature ^1H NMR spectra of $(Me_5Cp)_2ZrS_3$ (48) in $CD_2Cl_2/CFCl_3$ (1:1).


-80.0 ° C
-85.2 °
-87.2 °
-89.2 °
-90.2 °
-95.0 °
-100.0 °
-105.1 °
-114.9 °
-119.7 °
-124.5 °
-129.5 °
δ 2.0
1.0

Discussion

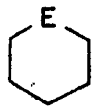
The room temperature ^{1}H NMR spectra of the complexes Cp_2ME_5 where M = Ti, Zr, Hf and E = S, Se consisted of two singlets of equal intensity when M = Ti but only one singlet when M = Zr or Hf in both series. At low temperatures each of the compounds gave two equally intense singlets. The magnitude of the signal separation followed the order Ti > Zr > Hf with the largest being 0.27 ppm for E = S and 0.42 ppm for E = Se when M = Ti (Table 7). For comparison, the chemical shift difference between the axial and equatorial protons of cyclohexanes is 0.4 to 0.5 ppm[426] but is 1.79 ppm for CH_2S_5 in CS_2 solution.[179]

The crystal structures of the complexes Cp_2MS_5 (see the end of this chapter and Fig. 13) showed that the average M-Cp distance followed the order Ti < Hf < Zr. Relative differences in the size or shape of the ME_5 ring might attenuate the magnitude of the signal separation, Δ. The crystal structures indicated that the MS_5 ring size as measured by the M to S3 distance (Table 9) followed the order Zr < Hf < Ti. The flattening of the MS_5 ring as measured by the two dihedral angles between the planes defined by S1-Ti-S5 and S1-S2-S4-S5, and S1-S2-S4-S5 and S2-S3-S4 (Fig. 13 and Table 9) increased in the order Zr < Hf < Ti also. The Cp-M-Cp angle followed this order too. Thus in the crystalline complexes Cp_2MS_5, the most puckered MS_5 ring is also the shortest and has the smallest Cp-M-Cp angle. However, the differences in the parameters for the three complexes is quite small so that the overall shapes of the MS_5 rings are very similar. It is not readily apparent from the crystal structures, then, why Δ follows the order Ti > Zr > Hf. It should be remembered, however, that the distances in the crystal structures may not necessarily correspond to those found in solution. In this regard it is worth noting that the pentamethylene heterocycles, $(CH_2)_5X$, for which the degree of flattening in solution can be accurately measured, often have solid-state structures with dihedral angles differing by 1° to 2° from the solution values.[426]

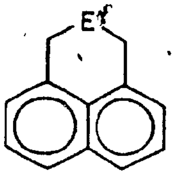
In analogy with the averaging of axial and equatorial protons of cyclohexanes[427] and pentamethylene heterocycles[426] the variable temperature ^1H NMR spectra of the complexes Cp_2ME_5 are consistent with ME_5 ring flipping.[406] In this way the axially- and equatorially-disposed Cp groups interconvert. The barriers follow the order Ti > Hf > Zr for E = S and for E = Se. Replacement of sulfur by selenium in the zirconium and hafnium complexes causes a slight increase in the barrier to ring reversal. The barrier for Cp_2TiSe_5 (107) is probably greater than that for Cp_2TiS_5 but it could not be measured because of decomposition. Köpf *et al.*[163] have reported that 107 decomposes at elevated temperatures in Me_2S_2 and Me_2Se_2. The coalescence temperature was reached but it was not specified.[163]

Riddell et al.[14] recently studied the stereochemical non-rigidity of the $Pt(S_5)_3^{2-}$ ion (2) using variable temperature ^{195}Pt NMR. They concluded that the dynamic process, presumed to be inversion of one PtS_5 chair, had a $\Delta G^{\ddagger}_{273}$ of 50.5 ± 1.3 kJ mol^{-1}. This barrier is close to those found for Cp_2MS_5 (M = Zr, Hf) but much lower than that for M = Ti (Table 7).

The factors underlying the differences in $\Delta G^{\ddagger}$ for ring reversal are not readily apparent. The magnitude of the barrier reflects the energy of the transition state with respect to the ground state. The transition state is less stable relative to the chair conformation because of an interplay of torsional forces, angle-bending strain, and non-bonding interactions.[426] The torsional barriers are often considered to be the most important factor in pentamethylene heterocycles (215).[426] For example, the $\Delta G^{\ddagger}$ decreases as ring puckering increases in the series tetrahydropyran (43.1 kJ mol^{-1}), thiane (39.3 kJ mol^{-1}), selenane (34.7 kJ mol^{-1}), and tellurane (30.5 kJ mol^{-1}). This has been attributed to a dominance of torsional strains of the C–E bonds over angle bending strains.[426] It is interesting to note, however, that the ring inversion barriers in a similar series of CH_2-E-CH_2 bridged peri-naphthalenes (216) followed the opposite trend.[428] The CH_2-naphthalene-CH_2



215



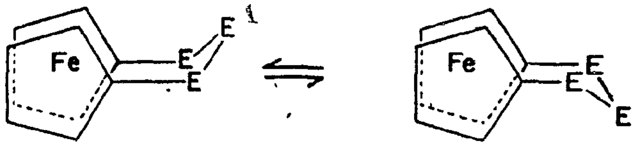
216

E = O, S, Se, Te

grouping maintains a nearly rigid geometry. Thus ring flipping will occur *via* a planar or nearly planar transition state. The C–E bond lengths, ring puckering, and angle strain during ring flipping increase in the order O < S < Se < Te. However, as the C–E bond lengthens the torsional interactions decrease. Thus the two effects would predict different orders in $\Delta G^{\ddagger}$ for ring reversal. The observed order is compatible with angle strain dominating over torsional strain in these cases.[428]

The mean M–S bond lengths in the complexes Cp_2MS_5 increased in the order Ti < Hf < Zr and the S–M–S bond angle increased in the same order (Table 9). Similar sulfur-sulfur bond lengths and angles were found in the three complexes. The same trends in molecular parameters are expected for the selenium analogs Cp_2MSe_5. By analogy with the *peri*-naphthalenes discussed above, the E–M–E angle strain in the complexes Cp_2ME_5 may increase in the order M = Ti < Hf < Zr for a given E as the size of the metal heteroatom increases. This should lead to an increase in $\Delta G^{\ddagger}$ in that order; the reverse order is observed experimentally (Table 7).

The torsional barriers of M-E bonds have not been reported and the observed trend in $\Delta G^{\ddagger}$ (Ti > Hf > Zr) may reflect their relative values. The M-E and E-E bonds are longer for E = Se than for E = S and this should reduce the torsional barriers and the steric interactions of the chalcogen lone pairs in the selenanes. With the metal remaining constant, these torsional barriers argue for lower ring reversal barriers when E = Se than when E = S, the reverse of what was observed. Abel et al.[95] determined the barriers to the bridge reversal process in several [3]-ferrocenophanes (41) including when E = S and Se. The torsional barrier about the Se-Se bond was calculated to be 5.8 kJ mol^{-1} less than that for the S-S bond.[95] The values of $\Delta G^{\ddagger}$ for bridge reversal were 80.4 ± 0.2 kJ mol^{-1} for E = S and 67.2 ± 0.1 kJ mol^{-1} for E = Se.



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It was of interest to study the effect of substituted Cp rings on the MS_x ring size and on the energy barrier to ring reversal. The metallacyclopolysulfanes containing the moieties $(RCp)_2Ti$ where R = Me and Me_3Si, CH_2Cp_2Ti, and $(Me_5Cp)CpTi$ all had TiS_5 rings. On the other hand the complexes bearing the $(Me_5Cp)_2M$ group

(M = Ti, Zr, Hf) contained MS_3 rings.

The methyl and trimethylsilyl groups have different electronic effects on cyclopentadienyl rings to which they are bonded. The latter group has a deshielding effect on the C_5H_4 protons in the complexes $(Me_3SiCp)_2MCl_2$ (M = Ti, Zr, Hf).[266] This effect has been attributed to a mesomeric (-M) effect involving silicon 3d orbitals dominating an inductive (+I) effect.[266] In $CDCl_3$ the chemical shift of the C_5H_5 protons of Cp_2TiCl_2 is δ 6.55 (s) while the C_5H_4 signals of $(Me_3SiCp)_2TiCl_2$ appear as two triplets at δ 6.57 and δ 6.79 having J(H-H) = 2.4 Hz. The Me substituent, however, has a shielding effect. Thus the C_5H_4 protons of $(MeCp)_2TiCl_2$ appear as triplets at δ 6.30 and δ 6.39 with J(H-H) = 2.6 Hz. In $(MeCp)_2TiCl_2$ the triplet at higher field has been assigned[429] to the protons α to the methyl substituent. In $(Me_3SiCp)_2TiCl_2$ it is assumed that the α protons resonate to lower field since the degree of electron withdrawal from the C_5H_4 ring is assumed to diminish with distance from the $SiMe_3$ substituent. In support of this proposal, the α protons of substituted ferrocenes $(RCp)_2Fe$ in which R is an electron-donating group appear at higher field than the β ones. When R is an electron withdrawing substituent the α protons resonate at lower field.[430]

In analogy with the assignment in $(MeCp)_2TiCl_2$ the two triplets at highest field in the spectrum of

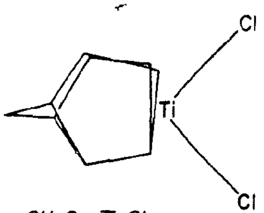
$(MeCp)_2TiS_5$ (<u>74</u>) are assigned to the protons α to the Me group (Fig. 8, Table 7). The decoupling experiments showed that the inner pair of triplets corresponded to C_5H_4 protons of one ring and the outer pair to protons of the other ring. Since the midpoint of the outer set of triplets is at higher field than that for the inner pair, the outer set is assigned to the axial ligand, $(MeCp)_a$, and the inner set to the equatorial ligand, $(MeCp)_e$. Similarly, the highest-field methyl singlet is assigned to the axial ring, Me_a.

The methyl resonance to higher field in the spectrum of $(Me_3SiCp)_2TiS_5$ (<u>77</u>) is assigned to the axial group in keeping with the assignment for Cp_2TiS_5 (<u>73</u>) and $(MeCp)_2TiS_5$ (<u>74</u>). The centers of the triplet pairs (inner and outer, Fig. 9) differ only marginally in chemical shift (0.01 ppm) with the inner pair to higher field. Thus, the inner triplets are tentatively assigned to the axial Me_3SiCp group. Assuming that the ring protons α to the Me_3Si group resonate at lower field than the β ones (<u>vide</u> <u>supra</u>), the following assignments (ax. = axial, eq. = equatorial) are tentatively made: α protons, δ 6.04 (ax.), δ 6.09 (eq.) and β protons, δ 5.77 (ax.), δ 5.75 (eq.) (Table 7). According to this analysis, the inner and outer pairs of triplets for <u>74</u> and <u>77</u> have opposite axial and equatorial assignments. It should be noted, however, that the assignment of these peaks is not crucial for an evaluation of the DNMR study.

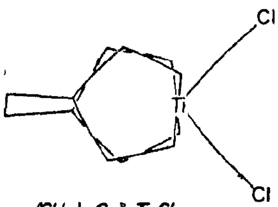
The $\Delta G^{\ddagger}$ values found for 74 and 77 are similar to those found for Cp_2TiS_5 (73) at the coalescence temperature (Table 7) and for CH_2S_5 (calculated to be 72.8 kJ mol^{-1},[431] experimentally > 60.0 kJ mol^{-1} [179]). The calculated $\Delta G^{\ddagger}$ for ring reversal for S_6 is much higher at 125.1 kJ mol^{-1}.[431]

The ^1H NMR spectrum of $(Me_5Cp)CpTiS_5$ (78) was unchanged from -101° to 124°C (Table 7). This is consistent with two possibilities, namely that the molecule is locked in one conformation over this temperature range or that the TiS_5 ring is flipping rapidly on the NMR time scale even at -101°C. The high barriers found for the other complexes containing TiS_5 rings argue against the latter possibility. Thus the molecule appears to be fixed in a chair conformation. The data, however, cannot assign the position of either ring with respect to being axial or equatorial. The X-ray crystal structure of $Cp(PMe_3)CoS_5$ (81) revealed the Cp group in the axial position.[175] The cone angle of the Cp ligand is ca. 136° while that for PMe_3 is 118°.[432] Thus the more sterically demanding ligand occupies the axial position. The tendency of 78 to crystallize as very thin plates from a variety of solvents has thus far prevented an X-ray crystallographic study.

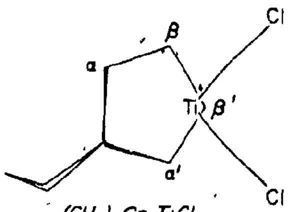
A few complexes containing bridged η-cyclopentadienyl ligands of the types $(CH_2)_x(\eta\text{-}C_5H_4)_2$ (x = 1, 2, 3) or $R_2M(\eta\text{-}C_5H_4)_2$ (M = Si, Ge, R = Me) are known. The crystal structures of $(CH_2)_xCp_2TiCl_2$ (x = 1,[433] 2,[434] 3[435]) showed that the methylene-bridged complex was highly strained. The ^1H NMR spectra of the *ansa*-titanocene[433] derivatives $(CH_2)_xCp_2TiX_2$ (x = 1, 2, 3; X = Cl, Me, CO) in $CDCl_3$ or C_6D_6 solutions all display an A_2B_2 spin pattern for the Cp protons consisting of two pseudo-triplets.[433] The solid-state molecular structures of the $(CH_2)_x$-bridged complexes revealed that the α positions of each ring were different as were the β positions.[433-435] The spectra were consistent with



$CH_2Cp_2TiCl_2$



$(CH_2)_2Cp_2TiCl_2$

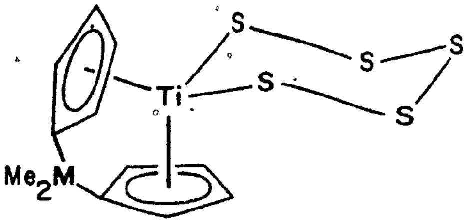


$(CH_2)_3Cp_2TiCl_2$

a rapid back-and-forth twisting motion of the C_5H_4 groups such that the two α positions in each ring became equivalent and similarly for the β positions. To interconvert the mirror images of $(CH_2)_3Cp_2TiCl_2$ both C_5H_4 ring twisting as well as reversal of the six-membered $(CH_2)_3Cp_2Ti$ ring are necessary.[433] Thus, the two pseudo-triplets correspond to the magnetically inequivalent α protons and β protons of both rings.

The magnitude of the separation of these two triplets for complexes with the same bridge length is very sensitive to the other ligands present such as Cl, Me, or CO. Smith et al.[433] concluded, and ^{13}C NMR data support the notion, that the magnitude was due to the degree of shifting of π-electron density from the sterically crowded bridgeheads towards the β positions. In the spectra of $(CH_2)_xCp_2TiX_2$[433] (x = 1-3, X = Cl, Me, CO) and $Me_2MCp_2TiX_2$ (M = Si, Ge; X_2 = Cl_2, S_5)[169] the ^{1}H NMR chemical shift of the high-field multiplet was most dependent on the nature of X. On this basis, and in keeping with the electron polarization model described above, the high-field multiplet was assigned to the β protons.

Köpf and Kahl[169] found that the compounds $Me_2MCp_2TiS_5$ (217) where M = Si and Ge, prepared in low yield from the dichlorides and aqueous $(NH_4)_2S_5$, gave ^{1}H NMR spectra wherein the signals for the axial and equatorial positions of only the β protons were resolved at ca. δ 5.5 and ca. δ 6.2, respectively (Table 7). The large chemical shift difference between the axial β and equatorial β protons (0.6 ppm) was primarily ascribed to the bending back of the C_5H_4 rings; the electronic effect of the Me_2Si substituent was thought to be minor.[436] Resolution of the axial and equatorial β protons is consistent



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with stereochemical rigidity on the NMR time scale at room temperature.

The DNMR study of $CH_2Cp_2TiS_5$ (79) was consistent with rapid TiS_5 ring flipping above room temperature. An average value of $\Delta G^{\ddagger} = 66.5 \pm 0.7$ kJ mol^{-1} was found (Table 7). On the basis of previous assignments the signals in the limiting spectrum at -7.1°C are assigned as follows: δ 6.50 (α, equatorial), δ 6.26 (α, axial), δ 4.61 (β, equatorial), δ 4.22 (β, axial) (Table 7, Fig. 10).

Thus, "tying-back" the Cp rings in Cp_2TiS_5 (73) with a bridging methylene group significantly lowers the energy barrier for TiS_5 ring reversal as compared to that for Cp_2TiS_5. There are probably several factors responsible for this lowering but it is difficult to state which are the most important. Tying-back the rings should decrease the extent of non-bonded interactions between the cyclopentadienyl rings and the sulfur atoms. Ring-carbon to sulfur distances shorter than the van der Waals distance of 3.40 Å[437] have been observed in the X-ray crystal structures of Cp_2TiS_5 (<u>73</u>),[166,167] Cp_2VS_5 (<u>80</u>),[167] and $Cp(PMe_3)CoS_5$ (<u>81</u>).[175] There is a much smaller Cp-Ti-Cp angle in $CH_2Cp_2TiCl_2$ (121°)[433] than in Cp_2TiCl_2 (131°).[438] This results in an increase of the Cl-Ti-Cl angle in $CH_2Cp_2TiCl_2$ (97.2° <u>vs</u>. 94.5°). Attempts at growing single crystals of $CH_2Cp_2TiS_5$ suitable for X-ray crystallographic purposes have been unsuccessful to date. It is not certain what effect tying-back the Cp rings would have on the structure of the TiS_5 ring and how it might lead to the lowering of the barrier for ring flipping.

Thus the introduction of a Me or $SiMe_3$ group into the Cp rings of Cp_2TiS_5 (<u>73</u>) only slightly lowers the barrier to TiS_5 ring reversal. However, tying-back the Cp rings with a CH_2 bridge lowers the barrier by <u>ca</u>. 13 kJ mol^{-1}. The DNMR study of $Cp_2Ti[S(CH_2)_3S]$ (<u>120</u>) led to an estimate of $\Delta G^{\ddagger}$ less than 34 kJ mol^{-1}, a barrier over 45 kJ mol^{-1} lower than that for <u>73</u> (Table 7). It is useful to compare $Cp_2Ti[S(CH_2)_3S]$ to platinum complexes which contain the same ligand. For the complexes $L_2Pt[S(CH_2)_3S]$ where L = PPh_3 and L_2 = dppe a slightly broadened quintet for the central CH_2 protons and a pair of overlapping triplets for the terminal CH_2 protons were observed.[378] This is consistent with the presence of PtS_2C_3 rings which are in rigid chair conformations, giving rise to axial and equatorial orientations for the protons. It is reasonable to expect that $Cp_2Ti[S(CH_2)_3S]$

would display a spectrum in which the signals for the protons of the axial and equatorial Cp ligands were resolved if it was rigid. The observation of only one triplet and one quintet for the CH_2 protons and one singlet for the Cp ligands down to -120°C is in accord with rapid TiS_2C_3 ring reversal occurring above this temperature. Thus, decreasing the sulfur content of the TiS_5 ring by replacing the central S_3 chain with three CH_2 groups lowers the barrier dramatically. However, it is not clear why the titanium complex differs so radically from the platinum complex.

Decreasing the sulfur content of rings of the type $(CH_2)_xS_{6-x}$ where x = 0 to 5 or of the X_3 bridge in the previously described [3]ferrocenophanes also lowered the $\Delta G^{\ddagger}$ for ring reversal (Table 8). The $\Delta G^{\ddagger}$ values for $(CH_2)_xS_{6-x}$ containing progressively longer chains of sulfur atoms have been established (Table 8). The increasing flexibility of the rings with decreasing sulfur content was attributed to the lower torsional barrier about C-S bonds compared to that for S-S bonds (ca. 29 to 50 kJ mol^{-1} in aliphatic disulfides).[443] The barriers to bridge reversal for S_3Cp_2Fe, $S_2CH_2Cp_2Fe$, and $S(CH_2)_2Cp_2Fe$ decreased in the order listed. It was proposed that this trend is probably due to the much higher torsional barrier of the S-S bond (assumed here to be 29.0 kJ mol^{-1})[94] relative to the C-C (15.5 kJ mol^{-1}) and C-S bonds (8.9 kJ

TABLE 8

$\Delta G^{\ddagger}$ Values for Ring Reversal in some Cyclic Polysulfides and [3]Ferrocenophanes

Six-membered Rings of the Type $S_x(CH_2)_{6-x}$

Compound	$\Delta G^{\ddagger\,a}$
$(CH_2)_6$	44.8[b]
$S(CH_2)_5$	39.3[c]
$S_2(CH_2)_4$	48.5[d]
$S_3(CH_2)_3$	55.2[e]
$S_4(CH_2)_2$	61.5[f]
S_5CH_2	>60.0[g]
S_6	125.1[f]

[3]Ferrocenophanes of the Type $S_x(CH_2)_{3-x}Cp_2Fe$

Compound	$\Delta G^{\ddagger\,a,h}$
$(CH_2)_3Cp_2Fe$	40.4
$S(CH_2)_2Cp_2Fe$	34.6
$S_2(CH_2)Cp_2Fe$	47.2
S_3Cp_2Fe	80.1

[a] In units of kJ mol^{-1} measured experimentally by the coalescence temperature method unless otherwise stated.

[b] Ref. 439.

[c] Ref. 440.

[d] Ref. 441.

[e] Ref. 442.

[f] Theoretical value. Ref. 431.

[g] Ref. 179. Theoretical value 72.8 kJ mol^{-1}, ref. 431.

[h] $\Delta G^{\ddagger}$ values calculated by lineshape analysis, ref. 94.

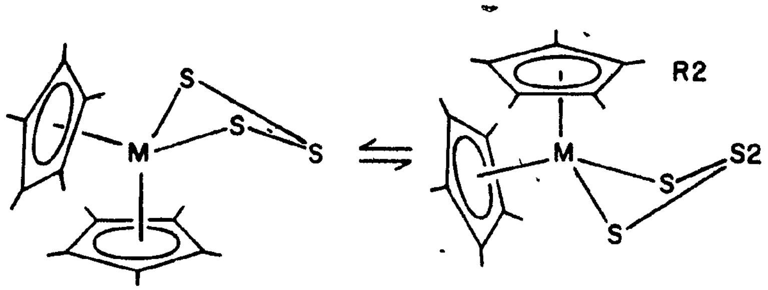
mol^{-1}) in these complexes.[94]

The Complexes $(Me_5Cp)_2MS_3$ (M = Ti, Zr, Hf)

In the title complexes and in the complexes Cp_2MS_5 two dynamic processes can be envisioned, one involving MS_x ring reversal and the other involving C_5 ring rotation. The DNMR studies of these complexes were consistent with the former process occurring at higher energy than the latter. Only for the permethylated complexes at very low temperatures was there evidence for a slowing down of the C_5 ring rotation.

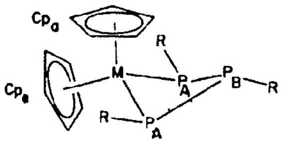
The ^1H NMR spectra of the complexes $(Me_5Cp)_2MS_3$ show a single line at room temperature. This did not change for the hafnium species 49 down to -130°C, but two peaks appeared at low temperatures for the titanium and zirconium complexes 47 and 48, respectively (Figures 11 and 12). The two peaks were unequal in intensity and poorly resolved for 47 at -90°C but were of nearly equal intensity and resolved for 48 at -95°C. Further cooling caused these peaks to collapse possibly due to the slowing of C_5 ring rotation.

In the regime where MS_3 ring flipping is slow the pseudoaxial and -equatorial Me_5Cp rings should appear as two singlets of equal intensity, provided that free rotation of the Me_5Cp rings still occurs. The crystal structure of $(Me_5Cp)_2TiS_3$ (47) (Figures 14 and 15) indicated



a possible steric interaction between the central sulfur atom S2 and the pseudoaxial Me$_5$Cp group R2. This would hinder the rotation of the axial ring more than the equatorial one. In both 47 and 48 the peak to higher field broadens most rapidly with a concurrent reduction in intensity. The onset of broadening of the signals due to the slowing down of C$_5$ ring rotation should occur at a higher temperature for the axial ring than for the equatorial one. On this basis the peak [illegible] higher field is once again assigned to the pseudoaxial Me$_5$Cp ligand. While the barriers to MS$_3$ ring reversal in these complexes are similar (Table 7) the degree of steric hindrance to C$_5$ ring rotation appears to be different. For 47 the broadening of the upfield signal occurs at a much higher temperature than for 48. This observation is consistent with the greater congestion anticipated for the titanium complex because of shorter Me$_5$Cp-M distances expected for M= Ti compared to M = Zr or Hf. Thus the barrier to rotation should be highest for the titanium complex. The ease of rotation of the two rings also depends on their methyl-methyl interactions. The X-ray crystal structure of $(Me_5Cp)_2TiCl_2$ revealed severely crowded Me_5Cp ligands.[444] Nevertheless, the ^1H NMR spectrum of this complex remained as one sharp singlet down to -50°C consistent with "free" rotation, with the Me_5Cp rings interlocked, as in meshed gears.[444] The lack of spectral changes for the complex $(Me_5Cp)_2HfS_3$ (49) is consistent with either a planar HfS_3 ring, which is considered unlikely, or with a barrier to ring reversal less than 30 kJ mol^{-1} (Table 7).

The sort of steric interactions discussed above were proposed in complexes of the type $Cp_2M(PR)_3$ where M = Ti, Zr, Hf and R = alkyl or aryl.[421] Their ^1H NMR spectra consisted of two broad triplets corresponding to the pseudoaxial and pseudoequatorial C_5H_5 ligands, Cp_a and Cp_e, respectively. It was assumed that J(P-H) would be larger for Cp_e than for Cp_a. Thus the one well resolved triplet was assigned to Cp_e and the unresolved one to Cp_a. The



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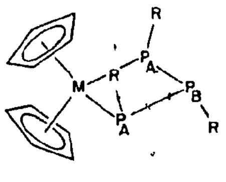

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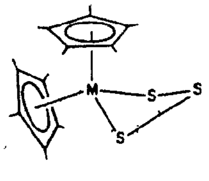
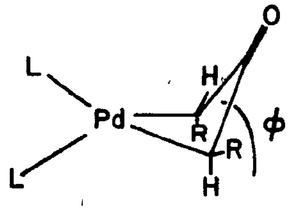


separation as well as the relative positions of these signals varied with the substituent, metal, and temperature. The temperature dependence of the magnitude of the separation was attributed to a variation in the fold-angle (defined as the dihedral angle between the planes P_A-M-P_A and P_A-P_B-P_A) between the extremes <u>218</u> and <u>219</u>.[421] The magnitude of the separation was thought to be dependent upon the degree of interaction between the Cp rings and the phosphorus atom lone pairs. Based on these assumptions, limiting structure <u>218</u> was assumed to prevail for R = Ph. Here the unresolved triplet corresponding to Cp_a appeared upfield from that for Cp_e. This is consistent with the presumed greater interaction of Cp_a with P_B compared to that of Cp_e with the two P_A atoms. When R = <u>t</u>-Bu the MP_3 ring was thought to be flattened as in <u>219</u> such that the interactions would be greatly decreased. Now the positions of the signals were reversed such that the signal for the Cp_a protons appeared downfield from the resolved triplet for the Cp_e protons. It was felt that this was due to a greater reduction in the Cp_a-P_B interaction compared with the Cp_e-P_A interactions.

According to the above model the signal for the pseudoaxial ring in the complexes $(Me_5Cp)_2MS_3$ should also appear at higher field than the pseudoequatorial ring. The more rapid broadening of the higher field peak observed for $(Me_5Cp)_2TiS_3$ (<u>47</u>) and $(Me_5Cp)_2ZrS_3$ (<u>48</u>) is consistent with this model as well.

Many compounds with four-membered rings bend in order to relieve torsional strain at the expense of a small amount of angle deformation.[445] The fold angle and barrier to ring reversal for cyclobutane are 30 ± 6° and ca. 5.9 kJ mol^{-1}, respectively.[446] Replacement of a CH_2 group by an L_2M moiety can profoundly affect the angle. Titanacyclobutanes of the type $Cp_2Ti[CH_2CRR'CH_2]$ are thought to be planar in solution but easily distorted. Theoretical studies have indicated that a similar structure is expected for the zirconium and hafnium analogs.[447] The X-ray crystal structures of the titanium complexes for which R = t-Bu, R' = H; R = Ph, R' = H; and R = R' = CH_3 revealed nearly planar metallacyclic rings.[416] Few measurements of the barrier to MC_3 ring reversal have been reported. The complexes $L_2Pd[CHRC(O)CHR]$ (220, L = PPh_3, $AsPh_3$, bipy; R = CO_2Me) have highly puckered MC_3 rings.[448] Their variable-temperature ^1H NMR spectra were consistent with PdC_3 ring reversal through a planar structure. As the puckering angle ϕ increased from 51.3° (L = bipy) to 52.7° (L = $AsPh_3$) to 54.0° (L = PPh_3) $\Delta G^{\ddagger}$ increased from 40.4 to 44.4 to 50.9 kJ mol^{-1}, respectively. The non-planarity of the PtC_3 ring and short Pd–C(O) distances were thought to indicate an allylic contribution to the bonding as shown in 221.

A structure in which an η-S_3 group rotates about the axis bonding it to the metal is also consistent with



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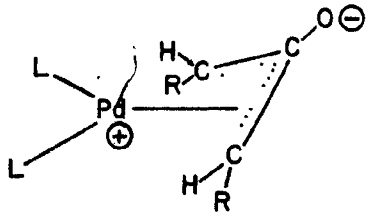

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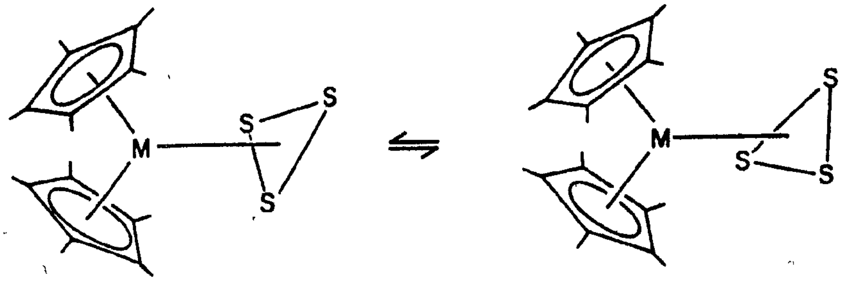
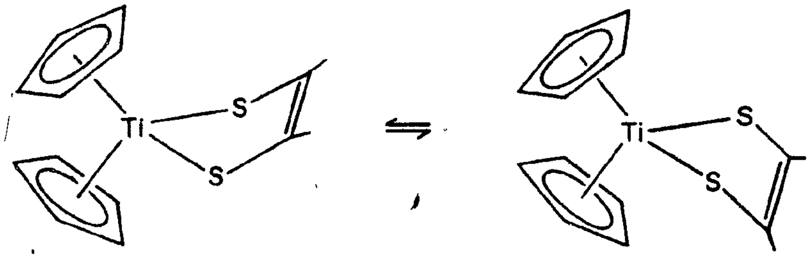
the DNMR data for the complexes $(Me_5Cp)_2MS_3$. The limiting structure is formally an adduct of neutral S_3 with $(Me_5Cp)_2M(II)$ or of the dianion S_3^{2-} with $(Me_5Cp)_2M(IV)$.



In these cases three equal sulfur-sulfur distances might be expected. The observed distances in $(Me_5Cp)_2TiS_3$ (47) (Figure 14, Table 10) are unequal. An intermediate structure might involve $(Me_5Cp)_2M(III)$ and an S_3^- ligand. Derivatives of titanium(II) and titanium(III) are generally paramagnetic. The sharp signals seen for the ^1H NMR spectrum of 47 favour the formulation as a titanium(IV) derivative.[449]

The X-ray crystal structure[104] of $(Me_5Cp)_2TiS_3$ (47) revealed a Ti-S (central) distance of 2.768(3) Å while the other Ti-S bond distances were 2.409(2) Å and 2.417(3) Å (Table 10). The Ti-S (central) distance is shorter than if the ring were planar in which case a distance of about 3.0 Å would be expected. Hence, a weak bonding interaction between the titanium and the central sulfur atom cannot be ruled out. A transannular interaction has also been implicated for the dithiolene complex 149. This molecule is conformationally flexible in solution. A variable temperature ^1H NMR study was consistent with a process involving folding of the TiS_2C_2 ring across the S····S axis *via* a planar transition state.[450] The $\Delta G^{\ddagger}$ for this process was 61.9 kJ mol^{-1}.[450]



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The X-ray crystal structure revealed a non-planar TiS_2C_2 five-membered ring, with a fold angle of 46.1°,[451] remarkably similar to the fold angle of 49° found in $(Me_5Cp)_2TiS_3$ (47).[104] Lauher and Hoffmann[337] found that a bent geometry was essential for a stabilizing interaction via donation from a donor orbital of the $S_2C_2H_2$ ligand to an empty acceptor orbital of the Cp_2Ti fragment. Thus, one can envision a similar donation from the central sulfur to the metal in the complexes $(Me_5Cp)_2MS_3$.

Titanium(III) complexes of the type $Cp_2Ti(\pi$-allyl) have been prepared.[452] The X-ray crystal structure of the η-1,2-dimethylallyl complex revealed an unsymmetrically bonded C_5H_9 ligand with the Ti-C (central) distance of 2.43 Å being greater than the Ti-C (terminal) distances of 2.35 Å. The π-allyl moiety made an angle of 56° with the line joining the center of the ligand with the metal atom.[453] It is interesting to note that the bis(allyl) complex $Cp_2Zr(C_3H_5)_2$ contains one σ-allyl and one π-allyl ligand such that an 18-electron zirconium(IV) species is achieved.[454] Donation of electron density from the central sulfur atom to the metal in the complexes $(Me_5Cp)_2MS_3$ could be a mechanism whereby an 18-electron M(IV) complex results. The barrier to rotation of π-allyl ligands have been measured. For example, the complex $CpMo(CO)_2(\eta-C_3H_5)$ has an activation energy for this process of 51.5 kJ mol^{-1}.[455] Thus, the variable-temperature ^1H NMR results of the complexes $(Me_5Cp)_2MS_3$ are also compatible with rotation of a trisulfane moiety. The data cannot distinguish between MS_3 ring flipping and S_3 group rotation although the former seems more likely.

The Crystal Structures of Cp_2MS_5 (M = Ti, Zr, Hf)

Although the crystal structures of many cyclopentadienyl-titanium compounds have been determined, comparatively few zirconium and hafnium species have been so studied. A few complete series in which the metal varies but the ligands remain the same have been examined. Notable examples of such series include the bis(η^5-indenyl) complexes $(\eta^5\text{-}C_9H_7)M(CH_3)_2$,[456] the dicarbonyls $Cp_2M(CO)_2$ (M = Ti,[457] Zr,[458] Hf [459]) and $(Me_5Cp)_2M(CO)_2$,[460] and the trimethylene-bridged complexes $(CH_2)_3Cp_2MCl_2$ (M = Ti,[434,435] Zr,[461] Hf [462]). The X-ray structures of the complexes Cp_2MS_5, where M = Ti (73),[166,167] Zr (75),[405,463] and Hf (76)[405,463] revealed that all three were isostructural, each containing a MS_5 ring in a chair conformation (Figure 13). Furthermore, the crystals of 75 and 76 were isomorphous with the crystal of 73 studied by Epstein et al.[166] A different crystalline modification of 73 has been examined by Muller et al.[167] Differences in structural parameters of the three molecules can be ascribed to differences in molecular structure rather than to packing forces in the isomorphous crystals. Details of the crystal structures of 75 and 76 and a comparison with the published structures of 73 have been reported elsewhere.[463] The more important parameters relevant to this thesis are mentioned below and are listed in Table 9. The volume of the unit cells followed the order Ti < Hf < Zr. This order was also

Figure 13. Perspective drawing of Cp_2MS_5 (M = Ti, Zr, Hf).

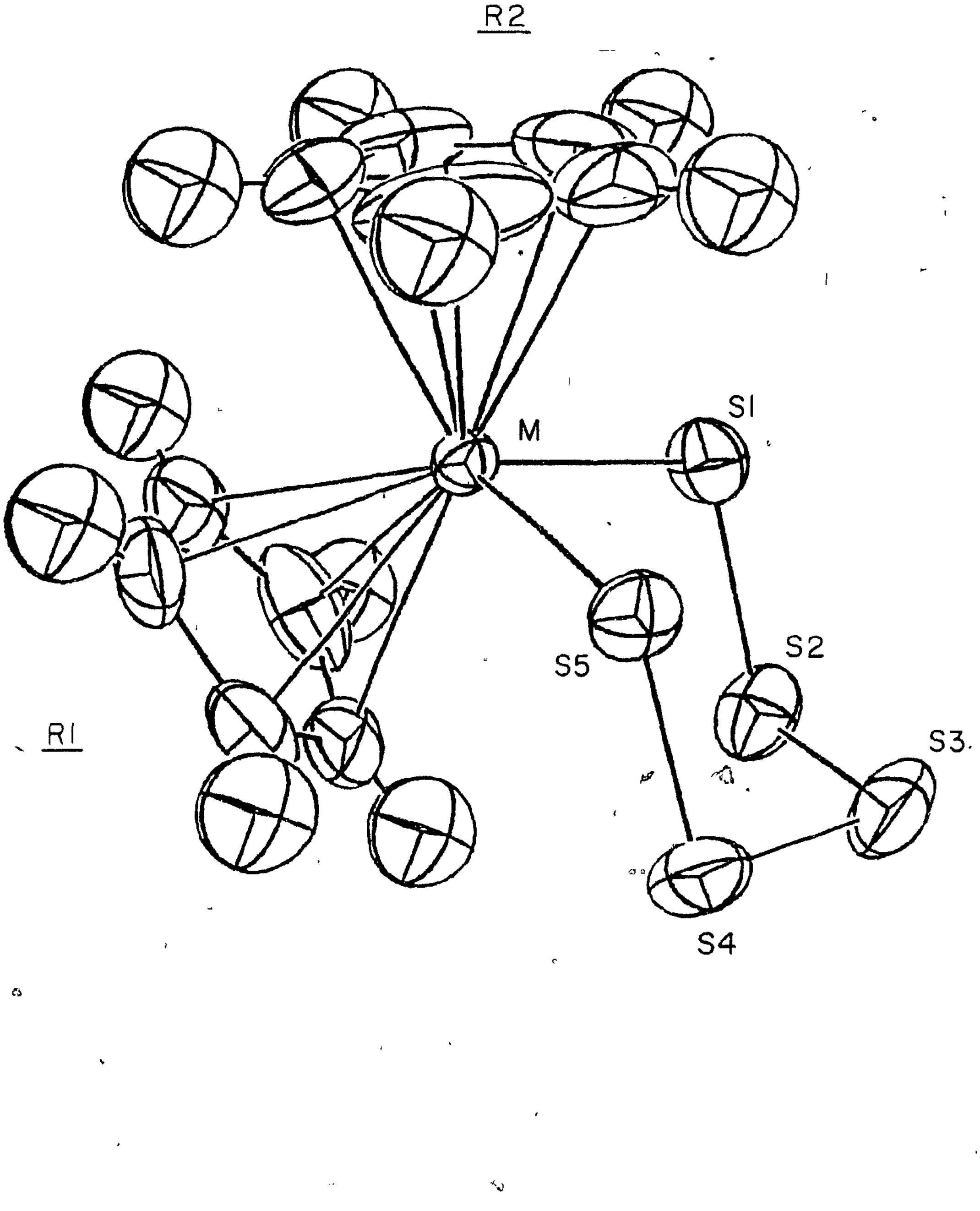
R2
M
S1
S2
S3.
S4
S5
R1

TABLE 9

Selected Bond Distances, Non-bonding Distances, Bond Angles, and Dihedral Angles for Cp_2MS_5 [M = Ti (73),[166] Zr (75),[405] Hf (76)[405]]

Bond Distances (Å)

	73	75	76		73	75	76
M-S1	2.4483(14)	2.544(1)	2.523(2)	S1-S2	2.0590(17)	2.059(1)	2.068(3)
M-S5	2.4219(11)	2.5265(1)	2.501(1)	S2-S3	2.0556(16)	2.048(1)	2.042(3)
Avg.	2.435	2.535	2.512				
M-R1	2.066	2.216	2.190	S3-S4	2.0665(18)	2.057(1)	2.062(3)
M-R2	2.071	2.206	2.118	S4-S5	2.0586(15)	2.057(1)	2.063(2)
				Avg.	2.060	2.055	2.059

Bond Angles (°)

	73	75	76		73	75	76
S1-M-S5	94.59(4)	97.77(3)	96.75	R1-M-R2	133.7	131.27	131.52
M-S1-S2	107.41(6)	102.69	103.71	R1-M-S1	110.7	111.66	111.47
M-S5-S4	108.58(5)	103.65	104.66	R1-M-S5	110.7	111.22	111.45
S1-S2-S3	105.24(6)	106.67(4)	106.17	R2-M-S1	100.5	100.43	101.36

TABLE 9 - cont'd

Bond Angles (°)

	73	75	76		73	75	76
S3-S4-S5	102.68(7)	104.18(5)	103.83	R2-M-S5	99.6	99.10	98.48
S2-S3-S4	106.71(7)	106.99(5)	106.79				

Non-bonding Distances (Å)

M•••S2	3.64	3.61	3.59	S1•••S5	3.580	3.819	3.756
M•••S4	3.64	3.61	3.62	S2•••S4	3.31	3.30	3.29
M•••S3	4.19	4.14	4.16				

Dihedral Angles (°)

S1-M-S5/ S1-S2-S4-S5	58	61	60	S1-S2-S4-S5/ S2-S3-S4	72	74	73

observed for the isostructural and isomorphous complexes $(\eta^5\text{-}C_9H_7)_2M(CH_3)_2$ (M = Ti, Zr, Hf) and has been attributed to the lanthanide contraction effect.[456] The covalent radius of titanium in a $Cp_2Ti(IV)$ complex has been estimated to be 1.43 Å.[464] The covalent radius of sulfur is 1.03 Å.[22] Hence a typical Ti-S single bond length may be calculated to be 2.46 Å; the observed average value of 2.435 Å in 73 is close to this value. The radius of the Ti^{4+} ion is about 0.12 Å smaller than those for the Zr^{4+} and Hf^{4+} ions. The M-S and M-Cp distances in Cp_2TiS_5 are smaller by about this amount.[463] The non-bonded transannular sulfur-sulfur distances S1···S5 follow the order Ti < Hf < Zr, consistent with the trend in the S1-M-S5 angles. However, the S2···S4 distances are nearly the same. The "end-to-end" M···S3 distances in the zirconium and hafnium complexes are slightly shorter than for the titanium complex by 0.05 Å and 0.03 Å, respectively (Table 9). In all three molecules the atoms S1, S2, S4, and S5 are nearly coplanar. The dihedral angles* for the pairs of planes S1MS5/S1S2S4S5 and S1S2S4S5/S2S3S4 are similar (Table 9) and indicate similar MS_5 ring shapes. The shortest S-S bond length is the S2-S3 bond in all three compounds. Although the S1-S2 and S4-S5 bond lengths are equal within experimental error in 73, 75, and 76, the two

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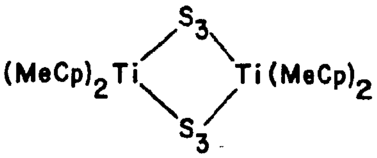
*The author thanks Dr. P. Bird, Concordia University, for calculating these angles.

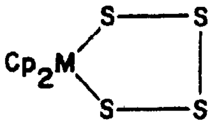
M-S bonds and the central S2-S3 and S3-S4 bonds are unequal in length. In each case the longer M-S1 bond is opposite the longer S3-S4 bond, and the shorter M-S5 bond lies opposite the shorter S2-S3 bond. Unequal Ti-S distances were also found for $Cp_2Ti(SPh)_2$ (<u>118</u>)[397] which are on average shorter (2.410 Å) than the average Ti-S distance in <u>73</u> (Table 9). The inequality of S-S bond lengths found in <u>73</u>, <u>75</u>, and <u>76</u> was also observed in Cp_2VS_5 (<u>80</u>)[167] and in Cp_2WS_4 (<u>59</u>).[136] The salts $M_2'S_5$ (M' = NH_4,[150] K,[151] Rb,[152] Tl[153]) which contain discrete S_5^{2-} chains, also displayed a variation in bond lengths. For the rubidium salt the two inner bond lengths were 2.054(8) Å and 2.109(7) Å, and the two outer bond lengths were 2.019(7) Å and 2.036(8) Å with the longest S-S bond adjacent to the shortest S-S bond. The S-S bonds in the Cp_2MS_5 molecules, with the exception of the short S2-S3 bonds, are all longer than those found in Rb_2S_5. Cyclohexasulfur, S_6, crystallizes in the chair conformation with all S-S bond lengths equal at 2.068(2) Å.[182] This distance is marginally greater than the average S-S distances of 2.060, 2.055, and 2.059 Å in <u>73</u>, <u>75</u>, and <u>76</u>, respectively. The S-S-S angles are larger in the Cp_2MS_5 molecules than those in S_6 [102.61(6)°].[182] Overall, the geometries of the MS_5 rings in the Cp_2MS_5 complexes are quite similar, especially for the Zr and Hf pair.

The X-ray Crystal Structure of $(Me_5Cp)_2TiS_3$ (47)

Organometallic compounds containing a chelating trisulfide ligand have hitherto not been reported. Hence, it was of interest to compare the X-ray crystal structure of $(Me_5Cp)_2TiS_3$ (47)[104,465] (Figure 14) to those found for $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46),[103] Cp_2TiS_5 (73)[166,167] (Figure 13), and Cp_2MS_4 [M = Mo (58),[133] W (59)[136]]. The crystal lattice consists of discrete molecules of 47 with the chelating S_3^{2-} and two Me_5Cp^- ligands arranged in a distorted tetrahedral fashion around each titanium atom (Figures 14 and 15). The structural parameters of 47 (Table 10) are compared with analogous features of 46 and 73 in Table 11. Of these three complexes, 47 has the largest ring-Ti-ring angle and the smallest S-Ti-S angle.



46



58 M = Mo
59 M = W

It has been noted elsewhere[438] that an expansion of the centroid-metal-centroid angle often leads to a reduction in the X-metal-X angle. This was observed in the homoleptic series Cp_2MS_5 (M = Ti, Zr, Hf). The larger centroid-Ti-centroid angle found in 47 is undoubtedly due

Figure 14. Perspective drawing of $(Me_5Cp)_2TiS_3$ (47).

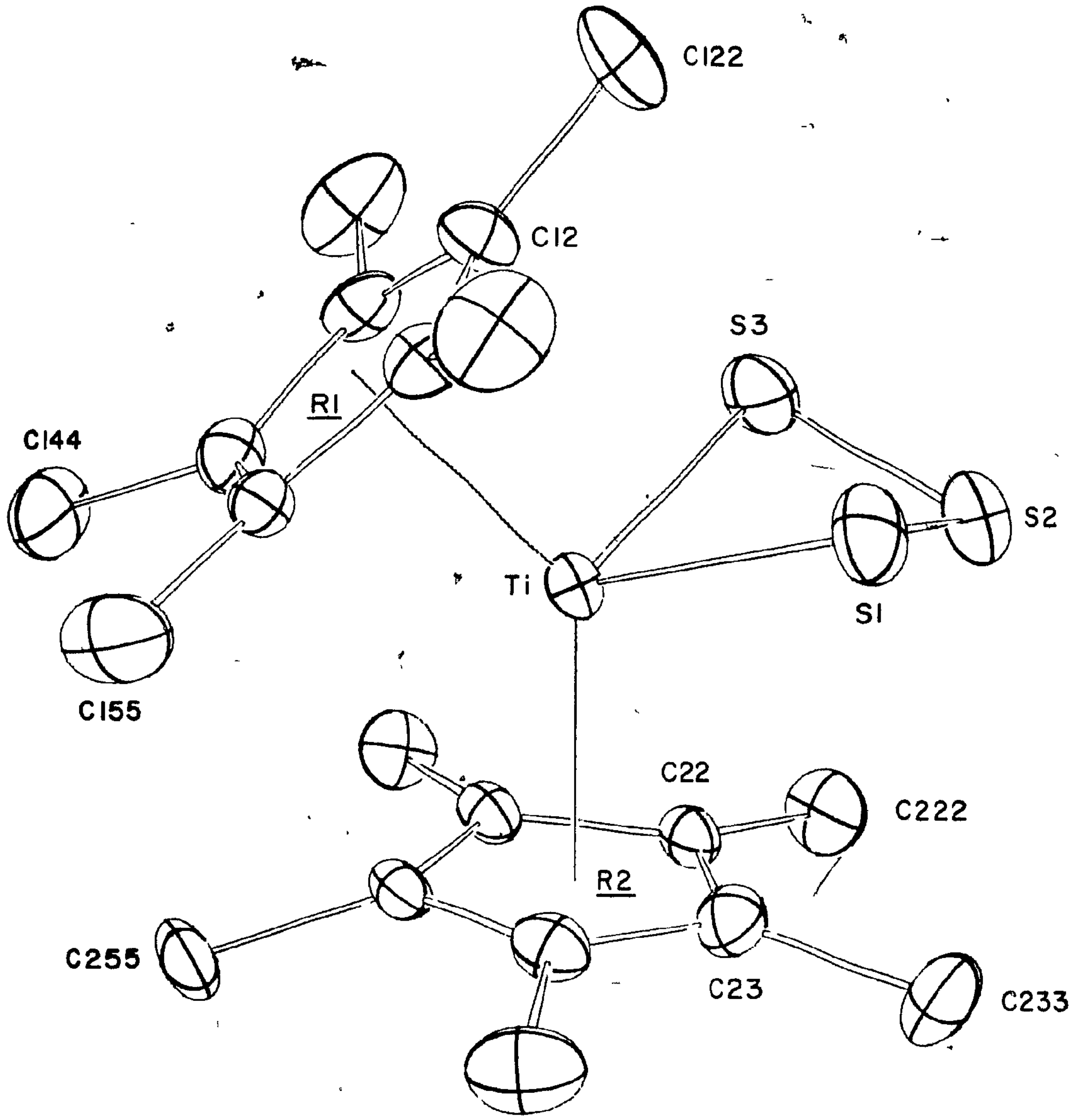

C122
C12
S3
R1
C144
S2
Ti
S1
C155
C22
C222
R2
C255
C23
C233

Figure 15. Perspective drawing of $(Me_5Cp)_2TiS_3$ (47) viewed down the Ti-R2 axis. Some methyl groups have been removed for clarity.

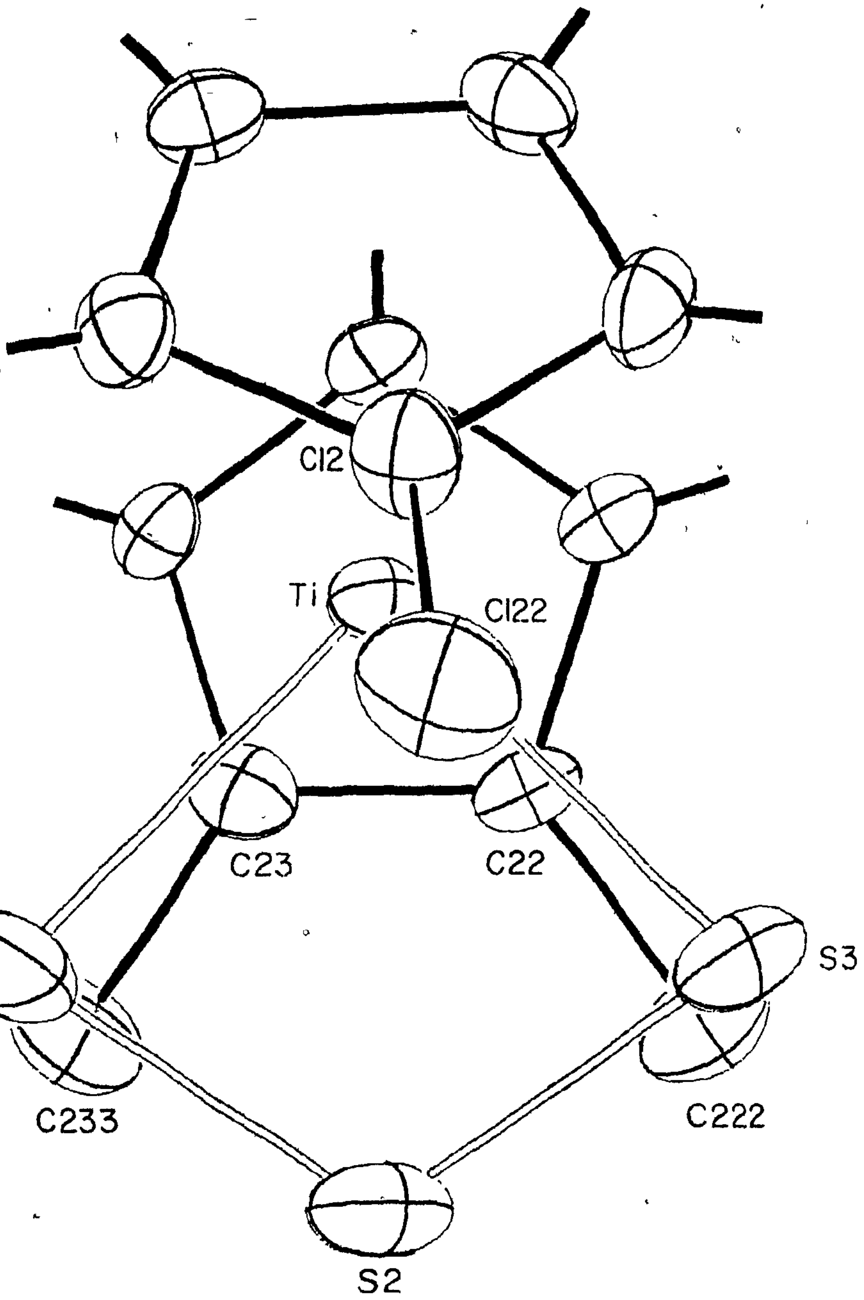

Cl2
Ti
Cl22
C23
C22
S1
S3
C233
C222
S2

TABLE 10

Selected Bond Distances, Non-bonding Distances, Bond Angles, and Dihedral Angles for $(Me_5Cp)_2TiS_3$ (47)[104,465]

Bond Distances (Å)

Ti—S1	2.409(2)	Ti—R1	2.129(1)	S1—S2	2.052(4)
Ti—S3	2.417(3)	Ti—R2	2.139(1)	S2—S3	2.029(3)
Ti···S2	2.768(3)			S1···S3	3.244(3)

Bond Angles (°)

S1-Ti-S3	84.44(9)	R1-Ti-S1	103.08(4)	R1-Ti-R2	136.85(3)
Ti-S1-S2	76.23(10)	R1-Ti-S3	102.08(5)		
Ti-S3-S2	76.44(9)	R2-Ti-S1	109.70(4)		
S1-S2-S3	105.27(12)	R2-Ti-S3	108.20(5)		

Dihedral Angles (°)

S1-Ti-S3 / S1-S2-S3	49°

TABLE 11

Comparison of Distance (Å) and Angle (°) Averages of $(Me_5Cp)_2TiS_3$ (47)[104] with those of $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46)[103] and Cp_2TiS_5 (73)[166]

	47	46	73
Distances			
Ti—S	2.413	2.425	2.435
S—S	2.041	2.056	2.060
Ti—Ring[a]	2.134	2.063	2.069
S···S[b]	3.244(3)	c	3.580
Angles			
Ring[a]-Ti-Ring[a]	136.85(3)	132.6(2)	133.7
S-Ti-S	84.44(9)	96.08(3)	94.59(4)
S-S-S	105.3(1)	109.07(6)	104.9

[a] Ring denotes the η-C_5H_5, η-C_5H_4Me, or the η-C_5Me_5 ligand as appropriate.

[b] "Bite" distance of the S_3 chain across the S-Ti-S angle.

[c] Not reported.

to the steric crowding of the permethylated cyclopentadienyl rings. A similar change was observed for Cp_2TiCl_2 (Cp-Ti-Cp angle 130.92°, Cl-Ti-Cl angle 94.54°)[438] and $(Me_5Cp)_2$-$TiCl_2$ (with corresponding angles 137.4° and 92.94°, respectively).[444] The crystal structures of $(Me_5Cp)_2TiCl_2$[444] and $(Me_5Cp)CpTiCl_2$[466] revealed staggered, planar π-bonded C_5 rings with the methyl groups bent out of the C_5 plane away from the metal atom [up to 0.49 Å out of plane for $(Me_5Cp)_2TiCl_2$ and 0.04-0.11 Å for $(Me_5Cp)CpTiCl_2$]. Similar features were found for <u>47</u>.[465] In the complexes <u>47</u>, $(Me_5Cp)CpTiCl_2$, and $(Me_5Cp)_2TiCl_2$ the maximum deviation occurs with the "backside" methyl groups (e.g., C144, C155, and C255 in <u>47</u>). Methyl-methyl and methyl-X (X = Cl or S, where appropriate) repulsions have been suggested as the cause of the deviations.[444] Significantly, the central sulfur atom S2 in <u>47</u> is oriented towards the space between the methyl groups on carbon atoms C22 and C23 (Figure 15). Steric interaction between S2 and the pseudoaxial ring R2 may contribute to the lengthening of the Ti-R2 distance relative to the Ti-R1 distance (Table 10) and to the greater R2-Ti-S(x) angles (x = 1,3) compared to the corresponding angles for the pseudoequatorial ring R1 (Table 10). In Cp_2TiS_5 (<u>73</u>) as well as in the zirconium and hafnium analogs the Cp(axial)-Ti-S(x) (x = 1 and 5) angles are about 10° greater than the Cp (equatorial)-Ti-S(x) angles. In <u>47</u>, this is reduced to about a 6° difference (see Tables 9 and 10). For 73 the cause of this tilting of the Cp_2Ti moiety relative to the S1-Ti-S5 plane was attributed to close non-bonding contacts between the axial ring and the two sulfur atoms S2 and S4.[167] The S1-Ti-S3 bond angle in 47 of 84.44(9)° is much smaller than the corresponding value of 99.3(3)° found in $Cp_2Ti(SPh)_2$[397] and 94.59(4)° found in 73.[166] It is quite close, however, to the S-Mo-S angle of 88.2(2)° found for Cp_2MoS_4 (58).[133] The Cp-metal-Cp angles in 58 and 47 are similar at 134° and 136.85(3)°, respectively. The S1···S3 "bite" distance of 3.244(3) Å in 47 is much shorter than the 3.580 Å value found for 73[167] which is close to the van der Waals distance of 3.60 Å for two sulfur atoms.[437] In both 47 and 73 the Ti-S bond lengths are unequal. A similar inequality was observed for $Cp_2Ti(SPh)_2$ which does not contain a TiS_x ring. The sulfur-sulfur bond lengths are different in 47, $[(MeCp)_2Ti(\mu\text{-}S_3)]_2$ (46), and 73 but the shortest on average occur in 47 at 2.041 Å (Table 11). In comparison, the S-S bond length in S_6 is 2.068(2) Å.[182] The shorter S-S bonds in 73 led to the suggestion of a degree of multiple bonding in these bonds.[166] Both the mean S-S bond distance and the S-S-S bond angle of 47 are close to those values found for the alkali metal trisulfides MS_3, where M = Ba,[36] Sr,[37] Na.[81] The parameters for these salts range from ca. 2.05 Å to 2.08 Å and 106.5° to 114.9°, respectively.

Although the transannular Ti···S2 distance is longer than the Ti-S bonding distances in 47 some interaction between these atoms as discussed earlier cannot be ruled out. The fold angle across the line connecting S1 with S3 in 47 (i.e., the dihedral angle between the planes defined by S1-Ti-S3 and S1-S2-S3) is 49°. In 73 the sulfur atoms S1, S2, S4, and S5 are coplanar. The fold angle across the S1···S5 axis [i.e., the dihedral angle between the planes defined by S1-Ti-S5 and S1-S2-S4-S5 (Figure 13)] is 58.1°.[166] The folding of the TiS_3 ring in 47 may be a mechanism whereby both torsional strain and angle strain are relieved in the molecule. The possible bonding interaction discussed above could also contribute to the degree of folding.

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

1) An improved route to the complex $Cp_2Ti(SH)_2$ was found and the new complexes $Cp_2Zr(SH)_2$ and $(Cp_2ZrS)_2$ were prepared.

2) Treatment of these bis(hydrosulfido) compounds with transfer reagents of the type $>N-S_x-N<$, where $>N$ = benzimidazolyl, phthalimidyl and $x = 1, 2$, gave the metallacyclohexasulfanes Cp_2MS_5. Anhydrous lithium polysulfide solutions prepared <u>in situ</u> reacted with the dichloro species Cp_2MCl_2 to form the Cp_2MS_5 complexes where M = Ti, Zr, and Hf. The complexes Cp_2MSe_5 were also prepared in the same way. Thus the tendency to form an ME_5 ring is characteristic of the Cp_2M residue and is not affected by the preparative route.

3) The compounds Cp_2ME_5, where M = Zr, Hf and E = S, Se are new.

4) The energy barriers to ME_5 ring reversal in the complexes Cp_2ME_5, where M = Ti, Zr, Hf and E = S, Se, follow the order Ti > Hf > Zr and Se > S. The complexes $(MeCp)_2TiS_5$ and $(Me_3SiCp)_2TiS_5$ have slightly lower barriers than Cp_2TiS_5. However, the new methylene-bridged compound $CH_2Cp_2TiS_5$ has a much lower barrier. The complex (Me_5Cp)-$CpTiS_5$ is stereochemically rigid up to 124°C.

5) The permethylated complexes $(Me_5Cp)_2MCl_2$ reacted with anhydrous solutions of lithium polysulfides

containing excess sulfur to give the novel metallacyclotetrasulfanes $(Me_5Cp)_2MS_3$. These are the first complexes to contain a chelating S_3^{2-} ligand. The barriers to ring reversal follow the order Ti ≃ Zr ≫ Hf and are much smaller than those for the Cp_2MS_5 complexes.

6) The complex $Cp_2Ti(SH)_2$ reacted with thiolato-transfer reagents of the type >NSR, where >N = phthalimidyl, R = $CHMe_2$, $4-C_6H_4Me$, and >N = succinimidyl, R = Ph, to give the new polysulfanes $Cp_2Ti(S_2R)_2$ when R = $CHMe_2$ and $Cp_2Ti(SR)(S_3R)$ when R = Ph and $4-C_6H_4Me$. The former is the first example of a compound containing two disulfano ligands, RS_2^-. The latter are the first examples of complexes bearing the MS_3R linkage.

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