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The Chemistry of Cyclopentadienyl Ruthenium Disulfanes, 2-Oxodisulfanes and 2-Dioxodisulfanes

by Darlene Trojansek

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

Deparment of Chemistry
McGill University
Montreal, Quebec
Canada

March, 1995

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To my parents

The Chemistry of Cyclopentadienyl Ruthenium Disulfanes, 2-Oxodisulfanes and 2-Dioxodisulfanes

Ph.D. Darlene Trojansek Chemistry

ABSTRACT

The complexes $CpRu(CO)_2SR$ ($Cp = \eta^5$-cyclopentadienyl; $R = 4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$) insert sulfur from S_8 to give $CpRu(CO)_2S_xR$ ($x = 1\text{-}3$) and undergo ligand exchange with R'_2S_y ($y = 2,3$) to give $CpRu(CO)_2S_xR'$ ($x = 1\text{-}3$). The mechanisms of these reactions are discussed. Treatment of $CpRu(CO)_2SH$ with the appropriate phthalimide sulfur transfer reagents REphth (phth = phthalimide; E = SS, SS(O); $R = 4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$) gave $CpRu(CO)_2ER$. The complexes $CpRu(CO)_2SSR$ undergo sulfur redistribution in solution to give $CpRu(CO)_2S_xR$ ($x = 1\text{-}3$) and insert sulfur from S_8 to give $CpRu(CO)_2SSSR$. The complexes $CpRu(CO)_2SS(O)R$ undergo spontaneous oxygen transfer in solution to form $CpRu(CO)_2SSR$ and $CpRu(CO)_2SS(O)_2R$. The reaction of $CpRu(CO)_2ER$ (E = S, SS, SS(O)) with PPh_3 in ambient light gave $CpRu(PPh_3)(CO)SR$. The complexes $CpRu(L)(CO)SS(O)_2R$ were prepared by oxidation of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ with $NaIO_4$ ($L = PPh_3$) and reaction of $CpRu(CO)_2SH$ with $RS(O)_2Cl$ ($L = CO$; $R = 4\text{-}C_6H_4Me$, C_6H_5). The reaction of $CpRu(CO)_2SS(O)_2R$ with PPh_3 gave $CpRu(PPh_3)(CO)SS(O)_2R$. The x-ray structures of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ were determined. Oxidation of $CpRu(PPh_3)(CO)SS(O)\text{-}4\text{-}C_6H_4Me$ by dimethyldioxirane (DMDO) gave $CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}4\text{-}C_6H_4Me$ which was immediately hydrolyzed by trace amounts of H_2O to give $CpRu(PPh_3)(CO)S(O)_3H$. Cyclic voltammetry (CV) studies of $CpRu(CO)_2ER$ (E = S, SS, SS(O), $SS(O)_2$) were performed. All of these complexes undergo irreversible sulfur-based oxidations.

La Chimie des Complexes Cyclopentadiényl Ruthénium Contenant Ligand des Disulfurés, 2-Oxodisulfurés et 2-Dioxodisulfurés

Ph.D. Darlene Trojansek Chemistry

RESUME

Les complexes $CpRu(CO)_2SR$ ($Cp = \eta^5$-cyclopentadiényl; R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) réagissent avec S_8 pour en transférer du soufre et donner $CpRu(CO)_2S_xR$ (x = 1-3). Ils échangent aussi un ligand avec R'_2S_y (y = 2,3) pour donner $CpRu(CO)_2S_xR'$ (x = 1-3). Les mécanismes de ces réactions sont discutés. Le choix approprié d'un agent de transfert de soufre à base de phthalimide REphth (phth = phthalimide; E = SS, SS(O); R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) permet de transformer $CpRu(CO)_2SH$ en $CpRu(CO)_2ER$. En solution, les complexes $CpRu(CO)_2SSR$ subissent une redistribution du soufre pour donner $CpRu(CO)_2S_xR$ (x = 1-3). Ils peuvent également transférer du soufre de S_8 pour donner $CpRu(CO)_2SSSR$. En solution, les complexes $CpRu(CO)_2SS(O)R$ réagissent spontannement pour transférer un oxygène et donner $CpRu(CO)_2SSR$ et $CpRu(CO)_2SS(O)_2R$. La réaction de $CpRu(CO)_2ER$ (E = S, SS, SS(O)) avec PPh_3, à la lumière ambiante, donne $CpRu(PPh_3)(CO)SR$. Les complexes $CpRu(L)(CO)SS(O)_2R$ ont été préparés soit par l'oxydation de $CpRu(PPh_3)(CO)SS(O)CHMe_2$ avec $NaIO_4$ (L = PPh_3) ou par la réaction de $CpRu(CO)_2SH$ avec $RS(O)_2Cl$ (L = CO; R = 4-C_6H_4Me, C_6H_5). La réaction de $CpRu(CO)_2SS(O)_2R$ avec PPh_3 donne $CpRu(PPh_3)(CO)SS(O)_2R$. Les structures des complexes $CpRu(CO)_2SS(O)C_6H_5$ et $CpRu(CO)_2SS(O)_2C_6H_5$ ont été confirmées par diffraction des rayons-x. L'oxydation de $CpRu(PPh_3)(CO)SS(O)$-4-C_6H_4Me par le diméthyldioxirane (DMDO) donne $CpRu(PPh_3)(CO)S(O)_2S(O)_2$-4-$C_6H_4Me$ qui est immédiatement hydrolysé par des traces de H_2O pour donner $CpRu(PPh_3)(CO)S(O)_3H$. Les complexes $CpRu(CO)_2ER$ (E = S, SS, SS(O), $SS(O)_2$)

ont été étudiés par voltampérométrie cyclique (CV). Tous montrent une oxydation irréversible a l'atome de soufre.

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General Abbreviations

Cp	η^5-cyclopentadienyl
$CH_2C_6H_5$	benzyl
C_3H_7	*n*-propyl
$CHMe_2$	*i*-propyl
$4\text{-}C_6H_4Me$	*p*-tolyl
phth	phthalimide
C_6H_5	phenyl
R	organic group
Me	methyl
Et	ethyl
Bu	butyl
M	transition metal
THF	tetrahydrofuran
DMDO	dimethyldioxirane
m-CPBA	*meta*-chloroperbenzoic acid
Å	Ångström (1 Ångström = 10^{-10} m)
e	electron
CV	cyclic voltammetry
NMR	nuclear magnetic resonance
IR	infrared
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Anal.	elemental analysis
Calcd.	calculated
FAB	fast atom bombardment

Abbreviations used in NMR

TMS	tetramethylsilane
s	singlet
d	doublet
t	triplet

sept	septet
m	multiplet
J	coupling constant
Hz	Hertz
ppm	part per million

Abbreviations used in IR

br	broad
m	moderate
s	strong
sh	shoulder
w	weak
ν	frequency

Abbreviations used in CV

br	broad
CVs	cyclic voltammograms
E	potential
GCE	glassy carbon electrode
Fc/Fc^+	ferrocene/ferrocinium
NHE	normal hydrogen electrode
SCE	saturated calomel electrode
I	current
V	volt
w	small
ν	sweep rate

LIST OF COMPOUNDS

Formula	R-group	Label
$CpRu(CO)_2SR$	H	**3**
	$4\text{-}C_6H_4Me$	**11a**
	C_6H_5	**11b**
	$CH_2C_6H_5$	**11c**
$CpRu(CO)_2SSR$	$4\text{-}C_6H_4Me$	**12a**
	C_6H_5	**12b**
	$CH_2C_6H_5$	**12c**
$(\mu\text{-}S_3)(CpRu(CO)_2)_2$		**4**
$CpRu(CO)_2SSSR$	$4\text{-}C_6H_4Me$	**13a**
$CpRu(CO)_2SS(O)R$	$4\text{-}C_6H_4Me$	**20a**
	C_6H_5	**20b**
	$CH_2C_6H_5$	**20c**
$CpRu(CO)_2SS(O)_2R$	$4\text{-}C_6H_4Me$	**19a**
	C_6H_5	**19b**
$CpRu((PPh_3)(CO)SS(O)_2R$	$CHMe_2$	**21**
$CpRu((PPh_3)(CO)S(O)_2S(O)_2R$	$4\text{-}C_6H_4Me$	**22**

Chapter 1.

General Introduction

1.1 Sulfur and its Sources

Sulfur is an element with a long history dating back to the first book in the Bible, Genesis, where it is referred to as "brimstone".[1] Sulfur which originated below the earth's crust is found in large quantities near active and extinct volcanoes in addition to hot springs all around the world.[2] One of the largest sources of sulfur is the salt domes around the Gulf of Mexico.[3] It is also found in sedimentary deposits as both sulfate salts such as anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$), and also as sulfides such as pyrites (FeS_2). All of these sources are substantial as sulfur accounts for 0.05% of the earth's crust. Sulfur also occurs in nature as H_2S and SO_2 in significant amounts, partially as a consequence of the large scale industrial desulfurization of petroleum fuels. H_2S gas is also produced in large amounts from the reduction of sulfate by microorganisms, and by the burning of coal which contains large amounts of metal sulfides.

Sulfur is essential to life and is a minor constituent of fats, body fluids and skeletal minerals.[2] The largest use of sulfur is for the production of sulfuric acid,[4] the most important manufactured chemical. Almost 80% of the sulfur mined in the world is transformed into sulfuric acid.[5] Sulfur is also used in the vulcanization of natural rubber, in crop dusting as a fungicide, and used extensively in making phosphate fertilizers.[2]

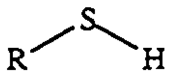
SO_2 is a major component in atmospheric air pollution. It has many sources including H_2S which is rapidly converted to SO_2 in the atmosphere[6] (Equation 1.1). Another source of SO_2 is from the combustion of pyrite, FeS_2, in coal used primarily for power generation[6] (Equation 1.2). Levels of SO_2 in the atmosphere as low as 1.3 ppm have been implicated as a cause of death in humans by irritation to the respiratory tract. Once in the atmosphere, SO_2 is converted to H_2SO_4, sulfuric acid, by the overall photochemical reaction[6] shown in Equation 1.3. The atmospheric H_2SO_4 is deposited in the earth's water system as rain, resulting in increased acidity of fresh water lakes and detrimental effects on some animals and vegetation in these water systems. From this environmental perspective, the incentive to decrease SO_2 emissions from industrial processes is great.

$$H_2S + {}^3\!/_2\,O_2 \longrightarrow SO_2 + H_2O \qquad (1.1)$$

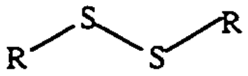
$$4\,FeS_2 + 11\,O_2 \longrightarrow 2\,Fe_2O_3 + 8\,SO_2 \qquad (1.2)$$

$$SO_2 + {}^1\!/_2\,O_2 + H_2O \xrightarrow{h\nu} H_2SO_4 \qquad (1.3)$$

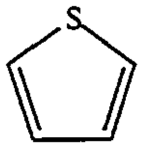
Western Canadians living in Alberta and British Colulmbia have become accustomed to the yellow mountains of elemental sulfur that line their skylines. These account for a large amount of the world's supply of sulfur. It originates from crude petroleum and natural gas. The sulfur in the crude oil and gas exists as mixtures of organic mercaptans (thiols), diaryl and dialkyl disulfides, and thiophenes. The sulfur must be removed from the crude petroleum fuels because it will poison the precious-metal catalysts that are used in reforming reactions in refineries. In addition, these organic mercaptans and sulfides are extremely malodorous. Finally, the atmospheric pollution caused by SO_2 produced during the combustion of petroleum-based fuels is no longer accepted in our environmentally conscious world.



thiol



disulfide



thiophene

The desulfurization of organosulfur compounds in the petroleum industry is accomplished via the heterogeneous catalytic hydrodesulfurization (HDS) reaction. In this process, sulfur is removed from organosulfur compounds in petroleum-based feed stocks by treatment with hydrogen gas at 400°C over molybdenum or tungsten catalysts supported on alumina[7] (Equation 1.4).

$$C_xH_yS + 2\,H_2 \xrightarrow[\text{catalyst}]{400^\circ C} C_xH_{y+2} + H_2S \qquad (1.4)$$

The hydrogen sulfide produced by the HDS process is extremely poisonous and in high concentration can cause death by respiratory paralysis.[4] However, it can be converted to harmless sulfur and water by means of the Claus Process (Equation 1.5). This reaction is a heterogeneous catalyzed process which is typically done over an alumina-based catalyst. Initially, some H_2S is partially oxidized to SO_2 and these two compounds then react together to give elemental sulfur and water.

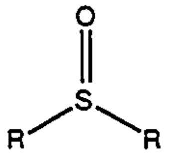
$$2\,H_2S + SO_2 \xrightarrow[\text{catalyst}]{\text{high temperature}} {}^3/_8\,S_8 + 2\,H_2O \qquad (1.5)$$

This process is efficient but considering the huge tonnage scale at which these reactions are performed, even a small amount of inefficiency will give a tremendous amount of unwanted sulfur-based contaminants.[8] These byproducts may poison the catalyst or be released into the atmosphere as environmentally unacceptable pollutants.[2] Although the reactions occurring in this process are poorly understood,[8,9] it is known that interaction of oxidized sulfur species on the surface of the catalyst leads to the formation of S-S bonds and is accompanied by oxygen transfer. One approach of organometallic chemists towards understanding this process is to model these reactions using homogeneous reactions involving transition metal complexes of sulfides, mercaptans and their oxidized derivatives.[10-13] Subsequently, the results of studies into the chemistry of certain oxidized sulfur ligands can be used to formulate possible mechanisms to explain the Claus Process. The overall Claus Process involves the oxidation of two sulfur atoms (H_2S) and the reduction of one sulfur atom (SO_2) to give sulfur chain growth or catenation. Thus, any process on a transition metal that mimics these events is of interest.

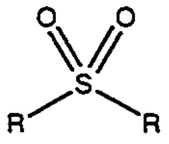
1.2 The Chemistry of Sulfur and its Oxidized Derivatives

There are many different forms of sulfur. Orthorhombic sulfur, S_α, is the most common and stable form at room temperature and consists of S_8 rings. At higher temperatures, S_α is transformed into monoclinic sulfur, S_β, which also exists as S_8 rings which are stacked differently.[2] Another form of sulfur, S_γ, is the least stable form of S_8.[2] Plastic sulfur, can be obtained by heating S_α at high temperatures[2] and exists as long helical chains. In polar solvents, approximately 1% of sulfur of S_α is present as S_6 and S_7 rings.[14] These smaller rings have slightly weaker S-S bonds (62.5 and 62.7 kcal mol^{-1}, respectively) than those found in S_8 rings (63.5 kcal mol^{-1}),[15,16] and this may contribute to their greater reactivity. Besides these ring sizes, sulfur is found in rings containing 12, 18, and 20 atoms.[14,17]

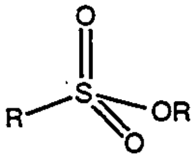
Sulfur can exist in many different oxidation states including -2, +2, +4 and +6 with coordination numbers of 4. The -2 oxidation state is commonly found in sulfides, RS_xR', and thiols, RSH, while the positive oxidation states are found in oxygen containing species such as R_2SO, R_2SO_2, R_2SO_3, and R_2SO_4.



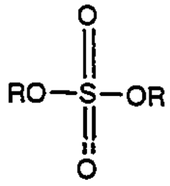
R_2SO



R_2SO_2



R_2SO_4



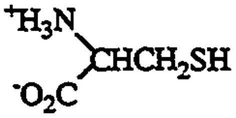
R_2SO_4

Sulfur oxides, S_xO_y, display differing stabilities. While SO_2 and SO_3 are stable, SO, S_2O and S_2O_2 are unstable.[18] SO rapidly disproportionates to S_2O and SO_2, with S_2O undergoing further decomposition (Equation 1.6).

$$3\,SO \longrightarrow S_2O + SO_2 \qquad (1.6)$$

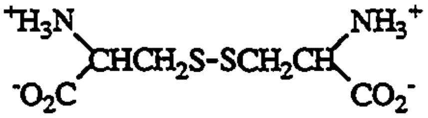
1.3 Organic Disulfides and Their Oxidized Derivatives

Sulfur exists in the -2 oxidation state in sulfides and thiols. The S-S unit in disulfides occurs regularly in organic and biological systems. Many protein molecules contain S-S linkages which play a crucial structural role in biological processes and are often essential for the bioactivity of the proteins. These linkages are formed when the amino acid cysteine, a thiol, is oxidized to cystine, a disulfide.[19]



$({}^{+}H_3N)({}^{-}O_2C)CHCH_2SH$

cysteine



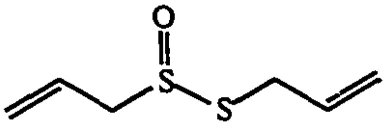
$({}^{+}H_3N)({}^{-}O_2C)CHCH_2S\text{-}SCH_2CH(NH_3^{+})(CO_2^{-})$

cystine

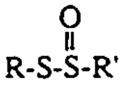
Applications of polysulfide products connected with industry are extensive. Disulfides serve as polymerization catalysts, regulators in emulsion polymerization, stabilizers in hydrocarbons and they are used in cutting oils. In lubricating oils, they improve film strength, prevent sludge formation, inhibit corrosion and serve as antioxidants.[20]

Organic disulfides, RSSR', are very stable compounds. By contrast, trisulfides, RSSSR', and tetrasulfides, RSSSSR', are generally less stable and may extrude sulfur to give the disulfide and a mixture of higher sulfides.[21] For example, attempted purification of *n*-butyl tetrasulfide, $(CH_3(CH_2)_2CH)_2S_4$ at room temperature gave a mixture of the disulfide and higher sulfides.[22]

Oxidized derivatives of disulfides also occur in nature. For example, allicin, or allyl 2-propene-1-thiosulfinate, is found in garlic.



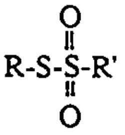
This class of oxidized disulfides are of interest due to the biological, antitumor, anti-viral and anti-fungal attributes of these compounds.[23] Industrially, they have found a use as surfactants for textiles[24] and as a solubilization agent in the dying of certain types of wool.[25] Generally, monooxidized disulfides are called thiosulfinates. Dioxidized disulfides can occur as *vic*-disulfoxides or thiosulfonates, and the trioxidized derivatives are called sulfinyl sulfones. Finally, the completely oxidized disulfides are called α-disulfones. Alkyl, aryl and some cyclic derivatives of all of these types of compounds excluding *vic*-disulfoxides have been isolated and studied in great detail.[26-32] *Vic*-disulfoxides have only been detected in low temperature NMR studies.[33] The organic oxidized disulfide compounds display varying reactivites depending on whether the R group is alkyl or aryl, and R = R'.


$R\text{-}S\text{-}\overset{\overset{O}{\|}}{S}\text{-}R'$

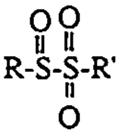
thiosulfinate


$R\text{-}\overset{\overset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{S}\text{-}R'$

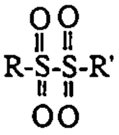
vic-disulfoxide


$R\text{-}S\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

thiosulfonate

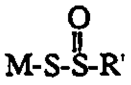

$R\text{-}\overset{\overset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

sulfinyl sulfone

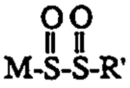

$R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

α-disulfone

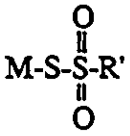
Nomenclature of polysulfide compounds has evolved over the years without great systemization. Generally, organic disulfides and their oxidized forms are named according to the "e-i-o" rule that corresponds to the oxidation number of sulfur of -2, 0, and +2, respectively. All organic compounds in this work will be named using this type of nomenclature. However, there are trends towards calling these compounds sulfanes. This term sulfane, referring to hydrogen polysulfides, was introduced in 1953 to be used in analogy to terms such as alkane and silane.[34] Sulfanes are named with a prefix indicating the number of sulfur atoms in the chain and the name of the alkyl or aryl groups that substitute the hydrogens. All metal compounds with sulfur containing ligands in this work will be named as sulfanes or oxosulfanes, (i.e. oxygen-containing sulfanes). Thus the above compounds where R is a metal center and R' is an alkyl or aryl group will be referred to as a metal -disulfane, -2-oxodisulfane, -1,2-dioxodisulfane, -2-dioxodisulfane, -1,2,2,-trioxodisulfane and -tetraoxodisulfane, respectively.


$M\text{-}S\text{-}\overset{\overset{O}{\|}}{S}\text{-}R'$

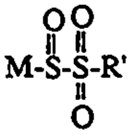
2-oxodisulfane


$M\text{-}\overset{\overset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{S}\text{-}R'$

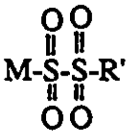
1,2-dioxodisulfane


$M\text{-}S\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

2-dioxodisulfane


$M\text{-}\overset{\overset{O}{\|}}{S}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

1,2,2-trioxodisulfane


$M\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}R'$

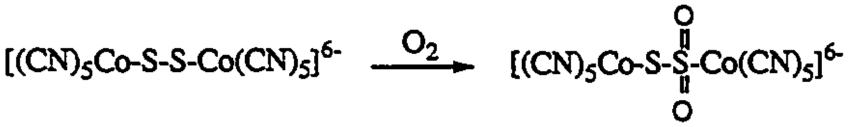
tetraoxodisulfane

1.4 Inorganic Sulfanes and their Oxidized Derivatives as Bridges

Inorganic analogs of disulfides and their derivatives are scarce. Many of them are salts of alkali or alkaline earth metals and relatively unstable.[2] For example Li_2S_3 disproportionates upon standing to give a mixture of sulfides, Li_2S_x ($x = 2\text{-}5$)[35] (Equation 1.7).

$$4\,Li_2S_3 \longrightarrow Li_2S_2 + Li_2S_3 + Li_2S_4 + Li_2S_5 \qquad (1.7)$$

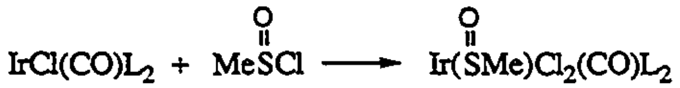
Symmetrical transition metal disulfanes with the formula MSSM exist and are generally stable complexes. Some examples of these include $K_6[(CN)_5CoSSCo(CN)_5]$,[36] $Li_4[(H_2O)_5CrSSCr(H_2O)_5]$,[37] $[(NH_3)_5RuSSRu(NH_3)_5]X_4$ ($X = Cl^-, Br^-, PF_6^-$)[38,39] and $CpFe(CO)_2SSFe(CO)_2Cp$.[40] There are also examples of $MSS(O)_2M$ and $MS(O)_2S(O)_2M$, such as $K_6[(CN)_5CoSS(O)_2Co(CN)_5]$, formed by the oxidation of its disulfide precursor (Equation 1.8), and the tetraoxodisulfanes $CpFe(CO)_2S(O)_2S(O)_2FeCp(CO)_2$,[41] $Cp^*M(CO)_3S(O)_2S(O)_2MCp^*(CO)_3$ ($M = Mo$, $Cp^* = \eta^5\text{-}C_5H_5$; $M = W$, $Cp^* = \eta^5\text{-}C_5Me_5$)[42] and $M(CO)_5S(O)_2S(O)_2M(CO)_5$ ($M = Mn, Re$).[41]



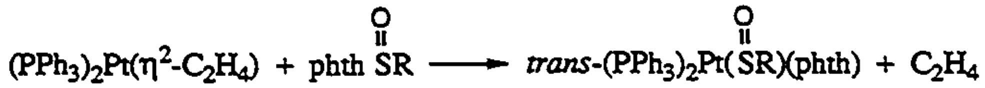
$$[(CN)_5Co\text{-}S\text{-}S\text{-}Co(CN)_5]^{6-} \xrightarrow{O_2} [(CN)_5Co\text{-}S\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Co(CN)_5]^{6-} \qquad (1.8)$$

1.5 Thiolates and Their Oxidized Derivatives Coordinated to One Metal Center

Metal thiolate complexes (MSR) are important in both biology and industry and have been studied extensively.[43] The oxidized species $MS(O)_xR$ ($x = 1,2$) have also been reported. Complexes of the type MS(O)R are rare due to their instability and tendency to form $MS(O)_2R$, which by contrast, are very stable. Some examples of MS(O)R complexes have been prepared by oxidative addition reactions. For example, $IrCl_2(CO)L_2S(O)Me$ (L = PPh_3; $PPPh_2Me$)[44] was prepared by oxidative addition of MeS(O)Cl to $IrCl(CO)L_2$ (Equation 1.9), and similarly, *trans*-$(PPh_3)_2Pt(phth)S(O)R$ (R = C_3H_7, C_4H_9, $C_{12}H_{25}$, $CH_2C_6H_5$, C_6H_5, 4-C_6H_4Me)[45] was prepared by oxidative addition of phthS(O)R to $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (Equation 1.10). By contrast, two oxidized cysteine derivatives, $[(en)_2CoS(O)CH_2CH_2NH_2][ClO_4]$[46] and $[(en)_2CoS(O)CH_2CH(COO)NH_2][ClO_4]$[47] were prepared by oxidation of the precursor thiolates by stoichiometric amounts of H_2O_2 (Equation 1.11); however, oxidation routes to MS(O)R are rarely successful due to the tendency to overoxidize the thiolate ligand to give $MS(O)_2R$.[48,49]



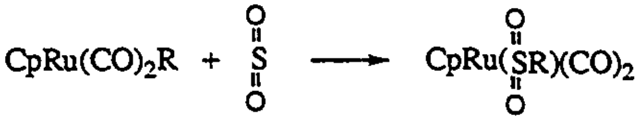
$$\mathrm{IrCl(CO)L_2} + \mathrm{Me\overset{\overset{O}{\|}}{S}Cl} \longrightarrow \mathrm{Ir(\overset{\overset{O}{\|}}{S}Me)Cl_2(CO)L_2} \qquad (1.9)$$



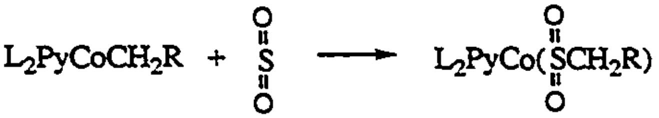
$$\mathrm{(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)} + \mathrm{phth\,\overset{\overset{O}{\|}}{S}R} \longrightarrow trans\text{-}\mathrm{(PPh_3)_2Pt(\overset{\overset{O}{\|}}{S}R)(phth)} + \mathrm{C_2H_4} \qquad (1.10)$$

$$\mathrm{[(en)_2Co(SCH_2R)]^{2+}} + \mathrm{H_2O_2} \longrightarrow \mathrm{[(en)_2Co(\overset{\overset{O}{\|}}{S}CH_2R)]^{2+}} + \mathrm{H_2O} \qquad (1.11)$$

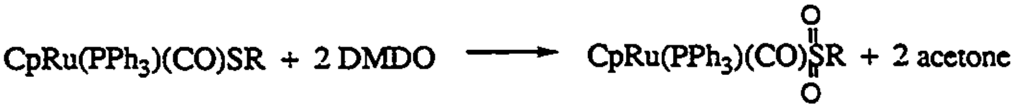
Complexes of the type $MS(O)_2R$ are more abundant than those of the type MS(O)R. There are three different preparative methods: 1) insertion of SO_2 into a M-C bond, 2) oxidation of the corresponding thiolate, 3) and condensation of two fragments (e.g. [M] + $[S(O)_2R]$ or $[MS(O)_2]$ + [R]). Some complexes prepared by the first route are $CpRu(CO)_2S(O)_2R$ (R = $CH_2C_6H_5$, C_6H_5)[50] and $L_2PyCoS(O)_2CH_2R$ (L = dimethylglyoximate, cyclohexaneglyoximate)[51] (Equations 1.12-1.13). Examples of complexes prepared by oxidation of the corresponding thiolate are $[(en)_2CoS(O)_2CH_2CH(COO)NH_2][ClO_4]$,[47] where the oxidizing agent was H_2O_2, and $CpW(CO)_3S(O)_2R$,[49] (R = Me and aryl) which was prepared by use of *m*-CPBA as the oxidizing agent. Another complex, $\mathrm{CpRu(PPh_3)(CO)S(O)_2R}$[48] (R = Me, 4-$\mathrm{C_6H_4Me}$, $\mathrm{C_6H_5}$) was prepared by oxidation with dimethyldioxirane (DMDO)[52] (Equation 1.14). In addition, nickel dithiolate complexes[53-57] such as (bme-daco)Ni (bme-daco = 1,5-bis(2mercapto-2-methylpropyl)-1,5-diazacyclooctanato)[53] have been oxidized to give a series of sulfinate and sulfenate ligands (Scheme 4.4). Finally, an example of a complex prepared by the third route is $\mathrm{CpRu(dppm)S(O)_2R}$[58] (R = Et, $\mathrm{CHMe_2}$), which was prepared by condensation of $\mathrm{CpRu(dppm)S(O)_2Cl}$ with LiR (Equation 1.15).



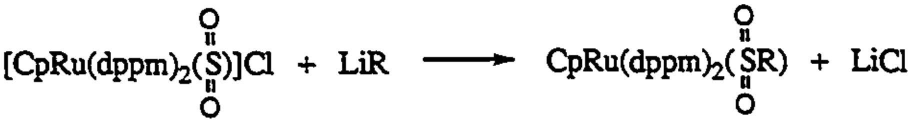
$$\mathrm{CpRu(CO)_2R} + \overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}} \longrightarrow \mathrm{CpRu(}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{R)(CO)_2} \qquad (1.12)$$



$$\mathrm{L_2PyCoCH_2R} + \overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}} \longrightarrow \mathrm{L_2PyCo(}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{CH_2R)} \qquad (1.13)$$



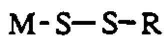
$$\mathrm{CpRu(PPh_3)(CO)SR} + 2\,\mathrm{DMDO} \longrightarrow \mathrm{CpRu(PPh_3)(CO)}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{R} + 2\ \mathrm{acetone} \qquad (1.14)$$



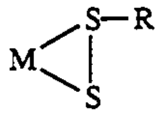
$$\mathrm{[CpRu(dppm)_2(}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{)]Cl} + \mathrm{LiR} \longrightarrow \mathrm{CpRu(dppm)_2(}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\mathrm{S}}}\mathrm{R)} + \mathrm{LiCl} \qquad (1.15)$$

1.6 Disulfanes and Their Oxidized Derivatives Coordinated to One Metal Center

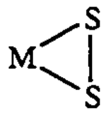
The $\mathrm{S_2R}$ ligand can bind to a metal center either via a sigma bond, η^1-$\mathrm{S_2R}$ or through side-on bonding, η^2-$\mathrm{S_2R}$. In the absence of an R group, persulfido complexes are formed η^2-$\mathrm{S_2}$.



η^1-S_2R

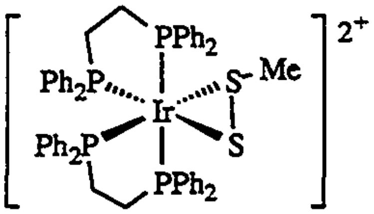


η^2-S_2R

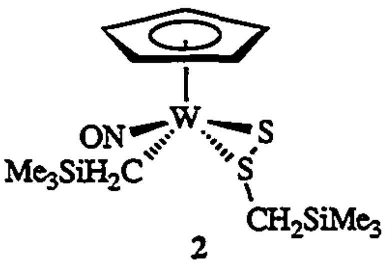


η^2-S_2

Examples of complexes with η^2-S_2 bonding include $Os(S_2)(CO)_2(PPh_3)_2$,[59] $[Ir(S_2)(dppe)_2]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane),[60] $[Rh(S_2)(dmpe)_2]Cl$ (dmpe = 1,2-bis(diphenylphosphino)methane),[61] and the cyclopentadienyl species $Cp_2Nb(S_2)Cl$[62] and $Cp_2Mo(S_2)$.[63] Compounds with the η^2-S_2R moiety include $[Os(\eta^2\text{-}S_2Me)(PPh_3)_2(CO)_2]ClO_4\cdot{}^1/_2\ C_6H_6$,[64] $[Ir(\eta^2\text{-}S_2Me)(dppe)_2][PF_6]_2$ (**1**)[65] and $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}S_2CH_2SiMe_3)$ (**2**),[66-68] for which the x-ray crystal structure was determined.



1



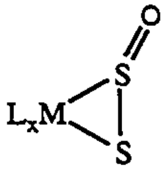
2

Complexes containing the η^1-S_2R ligand include $CpW(CO)_3SSR$ (R = $CH_2C_6H_5$, 4-C_6H_4Me),[69] $Cp_2Ti(X)SSR$ (X = SR, phth, Cl; R = $CHMe_2$, C_6H_5, 4-C_6H_4Me),[70] *cis*-$(PPh_3)_2Pt(phth)SSR$ (R = alkyl and aryl),[71] $CpRu(PPh_3)(CO)SSR$ (R = $CHMe_2$, C_3H_7, 4-C_6H_4Me),[72] $IrCl_2(PPh_3)_2(CO)SSC_6F_5$[73] and $Cu(tet\text{-}b)SSCH_2CO_2\cdot 3CH_3OH$ (tet-b = rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazocyclotetradodecane).[74] Many of these compounds were synthesized by condensation of the metal-thiol complex with the appropriate phthalimide sulfur transfer reagent (Equation 1.16). Similar condensation routes have also been used extensively in the preparation of unsymmetrical organic disulfides.

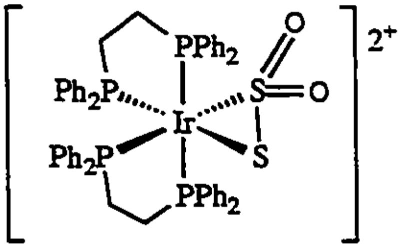
$$L_xM\text{-}SH + phthSR \longrightarrow L_xM\text{-}SSR + phthH \qquad (1.16)$$

This route offers many advantages since the reagents are solids, and the phthalimide by-product is easily removed.

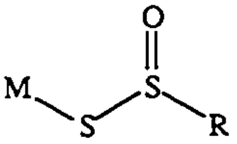
There are also some compounds containing the η^2-$S_2(O)$ moiety reported in the literature.



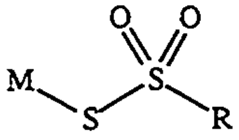
These include $[Ir(\eta^2\text{-}S_2O)(dppe)_2][PF_6]$,[75] $Cp_2NbCl(S_2O)$,[76]$(Cp^*Mn(CO)_2(S_2O)$ (Cp^* = η^5-C_5H_5)[77] and $(Cp^*Re(CO)_2(S_2O)$.[78] These compounds are generally made from the oxidation of S_2 units bound to metal centers. $[Ir(\eta^2\text{-}S_2O_2)(dppe)_2][PF_6]_2$ [75] has also been reported.



Examples of transition metal complexes containing a linear η^1-$S_2(O)_xR$ (x = 1 or 2) are rare. They include the complexes $CpRu(PPh_3)(CO)SS(O)R$ (L = PPh_3, CO; R = alkyl and aryl)[79-81] $CpW(CO)_3SS(O)R$ (R = $CH_2C_6H_5$, 4-C_6H_4Me)[69] and *cis*-$(PPh_3)_2Pt(phth)SS(O)R$ (R = alkyl and aryl).[82]

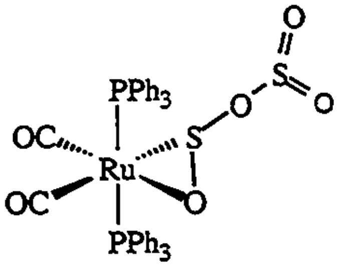


η^1-$S_2(O)R$



η^1-$S_2(O)_2R$

The monometallic tetraoxosulfane species, $Ru(CO)_2(\eta^2$-$S(O)\cdot SO_2)(PPh_3)_2$ has also been prepared and its X-ray structure was determined at -60°C.[83] This is the only example of a S_2O_4 ligand coordinated to a single metal center that has been reported in the literature.



1.7 Reasons for Studying Metal-sulfanes and Their Oxidized Derivatives

The object of this research is to make catenated sulfur ligands and their oxidized derivatives. Although organic compounds of the type RS_xO_yR',[84] (x = 1, 2 and y = 0 - 4), have been studied exhaustively, little is known about the metal analogs, MS_xO_yR'. Thus, it is of interest to prepare these compounds to observe the effect of a coordinated metal on the reactivity and stability of S_xO_yR'. For example, as mentioned earlier, *vic*-disufoxides have only been detected by low temperature NMR. The introduction of a metal might affect the stability to this *vic*-disulfoxide moiety . In addition, metal compounds containing a 1,2,2-trioxodisulfane ligand (M-S(O)S(O)$_2$R), 1,1,2-trioxodisulfane (M-S(O)$_2$S(O)R), or a 1,1,2,2-tetraoxodisulfane ligand (M-S(O)$_2$S(O)$_2$R), have not yet been synthesized. These compounds are of interest as possible models of intermediates in the Claus Process. The goal of this thesis was to make polysulfane and polyoxosulfane complexes of the type $CpRu(CO)_2S_xO_yR$ (x = 1-3; y = 0-2) and examine their chemistry.

Since this chemistry is focused on the ligand and not the metal center, the metal and the other surrounding ligands must meet certain criteria. First, the metal center must be stable and inert with respect to the chemistry about the sulfur containing ligand. In addition, the surrounding ligands should be strongly coordinated to the metal atom and not be labile. Thus, the metal fragment chosen for most of these studies was $CpRu(CO)_2$. The ruthenium atom is in the +2 oxidation state. The CO ligands are coordinated to the ruthenium atom via both a σ-bond and π-bond, the latter through back donation of electron density into π^*-antibonding orbital of the CO ligand from ruthenium d orbitals with the same symmetry.[85] The Cp ligand is also an electron withdrawing ligand. Thus, it was hoped that the Ru-S bond would be strong and that the $CpRu(CO)_2$ residue would be a good platform for the study of sulfane ligands and their oxidized derivatives. In addition, earlier work with the $CpRu(PPh_3)(CO)$ residue[72,79,86] suggested that the dicarbonyl analog should be productive.

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Chapter 2.

Preparation of $CpRu(CO)_2S_xR$ (x = 1-3; R = H, 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$)

2.1 Introduction

The ability of sulfur to catenate, that is exist as sulfur chains, is one of its best known characteristics. Allotropes with ring sizes up to S_{20} have been documented and rings of S_5, S_6, S_7 and S_8 are very common.[1] In addition, organic polysulfur compounds of the type RS_xR', where x ranges from 1 to greater than 20 are known. However, despite this tendency of sulfur to catenate, the metal substituted analogs of the type MS_xR, where x > 1 are relatively rare. There are many species known for x = 1 and these are referred to as metal thiolates. There are few compounds known for x = 2, metal disulfanes, and even fewer where x = 3, trisulfanes.

Many of the disulfane complexes, MSSR, have been prepared by a metathesis type reaction between the precursor metal thiol and the appropriate phthalimide sulfur transfer reagent (Scheme 2.1). For example, the complexes $CpW(CO)_3SSR$,[2] $Cp_2Ti(SSR)_2$[3] and $CpRu(PPh_3)(CO)SSR$[4] have been prepared in this way in good yields. These complexes display varying stabilities and reactivities. Other methods have also been employed to synthesize metal disulfane complexes. Thus, *cis*-$(PPh_3)_2Pt(phth)SSR$[5] was prepared by oxidative addition of phthSSR to $(PPh_3)_2Pt(C_2H_4)$, and $IrCl_2(PPh_3)_2(CO)SSC_6F_5$[6] was prepared by oxidative addition of $ClSSC_6F_5$ to *trans*-$IrCl(PPh_3)_2(CO)$. Cu(tet-b)$SSCH_2CO_3 \cdot 3CH_3OH$ (tet-b = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazocyclotetradodecane) was prepared by reaction of Cu(tet-b) with $HSCH_2CO_3H$ in the presence of base in methanol.[7]

Scheme 2.1

$$\mathrm{CpRu(PPh_3)(CO)SH} \xrightarrow{\mathrm{phthSR}} \mathrm{CpRu(PPh_3)(CO)SSR + phthH}$$

$$\mathrm{CpW(CO)_3SH} \xrightarrow{\mathrm{phthSR}} \mathrm{CpW(CO)_3SSR + phthH}$$

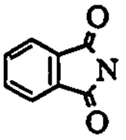
$$cis\text{-}\mathrm{Pt(PPh_3)_2(C_2H_4)} \xrightarrow{\mathrm{phthSSR}} cis\text{-}\mathrm{(PPh_3)_2Pt(phth)SSR + C_2H_4}$$

$$\mathrm{Cp_2Ti(SH)_2} \xrightarrow{\mathrm{2\ phthSR}} \mathrm{Cp_2Ti(SSR)_2 + 2\ phthH}$$

where R = alkyl

$$trans\text{-}\mathrm{IrCl(PPh_3)_2(CO)} \xrightarrow{\mathrm{ClSSC_6F_5}} \mathrm{IrCl_2(PPh_3)_2(CO)SSC_6F_5}$$

$$\mathrm{Cu(tet\text{-}b)^{2+} + 2\ HSCH_2CO_3H} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{base}} \mathrm{Cu(tet\text{-}b)SSCH_2CO_3{\cdot}3CH_3OH}$$



= phth

Complexes containing a trisulfane ligand, η^1-SSSR, are also very rare. The complexes CpRu(PPh$_3$)(CO)SSSR[4] and CpW(CO)$_3$SSSR[2] were prepared by reaction of the metal thiol precursor with the disulfide phthalimido transfer reagent, phthSSR (Scheme 2.2). The complex Cp$_2$Ti(SR)(SSSR),[3] where R = aryl, was prepared by reaction of the metal dithiol complex with the monosulfur transfer reagent phthSR whereupon the initial product, Cp$_2$Ti(SSR)$_2$, is thought to have rearranged.

Scheme 2.2

$$\mathrm{CpRu(PPh_3)(CO)SH} \xrightarrow{\mathrm{phthSSR}} \mathrm{CpRu(PPh_3)(CO)SSSR} + \mathrm{phthH}$$

$$\mathrm{CpW(CO)_3SH} \xrightarrow{\mathrm{phthSSR}} \mathrm{CpW(CO)_3SSSR} + \mathrm{phthH}$$

$$\mathrm{Cp_2Ti(SH)_2} \xrightarrow{\mathrm{2\ phthSR}} \mathrm{Cp_2Ti(SR)(SSSR)} + 2\ \mathrm{phthH}$$

where R = aryl

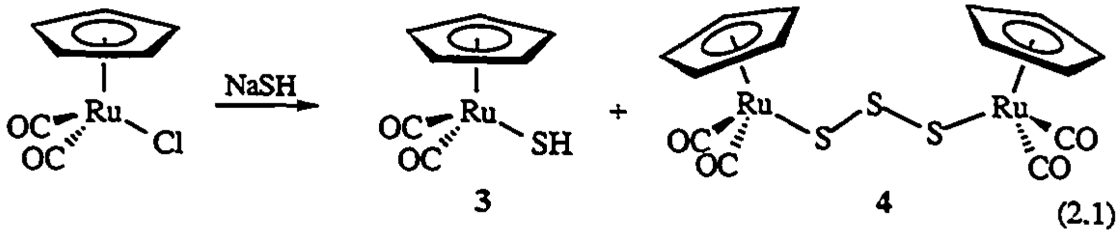
Due to the importance of metal-sulfur chemisry in biology[8] and industry,[9] it is of interest to investigate the chemistry of these simple catenated polysulfane species. Since only a handful of these complexes have been prepared, the synthesis and chemistry of more examples could give a better insight into the compounds. In this chapter the complexes $\mathrm{CpRu(CO)_2S_xR}$ (x = 2, R = 4-$\mathrm{C_6H_4Me}$, $\mathrm{C_6H_5}$, $\mathrm{CH_2C_6H_5}$; x = 3, R = 4-$\mathrm{C_6H_4Me}$) were prepared and characterized and some aspects of their reactivity towards small molecules was investigated. The analogous thiolato complexes, $\mathrm{CpRu(CO)_2SR}$ (R = 4-$\mathrm{C_6H_4Me}$, $\mathrm{C_6H_5}$,[10-12] $\mathrm{CH_2C_6H_5}$[10]) were prepared for comparison. The synthesis of the precursor to these disulfanes, $\mathrm{CpRu(CO)_2SH}$, is described as is $(\mu\text{-}\mathrm{S_3})(\mathrm{CpRu(CO)_2})_2$.

2.2 Results and Discussion

2.2.1 Preparation of $\mathrm{CpRu(CO)_2SH}$ and $(\mu\text{-}\mathrm{S_3})(\mathrm{CpRu(CO)_2})_2$

$\mathrm{CpRu(CO)_2SH}$ (3) was prepared as the precursor to the metal di- and trisulfanes. The reaction of $\mathrm{CpRu(CO)_2Cl}$ with NaSH in THF for 3 days at room temperature gave the corresponding thiolato metal complex, $\mathrm{CpRu(CO)_2SH}$ as the major product in 85% yield.

The reaction also gave a second product which usually accounted for approximately 15% of the total product distribution (^{1}H NMR: Cp = 4.82 ppm). This product was assigned as (μ-S_3)(CpRu(CO)$_2$)$_2$ (4) (Equation 2.1). The two products were distinguished by the positions of their Cp resonances in the ^{1}H NMR spectrum and were easily separated by column chromatography. Pure CpRu(CO)$_2$SH was obtained by recrystallization from THF/hexanes to give a yellow solid. CpRu(CO)$_2$SH is soluble in THF, EtOH, ether, and benzene, and slightly soluble in hexanes. It is air sensitive and also decomposes in the solid state to a brown oil at -16°C over time, with evolution of H_2S gas. Attempted recrystallization of the second product from ether/hexanes will be discussed below. The NMR spectrum of CpRu(CO)$_2$SH in C_6D_6 showed a peak due the SH proton at -2.93 which is characteristic of MSH species.[13] The IR spectrum in cyclohexane had strong bands at 1995 and 2043 cm^{-1} due to the ν(CO) stretching frequencies. The ν(CO) stretching frequency for CpRu(PPh$_3$)(CO)SH in toluene occurs at 1950 cm^{-1} reflecting the stronger M-C bond, due to the coordination of the electron donating PPh$_3$ ligand.

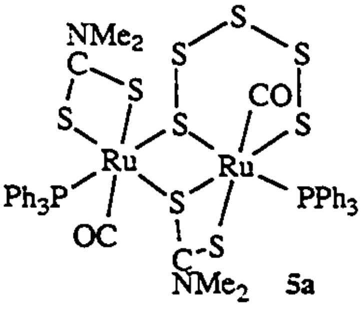


(2.1)

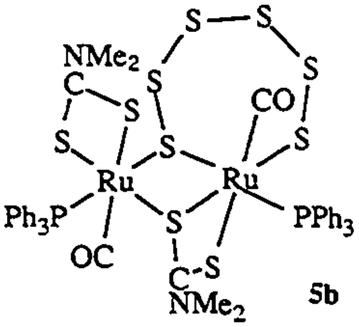
Other thiolato ruthenium complexes are known; e.g. CpRu(PPh$_3$)(CO)SH,[13] CpRu(PPh$_3$)$_2$SH[13,14] and Cp*Ru(PMe$_3$)$_2$SH[15] (Cp* = η^5-C_5Me_5). The first two compounds were prepared by similar methods to our preparation while the latter was prepared by treatment of Cp*Ru(PMe$_3$)$_2$OH with excess H_2S. The decomposition of CpRu(CO)$_2$SH with loss of H_2S was also observed for CpRu(PPh$_3$)$_2$SH and CpRu(PPh$_3$)(CO)SH.[13] Thus, although these metal thiolato complexes can be made, their relative instability and short shelve life dictates that they are used promptly in reactions.

The second product from the reaction of $CpRu(CO)_2Cl$ with NaSH in THF has been assigned as $(\mu\text{-}S_3)(CpRu(CO)_2)_2$. Unfortunately, it was contaminated by a species whose Cp peak appears in the NMR spectrum as a singlet at 4.62 ppm. This accounted for 2-10% of the integration in the Cp region of the NMR spectrum, depending on the preparation. Successive recrystallizations of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ served only to give samples enriched with the contaminant. Several attempts to grow crystals of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ suitable for x-ray analysis failed. $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ is a dark burgundy solid which is soluble in THF, moderately soluble in ether, and insoluble in hexanes. It reacts with CH_2Cl_2, is light, heat and air sensitive and decomposes over time at room temperature. $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ was identified based on its NMR, IR, and FAB mass spectra. The NMR spectrum of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ in C_6D_6 shows a single peak at 4.82 ppm, due to the equivalent Cp protons. The IR spectrum in toluene gave two strong bands at 1969 and 2024 cm^{-1} which have been assigned to the $\nu(CO)$ stretching frequencies. These bands are lower than the $\nu(CO)$ stretching frequencies of $CpRu(CO)_2SH$ (1995, 2043 cm^{-1} (cyclohexane)). The $\nu(S\text{-}S)$ stretching frequencies are expected to occur in the region 430-540 cm^{-1} which overlaps bands due to the Cp ligand.[16] Therefore, it was not possible to make the assignment of the $\nu(S\text{-}S)$ stretching frequency. The FAB mass spectrum showed peaks due to $(\mu\text{-}S_3)(CpRu(CO)_2)_2^+$, $(\mu\text{-}S_3)(CpRu(CO)_2)_2^+$ - S and $(\mu\text{-}S_3)(CpRu(CO)_2)_2^+$ - 2S, confirming the assignment of the trisulfane-bridged dinuclear species.

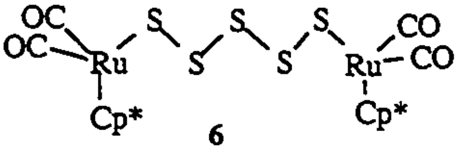
The formation of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ is in contrast to the reaction of $CpRu(PPh_3)_2Cl$ with NaSH which gave $CpRu(PPh_3)_2SH$ as the sole product.[13] However, there are numerous reports in the literature of polysulfane-bridged dinuclear complexes, many of which were prepared by addition of elemental sulfur to a dimer. These include the recently reported sulfur bridged compounds $(\mu\text{-}S_x)(Ru_2(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2)$ (x = 5 (**5a**), 6 (**5b**)) which were formed by the reaction of $RuH(S_2CNMe_2)(CO)(PPh_3)_2$ with elemental sulfur.[17] The compounds were obtained as a mixture of both the pentasulfane and hexasulfane bridged species which cocrystallized in a single crystal. They were both observed in the x-ray crystal structure. Another pentasulfane bridged compound, $(\mu\text{-}S_5)(CpRu(CO)_2)_2$ [18] (**6**), was prepared by the reaction of $(CpRu(CO)_2)_2$ with elemental sulfur under reflux or photolysis in benzene. This compound was only one of a mixture of several sulfane bridged compounds formed, and was isolated as microcrystals after numerous attempts of fractional crystallization. The compounds $(\mu\text{-}S_x)(CpFe(CO)_2)_2$, ($x = 1\text{-}4$) (**7a-d**) have been reported.[19] The crystal structures for $x = 3$ and 4 were determined and confirmed the polysulfane bridges. The compound $(\mu\text{-}S_4)(Cp^*Ru(CO)_2)_2$, (**8**) ($Cp^* = \eta^5\text{-}C_5Me_5$) was one of four products obtained from the irradiation of $(Cp^*Ru(CO)_2)_2$ with excess sulfur in THF.[20] $(\mu_2\text{-}S_2)((\mu\text{-}S)Cp^*Ru)_2$ ($Cp^* = \eta^5\text{-}C_5Me_4Et$) added CO to form $(\mu_2\text{-}S_2)_2Cp^*Ru(CO)_2)_2$[21] (**9**). $[(\mu\text{-}S_2)CpRu(PPh_3)_2]_2][PF_4]_2$ was prepared by reaction of $CpRu(PPh_3)_2Cl$ with elemental sulfur and silver salts,[22] and by reaction of $CpRu(PPh_3)_2Cl$ with $(Cp^*)TiS_5$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with $AgBF_4$. $[(MeCp)Ru(PPh_3)_2]_2(\mu\text{-}S_2)][SbF_6]_2$ reacted with $(NBu_4)_2S_6$ to give the cage and ring compounds $((MeCp)Ru(PPh_3)_2)_2S_x$ ($x = 4$ (**10a**), 6 (**10b**)).[23]



5a



5b



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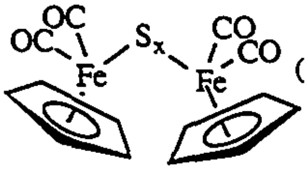
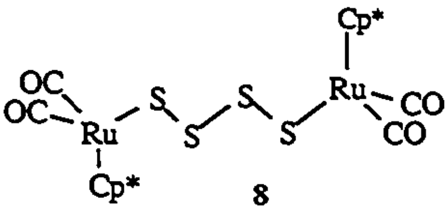


7a-d



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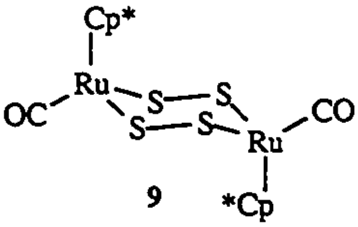

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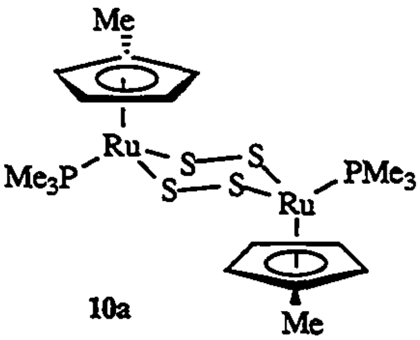
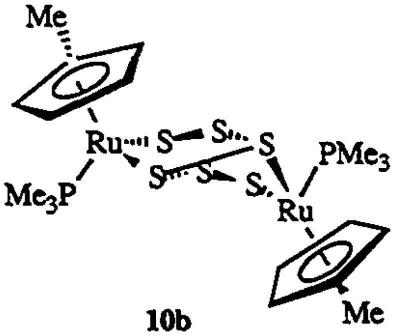


10a



10b

Although we did not succeed in the complete purification and isolation of (μ-S_3)($CpRu(CO)_2)_2$, the report of many other polysulfane-bridged species in addition to the spectroscopic evidence obtained makes the assignment of (μ-S_3)($CpRu(CO)_2)_2$ reasonable. In addition, since the pentasulfane dinuclear complex (μ-S_5)($CpRu(CO)_2)_2$ was isolated from a mixture of (μ-S_x)($CpRu(CO)_2)_2$, $x \geq 1$, it seems reasonable that the peak at 4.62

ppm may be due to the impurity associated with a different sized polysulfane bridged species, $(\mu\text{-}S_x)(CpRu(CO)_2)_2$, possibly where x = 2 or 4.

The isolation of the trisulfane bridged dinuclear complex instead of the other bridged species is of interest. Organic trisulfides tend to lose sulfur in polar solvents to give the corresponding disulfides. For example, upon attempted purification, both diethyltrisulfide and diphenyltrisulfide extruded sulfur to give the corresponding disulfides[24] (Equations 2.2-2.3). By analogy, one might have expected that $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ would lose sulfur to give the disulfane bridged species.

$$CH_3CH_2SSSCH_2CH_3 \longrightarrow CH_3CH_2SSCH_2CH_3 + {}^1/_8\, S_8 \qquad (2.2)$$

$$C_6H_5SSSC_6H_5 \longrightarrow C_6H_5SSC_6H_5 + {}^1/_8\, S_8 \qquad (2.3)$$

Clues to the stability of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ might be obtained by examining the properties and x-ray crystal structure of $(\mu\text{-}S_3)(CpFe(CO)_2)_2$.[19] The tetrasulfane bridged complex $(\mu\text{-}S_4)(CpFe(CO)_2)_2$ extruded sulfur to give the $(\mu\text{-}S_3)$ species. The tetrasulfane bridged species had a small S-S-S-S torsion angle of 50.95 (14)° compared to 74.47 (11)° and 80.52 (11)° found for Fe(1)-S-S-S and S-S-S-Fe(2), respectively, in the trisulfane species. The increased torsion angle in the latter species may contribute to its stability due to less steric hindrance. In addition, there were also large differences in the S-S bond lengths in the $(\mu\text{-}S_4)$ species, ranging from 2.022 (3) to 2.093 (3) Å which were not observed in the $(\mu\text{-}S_3)$ species. The longer bonds indicate weaker S-S bonds in the former. Thus, the relative stability of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ is consistent with that observed for the $CpFe(CO)_2$ systems.

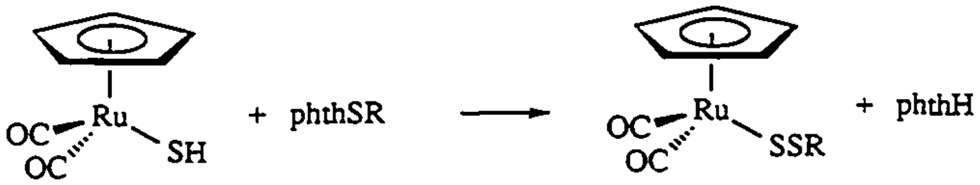
2.2.2 Preparation of $CpRu(CO)_2SR$

These thiolato compounds $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) (**11a-c**) were prepared so that they could be identified in reactions involving $CpRu(CO)_2S_xR$, where x = 2 and 3. The preparations were similar to those reported in literature for $CpRu(PPh_3)_2SR$ (R = 4-C_6H_4Me, C_3H_7, $CHMe_2$).[13] The compounds where R = C_6H_5 and $CH_2C_6H_5$ have been previously prepared by irradiation of solutions containing $(CpRu(CO)_2)_2$ and the disulfide.[12] However, as reported in the literature, $CpRu(CO)_2SCH_2C_6H_5$ was not fully characterized. The complex $CpRu(CO)_2SC_6H_5$ has also been made by reaction of $CpRu(CO)_2Cl$ with $(n\text{-}Bu)_3SnSPh$ in 38% yield.[11] The syntheses of $CpRu(CO)_2SR$ reported here (see Experimental Section) are improvements due to their simplicity and good yield.

2.2.3 Preparation of $CpRu(CO)_2SSR$

Synthesis

The reactions of $CpRu(CO)_2SH$ with the sulfur transfer reagents phthSR (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$, $CHMe_2$, C_3H_7) in THF at room temperature gave the corresponding disulfane complexes, $CpRu(CO)_2SSR$ (Equation 2.4). The compounds where R = 4-C_6H_4Me, C_6H_5 and $CH_2C_6H_5$ (**12a-c**) were isolated as pure crystalline solids whereas the alkyl analogs, R = $CHMe_2$ and C_3H_7 (**12d,e**), were isolated as oils, and could not be crystallized. The latter two compounds spontaneously decomposed in solution or as an oil over two days under N_2 at -16°C to a mixture of products including $(\mu\text{-}S_3)(CpRu(CO)_2)$ and R_2S_2, as identified by NMR. Due to their instability, they could not be fully characterized.



(2.4)

12a-c

a, R = 4-C_6H_4Me
b, R = C_6H_5
c, R = $CH_2C_6H_5$

The compounds $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) (**12a-c**) were crystallized from hexanes. The low yields of recrystallized products are due in part to their high solubility even in non-polar solvents. These complexes are very soluble in THF, ether, toluene, hexanes, and cyclohexane and decompose in CH_2Cl_2 and CS_2. The NMR spectrum for $CpRu(CO)_2SSR$ revealed one set of peaks due to the Cp and R protons, as expected with the proper integration and multiplicity (Table E.1). The IR spectra for all three compounds displayed strong bands due to the ν(CO) stretching frequencies in the ranges 1993-1996 and 2038-2043 cm^{-1} (Table E.2) similar to the ranges observed for $CpRu(CO)_2SSR$. Thus the additional sulfur atom does not have a large affect on the electron density on the ruthenium atom. This is in contrast to the IR spectra of $(\mu\text{-}S_3)(CpRu(CO)_2)$ where a shift in the ν(CO) stretching frequencies is observed. These stretching frequencies are higher than those found in $CpRu(PPh_3)(CO)SSR^4$ (1941-1954 cm^{-1}, toluene), reflecting the strong C-O bonds in $CpRu(CO)_2SR$, and resulting weaker M-C bonds. This increased stretching frequency results from an electron poorer ruthenium center when PPh_3, an electron donating ligand is substituted with a CO, a π-accepting ligand. The high resolution mass spectra of $CpRu(CO)_2SSR$ displayed the parent molecular ions and the elemental analyses were in good agreement with the calculated values.

The compounds in the solid state can be handled in air for prolonged periods of time without decomposition but they were stored under N_2. A sample of $CpRu(CO)_2SSCH_2C_6H_5$ stored under N_2 at room temperature decomposed over a period of two months to a dark burgundy red oil/solid. The NMR spectrum of this residue indicated it was a mixture of $(\mu\text{-}S_3)(CpRu(CO)_2)_2$, $CpRu(CO)_2SSCH_2C_6H_5$, $CpRu(CO)_2SCH_2C_6H_5$ and $(C_6H_5CH_2)_2S_2$ in the ratio of 3:1:1:1, respectively. In contrast, $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2SSC_6H_5$ can be stored indefinitely at room temperature under N_2. The decomposition of $CpRu(CO)_2SSCH_2C_6H_5$ resembles that of $CpRu(CO)_2SSR$, where R = $CHMe_2$ and C_3H_7, which also decompose to $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ and the corresponding R_2S_2, but at a much faster rate.

Further investigation of the compounds $CpRu(CO)_2SSR$ revealed that they were not stable in solution at room temperature and immediately started extruding sulfur to form some of the corresponding metal thiolates, $CpRu(CO)_2SR$. A sample of $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ in C_6D_6 at room temperature under N_2 for 19 hours displayed peaks in the NMR spectrum due to $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$, $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ in the ratio of 16:8:1, respectively. Thus, over time, some of the corresponding metal trisulfane, $CpRu(CO)_2SSSR$ was also formed. When solutions of $CpRu(CO)_2SSR$ were heated, sulfur loss and decomposition were accelerated, as detected in the NMR spectra. Therefore, in the light, solutions of $CpRu(CO)_2SSR$ are unstable. In contrast, a sample of $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ in C_6D_6 under N_2 in the absence of light heated at 70°C for 50 hours showed only 9% of the corresponding thiolate, $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and no peaks due to $(4\text{-}MeC_6H_4)_2S_2$, a product of decomposition. The remarkable decrease in the rate of sulfur loss in the dark implies that sulfur loss is photolytically activated.

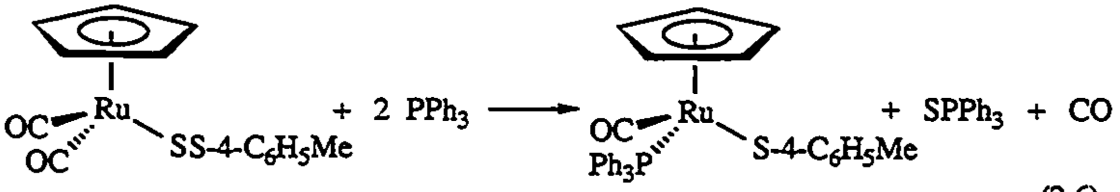
$$(CpRu(CO)_2)_2 + (CMe)_2S_2 \xrightarrow{\text{u.v.}} CpRu(CO)_2SC(Me)_3 + CpRu(CO)_2SSC(Me)_3 \tag{2.5}$$

There has been one other $CpRu(CO)_2SSR$ compound reported in the literature. $CpRu(CO)_2SSCMe_3$ has been prepared[12] by u.v. irradiation of a mixture of $(CpRu(CO)_2)_2$

and $(CMe_3)_2S_2$. However, it was not isolated and was obtained as a mixture of $CpRu(CO)_2SSCMe_3$ and $CpRu(CO)_2SCMe_3$ (Equation 2.5).

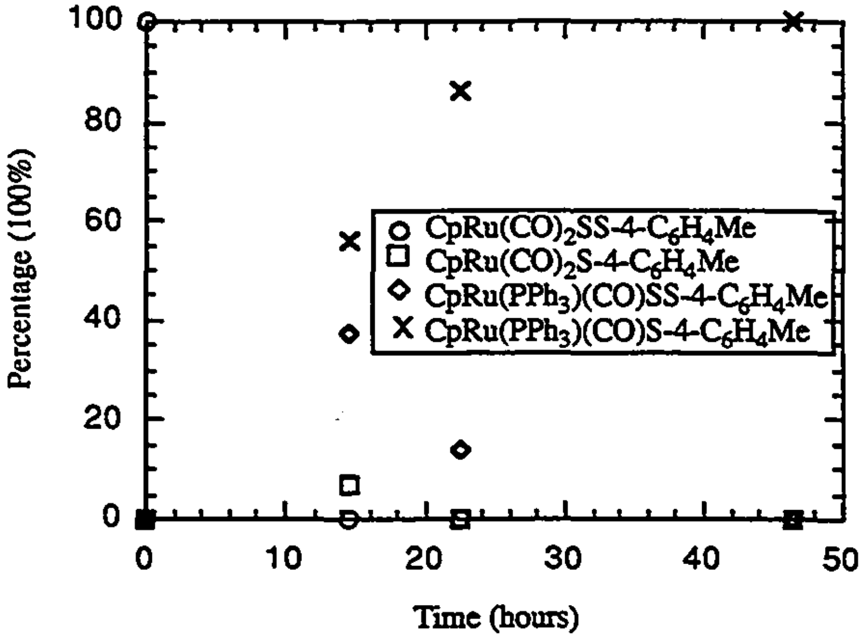
Reaction of $CpRu(CO)_2SSR$ with PPh_3

The reactivity of these ruthenium disulfanes with PPh_3, which is known to desulfurize metal disulfanes,[25] is exemplified by $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$, a prototypical complex. Reaction of $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ with 2.4 equivalents of PPh_3 in C_6D_6 gave $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ as the final product (Equation 2.6).



(2.6)

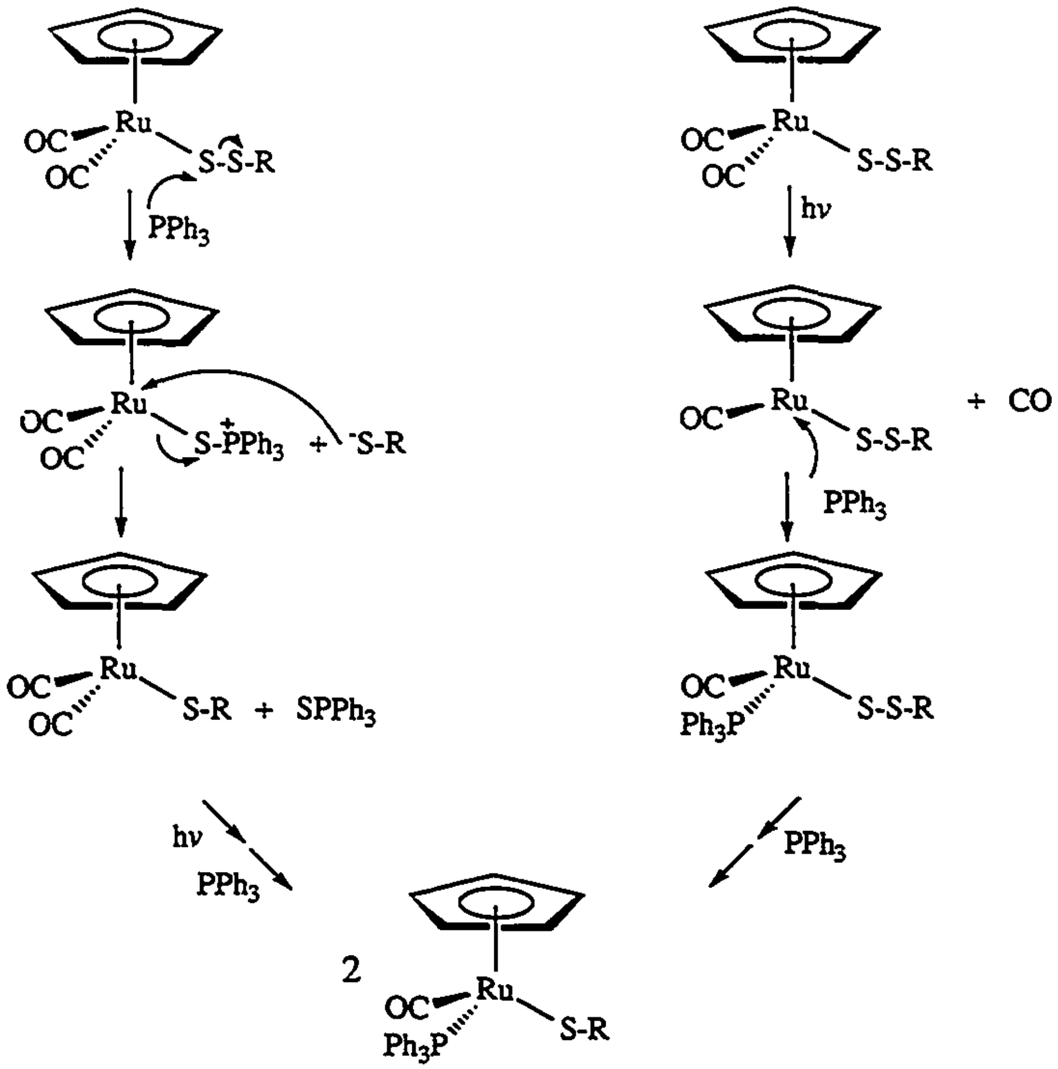
Figure 2.1 Reaction of $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ with a slight excess of two equivalents of PPh_3 at 42°C in C_6D_6.



As shown in Figure 2.1, sulfur was abstracted almost immediately from $CpRu(CO)_2SS$-4-C_6H_4Me to give $CpRu(CO)_2S$-4-C_6H_4Me. However, the phosphine substituted analogs, $CpRu(PPh_3)(CO)S$-4-C_6H_4Me and $CpRu(PPh_3)(CO)SS$-4-C_6H_4Me, were present in small amounts after 1.5 hours. They were identified by comparison of their spectra with the NMR and IR spectra of authentic samples. As the reaction proceeded, the peaks due to $CpRu(CO)_2S$-4-C_6H_4Me and $CpRu(PPh_3)(CO)SS$-4-C_6H_4Me grew and then diminished. Thus, the final product, $CpRu(PPh_3)(CO)S$-4-C_6H_4Me was formed by two routes: 1) desulfurization followed by PPh_3 substitution and, 2) the reverse, PPh_3 substitution followed by desulfurization. The first reaction is faster, as seen by the initial appearance of $CpRu(CO)_2S$-4-C_6H_4Me. Since CO substitution by PPh_3 does not occur immediately, perhaps CO dissociation from the metal must preceed PPh_3 association.

To determine if CO substitution by PPh_3 and sulfur abstaction by PPh_3 were photo- or thermally initiated, the reaction was performed in the dark. Heating $CpRu(CO)_2SS$-4-C_6H_4Me with 2.4 equivalent of PPh_3 in C_6D_6 at a higher temperature, 67°C, for 34 hours gave 40% of the PPh_3 substituted disulfane, $CpRu(PPh_3)(CO)SS$-4-C_6H_4Me, 25% of the sulfur extruded dicarbonyl thiolate, $CpRu(CO)_2S$-4-C_6H_4Me, and 35% of the final substituted product, $CpRu(PPh_3)(CO)S$-4-C_6H_4Me. Since the reaction was hindered in the dark even at higher temperatures, photo-assisted labilization of CO must be a major pathway to the product. A possible reaction path via both the initially desulfurized and PPh_3 substituted intermediates is outlined in Scheme 2.3. However, some PPh_3 substitution did occur, even in the absence of light and this was somewhat surprising. Therefore, the reaction of the parent thiolates with PPh_3 was examined.

Scheme 2.3

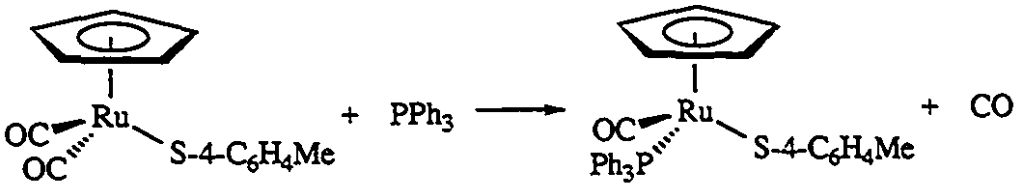


R = 4-C_6H_5Me

Reaction of $CpRu(CO)_2SR$ with PPh_3

The reaction of $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) with PPh_3 gave the phosphine-substituted complex $CpRu(PPh_3)(CO)SR$[13] as the sole product (Equation 2.7). The reaction with $CpRu(CO)_2S$-4-C_6H_4Me was complete in 3 hours at 67°C. By contrast, the reaction of $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) and

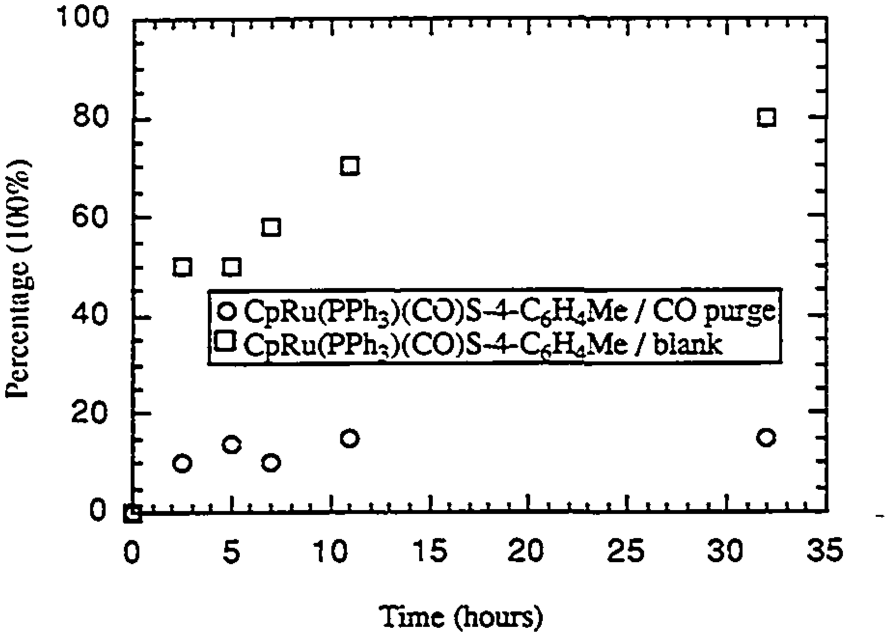
PPh_3 for 28 hours at 67°C in the absence of light gave only 10% of the phosphine-substituted product, $CpRu(PPh_3)(CO)SSR$. Thus, as with $CpRu(CO)_2SR$, CO substitution at ruthenium by PPh_3 is photo-assisted. The reaction was greatly accelerated by the addition of Et_3NO, a reagent known to convert a metal coordinated carbonyl group to CO_2.[26] This may indicate that CO dissociation is the rate determining step in this reaction.



(2.7)

To further probe the reaction of CO substitution, a NMR tube containing $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and 1.2 equivalents of PPh_3 in C_6D_6 was purged with a stream of CO and the reaction was monitored by NMR spectroscopy over a 27 hour period at room temperature. An identical NMR sample that was not purged with CO was monitored as the blank. After 2.5 hours, the NMR spectrum of the blank revealed peaks due to $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ in the ratio of 5:4. The NMR spectrum of the sample that had been purged with CO revealed the same set of peaks in the ratio of 1:10. This trend of slower reactivity of $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ towards PPh_3 substitution in the CO purged sample continued over time (Figure 2.2). Thus, excess CO may inhibit substitution by PPh_3 by inhibiting CO dissociation from ruthenium, indicating that loss of CO may be the rate determining step in this reaction.

Figure 2.2 Reaction of $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ with 1.2 equivalents of PPh_3 in C_6D_6 at 21°C, in the presence of and without CO. Note, 1.2 further equivalents of PPh_3 was added after 5 hours in both reactions.



However, if photolytic CO labilization from $CpRu(CO)_2SR$ occurred then one would expect that in the absence of PPh_3, loss of CO would result in the immediate dimerization of the unsaturated 16-electron complex, CpRu(CO)SR, to give $(CpRu(CO)SR)_2$ at a similar rate as that of CO substitution by PPh_3 to give $CpRu(PPh_3)(CO)SR$. When a sample of $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ was heated for 3 hours at 67°C in C_6D_6, only 3% was converted to *cis* and *trans*-$(CpRu(CO)S\text{-}4\text{-}C_6H_4Me)_2$. Thus, the reaction may not proceed by this proposed pathway.

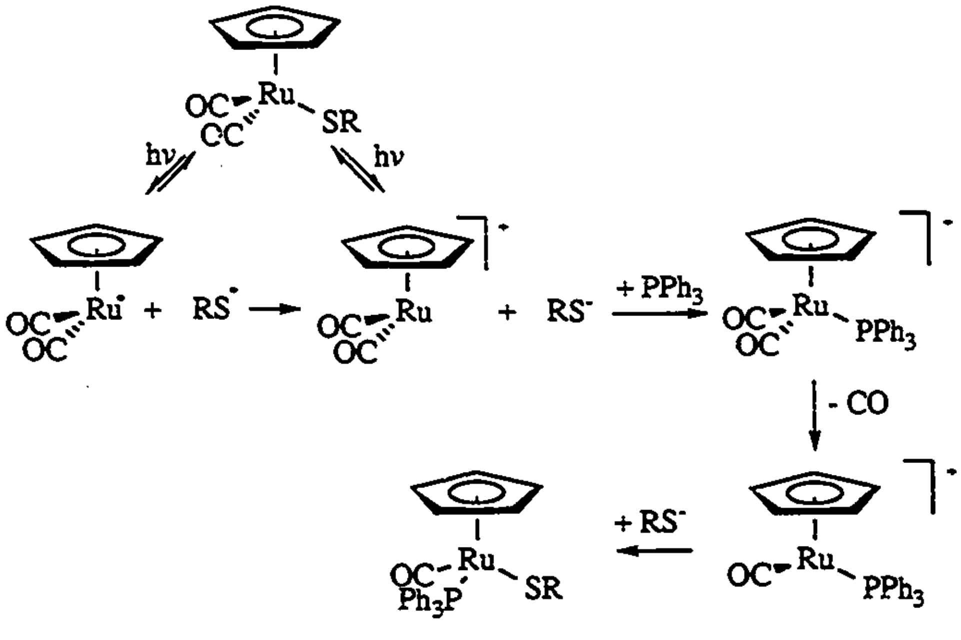
The photolytic behaviour of $CpM(CO)_2R$ (M = Fe, Ru; R = Me, $CH_2C_6H_5$, CH_2SiMe_3) has been investigated. Several studies indicate that irradiation of $CpM(CO)_2R$ results in CO dissociation and the formation of the 16-electron intermediate CpM(CO)R as the initial product[27-29] (Equation 2.8). The lack of homolysis of the M-R bond in these complexes may be attributed to $R^{\cdot}$ being unstable. Only one study reported that irradiation of $CpFe(CO)_2R$ (R = $CH_2C_6H_5$, CH_2SiMe_3) resulted in homolysis of the M-R bond to give M$^{\cdot}$ and R$^{\cdot}$, in addition to CO labilization.[30]

$$CpM(CO)_2R \xrightarrow{h\nu} CpM(CO)R + CO \qquad (2.8)$$

M = Fe, Ru; R = Me, $CH_2C_6H_5$, CH_2SiMe

Homolysis of the Ru-SR bond in $CpRu(CO)_2SR$ may be favourable due to the stability of RS$^{\cdot}$ (compared to R$^{\cdot}$) and give $[CpRu(CO)_2]^{\cdot}$ and RS$^{\cdot}$ (Scheme 2.4). Subsequently, RS$^{\cdot}$ may oxidize the metal fragment to give $[CpRu(CO)_2]^+$ and RS$^-$. Precedence for oxidation of the metal radical species is found in studies of the photolytic homolysis of the M-M bond in $Mn_2(CO)_{10}$ and $Cp_2W_2(CO)_6$ giving the monomer fragment $[M]^{\cdot}$,[31] where in the presence of one-electron oxidants, an electron was abstracted from the metal atom to give $[M]^+$. Alternatively, $[CpRu(CO)_2]^+$ and RS$^-$ may also be formed in one step by photoinitiated heterolytic cleavage of the Ru-SR bond.

Scheme 2.4



The next step of the mechanism may be PPh_3 association to give a $[CpRu(PPh_3)(CO)_2]^+$ intermediate which subsequently loses CO. This unsaturated fragment can then be attacked by the thiolate, RS^-, to give the final product. Precedence for these last series of events comes from the reaction between $[CpRu(CO)_2(CS)]^+$ and RS^- which gave CpRu(CO)(CS)(SR), resulting from CO loss (Equation 2.9).[32]

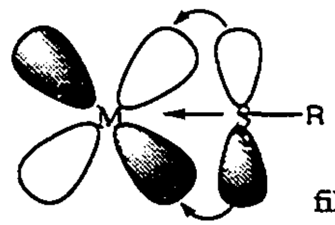
$$[CpRu(CO)_2(CS)]^+ + SR^- \longrightarrow CpRu(CO)(CS)SR + CO \qquad (2.9)$$

The reaction is relevant to others of this type reported in the literature. When a solution of $CpFe(CO)_2SC_6H_5$ and excess PMe_3 in toluene was refluxed for 3 hours $CpFe(PMe_3)(CO)SC_6H_5$ was obtained[33] in 49% yield (Equation 2.10). Similarly, the dicarbonyl compounds $CpRu(CO)_2X$, where X = Cl, Br and I, lost a CO ligand when refluxed[34] in xylene with a slight excess of PPh_3 (Equation 2.11). The reaction was determined to proceed via a dissociative mechanism. However, as mentioned earlier, these CO ligands are not normally thermally labile but the authors made no mention of this fact. It seems reasonable, therefore, that these reactions may also have been photo-assisted.

$$CpFe(CO)_2SC_6H_5 + PMe_3 \longrightarrow CpFe(PMe_3)(CO)SC_6H_5 + CO \qquad (2.10)$$

$$\underset{X = Cl, Br, I}{CpRu(CO)_2X + PPh_3} \longrightarrow CpRu(PPh_3)(CO)X + CO \qquad (2.11)$$

Kinetic exchange studies for the complexes $Cp^*Ru(PMe_3)_2X$ (X = SH, Me) found that the lone pairs on SH substantially accelerated PMe_3 dissociation and stabilized the $Cp^*Ru(PMe_3)X$ transition state compared to the complex for X = Me.[15] This was attributed to the formation of a M-SH π-bond in the former complex, via a lone pair on sulfur which stabilized the unsaturated complex. A molecular orbital explanation based on the Dewar-Chatt-Duncanson[35-37] representation of the π-donor ability of RS^- to a transition-metal is shown below.



empty metal d-orbital

filled sulfur p-orbital

The results of the CO substituted reactions by PPh_3 may also be explained by the theoretical studies that have been carried out on the effect of ligands containing lone pairs on metal complexes. *Ab initio* calculations on $CpRu(PH_3)X$ showed that Ru-X π-bonding decreased upon addition of PH_3 to give $CpRu(PH_3)_2X$. Since nucleophiles still attacked $Cp^*Ru(PH_3)X$ under mild conditions, it was concluded that this multiple bonding still leaves the complex operationally unsaturated.[38]

Other theoretical studies involved Fenske-Hall molecular orbital calculations and have been reported for $CpFe(CO)_2SH$.[39] The results indicated that the dπ-pπ orbital interaction between a filled metal d orbital and the filled sulfur 3p orbital destabilized the HOMO which is principally sulfur 3p in character.

The reactivity of $CpRu(PPh_3)_2SR$ has been attributed to similar electronic interactions. These compounds undergo facile ligand substitution, insert CS_2 to give the thioxanthates $CpRu(PPh_3)S_2CSR$,[11] and aggregate in the absence of ligands to give dimers and trimers.[40] Thus, as in the reactivity suggested by the studies and shown with $CpRu(PPh_3)_2SR$, the sulfur atom in $CpRu(CO)_2SR$ (and $CpRu(CO)_2SSR$) may tend to labilize a CO ligand.

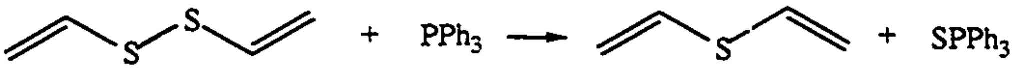
In summary, the ease of the reaction of $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ with PPh_3 to give the phosphine substituted complex $CpRu(PPh_3)(CO)S\text{-}4\text{-}C_6H_4Me$ was somewhat surprising at first. However, since the reaction was inhibited in the dark, it seems that it was photochemically induced by the ambient fluorescent lighting. The CO ligands of group 6 Cp-dicarbonyls are typically not thermally labile but are activated by photolysis.[41] However, it is not known if CO or SR labilization occurs, and indeed, the reaction may proceed by both routes. Analogous to this reaction, the reaction of CpRu(CO)$_2$SS-4-C$_6$H$_4$Me with PPh$_3$ to give CpRu(PPh$_3$)(CO)S-4-C$_6$H$_4$Me may also proceed via loss of RSS$^\cdot$ or RSS$^-$ via a photo-assisted pathways.

Desulfurization of MS$_x$R

A logical way to put our desulfurization results in context, is to compare them to those in literature. For example, spontaneous desulfurization of CpW(CO)$_3$SSR[2] gave the corresponding thiolate, CpW(CO)$_3$SR. The rate of desulfurization was greatly enhanced by PPh$_3$. However, the metal disulfane compounds, *cis*-(PPh$_3$)$_2$Pt(phth)SSR[5] and CpRu(PPh$_3$)(CO)SSR[4] do not undergo spontaneous sulfur extrusion, although the former was desulfurized in the presence of PPh$_3$. In addition, [Ir(η^2-S$_2$R)(dppe)$_2$]$^{2+}$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) reacts with 2 equivalents of PPh$_3$ to give [Ir(dppe)$_2$]$^+$, SPPh$_3$ and RSPPh$_3$$^+$.[42] Thus, the stability of metal disulfane complexes must depend on both the metal center and its ligand environment. The effect of light on these desulfurization reactions was not explored by the authors.

The CO ligands on the unstable disulfane complexes CpRu(CO)$_2$SSR and CpW(CO)$_3$SSR are excellent π-acceptors and may generate an electron deficient metal center. The PPh$_3$ ligand in the stable complexes CpRu(PPh$_3$)(CO)SSR is an excellent σ-donor and may give an electron rich metal center. Perhaps the metal center in complexes with many CO ligands is too electron poor to support sulfane ligands. A buildup of positive charge in the sulfur atom coordinated to the metal would promote desulfurization.

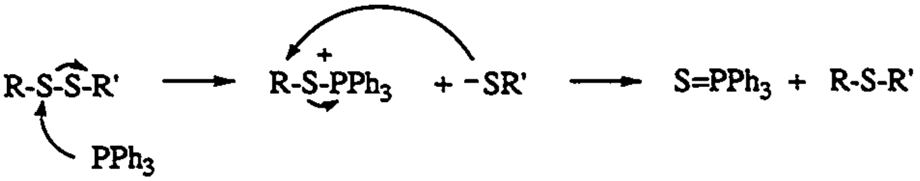
Organic disulfides are a stable class of compounds and normally are not desulfurized by PPh$_3$ unless activating terminal groups are present.[43,44] For example, diallyl disulfide is desulfurized by PPh_3 to give $SPPh_3$ and diallyl monosulfide[45] (Equation 2.12).



(2.12)

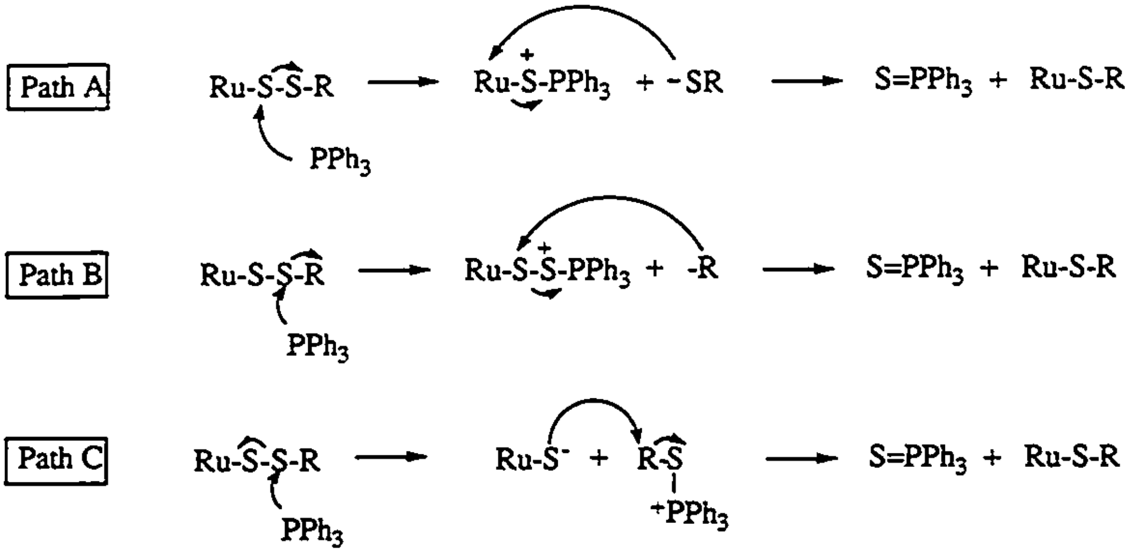
The desulfurization of "activated" organic disulfides by phosphines is thought to involve the formation of an intermediate phosphonium salt which undergoes subsequent back side attack by the thiolate anion to eliminate phosphine sulfide and give the corresponding sulfide (Scheme 2.5).

Scheme 2.5



The initial attack is postulated[44,46] to occur on the more negatively polarized sulfur atom in the case of a nonsymmetric disulfide. Unfortunately, the most negatively polarized sulfur atom in $CpRu(CO)_2SSR$ is difficult to predict, and thus, the sulfur attacked by PPh_3 can not be predicted based on this analogy to the organic systems (Scheme 2.5). Based on the leaving group ability, it is more likely the PPh_3 attacks the sulfur atom coordinated to the ruthenium atom as opposed to the sulfur atom bonded to R, because RS^-, is a better leaving group than R^-. These two paths are illustrated in Scheme 2.6 as Path A and Path B, respectively. Another possible mechanism is shown in Path C where attack by PPh_3 at the sulfur atom bonded to R results in S-S bond cleavage to form RuS^-. This nucleophile then attacks the R of $[R\text{-}S\text{-}PPh_3]^+$. Thus, PPh_3 desulfurization of $CpRu(CO)_2SSR$ most likely goes by Paths A or C.

Scheme 2.6

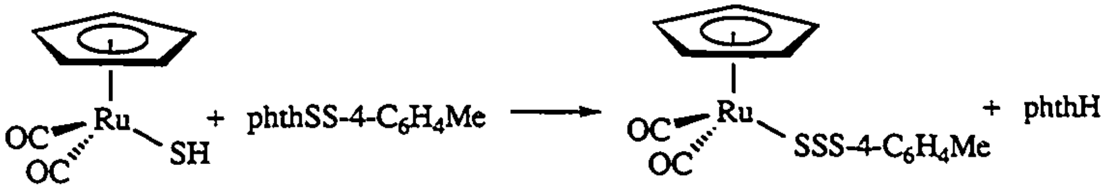


The instability of our and other disulfane compounds towards spontaneous desulfurization is inconsistent with these organic analogs. The metal center may have a large influence on the -SSR fragment compared to R.

2.2.4 Preparation of CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me

The reaction of CpRu(CO)$_2$SH with phthSS-4-C$_6$H$_4$Me in THF at -78°C gave one product, assigned as the trisulfane, CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me (**13a**), as identified by the NMR spectrum of the crude product (Equation 2.13). However, subsequent workup via column chromatography gave a mixture of CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me and CpRu(CO)$_2$SS-4-C$_6$H$_4$Me in the ratio of 9:1, in addition to a small amount of (4-MeC$_6$H$_4$)$_2$S$_2$. The latter may have prevented crystallization of CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me, since the presence of RS$_x$R tends to cause oils.[47] As a result, CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me was characterized by the NMR, IR, and mass spectra of the crude product. CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me underwent sulfur extrusion in solution even at -16°C to form

$CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$, $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and other unknown compounds (NMR). $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ also loses sulfur as an oil at -16°C. Thus, addition of an extra sulfur in $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ seems to give a product even less stable than $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ with respect to spontaneous sulfur loss.



13a

(2.13)

Spontaneous sulfur extrusion has been observed in the metal trisulfanes $CpW(CO)_3SSSR$[48] and $Cp_2Ti(SSR)X$.[3] By contrast, $CpRu(PPh_3)(CO)SSSR$ does not lose sulfur in solution.[4] Thus, as with metal disulfanes, the stability of metal trisulfanes seems to be dependent on both the metal center and ligand environment. This spontaneous desulfurization of $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ also parallels the reactivity in organic trisulfides which are known to spontaneously lose sulfur to give the corresponding disulfide, as discussed earlier (see Equations 2.2 and 2.3).[49]

2.3 Conclusions

The compounds $CpRu(CO)_2SH$ and $CpRu(CO)_2SSR$ (R = $4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$), rare examples of their type, were prepared and fully characterized. The disulfanes $CpRu(CO)_2SSR$ where R = $CHMe_2$ and C_3H_7 are unstable. Solutions of $CpRu(CO)_2SSR$ (R = $4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$) are stable in the dark but spontaneously lose a sulfur atom in the presence of light. The reaction of $CpRu(CO)_2SSR$ with PPh_3 gave $CpRu(PPh_3)(CO)SR$ via two pathways. The rate of reaction decreased in the dark implying a photo-assisted pathway. $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ was also prepared but spontaneously lost sulfur in solution. The thiolates $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) are very stable and react with PPh_3 to give $CpRu(PPh_3)(CO)SR$. A novel mechanism was proposed which involves the photo-assisted labilization of the Ru-SR bond.

Compared to $CpRu(PPh_3)(CO)S_xR$, the presence of two CO ligands decreased the stability of the $-S_xR$ (x = 2,3) ligand, possibly due to electonic factors. The factors that determine the ease of sulfur loss from MS_xR are not well understood. However, the increased π-acidity of CO decreased the electron density at the metal and may increase the $M\text{-}S_xR$ π-bonding. This may weaken the S-S bond.

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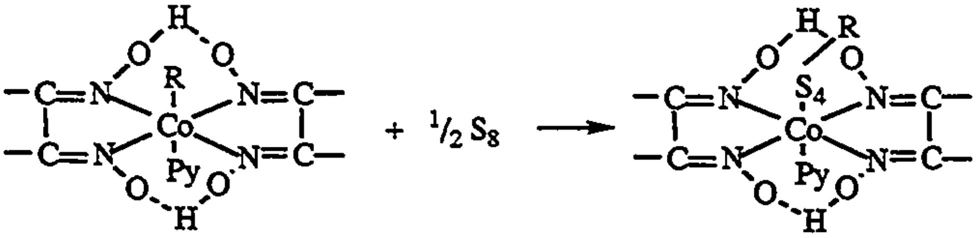
Chapter 3.

Sulfur Insertion Reactions with $CpRu(CO)_2S_xR$ (x = 1, 2) and Exchange Reactions with $CpRu(CO)_2SR$

3.1 Introduction

As discussed in Chapter 1, the ability of sulfur to catenate is well established and sulfur chains greater than 20 atoms in length can be formed.[1] Catenation may be viewed as successive insertions of sulfur into sulfur-sulfur bonds.

There are only a few reports of organometallic complexes which insert sulfur into metal-carbon sigma bonds and knowledge of the mechanisms and factors that influence sulfur insertion is elusive. The first example of sulfur insertion was reported for some alkyl- and aryl-cobaloximes.[2,3] These photolytically and thermally induced insertions gave organometallic tetrasulfanes as the most important products (Equation 3.1). Sulfur insertion may have proceeded in a stepwise fashion into Co-R to yield Co-S-R, followed by subsequent insertion to give Co-S_2-R, Co-S_3-R, and finally the product Co-S_4-R. The x-ray crystal structure of the organometallic tetrasulfane was not determined.

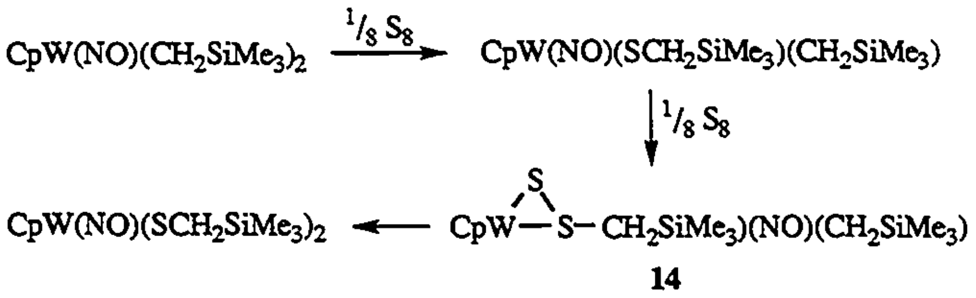


(3.1)

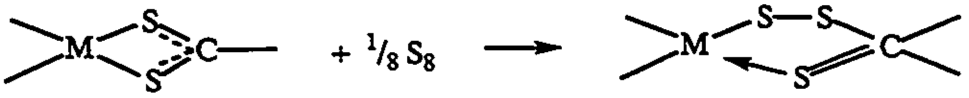
Another example of sulfur insertion involves the addition of one or two equivalents of sulfur to $CpW(NO)(CH_2SiMe_3)_2$ to give $CpW(NO)(SCH_2SiMe_3)(CH_2SiMe_3)$ and

$CpW(NO)(SCH_2SiMe_3)_2$, respectively[4-6] (Scheme 3.1). $CpW(NO)(\eta^2\text{-}S_2CH_2SiMe_3)(CH_2SiMe_3)$ (**14**) was isolated as an intermediate in the reaction of $CpW(NO)(SCH_2SiMe_3)(CH_2SiMe_3)$ with one equivalent of sulfur and its x-ray structure was determined. The slow rate of the reaction prevented decisive kinetic studies and mechanistic details of the insertion reaction were not determined. The authors concluded that sulfur insertion was complex and more complicated than first anticipated.

Scheme 3.1



Some metal 1,1-dithiocomplexes such as $Fe(p\text{-MePhDta})_2(p\text{-MePhDtaS})$,[7,8] $Ni(PhDtaS)_2$,[9] $Zn(PhDtaS)_2$,[9] $Ni(p\text{-}i\text{-PrPhDta})(p\text{-}i\text{-PrPhDtaS})_2$[10] and $Zn(p\text{-}i\text{-PrPhDtaS})_2$[10] (Dta = *p*-dithiocumate or dithiobenzoate) undergo sulfur insertion into the MS_2CX ring with the formation of MS_3CX, a five membered chelate (Equation 3.2). Early studies of these sulfur-addition reactions using radioactive ^{35}S were reported for $Ni(CS_3)^{2-}$ and concluded that sulfur inserted into the C-S bond, and not the M-S bond.[11] Later studies using ^{34}S with $Ni(PhDtaS)_2$ confirmed that sulfur inserted into the C-S bond.[12,13]



(3.2)

Sulfur insertion into a metal-thiolato bond has been postulated once before in the reaction of $Cu(tet\text{-}b)^{2+}$, where tet = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazocyclotetradoecane, with $HSCH_2CO_3H$ in the presence of KOH to give Cu(tet-b)$SSCH_2CO_2 \cdot 3CH_3OH$[14] (Equation 3.3). The mechanism of the formation of the copper disulfane is not known.

$$[Cu(tet\text{-}b)]^{2+} + KOH + 2\,HSCH_2CO_2H \longrightarrow Cu(tet\text{-}b)SSCH_2CO_2 + CH_3CO_2H + H_2O + H^+ + K^+ \quad (3.3)$$

Although all of these systems utilized elemental sulfur for the insertion reactions, it is not the only source of inserted sulfur. It has been known for a long time that organic polysulfides, RS_xR ($x > 2$) may spontaneously lose sulfur and, consequently provide sources of inserted sulfur.[15,16] For example, diethyltetrasulfide has been reported to give diethyl disulfide and free sulfur on distillation under reduced pressure.[17] The same authors reported that diethyl tetrasulfide gives diethyl disulfide and sulfur when distilling at atmospheric pressure. Taking this loss of sulfur one step further, some organic species transfer sulfur from one molecule to another. For example, a heated sample of Me_2S_3 in benzene at 80°C in the dark gives Me_2S_2 and Me_2S_4 as the initial products. Over time, the higher sulfanes (Me_2S_x ($x = 5,6$)) are also formed.[16] The mechanism is poorly understood even though the reaction has been studied by the use of a radical initiator, radical trap, polar and ionic solvents. From the results of the studies, the authors proposed that the thermal decomposition of Me_2S_3 to Me_2S_x occurred by an ionic mechanism.

There are at least two incentives for the study of sulfur insertion into and catenation of metal-sulfano species. First, MS_xR complexes for $x > 3$ are extremely rare and sulfur insertion may provide a synthetic route to their formation. Second, a metal-sulfane system which undergoes chain growth may model part of the Claus Process wherein sulfur chain growth occurs to give S_8.

In this chapter, insertion of sulfur into the complexes $CpRu(CO)_2S_xR$ (x = 1,2; R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) was investigated. In addition, sulfur transfer reactions of the complexes $CpRu(CO)_2SSR$, and exchange reactions between $CpRu(CO)_2S_xR$ with R'_2S_y, (y = 2,3) were also examined. Possible mechanisms for these reactions are discussed.

3.2 Results and Discussion

3.2.1 Identification of Products

Before describing the results from the insertion and exchange experiments, the methods used to identify the products and determine the amount of each product present in the reactions will be briefly presented. All of the procedures are described in detail in the Experimental Section. The compounds, $CpRu(CO)_2S_xR$ (x = 1,2; R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) were identified by comparison of their ^1H NMR shifts of the Cp and alkyl protons of their R groups (R = 4-C_6H_4Me, $CH_2C_6H_5$) to those of authentic samples. The ^1H NMR shifts for all of the compounds identified in these experiments are displayed in Table E.1. For example, the Cp peak due to $CpRu(CO)_2SSS$-4-C_6H_4Me (4.51 ppm) occurs 0.11 ppm downfield from that of $CpRu(CO)_2SS$-4-C_6H_4Me (4.40 ppm) and the Me peak (1.99 ppm) occurs 0.07 ppm upfield from that of $CpRu(CO)_2SS$-4-C_6H_4Me (2.06 ppm). The compounds $CpRu(CO)_2SSSR$ (R = C_6H_5, $CH_2C_6H_5$) were not synthesized; however, based on the shift of the peaks in the ^1H NMR spectra of $CpRu(CO)_2S_x$-4-C_6H_4Me (x = 2,3), the positions of the peaks were estimated. Thus, in the insertion reactions involving $CpRu(CO)_2S_xC_6H_5$ (x = 1,2), the Cp peak at 4.49 ppm (0.10 ppm downfield from that of $CpRu(CO)_2SSC_6H_5$ (4.39 ppm) was assigned to $CpRu(CO)_2SSSC_6H_5$. Likewise, in the insertion reactions involving

$CpRu(CO)_2S_xCH_2C_6H_5$ (x = 1,2), the Cp peak at 4.57 ppm (0.12 ppm downfield from that of $CpRu(CO)_2SSCH_2C_6H_5$ (4.43 ppm) and the CH_2 peak at 3.35 ppm (0.63 ppm upfield from that of $CpRu(CO)_2SSCH_2C_6H_5$ (3.98 ppm) were assigned to $CpRu(CO)_2SSSCH_2C_6H_5$. The ratio of the products present was obtained from integration of these same proton peaks.

Initial experiments were performed with the compounds for R = 4-C_6H_4Me, C_6H_5 and $CH_2C_6H_5$ to determine the effect of the R group on the rate of the reaction and product distribution.

3.2.2 Reactions of $CpRu(CO)_2SR$

$CpRu(CO)_2SR$ and 1 Equivalent of Sulfur

The NMR spectra of samples of $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5) in C_6D_6 treated with 1 gram equivalent of S_8 and heated at 45°C revealed Cp peaks due to the sulfur inserted products, $CpRu(CO)_2SSR$ and $CpRu(CO)_2SSSR$ after 21 hours. There were also peaks due to R_2S_2. The reactions equilibrated after 116 hours and were stopped. The solutions were dull orange in colour and there was dark precipitate in the NMR tubes, indicative of decomposition. The relative percentages of the products are given in Table 3.1. The reaction of $CpRu(CO)_2S$-4-C_6H_4Me with sulfur was also performed in the absence of light and, after 116 hours of heating, the product distribution was similar to that found in the light. However, there was less precipitate in the NMR tubes indicating less decomposition. This suggests that the observed decomposition was photolytically promoted.

In contrast to the above, a sample of $CpRu(CO)_2SCH_2C_6H_5$ in C_6D_6 treated with 1 gram equivalent of S_8 under the same conditions (light, 45°C, 116 hours) did not insert sulfur. The solution was light brown in colour and the NMR tube did not contain any precipitate. Peaks due to unreacted $CpRu(CO)_2SCH_2C_6H_5$ accounted for 76% of the integrated intensity in the NMR spectrum, and the Cp peaks due to inserted products $CpRu(CO)_2S_xCH_2C_6H_5$ (x = 2,3) were not present. Since aryl thiolate anions are better leaving groups than alkyl ones,[18] it is tempting to speculate that loss of RS^- may be a key step in the sulfur insertion

Table 3.1 Product distribution of soluble products after heating samples of $CpRu(CO)_2SR$ with $^1/_8$ equivalent of S_8 in C_6D_6 at 45°C for 116 hours.

R	$CpRu(CO)_2SR$	$CpRu(CO)_2SSR$	$CpRu(CO)_2SSSR$	Combined Unidentified
4-C_6H_4Me	70%	15%	15%	--
C_6H_5	47%	12%	15%	26%

CpRu(CO)₂SR without Added Sulfur

In order to determine the source of the inserted sulfur (either from a molecule of $CpRu(CO)_2SR$, or from the added sulfur), the same reactions were performed without added sulfur. Samples of $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) in C_6D_6 heated at 45°C for 4 days revealed at least 2 new Cp peaks in addition to the Cp peak due to unreacted $CpRu(CO)_2SR$ in their NMR spectra. There were also peaks due to R_2S_2. There was no precipitate in the NMR tubes and the colours of the solutions remained bright orange, indicative of less decomposition than in the reactions with added sulfur. The peaks that appeared in the NMR spectrum for $CpRu(CO)_2SC_6H_5$ and $CpRu(CO)_2SCH_2C_6H_5$ were identified as *cis*- and *trans*-$(CpRu(CO)(SC_6H_5))_2$ and *cis*- and *trans*-$(CpRu(CO)(SCH_2C_6H_5))_2$, respectively.[19] $(CpRu(CO)(S\text{-}4\text{-}C_6H_4Me))_2$ has not been previously reported in the literature but by analogy to the other compounds, the peaks at 4.58 and 4.35 ppm are most likely due to *cis*- and *trans*-$(CpRu(CO)(S\text{-}4\text{-}C_6H_4Me))_2$, respectively. Thus, heating solutions of CpRu(CO)SR gave *cis*- and *trans*-$(CpRu(CO)(SR))_2$ with loss of CO (Equation 3.4). The product distribution of the solutions after heating the solutions for 116 hours are given in Table 3.2. Based on the rate of conversion to the dimers from heated solutions of $CpRu(CO)_2SR$, the thermal stability of $CpRu(CO)_2SR$ decreases in the order $CpRu(CO)_2SCH_2C_6H_5 > CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me > CpRu(CO)_2SC_6H_5$.

$$2\ CpRu(CO)_2SR \xrightarrow{heat} cis\text{- and } trans\text{-}(CpRu(CO)SR)_2 + 2\,CO \qquad (3.4)$$

$$R = 4\text{-}C_6H_4Me,\ C_6H_5,\ CH_2C_6H_5$$

Table 3.2 Product distribution after heating samples of $CpRu(CO)_2SR$ in C_6D_6 at 45°C for 116 hours.

R	$CpRu(CO)_2SR$	*cis*- $(CpRu(CO)SR)_2$	*trans*- $(CpRu(CO)SR)_2$	Other Unidentified
$4\text{-}C_6H_4Me$	62%	25% (4.58 ppm)	13% (4.35 ppm)	--
C_6H_5	30%	51% (4.55 ppm)	19% (4.30 ppm)	--
$CH_2C_6H_5$	82%	7% (4.25 ppm)	7% (4.12, 4.18 ppm)	4%

In summary, heating solutions of $CpRu(CO)_2SR$ did not give the sulfur inserted products $CpRu(CO)_2SSR$ and $CpRu(CO)_2SSSR$. Therefore, the source of the inserted sulfur in the reactions of $CpRu(CO)_2SR$ with S_8 must be S_8.

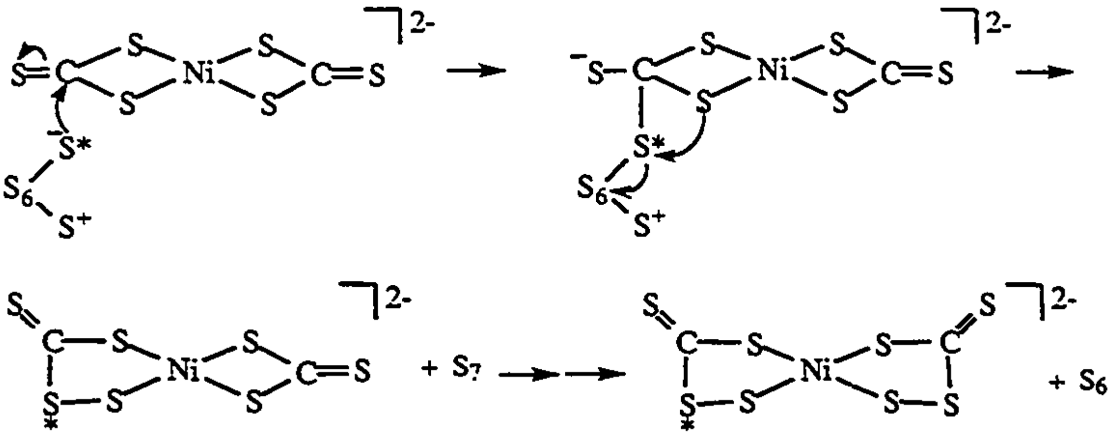
Proposed Mechanism of Sulfur Insertion into $CpRu(CO)_2SR$

The reaction of $CpRu(CO)_2SR$ (R = aryl) with S_8 gave $CpRu(CO)_2S_xR$ (x = 2,3). The reaction is not photo-activated and does not occur in the absence of S_8. This is the first example of sulfur insertion into a metal-thiolate bond giving higher sulfanes as products.

The novelty of sulfur insertion into $CpRu(CO)_2SR$ is realized as there are no examples of sulfur insertion into organic sulfides, RSR. The only data found on the thermal activity of organic sulfides date back to 1951 which reports the products as hydrogen sulfide, thiols and gaseous hydrocarbons.[20]

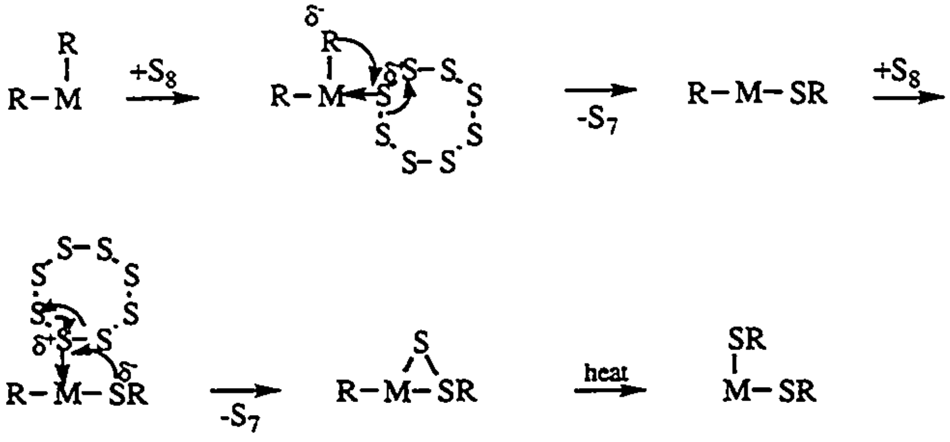
As mentioned in the introduction, sulfur insertion into metal complexes containing a chelating S_2CX group have been studied. Based on sulfur insertion studies of $[Ni(CS_3)_2]^{2-}$ with labeled sulfur (^{35}S), a mechanism involving attack from S_8 onto the electrophilic carbon atom was proposed (Scheme 3.2).[11] However, this mechanism is not applicable to the formation of $CpRu(CO)_2S_xR$ complexes (x = 2,3, R = aryl) because nucleophilic attack of sulfur at an aromatic carbon is unlikely.

Scheme 3.2



The complex $CpW(NO)(CH_2SiMe_3)_2$ also underwent S_8 insertion into metal-carbon bonds[4-6] (Scheme 3.3). The mechanism was postulated to proceed via precoordination of S_8 to the unsaturated 16-electron metal center followed by migration of $Me_3SiH_2C^-$ to a sulfur atom and loss of S_7. The second sulfur atom could be inserted by S_8 precoordination to the tungsten atom followed by intramolecular attack by $Me_3SiH_2CS^-$ onto the coordinated S_8 ring and subsequent loss of S_7. The last part of this mechanism involving attack of $Me_3SiH_2CS^-$ onto the coordinated S_8 ring is attractive to our $CpRu(CO)_2SR$ system because it accounts for the result that insertion only occurred when R is an aromatic group. However, precoordination of S_8 to the ruthenium atom would necessitate CO dissociation to give a 16-electron unsaturated ruthenium complex followed by CO association, which is unlikely. Therefore, a similar mechanism to the one proposed in Scheme 3.3 appears unlikely in explaining sulfur insertion in $CpRu(CO)_2SR$.

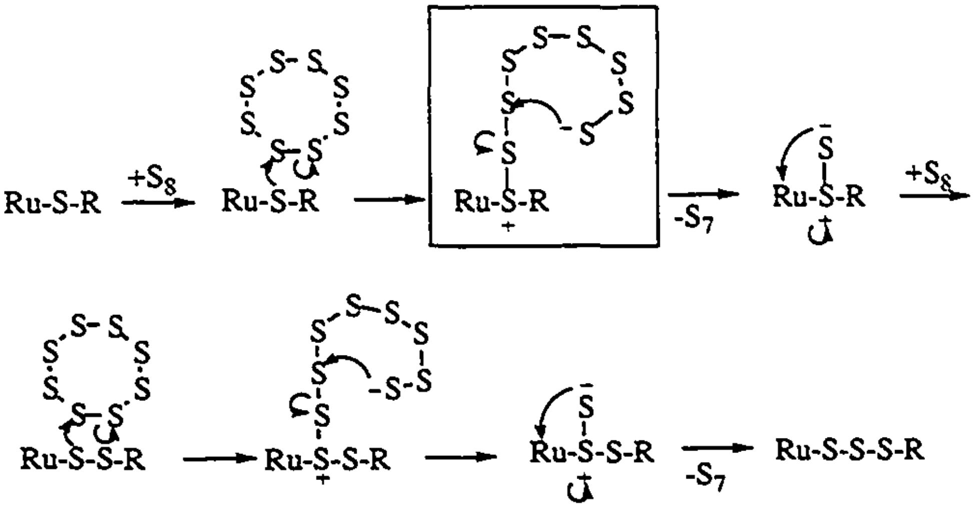
Scheme 3.3



$M = CpW(NO)$; $R = CH_2SiMe_3$

Since $CpRu(CO)_2SR$ does not possess an overall negative charge (as $Ni(CS_3)^{2-}$) or an unsaturated 16-electron metal center (as $CpW(NO)(CH_2SiMe_3)_2$) perhaps the mechanism for the formation of $CpRu(CO)_2S_xR$ ($x = 2,3$) from the reaction of $CpRu(CO)_2SR$ with S_8 does not proceed via nucleophilic attack *from* S_8 as shown in Schemes 3.2 and 3.3 but instead involves nucleophilic attack *onto* S_8. The mechanism proposed in Scheme 3.4 proceeds via nucleophilic attack from the thiolate sulfur atom onto a sulfur atom in the S_8 ring, causing the ring to open. Subsequent loss of S_7 [21] gives a disulfur intermediate which can rearrange to give the ruthenium disulfane, $CpRu(CO)_2SSR$. This disulfane can then react with S_8 (or S_7) to insert another sulfur atom and give $CpRu(CO)_2SSSR$.[21]

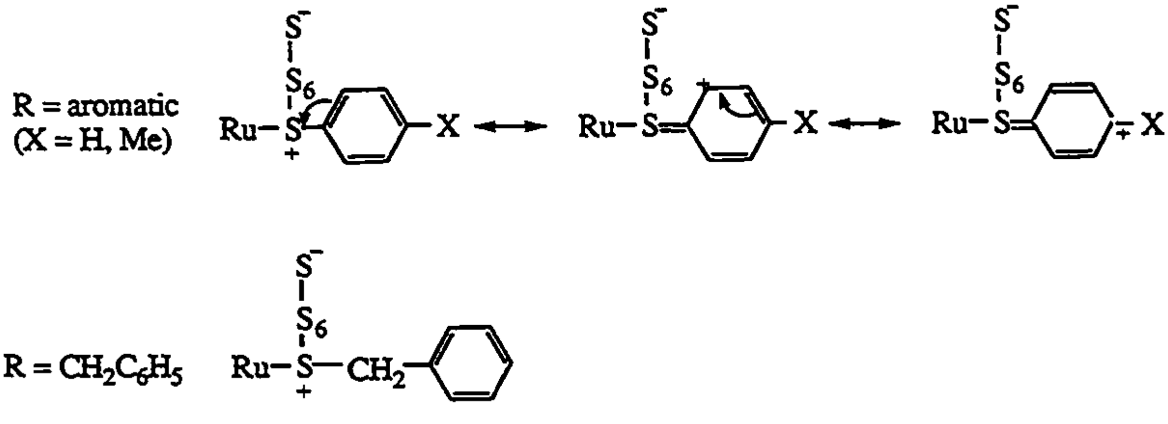
Scheme 3.4



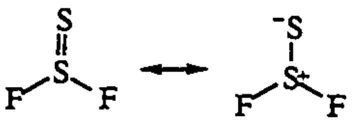
Note, the Cp and CO ligands are not shown for clarity.

The mechanism in Scheme 3.4 also accounts for the lack of sulfur insertion in $CpRu(CO)_2SCH_2C_6H_5$. The boxed intermediate in Scheme 3.4 is redrawn in Scheme 3.5 as resonance stabilized structures when R is an aryl group. However, when R is $CH_2C_6H_5$ there are no resonance structures which will stabilize the positive charge on the sulfur atom; consequently this intermediate may be unstable for $CpRu(CO)_2SCH_2C_6H_5$ and no sulfur insertion is observed.

Scheme 3.5



Existing x-ray crystal structures of some disulfur compounds support the S^+-S^- structure in Scheme 3.4. The compounds F_2S_2[22] (**15**), *O,O*-bicyclohexyl-1,1'-diyl thiosulphite[23] (**16**) and $Cp^*{}_2Cr_2S_5$ ($Cp^* = \eta^5$-C_5Me_5)[24] (**17**) contain rare S_2 moieties. **17** also contains a novel η^2-S_2 ligand bridging the metal centers. The structures of these complexes are shown below along with their S^+-S^- (thiosulfoxide) resonance structure.



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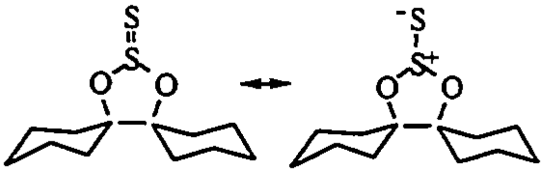

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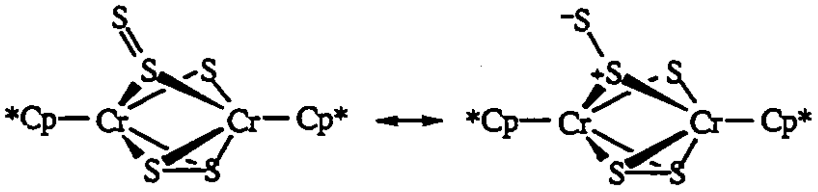
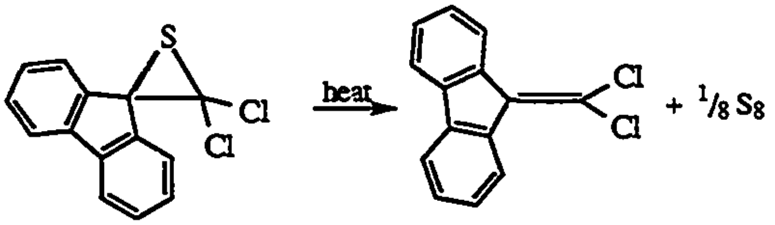


17

Disulfur or thiosulfoxide intermediates have also been postulated in organic sulfur extrusion mechanisms. For example, a thiosulfoxide intermediate is implicated in the extrusion of sulfur in the thermal decomposition of 3',3'-dichlorospiro[fluorene-9,2'-thiirane][25] (Equation 3.5). The loss of sulfur proceeds by both uni- and bimolecular ionic mechanisms involving the formation of a zwitterionic S_2 moiety (S^+-S^-) followed by growth of sulfur atoms to give the sulfur extruded product and S_8.



(3.5)

In summary, the mechanisms reported in the literature for sulfur insertion are not applicable to $CpRu(CO)_2SR$ complexes. Instead, a new mechanism involving nucleophilic attack from the sulfur atom onto S_8 followed by rearrangement to give a disulfur intermediate (S^+-S^-) has been postulated to account for sulfur insertion into $CpRu(CO)_2SR$ complexes.

3.2.3 $CpRu(CO)_2SR$ with excess R_2S_x, (x = 2,3)

Since sulfur inserts into $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5), other sulfur containing compounds were examined as possible sources of sulfur.

$CpRu(CO)_2SC_6H_5$ and (4-$C_6H_4Me)_2S_3$

Organic trisulfides can extrude sulfur in solution and are potential sources of sulfur. Treatment of $CpRu(CO)_2SC_6H_5$ with 6 equivalents of (4-$MeC_6H_4)_2S_3$ in C_6D_6 at 67°C for 57 hours gave peaks in the NMR spectrum due to $CpRu(CO)_2SC_6H_5$, $CpRu(CO)_2SSC_6H_5$, $CpRu(CO)_2S$-4-C_6H_4Me, $CpRu(CO)_2SS$-4-C_6H_4Me and $CpRu(CO)_2SSS$-4-C_6H_4Me in relative percentages of 8, 6, 27, 46 and 13%, respectively (Scheme 3.6). Surprisingly, the majority of these products contained the 4-C_6H_4Me group from the organic trisulfide. Thus, (4-$MeC_6H_4)_2S_3$ undergoes exchange with $CpRu(CO)_2SC_6H_5$. In addition, (4-$MeC_6H_4)_2S_3$ is also a source of inserted sulfur, but is less effective than elemental sulfur.

Scheme 3.6

$CpRu(CO)_2SC_6H_5$ + 6 $(4\text{-}C_6H_4Me)_2S_3$ $\longrightarrow$

$CpRu(CO)_2SC_6H_5$ 8%

$CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ 27%

$CpRu(CO)_2SSC_6H_5$ 6%

$CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ 46%

$CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ 13%

In an attempt to determine whether or not the reaction was photo-activated, the reaction was performed in the absence of light. Treatment of $CpRu(CO)_2SC_6H_5$ with 6 equivalents of $(4\text{-}MeC_6H_4)_2S_3$ under the same conditions (C_6D_6, 67°C, 57 hours) but in the absence of light gave peaks in the NMR spectrum due to $CpRu(CO)_2S\text{-}4C_6H_4Me$ and $CpRu(CO)_2SC_6H_5$, 15 and 85%, respectively. Therefore, the inhibition of ligand exchange in the dark, and the lack of sulfur insertion suggest that these ligand reactions are photo-initiated.

$CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and $(C_6H_5CH_2)_2S_3$

Treatment of $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ with 6 equivalents of $(C_6H_5CH_2)_2S_3$ in C_6D_6 at 67°C for 57 hours gave peaks due to $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$, $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$, $CpRu(CO)_2SCH_2C_6H_5$, and $CpRu(CO)_2SSSCH_2C_6H_5$ in relative percentages of 52, 3, 31 and 5%, respectively (Scheme 3.7). There were also peaks due to $(4\text{-}MeC_6H_4)_2S_2$. There were no peaks due to the disulfanes $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ or $CpRu(CO)_2SSCH_2C_6H_5$. The solution remained bright yellow and there was no precipitate in the NMR tube. $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ undergoes ligand exchange with $(C_6H_5CH_2)_2S_3$, but to a lesser extent than does $CpRu(CO)_2SC_6H_5$ with $(4\text{-}MeC_6H_4)_2S_3$, and gives less sulfur atom transfer. Nevertheless, these reactions appear to be reasonably general for $CpRu(CO)_2SR$ where R = aryl.

Scheme 3.7

$$\begin{array}{cccc}
\mathrm{CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me} & & \mathrm{CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me} & \mathrm{CpRu(CO)_2SCH_2C_6H_5} \\
 & & 52\% & 31\% \\
+ & \longrightarrow & & \\
\mathrm{6\ (C_6H_5CH_2)_2S_3} & & \mathrm{CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me} & \mathrm{CpRu(CO)_2SSSCH_2C_6H_5} \\
 & & 3\% & 5\% \\
 & & \multicolumn{2}{c}{+\ \text{unidentified } 12\%}
\end{array}$$

The reaction of $CpRu(CO)_2S$-4-C_6H_4Me with 6 equivalents of $(C_6H_5CH_2)_2S_3$ under the same conditions (C_6D_6, 67°C, 57 hours) was performed in the absence of light. The products obtained were $CpRu(CO)_2SCH_2C_6H_5$ and unreacted $CpRu(CO)_2S$-4-C_6H_4Me in 15% and 85%, respectively. This is similar to the reaction of $CpRu(CO)_2SC_6H_5$ with $(4\text{-}MeC_6H_4)_2S_3$ in the dark and also suggests that ligand exchange is photo-initiated.

$CpRu(CO)_2S$-4-C_6H_4Me and $(C_6H_5CH_2)_2S_2$

Since ligand exchange occurred between $CpRu(CO)_2SR$ and organic trisulfides, it was of interest to see if any reaction would occur between the thiolato complexes and disulfides. Treatment of $CpRu(CO)_2S$-4-C_6H_4Me with 6 equivalents of $(C_6H_5CH_2)_2S_2$ in C_6D_6 at 67°C for 57 hours gave peaks due to unreacted $CpRu(CO)_2S$-4-C_6H_4Me and to $CpRu(CO)_2S_xCH_2C_6H_5$ (x = 1-3) (Scheme 3.8). There were no unidentified Cp peaks in the NMR spectrum and no precipitation in the NMR tube. The reaction between the organic disulfides $(C_6H_5CH_2)_2S_2$ and $(4\text{-}C_6H_4Me)_2S_2$ under the same conditions gave three new CH_2 and Me peaks accounting for a total of 5% of the total integration. It is likely that these products are due to $C_6H_5CH_2SS\text{-}4\text{-}C_6H_4Me$, $C_6H_5CH_2S\text{-}4\text{-}C_6H_4Me$, $(C_6H_5CH_2)_2S$ and $(4\text{-}C_6H_4Me)_2S$. Thus, these organic disulfides are photo-activated only to a small extent.

Scheme 3.8

$$\begin{array}{ccccc}
\mathrm{CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me} & & \mathrm{CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me} & & \mathrm{CpRu(CO)_2SCH_2C_6H_5} \\
 & & 68\% & & 13\% \\
+ & \longrightarrow & & & \\
6\,(\mathrm{C_6H_5CH_2})_2\mathrm{S_2} & & \mathrm{CpRu(CO)_2SSCH_2C_6H_5} & & \mathrm{CpRu(CO)_2SSSCH_2C_6H_5} \\
 & & 10\% & & 7\%
\end{array}$$

The ligand exchange reaction between $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and $(C_6H_5CH_2)_2S_2$ is surprising because disulfides do not to dissociate to an appreciable extent in nonpolar solvents and do not extrude sulfur.[26] There was no reaction in the absence of light implying that ligand exchange and sulfur insertion between $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ and $(C_6H_5CH_2)_2S_2$ may be photo-initiated.

Proposed Mechanism for Ligand Exchange

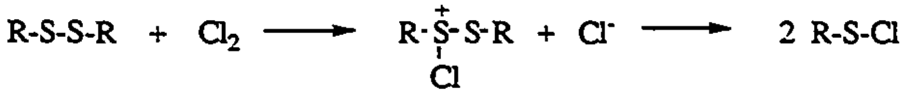
The photosensitive ligand exchange and sulfur insertion reactions between $CpRu(CO)_2SR$ and R'_2S_2 and R'_2S_3 to give $CpRu(CO)_2S_xR$ and $CpRu(CO)_2S_xR'$ ($x = 1\text{-}3$) are new. Prior to a discussion of these reactions, the photochemistry of di- and trisulfides will be briefly reviewed.

The sulfur-sulfur bond of disulfides may be cleaved both homolytically and heterolytically. Homolytic cleavage of the disulfide bond may be induced either photolytically or thermally at temperatures above 125°C.[27] For example, unsymmetrical disulfides dissociate at 170°C to give symmetrical disulfides.[20]

$$\text{R-S-S-R} \xrightarrow{h\nu} 2\,\text{R-S}^{\cdot}$$

$$\text{R-S-S-R} + \text{R'-S-S-R'} \rightleftharpoons 2\,\text{R-S}^{\cdot} + 2\,\text{R'-S}^{\cdot} \rightleftharpoons 2\ \text{R'-S-S-R}$$

Heterolytic cleavage of the sulfur-sulfur bond of disulfides may be induced by both electrophilic and nucleophilic reagents. For example, in the presence of an electrophile, a sulfur atom may act as Lewis base.[28] An example of electrophilic scission of a sulfur-sulfur bond is the chlorinolysis of a disulfide.[29]



$$\text{R-S-S-R} + \text{Cl}_2 \longrightarrow \text{R-}\underset{\text{Cl}}{\overset{+}{\text{S}}}\text{-S-R} + \text{Cl}^{-} \longrightarrow 2\ \text{R-S-Cl}$$

Organic trisulfides also undergo photolytic or homolytic cleavage to form RS$^{\cdot}$ and RSS$^{\cdot}$ radicals, allowing exchange of end groups and disproportionation to di- and polysulfides. Extrusion of sulfur from some trisulfides has also been reported.[18,30-32] As discussed with the organic disulfides, trisulfides are also susceptible to electrophilic and nucleophilic attack.

$$\text{R-S-S-S-R} \xrightleftharpoons{h\nu \text{ or } \Delta} \text{R-S}^{\cdot} + \text{RSS}^{\cdot} \rightleftharpoons \text{R-S-S-R} + \text{R-S-S-S-S-R}$$

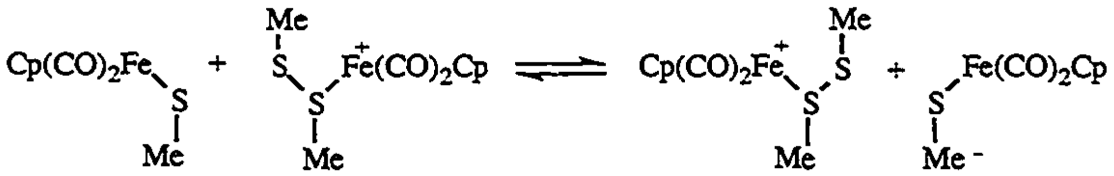
$$\text{R-S-S-S-R} + {}^{*}\text{S}_8 \xrightleftharpoons{\Delta} \text{R-S-}{}^{*}\text{S-S-R} + \text{S}_8$$

$$\text{R-S-S-S-R} + \text{R'-S-S-S-R'} \xrightleftharpoons{\Delta} 2\ \text{R-S-S-S-R'}$$

$$\text{R-S-S-S-R} + \text{R-}{}^{*}\text{S-}{}^{*}\text{S-R} \xrightleftharpoons{\Delta} \text{R-}{}^{*}\text{S-S-}{}^{*}\text{S-R} + \text{R-S-S-R}$$

Surprisingly little work has addressed the photochemical behaviour of organic sulfides, RSR'. Studies with RSCl (R = aromatic) in the presence HR' (saturated alkanes) gave RSR' as the major product with RSSR , R'Cl and HCl as minor products.[33] Thus, the S-Cl bond undergoes photoinitiated homolytic cleavage.

Although there are many thiolato metal complexes known,[34-37] none has been reported to undergo ligand exchange with organic di- and trisulfides. A rapid exchange of uncoordinated thiolate cations, MeS^+, with coordinated thiolate ligands on two different $CpFe(CO)_2SMe$ molecules is the closest analogy. Nucleophilic attack from the sulfur atom of the thiolate group without the coordinated MeS^+, onto the sulfur atom of MeS^+ which is coordinated to iron has been proposed to account for this reactivity[38] (Equation 3.6).



(3.6)

As the reactions were photoinitiated, a mechanism similar to the homolytic reactions of organic di- and trisulfides can be envisioned to explain the ligand exchange reactions between $CpRu(CO)_2SR$ and R'_2S_x (x = 2,3) (Scheme 3.9). In Path A, homolysis of the Ru-SR bond in $CpRu(CO)_2SR$ would give $Cp(CO)_2Ru^{\cdot}$ and $RS^{\cdot}$ (1) and homolysis of R'SSR' gives 2 $R'S^{\cdot}$ (2). $R'S^{\cdot}$ can subsequently recombine with $Cp(CO)_2Ru^{\cdot}$ to give the substituted thiolate, $CpRu(CO)_2SR'$ (3). There is no source of inserted sulfur (disulfides do not extrude sulfur) to account for the formation of $CpRu(CO)_2SR'$ (x = 2,3) and homolytic cleavage of the S-R' and RuS-R bonds (which would account for $CpRu(CO)_2SR'$ (x = 2,3)) is unlikely. Thus, Path A in Scheme 3.9 only accounts for the formation of $CpRu(CO)_2SR'$.

By contrast, the reaction between $CpRu(CO)_2SR$ and R'_2S_3 (Path B) accounts for the formation of $CpRu(CO)_2S_xR'$ (x = 1,2) by recombination of $Cp(CO)_2Ru^{\cdot}$ with $RS^{\cdot}$ (3) and $RSS^{\cdot}$ (4), respectively. $CpRu(CO)_2SSSR'$ can be obtained by recombination of

$CpRu(CO)_2S^{\cdot}$ (from homolytic cleavage of the RuS-SR' bond (5)) and $R'SS^{\cdot}$ (7) (from R'SSSR'). Another route to the formation of $CpRu(CO)_2SSSR'$ (in addition to $CpRu(CO)_2S_xR$ (x = 2,3)) is via insertion of sulfur into $CpRu(CO)_2SR$ (R'SSSR' loses sulfur in solution). Thus, this mechanism accounts for all of the products observed between $CpRu(CO)_2SR$ and R'_2S_3.

Scheme 3.9

$\boxed{\text{Path A}}$

$$(1)\quad \text{Ru-SR} \rightleftharpoons \text{Ru}^{\cdot} + {}^{\cdot}\text{SR}$$

$$(2)\quad \text{R'-S-S-R'} \rightleftharpoons 2\,\text{R'-S}^{\cdot}$$

$$(3)\quad \text{Ru}^{\cdot} + {}^{\cdot}\text{SR'} \rightleftharpoons \boxed{\text{Ru-SR'}}$$

$\boxed{\text{Path B}}$

$$(1)\quad 2\,\text{Ru-SR} \rightleftharpoons 2\,\text{Ru}^{\cdot} + 2\,{}^{\cdot}\text{SR}$$

$$(2)\quad \text{R'SSSR'} \rightleftharpoons \text{R'S}^{\cdot} + {}^{\cdot}\text{SSR'}$$

$$(3)\quad \text{Ru}^{\cdot} + {}^{\cdot}\text{SR'} \rightleftharpoons \boxed{\text{Ru-SR'}}$$

$$(4)\quad \text{Ru}^{\cdot} + {}^{\cdot}\text{SSR'} \rightleftharpoons \boxed{\text{Ru-SSR'}}$$

$$(5)\quad \text{Ru-S-SR} \rightleftharpoons \text{RuS}^{\cdot} + {}^{\cdot}\text{SR}$$

$$(6)\quad \text{R'SSSR'} \rightleftharpoons \text{R'S}^{\cdot} + {}^{\cdot}\text{SSR'}$$

$$(7)\quad \text{RuS}^{\cdot} + {}^{\cdot}\text{SSR'} \rightleftharpoons \boxed{\text{RuSSSR'}}$$

$$(8)\quad \text{R'S}^{\cdot} + {}^{\cdot}\text{SR} \rightleftharpoons \text{R'SSR}$$

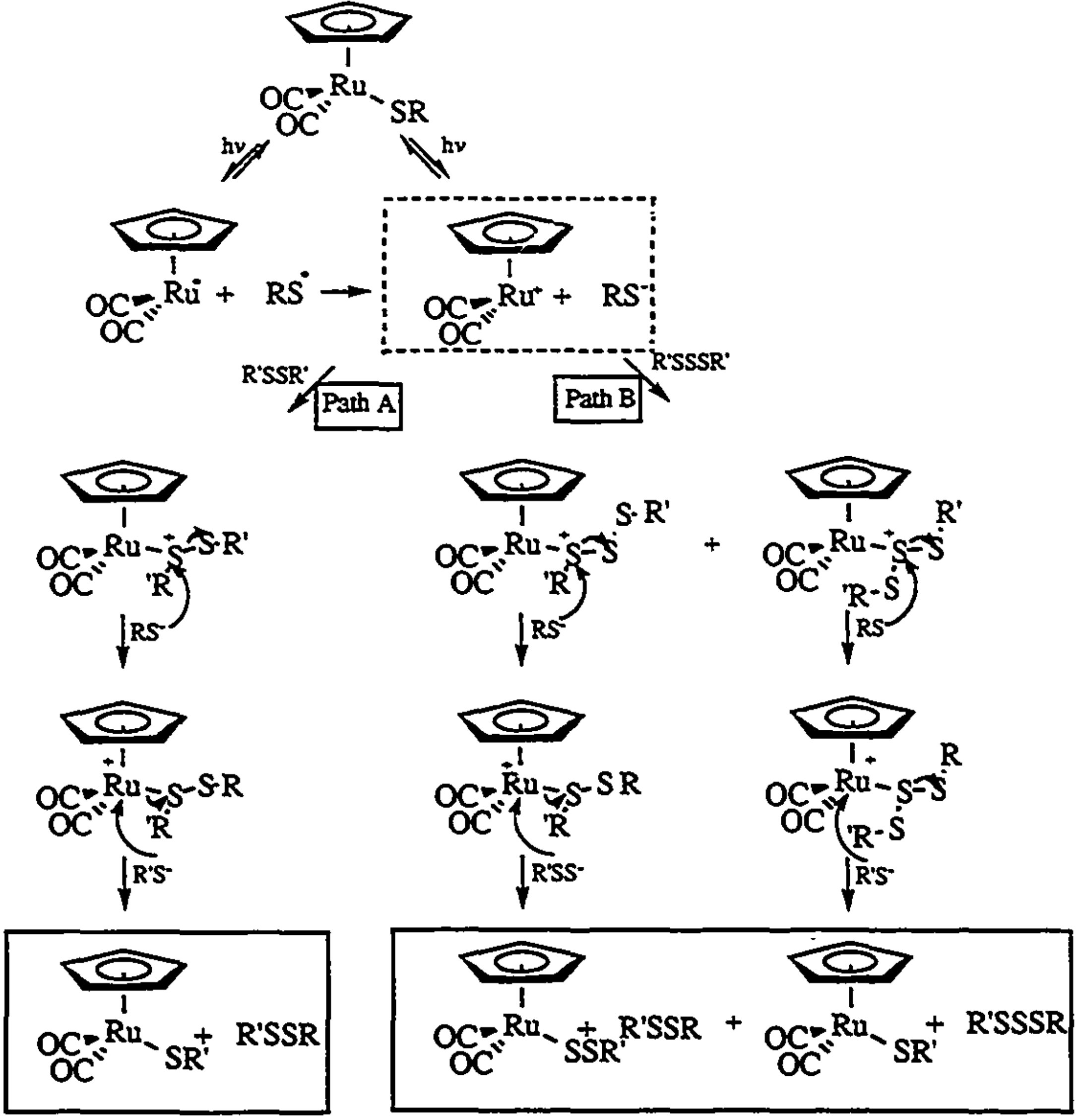
Note, the Cp and CO ligands are omitted for clarity.

Another mechanism which accounts for the products obtained in Scheme 3.9 is presented in Scheme 3.10. As speculated in Chapter 2, photolysis of $CpRu(CO)_2SR$ may lead to homolysis of the Ru-SR bond and give $[CpRu(CO)_2]^{\cdot}$ and $RS^{\cdot}$. One electron oxidation of $[CpRu(CO)_2]^{\cdot}$ by $RS^{\cdot}$ gives $[CpRu(CO)_2]^+$ and RS^-. Alternatively, $[CpRu(CO)_2]^+$ and RS^- may also be formed by photo-initiated heterolytic cleavage of the Ru-SR bond. $[CpRu(CO)_2]^+$ may be attacked by the disulfide. This step is supported by the ability of disulfides to act as Lewis bases in the presence of an electrophile[28,29] and the reports of mononuclear transition metal complexes that contain a RSSR ligand.[39,40]

Nucleophilic attack by RS$^-$ gives R'S$^-$ as the leaving group which can attack the metal to give the product, CpRu(CO)$_2$SR'. As with the mechanism in Path A of Scheme 3.9, this mechanism still does not account for CpRu(CO)$_2$S$_x$R' (x = 2,3).

A similar mechanism is illustrated for R'$_2$S$_3$ (Path B). Attack at a terminal or central sulfur of [CpRu(CO)$_2$(R'SSSR')]$^+$ gives CpRu(CO)$_2$S$_x$R' (x = 1,2). Insertion of S$_8$ (from R'SSSR') accounts for the other products.

Scheme 3.10



In summary, both Schemes in 3.9 and 3.10 account for the products observed between the reaction of $CpRu(CO)_2SR$ and R'_2S_3, however neither one can account for all of the products of observed between $CpRu(CO)_2SR$ and R'_2S_2.

3.2.4 Reactions of $CpRu(CO)_2SSR$

$CpRu(CO)_2SSR$

As previously mentioned in Chapter 2, the compounds $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) spontaneously lose sulfur in solution to give the corresponding thiolates, $CpRu(CO)_2SR$. Thus, to examine the thermal extrusion of sulfur from these complexes, samples of $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) were heated at 45°C. The peaks in the NMR spectra after 20 hours of heating were due to $CpRu(CO)_2SR$ and $CpRu(CO)_2SSR$. The reaction equilibrated after 116 hours and the NMR spectra revealed peaks due to $CpRu(CO)_2S_xR$ (x = 1-3) with the relative percentages of the products displayed in Table 3.3. The solutions were orange in colour and there was no precipitate in the NMR tubes. Thus, the complexes $CpRu(CO)_2SSR$ extrude sulfur to give the thiolate species $CpRu(CO)_2SR$ and insert sulfur to give the trisulfanes. In addition, the product distribution of $CpRu(CO)_2S_xR$ (x = 1-3) is independent of the R group.

Table 3.3 Product distribution after heating samples of $CpRu(CO)_2SSR$ in C_6D_6 at 45°C for 116 hours.

R	$CpRu(CO)_2SR$	$CpRu(CO)_2SSR$	$CpRu(CO)_2SSSR$	OtherUnidentied (% of all peaks)
4-C_6H_4Me	62%	19%	19%	(21%)
C_6H_5	53%	31%	16%	(7%)
$CH_2C_6H_5$	53%	34%	13%	(14%)

The percentage of $CpRu(CO)_2SR$, $CpRu(CO)_2SSR$ and $CpRu(CO)_2SSSR$ excludes Other Unidentified (i.e. Σ (MSR + MSSR + MSSSR) = 100%). Other Unidentified refers to combined unidentified Cp peaks (i.e. Σ (MSR + MSSR + MSSSR + Other Unidentified) = 100%)

To determine if sulfur extrusion and sulfur insertion were photo-initiated, a sample of $CpRu(CO)_2SS$-4-C_6H_4Me was heated in C_6D_6 at 45°C but in the absence of light. After 100 hours, the relative percentages of peaks in the NMR spectrum due to $CpRu(CO)_2S_x$-4-C_6H_4Me (x = 1-3) were 9, 88 and 3%, respectively. These results indicate that the amount of the sulfur extruded product, $CpRu(CO)_2S$-4-C_6H_4Me is much less than in the reaction that was performed in the light. Thus, sulfur loss from the disulfane seems to be photolytically activated. In addition, there is much less of the trisulfane product (3%) than in the reaction in the light. However, it cannot be determined if the decrease in the amount of inserted product is a result of decreased amounts of sulfur in solution (from less sulfur extrusion) or simply because the insertion reaction is also photo-initiated.

$CpRu(CO)_2SSR$ and one Equivalent of Sulfur

It was of interest to examine the effect of an additional source of sulfur on the relative amount of $CpRu(CO)_2SSSR$ formed. The compounds $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) were treated with 1 equivalent of S_8 in C_6D_6 at 45°C. The integration of peaks due to $CpRu(CO)_2S_xR$ (x = 1-3) in the NMR spectra for 116 hours revealed some interesting differences in the reactions for the different R groups (Table 3.4). The solutions were light brown in colour and there were small amounts of dark precipitate in the NMR tubes, indicative of decomposition. The results of these reactiions can be summarized as follows. (1) $CpRu(CO)_2SSCH_2C_6H_5$ had the slowest reactivity and gave the greatest percentage of unidentified products. (2) $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ extrudes sulfur to give the thiolato complex to a greater extent than $CpRu(CO)_2SSC_6H_5$ and $CpRu(CO)_2SSCH_2C_6H_5$. (3) Both $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2SSC_6H_5$ inserted sulfur to the same extent and gave equal amounts of $CpRu(CO)_2SSSR$. These reactions demonstrate that adding sulfur gave increased amounts or $CpRu(CO)_2SSSR$ compared to samples without the added sulfur.

Table 3.4 Product distribution after heating samples of $CpRu(CO)_2SSR$ with 1 equivalent of S_8 in C_6D_6 at 45°C for 116 hours.

R	$CpRu(CO)_2SR$	$CpRu(CO)_2SSR$	$CpRu(CO)_2SSSR$	Other Unidentified (% of all peaks)
$4\text{-}C_6H_4Me$	50%	18%	32%	(23%)
C_6H_5	24%	28%	33%	(15%)
$CH_2C_6H_5$	35%	43%	22%	(51%)

The percentage of $CpRu(CO)_2SR$, $CpRu(CO)_2SSR$ and $CpRu(CO)_2SSSR$ excludes Other Unidentified (i.e. Σ (MSR + MSSR + MSSSR) = 100%). Other Unidentified refers to combined unidentified Cp peaks (i.e. Σ (MSR + MSSR + MSSSR + Other Unidentified) = 100%)

3.2.5 Further Studies with $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$

Studies directed towards enhancing sulfur insertion into $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ were undertaken since preliminary results suggest that $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ inserts sulfur to a greater extent than $CpRu(CO)_2SSCH_2C_6H_5$. In all experiments, both the Cp and Me resonances in the NMR spectra of the mixtures were used to determine the product distribution.

The results of the following experiments will be reported as the percent of $CpRu(CO)_2S_x$-4-C_6H_4Me (x = 1-3) formed as determined from the equation $CpRu(CO)_2SR$ + $CpRu(CO)_2SSR$ + $CpRu(CO)_2SSSR$ = 100%, that is excluding unidentified products. The term "unidentifed" refers to all non-identifiable Cp peaks, i.e. any peaks besides those of $CpRu(CO)_2S_x$-4-C_6H_4Me, where x = 1-3. The amount of unidentified products will also be given for each experiment and will be obtained from the equation $CpRu(CO)_2SR$ + $CpRu(CO)_2SSR$ + $CpRu(CO)_2SSSR$ + unidentified = 100%. However, it must be kept in mind that the unidentified products may actually be a mixture of higher metal sulfanes, $CpRu(CO)_2S_xR$ (x > 3) which cannot be characterized.

$CpRu(CO)_2SS$-4-C_6H_4Me and Excess Sulfur

Since 1 equivalent of sulfur increased the amount of $CpRu(CO)_2SSSR$ formed, $CpRu(CO)_2SS$-4-C_6H_4Me was treated with 8 equivalents of sulfur, in C_6D_6 at 45°C to determine if insertion to form the trisulfane could be enhanced. The results with respect to the reaction with one equivalent of sulfur are:

(1) The reaction with 8 equivalents of sulfur contained twice the amount of $CpRu(CO)_2SSS$-4-C_6H_4Me at equilibrium (60% vs. 27%).

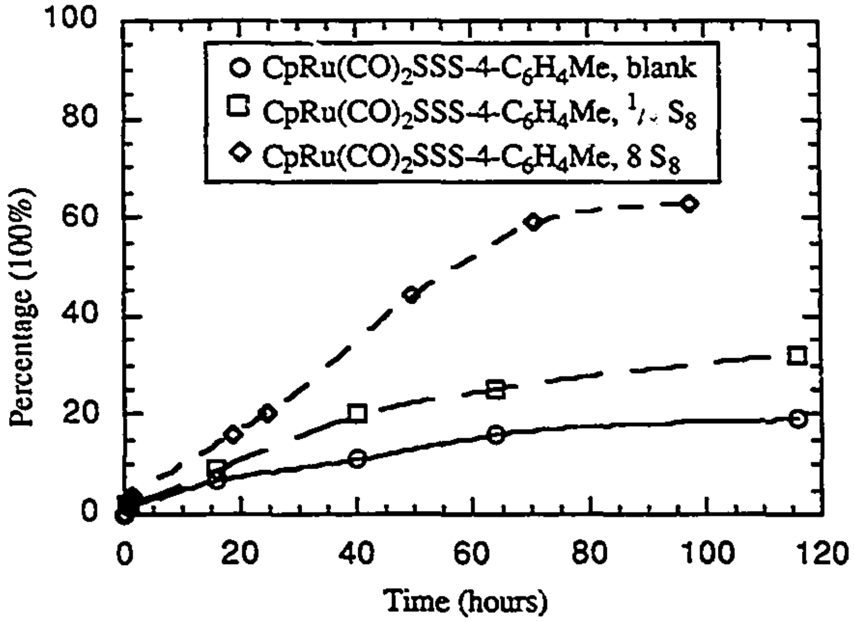
(2) The reaction consumes $CpRu(CO)_2SS$-4-C_6H_4Me more quickly and the reaction equilibrates faster (70 vs. 50 hours).

(3) The rate of sulfur extrusion to form $CpRu(CO)_2S$-4-C_6H_4Me is decreased and, at equilibrium, the concentration of $CpRu(CO)_2S$-4-C_6H_4Me is one half that in the experiment with 1 equivalent (22% vs. 50%)

(4) The amount of unidentified peaks is increased (60% vs. 40%) and decomposition is enhanced (more precipitate).

A graph showing the rate of $CpRu(CO)_2SSS$-4-C_6H_4Me formation in the presence of 1 equivalent, 8 equivalents and without sulfur is shown below (Figure 3.1). The graph clearly illustrates that the addition of excess sulfur to CpRu(CO)$_2$SS-4-C$_6$H$_4$Me greatly enhances the formation of CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me.

Figure 3.1 Formation of CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me in C$_6$D$_6$ at 45°C from CpRu(CO)$_2$SS-4-C$_6$H$_4$Me, reaction with 1 equivalent of S$_8$, and reaction with 8 equivalents of S$_8$.



To determine the effect of light on the reactions, two samples of CpRu(CO)$_2$SS-4-C$_6$H$_4$Me with 8 equivalents of S$_8$ in C$_6$D$_6$ at 67°C were monitored for 116 hours; one in the light and the other in the dark. The results from these experiments are summarized for the reaction in the dark with respect to the reaction in the light.

(1) The reaction in the dark contained less CpRu(CO)$_2$S-4-C$_6$H$_4$Me (5% vs. 26%), more CpRu(CO)$_2$SS-4-C$_6$H$_4$Me (73% vs. 31%) and less CpRu(CO)$_2$SSS-4-C$_6$H$_4$Me (22% vs. 43%).

(2) The number of unidentified peaks decreased and they accounted for less of the overall product distribution (10% vs. 40%).

After 2 days of further heating, the product percentage of $CpRu(CO)_2S_x$-4-C_6H_4Me (x = 1-3) for the reaction in the dark was to 6, 35 and 59%, respectively, with 25% of the Cp peaks due to unidentified products. In contrast, over 80% of the peaks in the reaction which was performed in the light were unidentified. These experiments imply that sulfur insertion and extrusion of $CpRu(CO)_2SS$-4-C_6H_4Me proceeds slower in the dark, but the equilibrium concentrations are similar to those obtained from the reactions in the light. In addition, the light seems to increase the formation of unidentified products.

Temperature Effect

Since the reactions were relatively slow and proceeded sometimes over 4 days at 45°C, the effect of higher temperatures on the insertion reactions was examined. Samples of $CpRu(CO)_2SS$-4-C_6H_4Me without sulfur and in the presence of 1 equivalent of S_8 were heated at 67°C in C_6D_6 for 116 hours and the results compared to the same reactions performed at 45°C. The higher temperature reactions equilibrated faster (50 hours) than the same reactions at 45°C (100 hours) and there were no significant differences in the product distribution of the reactions at the different temperatures. In addition, the amount of unidentified products was only slightly enhanced at the higher temperatures. Thus, further reactions were performed at 67°C.

Solvent Effect, C_6D_6 Versus THF-d_8

The rate of a reaction which proceeds via an ionic mechanism can depend on the polarity of the solvent while a radical reaction is usually independent of solvent polarity.[30] The reaction of $CpRu(CO)_2SS$-4-C_6H_4Me with 8 equivalents of sulfur was performed in C_6D_6 and THF-d_8 at 67°C and after 48 hours there was no significant difference in either the rate of sulfur insertion or the product distribution at equilibrium. Thus, the polarity of the solvent does not have a drastic effect on the rate of sulfur extrusion, sulfur insertion, or decomposition. This lack of solvent effect is in accordance with a free radial reaction.

However, the lack of solvent effect may also be a consequence of the long duration of the reaction, up to 4 days.

Miscellaneous Reagents

Other reagents can be added to increase the amount of the insertion products. Bases have been reported to catalyse some organic sulfur extrusion reactions.[41] Thus, two different reactions between $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and 8 equivalents of sulfur at 67°C were performed in the presence of either: 1) 0.2 equivalents of NH_3 or 2) 0.2 equivalents of NEt_3. The addition of bases did not have an effect on the reactions. Therefore, these sulfur extrusion and sulfur insertion reactions of $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ are not base catalyzed.

Radical reactions are accelerated in the presence of a radical initiator and inhibited in the presence of a radical trap. Thus, the reactions between $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and 8 equivalents of sulfur at 67°C were performed with the addition of: 1) 5% galvinoxyl, a radical initiator or 2) 0.3 equivalents of 2,2-diphenyl-1picrylhydrazyl hydrate, a free radical. The radical initiator had no effect on the reaction while the radical trap greatly enhanced decomposition. These results suggest that sulfur insertion does not proceed via a radical mechanism.

Reaction in the presence of CO

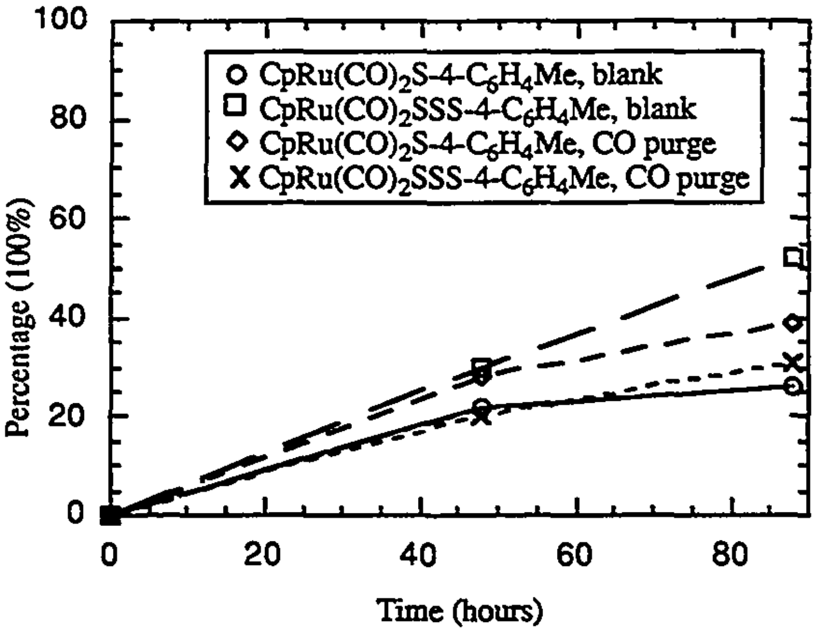
An NMR tube containing $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and 1 equivalent of S_8 in C_6D_6 was purged with CO gas (40 mL, 1.7 mmol) (syringe) and heated at 67°C for 88 hours. The results of the reaction in Figure 3.2 are listed with respect to the results of the same reaction but without CO gas (blank).

(1) The solution remained clear and bright yellow while the blank reaction was a dull yellow colour and contained some precipitate.

(2) There was somewhat more $CpRu(CO)_2S$-4-C_6H_4Me (39% vs. 26%) and less $CpRu(CO)_2SSS$-4-C_6H_4Me (31% vs. 52%).

(3) The percentage of unidentified Cp peaks was equal in each reaction.

Figure 3.2 Formation of $CpRu(CO)_2S_x$-4-C_6H_4Me (x = 1,3) from reaction of $CpRu(CO)_2SS$-4-C_6H_4Me with 8 equivalents of S_8 in C_6D_6 at 67°C for blank, and reaction purged with CO.



Reaction with SO_2

The addition of SO_2 is of special interest because it pertains to the Claus Process (catenation to form S_8). A sample of $CpRu(CO)_2SS$-4-C_6H_4Me (7.0 mg, 0.019 mmol) in C_6D_6 that had been purged with SO_2 gas (40 ml, 1.7 mmol) (syringe) was heated at 67°C for two days. An identical sample without SO_2 was also monitored. The results are listed with respect to the results of the same experiment but without SO_2 (blank).

(1) The reaction with SO_2 contained less $CpRu(CO)_2S$-4-C_6H_4Me (34% vs. 47%), equal amounts of $CpRu(CO)_2SS$-4-C_6H_4Me (29% vs. 34%) and more $CpRu(CO)_2SSS$-4-C_6H_4Me (37% vs. 19%).

(2) There were more unidentified products and they accounted for a larger percentage of the product distribution (50% vs. 25%). In addition there was more (4-$MeC_6H_4)_2S_2$ present (70% vs. 47%).

The absence of light did not affect the relative amounts of $CpRu(CO)_2S_xR$ (x = 2,3) formed and there was approximately the same amount of $(4\text{-}MeC_6H_4)_2S_2$ present.

Reaction with SO_2 and Excess Sulfur

In order to determine if the amount of insertion with added SO_2 could be further increased, the reaction was performed in the presence of SO_2 and excess sulfur. Thus, $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ (7.0 mg, 0.019 mmol) and 8 equivalents of S_8 in C_6D_6 was purged with SO_2 gas (40 ml, 1.7 mmol) (syringe) and heated at 67°C for two days. The results are given with respect to the same reaction purged with SO_2 gas but without added S_8 (blank).

(1) The reaction with SO_2 and S_8 contained less $CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$ (14% vs. 34%), less $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ (16% vs. 29%) and more $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ (70% vs. 37%).

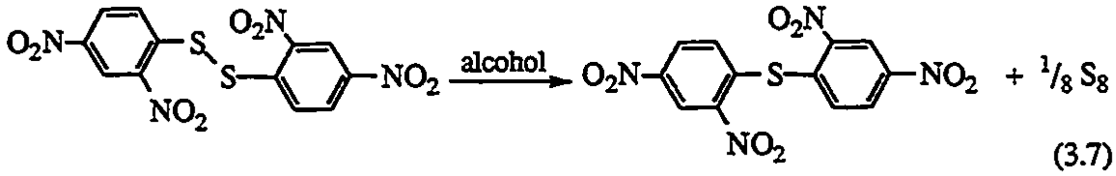
(2) Similar amounts of $(4\text{-}MeC_6H_4)_2S_2$ were present (75% vs. 70%).

The same reaction in the absence of light had almost identical product distribution but less $(4\text{-}MeC_6H_4)_2S_2$ (50%). The combination of excess sulfur and SO_2 gas gave the largest amount of sulfur insertion.

Discussion

The transfer of sulfur in the complexes $CpRu(CO)_2SSR$ to give a mixture of $CpRu(CO)_2S_xR$ (x = 1-3) is new and has not been observed in transition metal sulfano complexes. The initial formation of $CpRu(CO)_2SR$ followed by the formation of $CpRu(CO)_2SSSR$ suggests that the extruded sulfur is reinserted into $CpRu(CO)_2SSR$ to give $CpRu(CO)_2SSSR$. Since two processes (extrusion and insertion) are occurring, discerning the mechanisms of each of these processes may be complicated.

The inhibition of sulfur loss from $CpRu(CO)_2SSR$ in the absence of light suggests a photo-initiated pathway for sulfur extrusion. This pathway may be initiated by the loss of $RSS^{\cdot}$ via a route similar to the loss of $RS^{\cdot}$ proposed in Scheme 3.10. The mechanisms of sulfur extrusion in organic compounds are not clearly understood and are thought to go by different routes.[42] The lowest energy pathway for organic sulfur extrusion has been determined to be either loss of a sulfur chain fragment or diatomic sulfur, S_2, which can recombine to form S_8. Organic extrusion reactions can be thermally, photolytically, or base induced, and are solvent dependent, being faster in polar solvents.[42] However, organic sulfides undergo sulfur extrusion only if they contain activating groups and the reactions are either base or solvent induced. For example, bis(2,4-dinitrophenyl) disulfide undergoes extrusion of an atom of sulfur to form bis(2,4-dinitrophenyl) sulfide when heated in alcohol, but no extusion was observed when the disulfide was heated in non-polar solvents[43] (Equation 3.7).



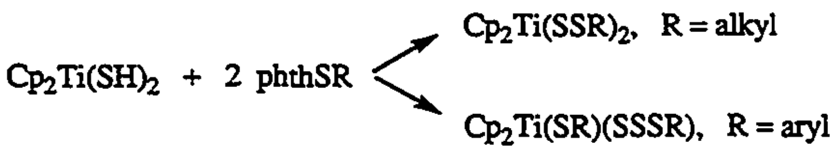
(3.7)

It is more difficult to speculate on a mechanism of sulfur insertion with metal disulfanes than with metal thiolates because 1) the reactivities of the two sulfurs in the ligands are unknown and 2) there is no literature precedence. The information obtained from studying the reaction of $CpRu(CO)_2SSR$ with sulfur under different conditions gave contradictory results with respect to an ionic or radical pathway for sulfur insertion. On one hand, the lack of solvent effect on the rate of sulfur insertion seems to indicate a radical pathway, but in contrast, the lack of acceleration in the rate of $CpRu(CO)_2SSSR$ formation with the addition of a radical initiator seems to indicate an ionic route. This ionic pathway to sulfur insertion is also supported by the procession of the reaction even in the absence of light. The role of CO in decreasing the amount of $CpRu(CO)_2SSSR$ formed is not understood. The mechanism for sulfur insertion may be similar to that of ligand exchange proposed in Scheme 3.10.

The largest increase in the amount of $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ formed was obtained from the reaction with SO_2. The large increase in both the amount of $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ and $(4\text{-}MeC_6H_4)_2S_2$ formed may be a result of SO_2 weakening the S-S or Ru-S bond possibly by behaving as a Lewis acid and accepting electrons from one of the lone pairs of the sulfur atoms from the disulfane ligand. This may suggest that the reaction of S_8 insertion into $CpRu(CO)_2SSR$ proceeds by an ionic route. Studies on the mechanism of SO_2 insertion into $CpFe(CO)_2R$ to give $CpFe(CO)_2S(O)_2R$ in organic solvents indicate that a radical pathway seems unlikely, as we have suggested.[44] The observation that SO_2 greatly enhanced the formation of $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ suggests that SO_2 may act as a catalyst which may be relevant to the Claus Process.

There is one example of rearrangement of a metal disulfane compound in the literature. The compound $Cp_2Ti(SH)_2$ was reacted with 2 equivalents of phthSR to give $Cp_2Ti(SSR)_2$, where R = alkyl, and $Cp_2Ti(SR)(SSSR)$, where R = aromatic[45](Scheme 3.11).

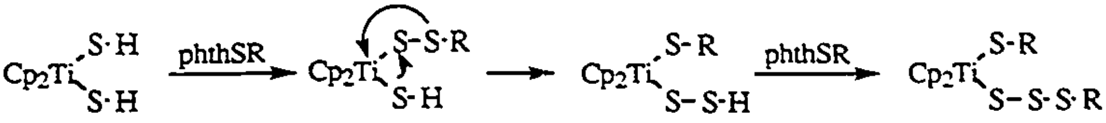
Scheme 3.11



Rearrangement of the intermediate $Cp_2Ti(SH)(SSR)$ followed by subsequent reaction with phthSR has been proposed to give the mixed thiolate-trisulfane compound (Scheme 3.12).

It was reasoned that this reactivity was seen only for aryl groups because aryl thiolate anions are better leaving groups than alkyl ones.[18]

Scheme 3.12



where R = aryl

Our system most likely does not follow this type of rearragement since S_8 is involved in the insertions.

3.3 Conclusions

The novel reactions of $CpRu(CO)_2SR$ involving sulfur atom insertion and ligand exchange with R_2S_y ($y = 2,3$) exemplify the influence of a metal system on a thiolate ligand. Studying these reactions has allowed us to propose mechanisms to account for ligand substitution such as photo-initiated $RS^{\cdot}$ labilization. Although these mechanisms cannot be definitively proved, these studies have illustrated that metal thiolato complexes may behave in a variety of different ways.

The sulfur transfer of $CpRu(CO)_2SSR$ in solution to give $CpRu(CO)_2S_xR$ ($x = 1$-3) and the insertion of added sulfur (S_8) to enhance the formation of $CpRu(CO)_2SSSR$ is also surprising. The amount of sulfur inserted product was maximized by the addition of SO_2 and elemental sulfur. Attempts to discern the mechanism of sulfur insertion showed that the reaction is complicated. Once again, it is difficult to discern the reactivity of MSSR since it cannot be concluded if the reactivity occurs as a result of labilization of the M-S or S-S , or both bonds.

3.4 References

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Chapter 4.

The Preparation of $CpRu(L)(CO)S_2O_yR$ ($y = 1, 2$; $L = CO$; $R =$ 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$ and $y = 4$, $L = PPh_3$; $R =$ 4-C_6H_4Me)

4.1 Introduction

The Claus Process, as discussed in Chapter 1, is the industrial reaction which converts H_2S to harmless sulfur and water (see Equation 1.5). In this transformation, H_2S and SO_2 react together on the surface of the catalyst to give the products.[1,2] However, studies have generally not been successful in determining the mechanisms of these transformations.[3-6] Thus, the preparation and study of complexes containing sulfur oxide ligands, which may be models of possible intermediates, is a reasonable approach towards gaining insight into the Claus Process.

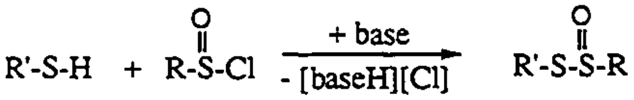
The synthesis and study of MS_2O_xR', requires familiarity with both the inorganic and organic literature. Thus, the preparative routes to the organic compounds RS_2O_xR', where $x = 1$-4, which have been studied exhaustively, will be reviewed briefly before discussing the literature of metal species with oxidized sulfane ligands.

4.1.1 Syntheses of Organic Compounds, RS_2O_xR'

Organic disulfides and their oxidized derivatives, RS_2O_xR' ($x = 1$-4) are well known and their preparations are well established. Thiosulfinates (RSS(O)R') are prepared by peracid oxidation of disulfides when $R = R'$[7] (Equation 4.1). However, for $R \neq R'$, a non-oxidative approach is preferred due to the nonregioselectivity of most oxidants, which result in a mixture of thiosulfonates.[8,9] Generally, nonsymmetric thiosulfinates are prepared by condensation reactions between sulfinyl chlorides and thiols in the presence of base[10] (Equation 4.2). Thiosulfinates are typically unstable and readily disproportionate into disulfides and thiosulfonates[11-16] (Equation 4.3).

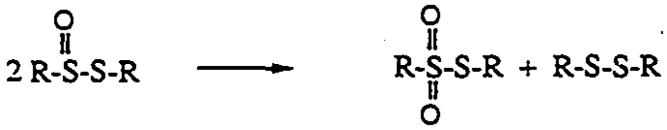
$$2\ R'\text{-}S\text{-}S\text{-}R \xrightarrow{[O]} R'\text{-}\overset{\overset{O}{\|}}{S}\text{-}S\text{-}R + R'\text{-}S\text{-}\overset{\overset{O}{\|}}{S}\text{-}R$$

(4.1)



$$R'\text{-}S\text{-}H + R\text{-}\overset{\overset{O}{\|}}{S}\text{-}Cl \xrightarrow[\text{- [baseH][Cl]}]{\text{+ base}} R'\text{-}S\text{-}\overset{\overset{O}{\|}}{S}\text{-}R$$

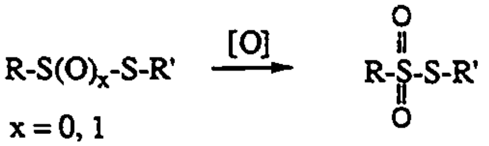
(4.2)



$$2\ R\text{-}\overset{\overset{O}{\|}}{S}\text{-}S\text{-}R \longrightarrow R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}S\text{-}R + R\text{-}S\text{-}S\text{-}R$$

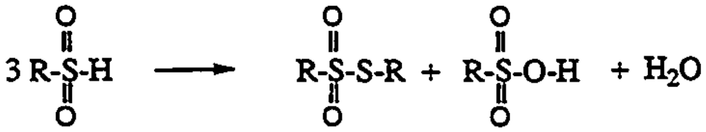
(4.3)

On the other hand, thiosulfonates ($RSS(O)_2R'$) are an extremely stable class of compounds.[17-19] They can be prepared by oxidation of disulfides or thiosulfinates (Equation 4.4) or by disproportionation of the sulfinic acid, RSO_2H[20] (Equation 4.5).



$$\underset{x = 0, 1}{R\text{-}S(O)_x\text{-}S\text{-}R'} \xrightarrow{[O]} R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}S\text{-}R'$$

(4.4)



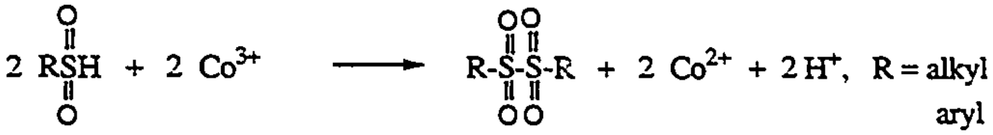
$$3\ R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}H \longrightarrow R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}S\text{-}R + R\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}O\text{-}H + H_2O$$

(4.5)

Sulfinylsulfones ($RS(O)S(O)_2R'$) can also be prepared by oxidation of a disulfide, thiosulfinate, or thiosulfonate precursor. However, they are unstable and undergo thermal decomposition to give sulfenyl sulfonic acids ($RSOS(O)_2R'$) which can subsequently undergo further reaction[20,21] (Equation 4.6).

$$\mathrm{R\text{-}\overset{\overset{O}{\|}}{S}\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}R} \xrightarrow{\text{heat}} \mathrm{R\text{-}S\text{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}R} \qquad (4.6)$$

Lastly, α-sulfones ($RS(O)_2S(O)_2R'$) are also known as a stable class of compounds,[22] although under certain conditions they may react with H_2O, or other nucleophiles.[23] The chief route to these is through oxidation of sulfinic acid salts or disulfides using $KMnO_4$, H_2O_2 or CH_3CO_3H, although yields are low.[11,24] A new method has been described which uses a Co(III) species to oxidize an alkyl or aryl sulfinic acid[25] (Equation 4.7).



$$2\ \mathrm{R\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}H} + 2\ \mathrm{Co^{3+}} \longrightarrow \mathrm{R\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}R} + 2\ \mathrm{Co^{2+}} + 2\,\mathrm{H^+},\ \ \mathrm{R} = \begin{array}{l}\text{alkyl}\\ \text{aryl}\end{array} \qquad (4.7)$$

In summary, the compounds RS_2O_yR' can be prepared by two types of reactions. One involves the oxidation of an RS_2O_yR' precursor as in Equations 4.1 and 4.5, while the other involves the joining or adding of two fragments of RSO_x and $R'SO_y$ as in Equations 4.2, 4.4 and 4.7. The latter route results in better selectivity and higher yields.

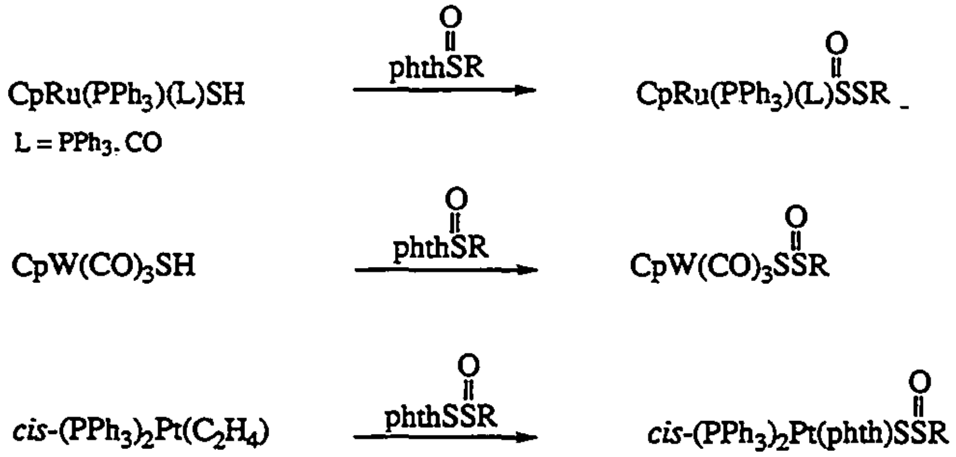
4.1.2 Syntheses of Transition Metal Complexes Containing the S_xO_y Moiety

By contrast to the organic compounds, the metal analogs, MS_2O_xR', are rare and there are few investigations into their chemistry. Consequently, a brief summary of the preparations for complexes MS_2O_xR, where x = 1-4, will be presented. In addition, oxidative routes to metal complexes containing oxidized sulfur ligands will be descibed.

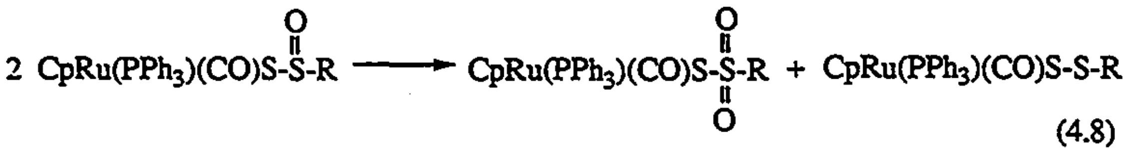
Metal complexes containing a 2-oxodisulfane ligand, -SS(O)R, have been synthesized by a non-oxidative route involving the reaction of the parent thiolato metal complex with a phthalimide sulfinyl transfer reagent, phthS(O)R (Scheme 4.1). For example, the complexes $CpRu(L)(CO)SS(O)R$ ($L = PPh_3$, CO; R = alkyl and aryl)[26-28] and $CpW(CO)_3SS(O)R$[29] ($R = CH_2C_6H_5$, $4\text{-}C_6H_4Me$) were prepared in good yields in this manner. The complexes *cis*-$(PPh_3)_2Pt(phth)SS(O)R$[30] (R = alkyl and aryl) were prepared by oxidative addition of $phthSS(O)R$ to *cis*-$(PPh_3)_2Pt(C_2H_4)$. Thus, these condensation routes are good for the synthesis of complexes of the type $MSS(O)R$.

Interestingly, these 2-dioxodisulfane complexes display differing reactivities. For example, the compounds $CpRu(PPh_3)(CO)SS(O)R$ are more stable than $CpW(CO)_3SS(O)R$ with respect to oxygen transfer in solution.

Scheme 4.1



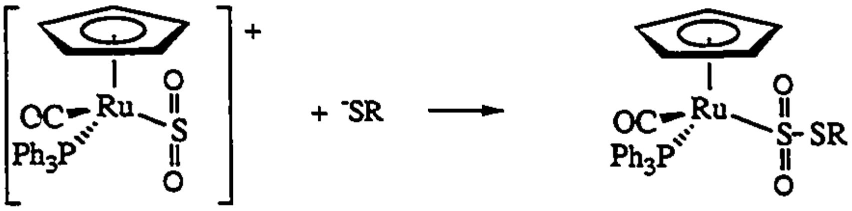
By contrast, the only metal complex containing a $-SS(O)_2R$ ligand that has been reported in the literature is $CpRu(PPh_3)(CO)SS(O)_2\text{-}4\text{-}C_6H_4Me$ which was prepared by oxygen transfer from $CpRu(PPh_3)(CO)SS(O)\text{-}4\text{-}C_6H_4Me$[26] (Equation 4.8).



$$2\ CpRu(PPh_3)(CO)S\text{-}\overset{O}{\overset{\|}{S}}\text{-}R \longrightarrow CpRu(PPh_3)(CO)S\text{-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-}R + CpRu(PPh_3)(CO)S\text{-}S\text{-}R \qquad (4.8)$$

In addition to this complex, a cobalt dimer containing a bridging dioxodisulfane ligand has been reported.[31] $[(NC)_5CoSS(O)_2Co(CN)_5]^{6-}$ was prepared by air oxidation of the corresponding symmetrical disulfane bridged dimer (see Equation 1.7).

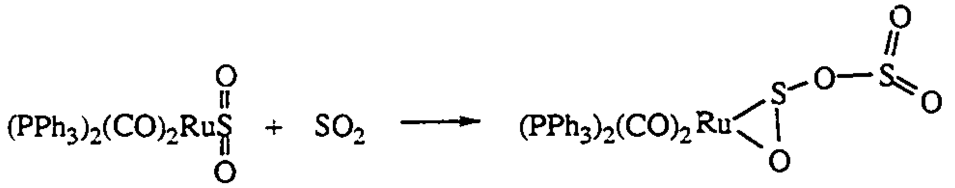
Complexes of the type $MS(O)_2SR$ have recently been prepared by non-oxidative routes. The complexes $CpRu(PPh_3)(CO)S(O)_2SR$ ($R = C_3H_7$, $CHMe_2$) were synthesized by reaction of $[CpRu(PPh_3)(CO)S(O)_2][SbF_6]$ with HSR in the presence of Na_2CO_3 and $MgSO_4$[32] (Equation 4.9). These compounds are extremely H_2O sensitive and readily hydrolyze to give $CpRu(PPh_3)(CO)S(O)_3H$. In addition, the square planar complexes, *trans*-$(PPh_3)_2Pt(phth)S(O)_2SR$ (R = alkyl and aryl) were prepared by oxidative addition of phthSR to $(PPh_3)_3PtS(O)_2$ (Equation 4.10).[32] These are stable complexes and the x-ray structure was determined for $R = CH_2C_6H_5$. The different stabilities of these $MS(O)_2SR$ complexes, suggest that the metal center and surrounding ligands must play an important role in stabilizing the $-S(O)_2SR$ ligand.



(4.9)

(4.10)

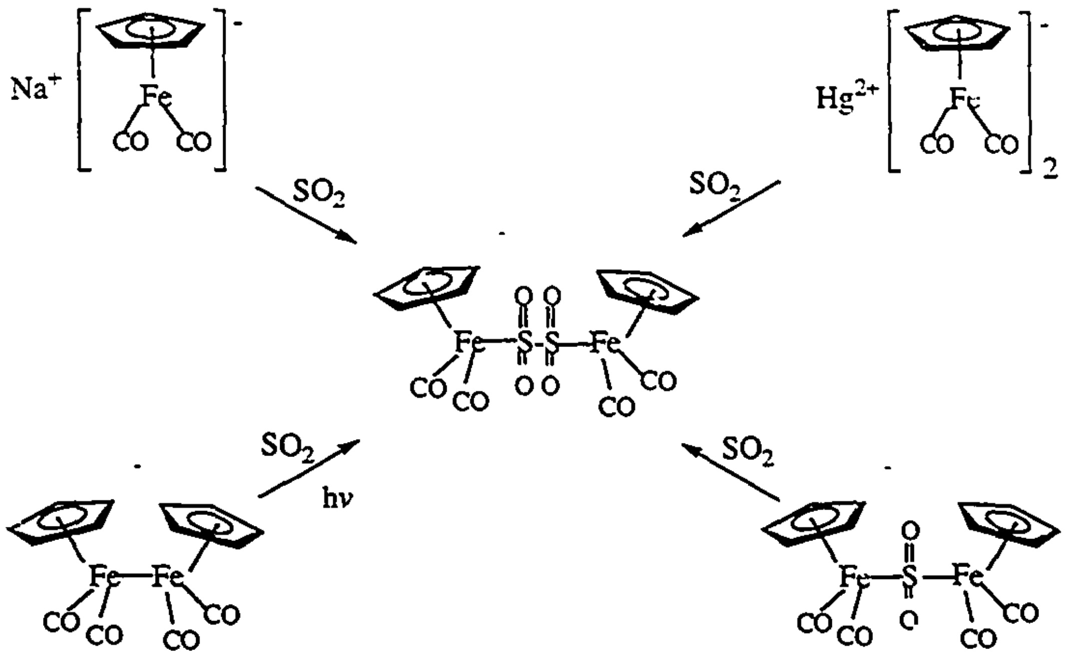
There are no compounds of the type $MS(O)S(O)_2R$ and $MS(O)_2S(O)_2R$ yet reported in the literature. However, a compound containing a bidentate sulfanato ligand of the type $M(\eta^2\text{-}SO_2)OS(O)$ has been prepared. The crystal structure of $Ru(PPh_3)_2(CO)_2(\eta^2\text{-}SO_2\cdot SO_2)(PPh_3)_2$ was determined at -60°C.[33] It was made by addition of excess SO_2 to $Ru(PPh_3)_2(CO)_2(SO_2)$ (Equation 4.11).

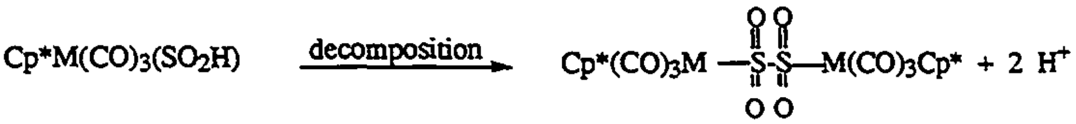


(4.11)

There have been reports of transition metal complexes bridged by the $S(O)_2S(O)_2^{2-}$ ligand (Scheme 4.2). $(CpFe(CO)_2)_2S_2O_4$ was synthesized by four different non-oxidative methods:[34] 1) reaction of $Na[CpFe(CO)_2]$ with a large excess of SO_2 2) reaction of $[CpFe(CO)_2]_2[Hg]$ with SO_2, 3) photolysis of $(CpFe(CO)_2)_2$ and SO_2, and 4) reaction of $(CpFe(CO)_2)_2)SO_2$ with SO_2. Photolysis reactions were also used to prepare $(M(CO)_5)_2S_2O_4$, where M = Mn and Re,[34] and $[Cp^*M(CO)_3]_2S_2O_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo, W), the latter being a decomposition product of $Cp^*M(CO)_3(S(O)_2H)$. The x-ray crystal structure for the molybdenum complex has been determined.[35] Thus, condensation routes are also possible for the synthesis of MS_2O_4R, if the necessary fragments are available.

Scheme 4.2



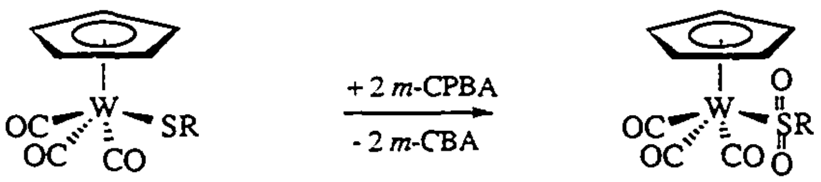


$$Cp^*M(CO)_3(SO_2H) \xrightarrow{\text{decomposition}} Cp^*(CO)_3M-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-M(CO)_3Cp^* + 2\ H^+$$

M = Mo, Cp* = η^5-C_5H_5; M = W, Cp* = η^5-C_5Me_5

Oxidative Routes

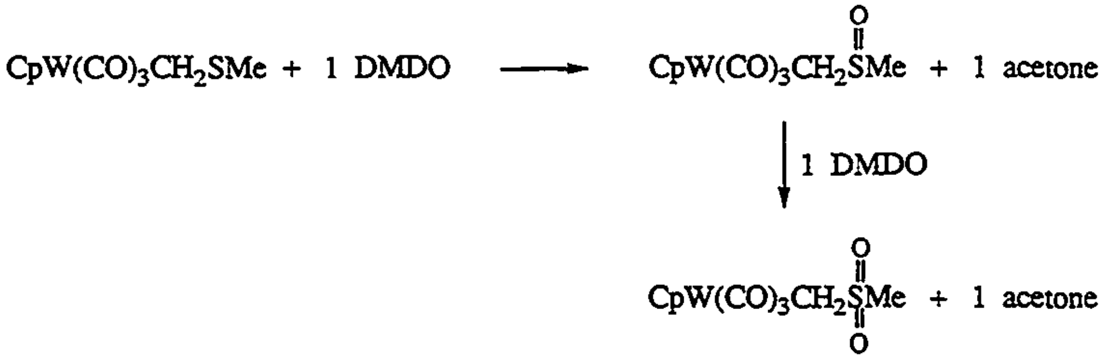
Reports of oxidation of thiolato ligands are fairly common. For example, the complexes $CpW(CO)_3S(O)_2R$ (R = Me and aryl) were prepared by oxidation of the thiolate, $CpW(CO)_3SR$, with *m*-CPBA[36] (Equation 4.12). Interestingly, the reaction could not be stopped to give the mono-oxygenated complexes $CpW(CO)_3S(O)R$.



(4.12)

The products $CpW(CO)_3CH_2S(O)Me$ and $CpW(CO)_3CH_2S(O)_2Me$ were also isolated after the oxidation of $CpW(CO)_3CH_2SMe$ with either one or two equivalents of dimethyldioxirane (DMDO), respectively (Scheme 4.3).[37]

Scheme 4.3



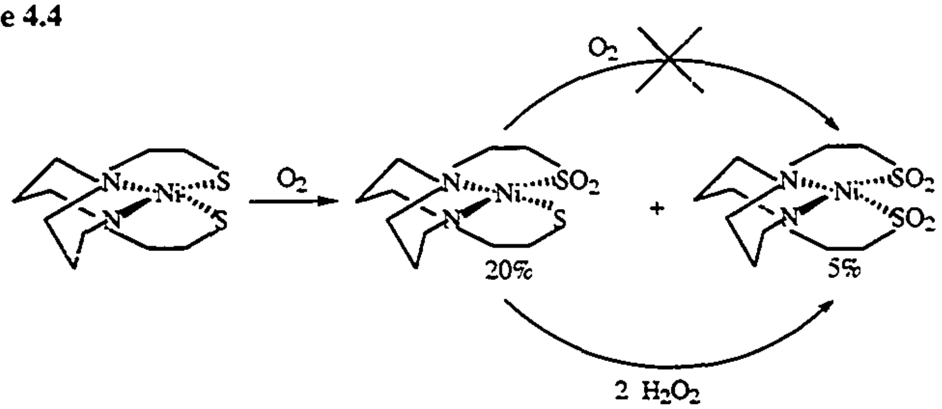
$$\mathrm{CpW(CO)_3CH_2SMe} + 1\ \mathrm{DMDO} \longrightarrow \mathrm{CpW(CO)_3CH_2\overset{\overset{O}{\|}}{S}Me} + 1\ \text{acetone}$$

$$\Big\downarrow 1\ \mathrm{DMDO}$$

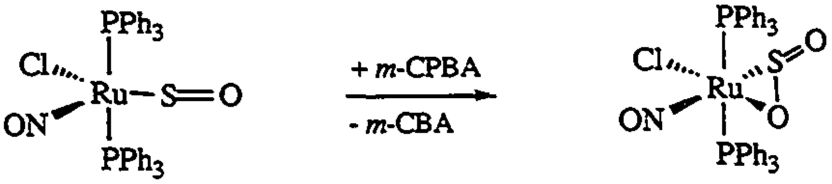
$$\mathrm{CpW(CO)_3CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}Me} + 1\ \text{acetone}$$

Oxidation of the *cis*-dithiolato complex, Ni(bme-daco) (bme-daco = N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane) with 1 and 2 equivalents of O_2 gave the mono- and bis-dioxosulfano nickel complexes, respectively.[38] The bis-dioxosulfane was also prepared from the mono-dioxosulfane by H_2O_2 oxidation (Scheme 4.4).

Scheme 4.4

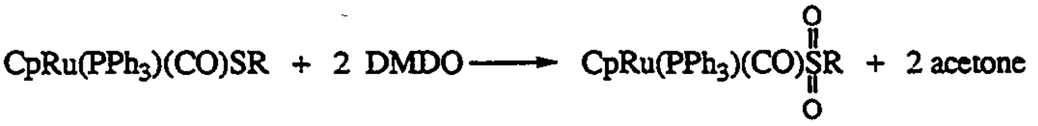


Oxidation of RuCl(NO)(SO)(PPh$_3$)$_2$ which contains a terminal bent M-SO function, with *m*-CPBA gave RuCl(NO)(η^2-SO$_2$)(PPh$_3$)$_2$ (Equation 4.13).[39]



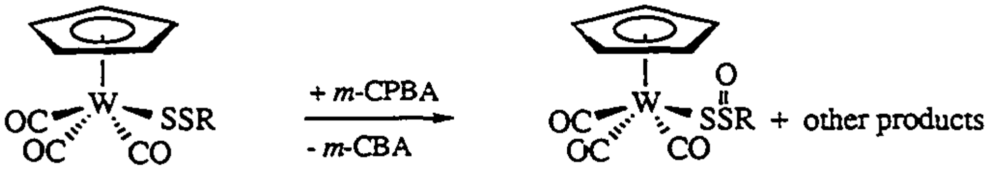
(4.13)

Finally, dimethyldioxirane (DMDO) oxidized the thiolato complexes CpRu(PPh$_3$)(CO)SR (R = Me, 4-C$_6$H$_4$Me, C$_6$H$_5$) at -40°C to give CpRu(PPh$_3$)(CO)S(O)$_2$R[37] (Equation 4.14).



$$\mathrm{CpRu(PPh_3)(CO)SR} + 2\ \mathrm{DMDO} \longrightarrow \mathrm{CpRu(PPh_3)(CO)}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{R} + 2\ \mathrm{acetone} \quad (4.14)$$

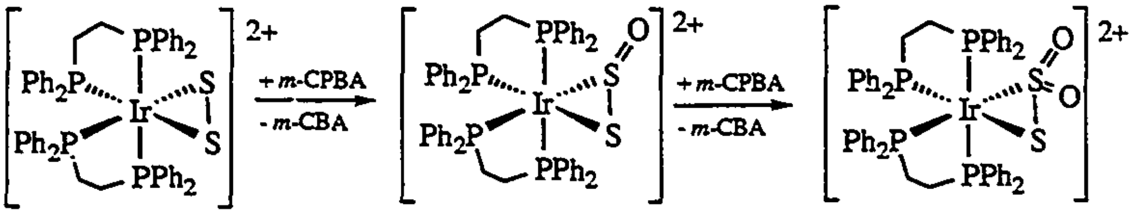
The complexes containing an oxidized disulfane ligand, MS$_x$O$_y$R, have been prepared mainly by a condensation route. However, complexes of this type have also been prepared via oxidation of the corresponding disulfane, oxodisulfane or dioxodisulfane metal complex. For example, oxidation of the disulfane ligand of $CpW(CO)_3SSR$ by *m*-CPBA gave a mixture of compounds including $CpW(CO)_3SS(O)R$[40] (Equation 4.15).



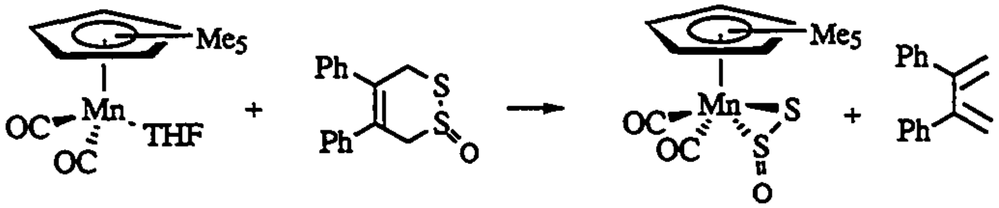
(4.15)

The stepwise oxidation of $[Ir(\eta^2\text{-}S_2)(dppe)_2][PF_6]$, by *m*-CPBA gave $[Ir(\eta^2\text{-}S_2O)(dppe)_2][PF_6]$ followed by $[Ir(\eta^2\text{-}S_2O_2)(dppe)_2][PF_6]$, both of which were stable[41] (Scheme 4.5).[41]

Scheme 4.5



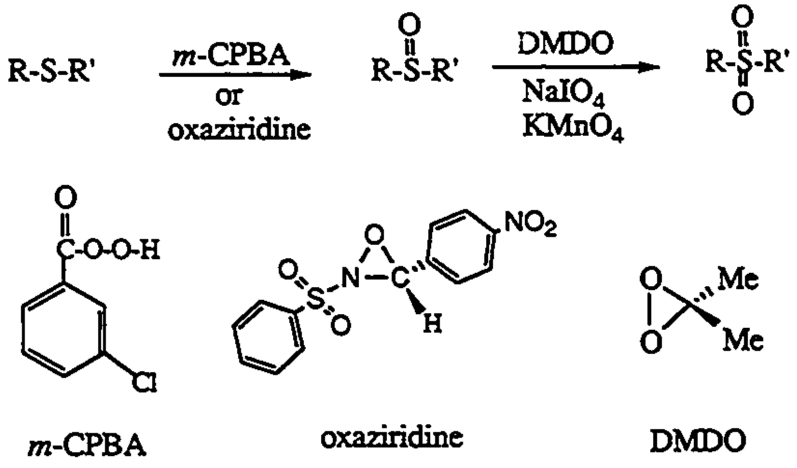
Metal complexes containing a disulfur monoxide moiety (S_2O) have also been prepared; oxidation of $Cp^*Mn(CO)_2(\eta^2\text{-}S_2)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with O_2 gave $Cp^*Mn(CO)_2(\eta^2\text{-}S_2O)$.[42] Interestingly, the latter was also prepared by a non-oxidative approach involving a transition metal assisted retro Diels-Alder reaction[43] (Equation 4.16).



(4.16)

Thus, oxidation reactions involving thiolate ligands are good routes for obtaining the oxidized sulfoxide and sulfone ligands. However, oxidation of disulfane ligands may be more complicated since there are two sites of attack for the oxidant. Oxidations can be "tuned" to obtain the desired regiospecificity by selecting the appropriate oxidant. For example, an electrophilic oxidant such as *m*-CPBA or oxaziridine[44-47] will preferentially oxidize sulfides to sulfoxides rather than sulfoxides to sulfones. In contrast, nucleophilic oxidants such as DMDO,[37,48-53] $NaIO_4$[54] and $KMnO_4$[55] can selectively oxidize sulfoxides to sulfones (Scheme 4.6). Oxaziridines are sterically bulky oxidants which can oxidize an open area in preference to a sterically hindered site. The structures of *m*-CPBA, 2-benzenesulfonyl-3-(*p*-nitrophenyl)oxaziridine and dimethyldioxirane (DMDO) are illustrated in Scheme 4.6. DMDO has been used extensively as a specific sulfur oxidant in organic chemistry[53,56] in addition to oxidizing other functional groups. DMDO is also advantageous because the reaction byproduct, acetone, is inert and easily removed.

Scheme 4.6



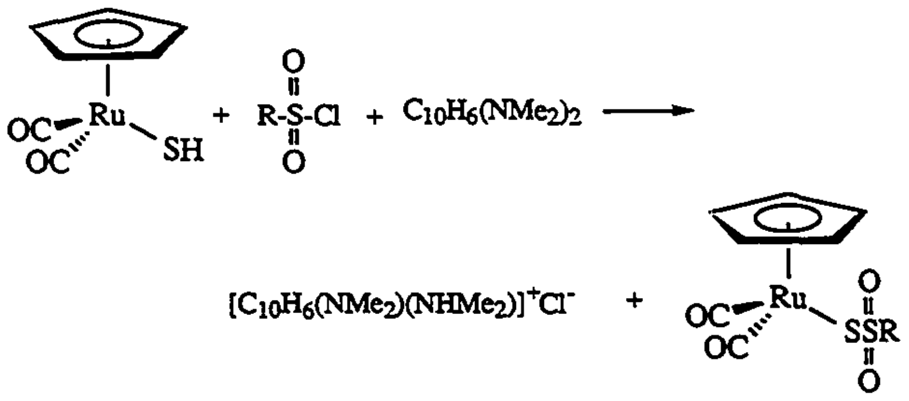
As part of our investigation of the reactivity of sulfur containing ligands, the complexes $CpRu(CO)_2SS(O)R$ have been prepared and their reactivity examined. A new preparative route to $CpRu(CO)_2SS(O)_2R$ is reported and the chemistry of these compounds studied. In addition, oxidation of $CpRu(PPh_3)(CO)SS(O)_xR$ ($x = 0, 1$) was examined and is discussed in comparison to oxidations of organic analogs.

4.2 Results and Discussion

4.2.1 $CpRu(CO)_2SS(O)_2R$

Synthesis and Characterization

Treatment of $CpRu(CO)_2SH$ with $ClS(O)_2R$ ($R = 4\text{-}C_6H_4Me$, C_6H_5) in THF at 0°C in the presence of 1,8-bis(dimethylamino)naphthalene, gave the corresponding 2-dioxodisulfane compounds, $CpRu(CO)_2SS(O)_2R$ (**19a,b**), as determined by the NMR spectrum of the crude products (Equation 4.17).



(4.17)

19a,b a, $R = 4\text{-}C_6H_4Me$
b, $R = C_6H_5$

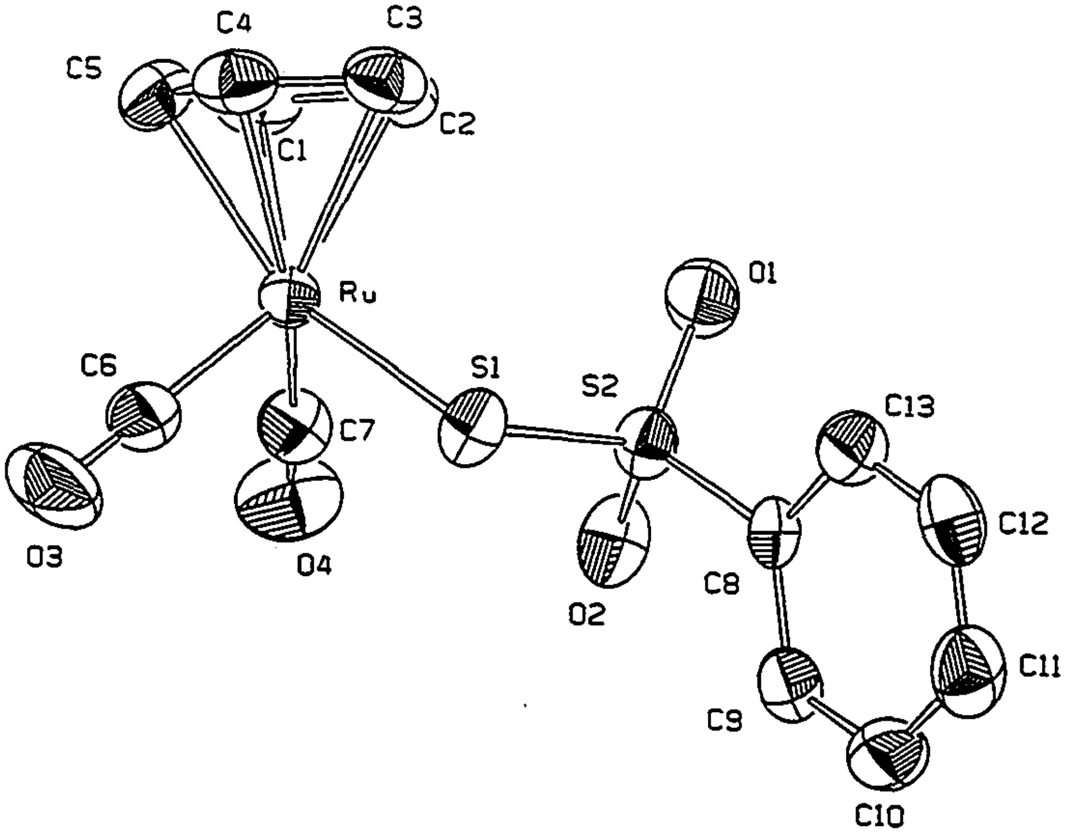
These reactions proceeded by an immediate colour change from yellow to bright red ($R = 4\text{-}C_6H_4Me$) or orange ($R = C_6H_5$) and precipitation of 1,8-bis(dimethylamino)naphthalene hydrochloride, which was removed by filtration. Isolation of the pure compounds was achieved by continuous extraction of the crude products with ether followed by crystallization from ether. The complex $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me was also formed when NEt_3 was used, but the yield was lower (34%) than when 1,8-bis(dimethylamino)naphthalene was used (53%). Treatment of $CpRu(CO)_2SH$ with $ClS(O)_2CH_2C_6H_5$ in the presence of 1,8-bis(dimethylamino)naphthalene at 0°C and -78°C gave a mixture of products that were not due to $CpRu(CO)_2SS(O)CH_2C_6H_5$, $CpRu(CO)_2SSCH_2C_6H_5$ or $CpRu(CO)_2SCH_2C_6H_5$, as identified by NMR.

The compounds $CpRu(CO)_2SS(O)_2R$ (R = 4-C_6H_4Me, C_6H_5) were isolated as air stable orange crystals in good yields (44-53%). The NMR and IR spectra (Tables E.1 and E.2) were as expected. The high resolution mass spectra of the compounds displayed the parent molecular ions and their elemental analyses were in excellent agreement with the calculated values. These compounds are soluble in THF and H_2O, moderately soluble in toluene and ether, slightly soluble in cyclohexane and insoluble in hexanes. The compounds are stable in solution under N_2 indefinitely but decompose when subjected to chromatography on alumina.

X-ray Crystal Structure of $CpRu(CO)_2SS(O)_2C_6H_5$

The x-ray crystal structure of $CpRu(CO)_2SS(O)_2C_6H_5$ was determined and an ORTEP diagram is shown in Figure 4.1. Appendix 1 contains tables of the x-ray data, the atom coordinates, the anisotropic thermal factors, and the bond lengths and angles (Tables 1 to 4 respectively). The structure of the complex approximates a piano stool with the carbonyl and dioxodisulfane ligands as the legs. The Ru-S1, S1-S2, S2-O1 and S2-O2 bond lengths (2.391(2), 2.037(2), 1.444(4) and 1.444(4) Å, respectively) are similar to those of $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me[26] (2.383(2), 2.023(3), 1.444(8) and 1.435(6) Å, respectively), the only other metal complex containing a 2-dioxodisulfane ligand to be structurally characterized. The S2 atom has a tetrahedral geometry with O1-S2-O2 and S1-S2-C8 angles of 116.5(3) and 107.9(3)°, respectively (same angles for $CpRu(CO)(PPh_3)SS(O)_2$-4-C_6H_4Me are 117.4(3) and 107.0(3)°). The bond lengths and

Figure 4.1 ORTEP drawing of $CpRu(CO)_2SS(O)_2C_6H_5$. Selected bond lengths (Å) and angles (°); Ru-S1, 2.391(2); S1-S2, 2.037(2); S2-O1, 1.444(4); S2-O2; 1.444(4); O1-S2-O2; 116.5(3); S1-S2-O1, 111.1(2); S1-S2-O2, 112.1(2); S1-S2-C8, 107.9(3)°. Ellipsoids are drawn at 30% probability and the H atoms have been omitted.



bond angles for these two structures are not significantly different suggesting that the different R group, and the substitution of a PPh_3 for a CO ligand does not effect the geometry of the -$SS(O)_2R$ ligand.

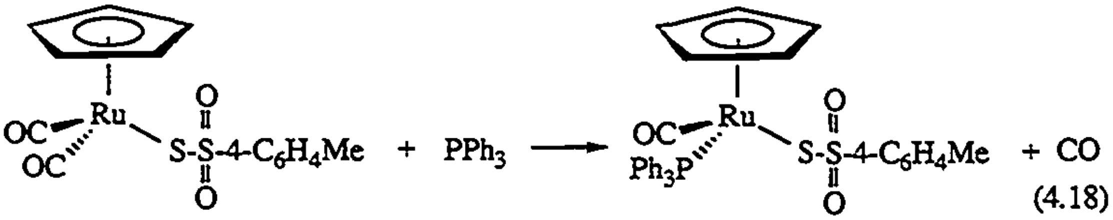
Stability

The stability of $CpRu(CO)_2SS(O)_2R$ (R = 4-C_6H_4Me, C_6H_5) was examined by heating them to test for SO_2 extrusion giving the thiolate, $CpRu(CO)_2SC_6H_5$, as is observed for some organic thiosulfonates ($RSS(O)_2R'$).[17-19] The compounds were stable in sealed NMR tubes in C_6D_6 heated at 70°C for 17 hours (less than 2% decomposition). In addition, a solid sample of $CpRu(CO)_2SS(O)_2C_6H_5$ heated at 124°C in a Schlenk tube under nitrogen for 16 hours, showed less than 20% decomposition (NMR). No peaks in the NMR spectrum due to $CpRu(CO)_2SS(O)C_6H_5$, $CpRu(CO)_2SSC_6H_5$ or $CpRu(CO)_2SC_6H_5$ were observed.

The reactivity of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me was also tested by treating the compound with H_2O and H_2S. A sample of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me in H_2O for 2 days showed approximately 15% decomposition (NMR). In the case of H_2S (20 equivalents), a sample of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me was stable in C_6D_6 for 2 days at 67°C. The robustness of $CpRu(CO)_2SS(O)_2R$ towards H_2S and H_2O, is in contrast to most organometallic complexes. Thus, the complexes $CpRu(CO)_2SS(O)_2R$ are exceptionally stable, parallelling their organic counterparts, $RSS(O)_2R'$.

Reaction With PPh_3

To determine if $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me could be deoxygenated, it was treated with PPh_3 which abstracts oxygen from organic thiosulfonates ($RSS(O)_2R'$) to give RSSR' and two equivalents of $OPPh_3$. In some cases, subsequent desulfurization occcurs to give the sulfide, RSR' and $SPPh_3$.[57,58] Treatment of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me with 5 equivalents of PPh_3 in C_6D_6 at room temperature for 2 hours selectively gave the phosphine substituted product, $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me[26] (Equation 4.18). This compound was identified by comparison of its NMR (^1H and ^{31}P) and IR spectra to those of an authentic sample. Even after heating the reaction mixture at 67°C for 24 hours, neither the oxygen nor the sulfur atoms were abstracted from the -$SS(O)_2$-4-C_6H_4Me ligand. Thus, $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me is more stable than $CpRu(CO)_2SS$-4-C_6H_4Me towards PPh_3 where sulfur abstraction was observed.



(4.18)

A study of the deoxygenation of a series of organic thiosulfonate compounds ($RSS(O)_2R'$) by PPh_3 to give the corresponding disulfides (RSSR')[59] concluded that deoxygenation occurred via nucleophilic attack of PPh_3 on the sulfenyl sulfur (S^{2-}). The stability of our metal analogs, $CpRu(CO)_2SS(O)_2R$ to PPh_3 may be due to steric hindrance of the sulfenyl sulfur by the metal center and surrounding ligands.

Athough PPh_3 did not react with the -$SS(O)_2R$ ligand, it did substitute a CO ligand at the metal center. However, treatment of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me with 5 equivalents of PPh_3 in C_6D_6 under more severe conditions (67°C for 34 hours) but in the absence of light gave only 50% conversion to $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me. The considerable decrease in the rate of CO substitution in the absence of light implicates a photolytically assisted reaction, as observed in the reactions of $CpRu(CO)_2S$-4-C_6H_4Me and $CpRu(CO)_2SS$-4-C_6H_4Me with PPh_3 (Chapter 2). The mechanism of CO substitution may involve the loss of $^-SS(O)_2R$ or $^\cdot SS(O)_2R$ and proceed similarly to the route proposed in Scheme 2.4.

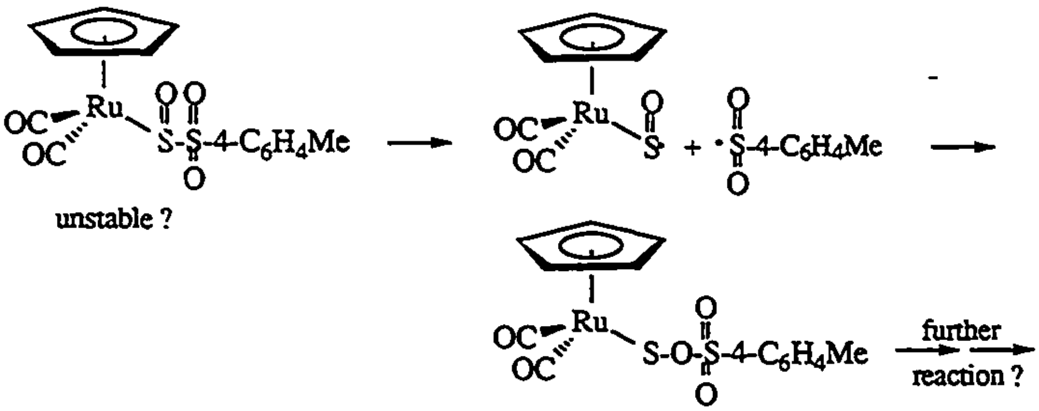
Attempted Oxidation

2-benzenesulfonyl-3-(4-nitrophenyl)oxaziridine[44,45,47] is an electrophilic oxidizing agent which specifically oxidizes organic sulfides to sulfoxides, and disulfides to thiosulfinates, in preference to sulfoxides to sulfones, or thiosulfinates to thiosulfonates.[46] Subsequent oxidation to the sulfone or thiosulfinate in the presence of excess oxidant is slow due to the presence of the less nucleophilic sulfoxide center and the increased steric hindrance. $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me was treated with 2.1 equivalents of 2-benzenesulfonyl-3-(*p*-nitrophenyl)oxaziridine in THF at room temperature for 10 minutes. The NMR spectrum of the resulting yellow oil in C_6D_6 showed 3 peaks in the Cp region (5.33, 4.59 and 4.45 ppm) in the ratio of 4:10:1, respectively and corresponding peaks in the alkyl region. None of the peaks are due to known compounds, and thus, may be due to oxidized compounds such as $CpRu(CO)_2S(O)S(O)_2$-4-C_6H_4Me or $CpRu(CO)_2S(O)_2S(O)_2$-4-C_6H_4Me. The reaction was repeated at -40°C for 45 minutes. The NMR spectrum in C_6D_6 displayed 5 peaks in the Cp region (the major one appearing at 4.51 ppm). Attempts at isolation of the products were unsuccessful. Although the reaction of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me with the oxaziridine might have been expected to give 1,2,2-trioxodisulfane, a mixture of products was obtained. Further oxidation to the 1,1,2,2-tetraoxosulfane product was not expected due to the electron deficient sulfinyl sulfur and the increased steric hindrance.[45]

Meta-perchlorobenzoic acid (*m*-CPBA) is also an electrophilic oxidizing agent. Treatment of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me with 2 equivalents of *m*-CPBA at different temperatures (0°C, 2.5 hours; -40°C, 2 hours; -78°C, 3 hours) gave several products (NMR) that were not due to $CpRu(CO)_2S$-4-C_6H_4Me, $CpRu(CO)_2SS$-4-C_6H_4Me or $CpRu(CO)_2SS(O)$-4-C_6H_4Me. Therefore, *m*-CPBA is not a selective reagent for oxidizing the sulfenyl (S^{2-}) sulfur atom of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me, possibly because it is smaller and more reactive than the oxaziridine.

The presence of multiple products may be rationalized by noting that aryl sulfinyl sulfones ($ArS(O)S(O)_2Ar$) thermally decompose via initial homolytic dissociation of the $S(O)$-$S(O)_2$ bond followed by recombination of the fragments to give the sulfenyl sulfonate[21] (Equation 4.6). This S-S bond fission is very fast.[60] By analogy, if the 1,2,2-trioxodisulfane moiety was formed, the $S(O)$-$S(O)_2$ bond may also be expected to break homolytically to give a sulfenyl sulfonate product ($MSOS(O)_2R$) which could undergo further reaction (Scheme 4.7). A similar scheme involving initial heterolytic cleavage giving $[CpRu(CO)_2S(O)]^-$ and $^+[S(O)_2$-4-$C_6H_4Me]$ can also be envisioned.

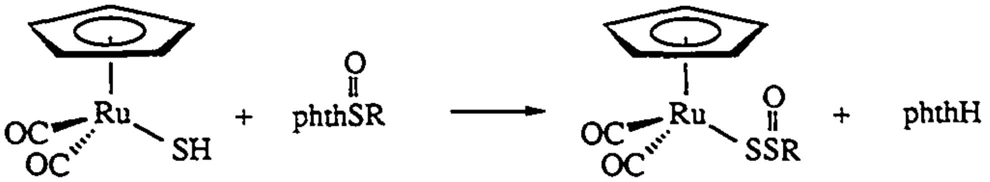
Scheme 4.7



4.2.2 $CpRu(CO)_2SS(O)R$

Synthesis and Characterization

Treatment of $CpRu(CO)_2SH$ with the phthalimide thiosulfinyl transfer reagents, phthS(O)R (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) in THF gave $CpRu(CO)_2SS(O)R$ (**20a-c**), in addition to other products, depending on the R groups (Equation 4.19).



(4.19)

20a-c a, R = 4-C_6H_4Me
b, R = C_6H_5
c, R = $CH_2C_6H_5$

The reaction of $CpRu(CO)_2SH$ with $phthS(O)CH_2C_6H_5$ gave 1 major product, $CpRu(CO)_2SS(O)CH_2C_6H_5$, which was isolated but, the reaction with $phthS(O)C_6H_5$ gave 1 major product (NMR), $CpRu(CO)_2SS(O)C_6H_5$, which could not be isolated. The reaction with phthS(O)-4-C_6H_4Me gave a mixture of products (NMR) including $CpRu(CO)_2SS(O)$-4-C_6H_4Me, which could not be isolated. The two aryl products were isolated as mixtures containing both $CpRu(CO)_2SS(O)R$ and $CpRu(CO)_2SS(O)_2R$. The reaction of $CpRu(CO)_2SH$ with $phthS(O)CHMe_2$ in THF at room temperature for 20 minutes gave a product which was likely $CpRu(CO)_2SS(O)CHMe_2$ as its ^1H NMR spectrum displayed resonances at 1.27, 1.35 (dd, Me_2), 2.98 (septet, CH) and 4.71 ppm (s, Cp). The observation of two Me peaks is consistent with the presence of the chiral S(O) center. The product was unstable and decomposed in solution overnight at -16°C to a mixture containing $(\mu\text{-}S)_3(CpRu(CO)_2)_2$ as the major product, as identified by NMR and the colour change from orange to deep burgandy.

The reaction of $CpRu(CO)_2SH$ with phth(O)R is similar to methods used to synthesize CpRu(L)(CO)SS(O)R (L = PPh_3,[27,28] CO[26,28]) and $CpW(CO)_3SS(O)R$.[29] This non-oxidative route to complexes of the type MSS(O)R parallels the non-oxidative approaches for synthesizing unsymmetrical thiosulfinates (RSS(O)R') illustrating a similarity between the organic and inorganic chemistries.

$CpRu(CO)_2SS(O)CH_2C_6H_5$

$CpRu(CO)_2SS(O)CH_2C_6H_5$ was obtained in 31% yield and its NMR and IR spectra (Tables E.1 and E.2) were as expected. The high resolution mass spectrum detected the parent molecular ion and the elemental analysis was in agreement with calculated values. $CpRu(CO)_2SS(O)CH_2C_6H_5$ is very soluble in THF, moderately soluble in ether, toluene, benzene, and only slightly soluble in cyclohexane and hexanes.

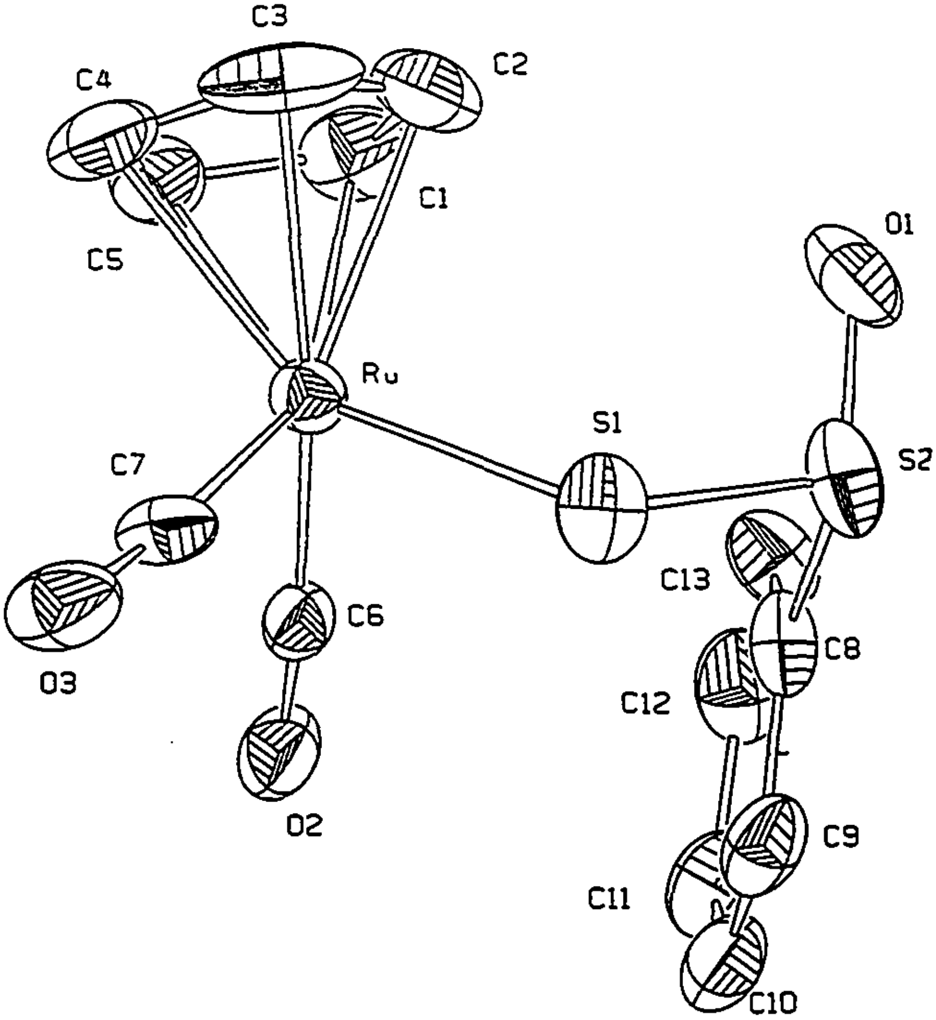
$CpRu(CO)_2SS(O)C_6H_5$

The crude product from the reaction of $CpRu(CO)_2SH$ and $phthS(O)C_6H_5$ in THF at room temperature contained $CpRu(CO)_2SS(O)C_6H_5$ in greater than 95% yield, as identified by NMR. Recrystallization from THF/hexanes gave an orange oil and yellow crystals. The crystals were recrystallized from THF/hexanes to give $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ in the ratio of 9:1; the latter being most likely the result of oxygen transfer. This sample was used for spectroscopic analysis and further reactions. The orange oil contained almost equal amounts of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ and was discarded. The high resolution mass spectrum displayed peaks due to the parent molecular ion, $CpRu(CO)_2SS(O)C_6H_5^{+\cdot}$, to $CpRu(CO)_2SS(O)_2C_6H_5^{+\cdot}$ and to $CpRu(CO)_2SSC_6H_5^{+\cdot}$. The mixture of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ is soluble in THF, moderately soluble in toluene, ether and C_6D_6, and slightly soluble in cyclohexane and hexanes.

X-ray Structure of $CpRu(CO)_2SS(O)C_6H_5$

The crystal used for x-ray analysis was chosen from the crystals obtained by recrystallization from THF/hexanes. All of the crystals were identical in appearance and the NMR spectra indicated a mixture of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ in the ratio of 9:1. The structure of $CpRu(CO)_2SS(O)C_6H_5$ is shown in Figure 4.2.

Figure 4.2 ORTEP drawing of $CpRu(CO)_2SS(O)C_6H_5$. Selected bond lengths (Å) and angles (°); Ru-S1, 2.391(3); S1-S2, 2.050(4); S2-O1, 1.488(9); S1-S2-O1, 111.9(4); S1-S2-C8, 101.6(4)°. Ellipsoids are drawn at 50% probability and the H atoms have been omitted.



Appendix 2 contains tables of the crystallographic data, atomic coordinates, theanisotropic thermal factors, and the bond lengths and angles (Tables 1 to 4, respectively). There is no disorder in the oxygen atom coordinated to the sulfur atom. The structure of $CpRu(CO)_2SS(O)C_6H_5$ is a piano stool with the two CO and the $-SS(O)C_6H_5$ ligands as the legs.

The x-ray structures of $CpRu(PPh_3)_2SS(O)CH_2C_6H_5$,[27] $CpRu(PPh_3)(CO)SS(O)CH_2C_6H_5$[28] and $CpRu(PPh_3)(CO)SS(O)CHMe_2$[61] are also known. The bond lengths and bond angles in all these compounds are similar (Table 4.1).

Table 4.1 Selected bond lengths from the x-ray crystal structures of transition metal complexes containing a -SS(O)R ligand.

	Ru-S1 (Å)	S1-S2 (Å)	S2-O (Å)	ref.
$CpRu(CO)_2SS(O)C_6H_5$	2.391(3)	2.050(4)	1.488(9)	this work
$CpRu(PPh_3)(CO)SS(O)CHMe_2$	2.3794(22)	2.076(3)	1.448(10)[a] 1.358(21)[a]	26
$CpRu(PPh_3)(CO)SS(O)CH_2C_6H_5$	2.377(3)	2.086(3)	1.502(6)	28
$CpRu(PPh_3)_2SS(O)CH_2C_6H_5$[b]	2.420(3)[c] 2.423(3)[c] 2.420(3)[c]	2.044(4)[c] 2.055(4)[c] 2.053(4)[c]	1.537(11) 1.529(12) 1.452(15)[a,d] 1.523(26)[a,d]	27

[a] The oxygen atom was disordered over two different positions resulting in two S-O bond lengths.
[b] Three independent molecules were found in the unit cell.
[c] Large thermal motion tended to lengthen these values.
[d] The value was corrected for thermal motion.

$CpRu(CO)_2SS(O)$-4-C_6H_4Me

The reaction of $CpRu(CO)_2SH$ with phthS(O)-4-C_6H_4Me at room temperature gave a complex mixture of products including $CpRu(CO)_2SS(O)$-4-C_6H_4Me, $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me, $CpRu(CO)_2SS$-4-C_6H_4Me and $CpRu(CO)_2S$-4-C_6H_4Me, in addition to 9 other unknown products as detected by NMR (see Table E.1 for ^1H NMR shifts). Column chromatography of the crude product obtained from the room temperature reaction gave a fraction containing $CpRu(CO)_2SS(O)$-4-C_6H_5Me, $CpRu(CO)_2S$-4-C_6H_5Me, $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me and $CpRu(CO)_2SS$-4-C_6H_5Me, recrystallization of which gave a mixture of $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me and $CpRu(CO)_2SS(O)$-4-C_6H_5Me in the ratio of 10:1. Concentration of the mother liquors gave orange crystals which contained $CpRu(CO)_2SS(O)$-4-C_6H_5Me and $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me in the ratio of 4:1, as deduced by NMR analysis. This enriched sample was used for spectroscopic characterization. The high resolution mass spectrum displayed molecular ions due to $CpRu(CO)_2SS(O)$-4-$C_6H_5Me^{+\cdot}$, $CpRu(CO)_2SS(O)_2$-4-$C_6H_5Me^{+\cdot}$ and $CpRu(CO)_2S(O)_2$-4-$C_6H_5Me^{+\cdot}$. This mixture is soluble in THF, moderately soluble in toluene and slightly soluble in cyclohexane and hexanes.

The stability of $CpRu(CO)_2SS(O)R$ (R = $CHMe_2$, 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) depends on the R group; R = $CH_2C_6H_5$ being the only one isolated. This is in contrast to the disulfane analogs, where $CpRu(CO)_2SSCH_2C_6H_5$ is less stable than $CpRu(CO)_2SS$-4-C_6H_4Me and $CpRu(CO)_2SSC_6H_5$ (Chapter 2). The least stable 2-oxodisulfane compound was $CpRu(CO)_2SS(O)CHMe_2$ which quickly decomposed as an oil or in solution to (μ-S_3)$(CpRu(CO)_2)_2$, $(CHMe_2)_2S_2$ and other unknown compounds. This mirrors the instability of $CpRu(CO)_2SSCHMe_2$ which also decomposed rapidly (Chapter 2). The compounds $CpRu(CO)_2SS(O)$-4-C_6H_4Me and $CpRu(CO)_2SS(O)C_6H_5$ were isolated as mixtures containing $CpRu(CO)_2SS(O)_2R$ due to the tendency to spontaneously transfer oxygen (discussed in the next section).

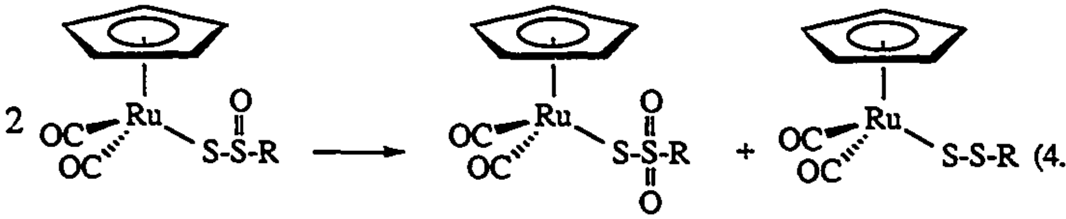
The compounds $CpW(CO)_3SS(O)R$ were previously observed to be fairly unstable and thus, difficult to characterize[29] as was the case with our compounds. The compounds $CpRu(PPh_3)(CO)SS(O)R$ were surprisingly stable in solution and to air for short periods of time.[61] Thus, it seems that relatively electron poor metal centers, as is the case with $CpRu(CO)_2SS(O)R$ and $CpW(CO)_3SS(O)R$, do not form stable compounds containing 2-oxodisulfane ligands.

The instabilty of the 2-dioxodisulfanes in general and the increased reactivity for R = 4-C_6H_4Me and C_6H_5, compared to R = $CH_2C_6H_5$ for CpRu(CO)$_2$SS(O)R parallels that found in the organic analogs. Aromatic thiosulfonates decompose to some extent during recrystallization and are more difficult to purify than the alkyl compounds.[11]

Reactivity of CpRu(CO)$_2$SS(O)R

The complexes CpRu(CO)$_2$SS(O)R are air stable in the solid state over a period of several days. There was no change in the ratio of CpRu(CO)$_2$SS(O)C_6H_5 to CpRu(CO)$_2$SS(O)$_2C_6H_5$ from the initial value of 9:1 upon exposure to air for 3 days (NMR). Similar air stability was also observed for the analogous compounds: CpRu(PPh$_3$)(CO)SS(O)R,[26] CpW(CO)$_3$SS(O)R,[29] CpRu(PPh$_3$)(L)SS(O)$CH_2C_6H_5$ (L = CO,[27] PPh$_3$)[28] and organic compounds of the type RSS(O)R'.[11-16] However, CpRu(CO)$_2$SS(O)R slowly reacted over two weeks in air to give CpRu(CO)$_2$SS(O)C_6H_5, CpRu(CO)$_2$SS(O)$_2C_6H_5$, CpRu(CO)$_2$SSC_6H_5 and CpRu(CO)$_2$SC_6H_5 in the ratio of 57 : 12 : 1 : 1, respectively, as detected by NMR. This mixture of products is enriched in CpRu(CO)$_2$SS(O)$_2C_6H_5$ compared to the original sample due to air oxidation.

The compounds CpRu(CO)$_2$SS(O)R also spontaneously undergo oxygen transfer in solution to give the 2-dioxodisulfane, CpRu(CO)$_2$SS(O)$_2$R, and disulfane, CpRu(CO)$_2$SSR (Equation 4.20).



(4.20)

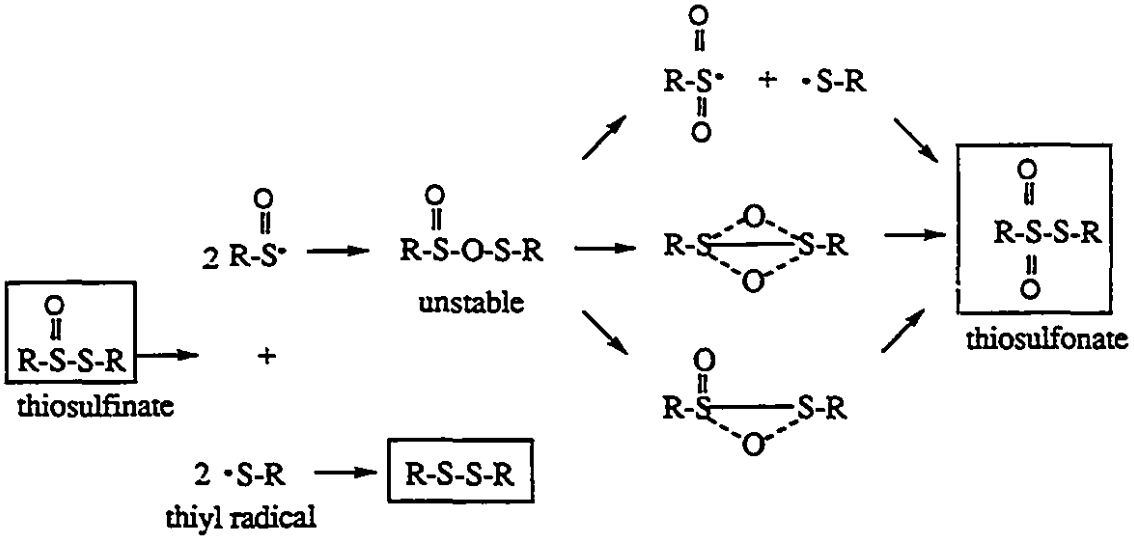
R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$

A sample containing a mixture of $CpRu(CO)_2SS(O)$-4-C_6H_4Me and $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me (4:1) in C_6D_6 heated at 50°C for 48 hours gave two compounds. $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me and $CpRu(CO)_2S$-4-C_6H_4Me, in the ratio of 8:1 (NMR), in addition to some $(4\text{-}MeC_6H_4)_2S_2$. A sample of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ (9:1) in C_6D_6 heated at 45°C for 66 hours gave $CpRu(CO)_2SS(O)_2C_6H_5$, $CpRu(CO)_2SC_6H_5$ and $CpRu(CO)_2SSC_6H_5$ in the ratio of 6:2:1 (NMR), respectively. A sample of $CpRu(CO)_2SS(O)CH_2C_6H_5$ in in C_6D_6 heated at 50°C for 4 days gave $CpRu(CO)_2SS(O)_2CH_2C_6H_5$, $CpRu(CO)_2SS(O)CH_2C_6H_5$ and $CpRu(CO)_2SSCH_2C_6H_5$ in the ratio of 3:2:1.5:1 (NMR), respectively. Although $CpRu(CO)_2SS(O)_2CH_2C_6H_5$ has not been synthesized, the peaks that grew in the NMR spectrum of a solution of $CpRu(CO)_2SS(O)CH_2C_6H_5$ in C_6D_6 at 67°C, (CH_2, 3.91; Cp, 4.49) are assigned to $CpRu(CO)_2SS(O)_2CH_2C_6H_5$, based on the observed results for R = 4-C_6H_4Me and C_6H_5. There were also peaks in the NMR spectrum due to $CpRu(CO)_2SSCH_2C_6H_5$ and $CpRu(CO)_2SCH_2C_6H_5$, the other oxygen transfer product, and the latter's sulfur extruded product, respectively. Thus, oxygen transfer occurs more readily for R = 4-C_6H_4Me and C_6H_5 compared to R = $CH_2C_6H_5$. The reaction is not affected by the absence of light.

This disproportionation reaction was also performed on a preparatory scale. A mixture of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ (9:1) was refluxed in toluene for 1 hour. This gave $CpRu(CO)_2SS(O)_2C_6H_5$, $CpRu(CO)_2SC_6H_5$ and $CpRu(CO)_2SSC_6H_5$ in the ratio of 5:1.5:1 respectively, as determined by NMR. The resulting dark brown coloured solution was reduced to dryness under vacuum to give a brown solid which was washed with hexanes (2 x 50 mL), and extracted with ether (3 x 5 mL). Concentration of the dark brown coloured extracts under vacuum gave light brown crystals of $CpRu(CO)_2SS(O)_2C_6H_5$ in 28% yield.

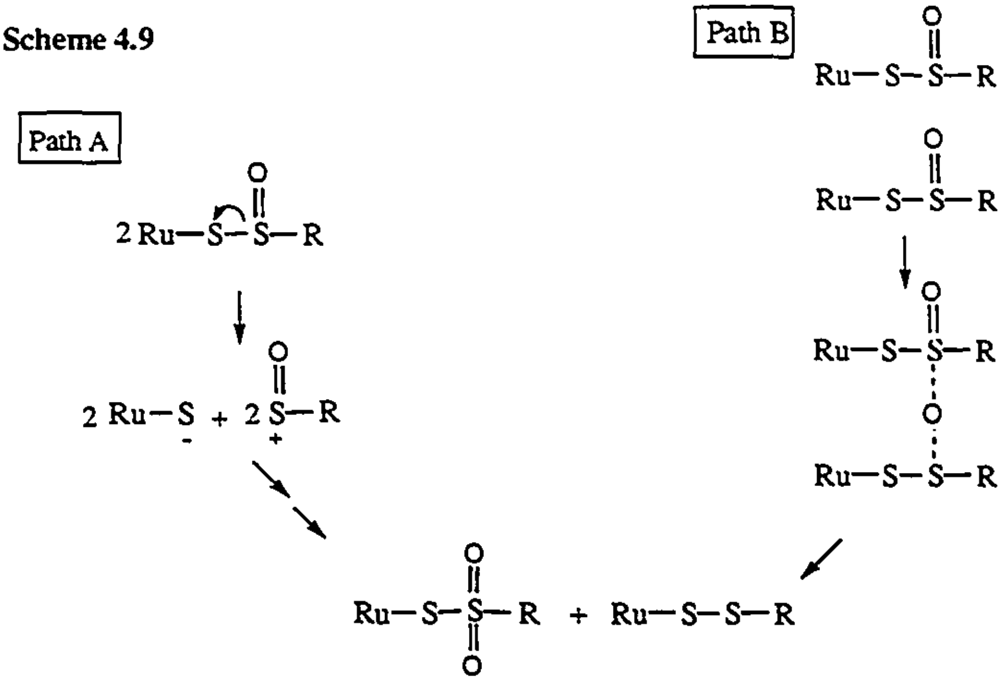
Thiosulfinates (R'SS(O)R) are typically unstable and readily disproportionate into disulfides and thiosulfonates via sulfinyl radicals, *vic*-disulfoxides and/or *OS*-sulfenyl sulfinates or an ionic mechanism.[13,16] This disproportionation involves cleavage of the S-S(O) bond. Some of the possible routes of disproportionation are shown in Scheme 4.8. Generally, thiosulfinates are unstable when R is an aryl group and easily disproportionate to the corresponding disulfide and thiosulfonate due to a weaker S-S(O) bond resulting from the electron withdrawing effect of the aryl group. By contrast, the compounds CpRu(PPh$_3$)(CO)SS(O)R are stable in solution and do not undergo oxygen transfer, as observed in our complexes.

Scheme 4.8



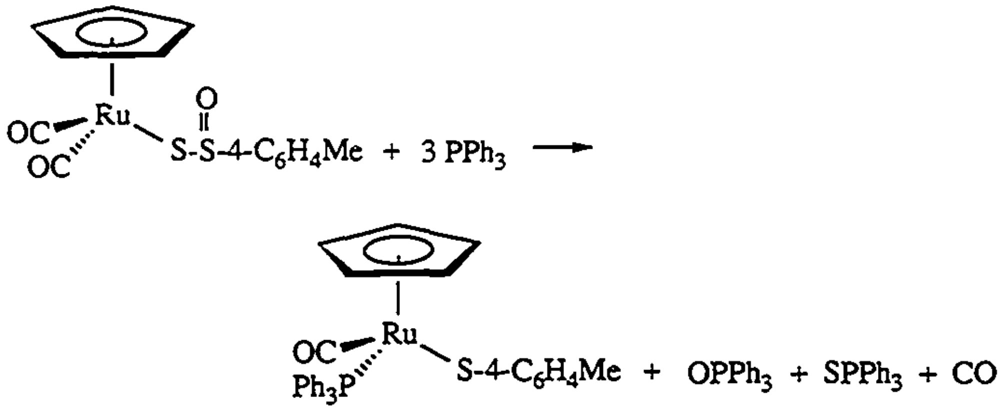
Two possible routes for oxygen transfer will be proposed. The first is similar to the disproportionation of organic thiosulfinates and involves initial cleavage of the S-S(O) bond to give the possible intermediates shown in Path A of Scheme 4.9. These ions can then rearrange and recombine similarly to the ways reported for the organic compounds[11,12,62,63] (Scheme 4.8) to give the observed 2-dioxodisulfane compounds, in addition to the disulfane, as observed. Another possible route is intermolecular oxygen transfer between two molecules of CpRu(CO)$_2$SS(O)R and is shown in Path B. Both of these paths account for both the formation of the 2-dioxodisulfane and the disulfane products.

Scheme 4.9



Reaction With PPh_3

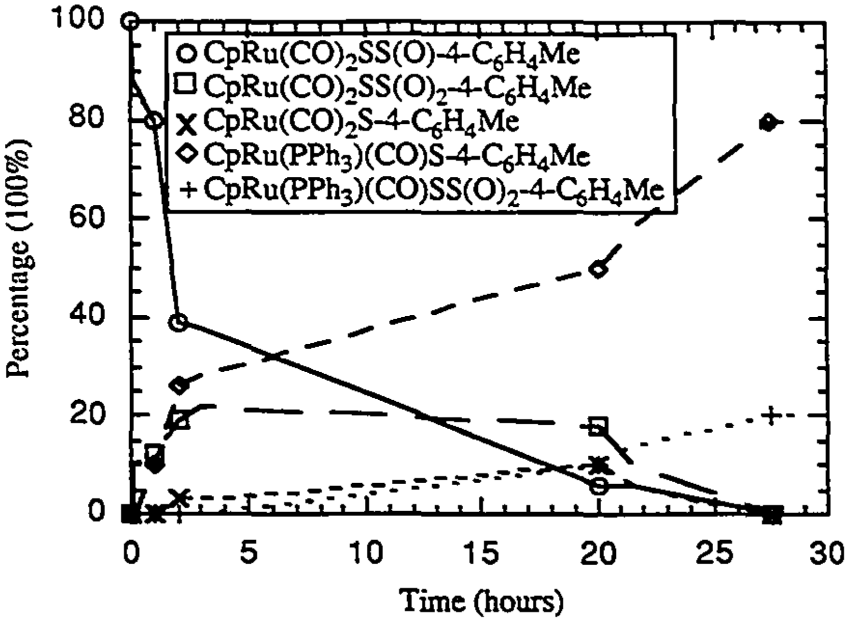
To determine whether PPh_3 could remove the oxygen atom from $CpRu(CO)_2SS(O)R$, a mixture of $CpRu(CO)_2SS(O)$-4-C_6H_4Me and $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me in the ratio of 10:1, was treated with PPh_3 (3.5 equivalents) in C_6D_6 for 22 hours at room temperature. $CpRu(PPh_3)(CO)S$-4-C_6H_4Me and $CpRu(PPh_3)(CO)SS(O)_2$-4-C_6H_4Me, in the ratio of 7:1, respectively, were identified by NMR (Equation 4.21). Peaks due to $OPPh_3$, $SPPh_3$ and $(4\text{-}MeC_6H_4)_2S_2$ were also present in the spectra. Thus, the major product is the result of the net loss of SO and CO substitution. The major product in the absence of light was $CpRu(CO)_2S$-4-C_6H_4Me.



(4.21)

The reaction was repeated with 1.2 equivalents of PPh_3 and monitored over time by NMR. None of the expected intermediate $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ was detected. 1.5 additional equivalents of PPh_3 was added after 20 hours and the results are displayed in Figure 4.3. Thus, it seems that desulfurization and CO subsitution are rapid reactions. PPh_3 deoxygenates organic thiosulfinates to the corresponding disulfides, prior to desulfurization to the sulfide.

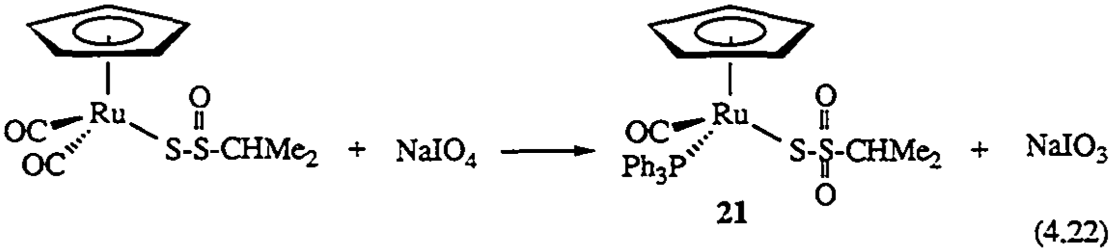
Figure 4.3 The reaction of $CpRu(CO)_2SS(O)$-4-C_6H_4Me with 1.2 equivalents of PPh_3 at 67°C in C_6D_6. 1.5 additional equivalents of PPh_3 were added after 20 hours.



4.2.3 Oxidative Routes to $CpRu(PPh_3)(CO)S_2(O)_yR$

Reaction of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ with $NaIO_4$

Treatment of $CpRu(PPh_3)(CO)SS(O)CHMe_2$[26] with a slight excess of $NaIO_4$ (10% w/w supported on silica[64]) in THF at room temperature for 30 hours gave the 2-dioxodisulfane product, $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$ (**21**), in 30% yield (Equation 4.22). The NMR and IR spectra were as expected (Tables E.1 and E.2). The high resolution mass spectrum identified the parent molecular ion, $CpRu(PPh_3)(CO)SS(O)_2CHMe_2^{+\cdot}$.



21

(4.22)

$CpRu(PPh_3)(CO)SS(O)CHMe_2$ undergoes spontaneous oxygen transfer to give $CpRu(PPh_3)(CO)SSCHMe_2$[65] and $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$; however, this reaction is very slow under the conditions employed for the oxidation reaction above. $NaIO_4$ is a nucleophilic oxidant and the oxidation of the electron poor 2-oxo-sulfur[66] was expected. Treatment of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ with $KMnO_4$ (3% w/w on 4 Å molecular sieves[55]) also gave $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$, as determined by NMR, but the reaction was slower than that with supported $NaIO_4$. $KMnO_4$ is also a nucleophilic oxidant and was expected to give reactivity similar to $NaIO_4$.

Treatment of $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$ with 1 equivalent of *m*-CPBA gave a mixture of products as shown by multiple peaks in the ^1H NMR spectrum. Oxidation most likely occurred at the 1-sulfenyl sulfur to give the 1,2,2-trioxodisulfane complex, which may have been unstable and decomposed.

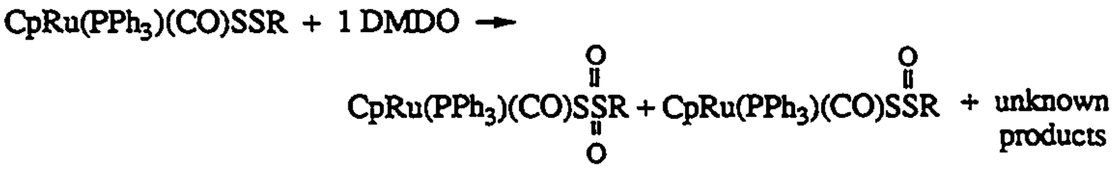
Reactions of $CpRu(CO)(PPh_3)SS(O)_xR$ ($x = 0, 1$) with Dimethyldioxirane (DMDO)

Many oxidation reactions were performed between dimethyldioxirane (DMDO) and the disulfanes $CpRu(PPh_3)(CO)SSR$ (R = $4\text{-}C_6H_4Me$, C_6H_5, $CHMe_2$, C_3H_7) or the 2-oxodisulfanes, $CpRu(PPh_3)(CO)SS(O)R$ (R = $4\text{-}C_6H_4Me$, $CHMe_2$). DMDO was prepared and its concentration determined according to the literature procedure.[50] The concentration ranged from 0.06 to 0.10 M, depending on the particular preparation.

DMDO was stored over 4 Å Molecular Sieves at -16°C for up to 2 weeks after preparation to prevent H_2O contamination. However, this was not always achieved as evidenced by the peak due to H_2O which was present in the NMR spectra of many of the crude reaction products. The concentration of DMDO was redetermined after storage in the freezer for 1 week because DMDO solutions slowly decrease in concentration over time.[50] All DMDO oxidations were performed at -40°C with great care taken to ensure that O_2 and H_2O were excluded. In each case, the oxidations were performed using a slight excess of DMDO. However, addition of a large excess of oxidant gave mixtures of unknown compounds, as indicated by NMR. The optimum solvent for the reaction was THF with a small amount of acetone (20%) if the concentration of DMDO exceeded 0.08 M.

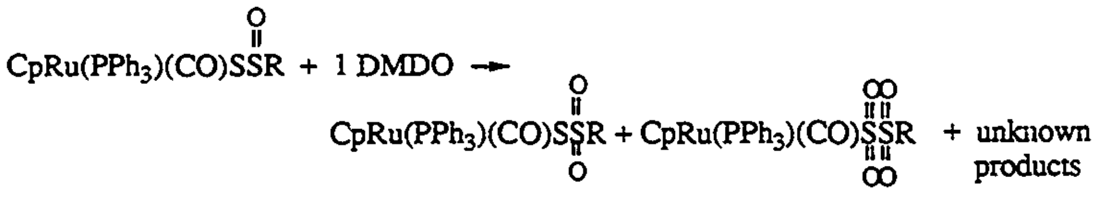
Reactions with 1 or 2 Equivalents of DMDO

Treatment of $\mathrm{CpRu(PPh_3)(CO)SSR}$ (R = $\mathrm{CHMe_2}$, 4-$\mathrm{C_6H_4Me}$) with 1 or 2 equivalents of DMDO in CH_2Cl_2 at -40°C for 20 minutes resulted in a mixture of products as determined by NMR, containing at least 7 peaks in the Cp region. Peaks due to $\mathrm{CpRu(PPh_3)(CO)SS(O)_2R}$, unreacted $\mathrm{CpRu(PPh_3)(CO)SSR}$, and $\mathrm{CpRu(PPh_3)(CO)SS(O)R}$ were identified by NMR, the latter as a minor component (Equation 4.23). These results demonstrate that the oxidation of $\mathrm{CpRu(PPh_3)(CO)SSR}$ with DMDO gives a mixture of the 2-dioxodisulfane and the 2-oxodisulfane products. This is similar to the oxidation of $\mathrm{CpRu(PPh_3)(CO)SR}$ by DMDO where only $\mathrm{CpRu(PPh_3)(CO)S(O)_2R}$ could be isolated [37] (Equation 4.14).



$$\mathrm{CpRu(PPh_3)(CO)SSR} + 1\ \mathrm{DMDO} \rightarrow \mathrm{CpRu(PPh_3)(CO)S}\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{\|}}{\mathrm{S}}}}\mathrm{R} + \mathrm{CpRu(PPh_3)(CO)S}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{R} + \text{unknown products} \qquad (4.23)$$

The oxidation of $CpRu(PPh_3)(CO)SS(O)R$[61] ($R = CHMe_2$, $4\text{-}C_6H_4Me$) with 1 equivalent of DMDO in acetone at -40°C for 20 minutes gave $CpRu(PPh_3)(CO)SS(O)_2R$, a small amount of $CpRu(PPh_3)(CO)S(O)_2S(O)_2R$ (to be discussed later), unreacted $CpRu(PPh_3)(CO)SS(O)R$ and a mixture of unidentifiable products, as identified by its NMR spectrum (Equation 4.24).



$$CpRu(PPh_3)(CO)S\overset{O}{S}R + 1\ DMDO \rightarrow CpRu(PPh_3)(CO)S\overset{O}{\underset{O}{S}}R + CpRu(PPh_3)(CO)\overset{OO}{\underset{OO}{SS}}R + \text{unknown products}$$

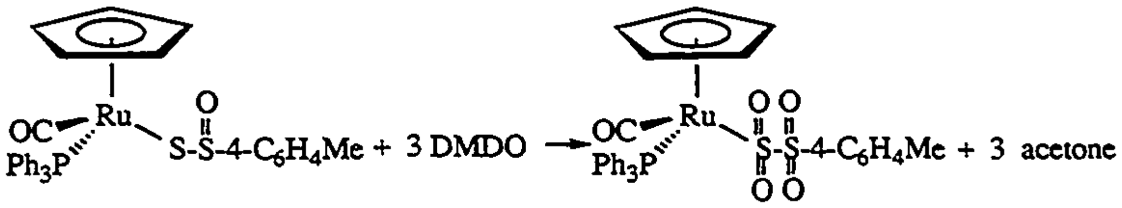
$R = CHMe_2$, $4\text{-}C_6H_4Me$ (4.24)

This reaction also suggests that DMDO oxidizes the electron poor 2-oxo-sulfur atom in preference to the 1-sulfur atom, as expected from a nucleophilic oxidant.

$CpRu(PPh_3)(CO)SS(O)\text{-}4\text{-}C_6H_4Me$ with 3.3 DMDO

At this point, it was concluded that partly oxidized products of the type $CpRu(PPh_3)(CO)S(O)_xS(O)_yR$, where x and y are not both equal to 2, could not be obtained by oxidation of $CpRu(PPh_3)(CO)SSR$ or $CpRu(PPh_3)(CO)SS(O)R$ with stoichiometric amounts of DMDO. Therefore, the target product became the completely oxidized 1,2-tetraoxodisulfanes, $CpRu(PPh_3)(CO)S(O)_2S(O)_2R$, and subsequent reactions were performed with 4.4 equivalents of DMDO for $CpRu(PPh_3)(CO)SSR$ and 3.3 equivalents for $CpRu(PPh_3)(CO)SS(O)R$. The reactions were monitored by NMR, and after all the starting ruthenium compound had been consumed, the solution was stripped to dryness under vacuum to remove all solvents and any excess oxidant. The products decomposed on alumina and were recrystallized.

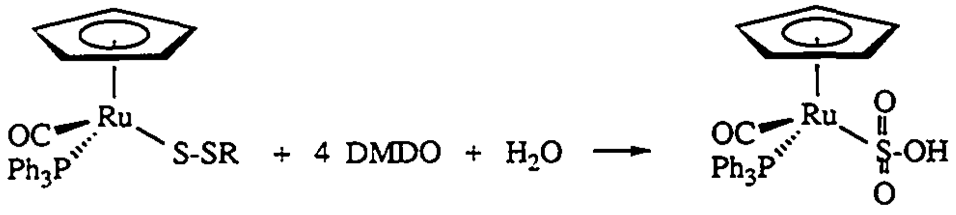
Treatment of $CpRu(PPh_3)(CO)SS(O)\text{-}4\text{-}C_6H_4Me$ with 3.3 equivalents of DMDO gave a yellow solid whose NMR spectrum was consistent with its formulation as $CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}4\text{-}C_6H_4Me$ (22) (Equation 4.25). The IR spectrum in nujol gave bands at 1955 cm^{-1} due to the $\nu(CO)$ stretching frequency and at 1308 and 1262 cm^{-1} due to the $\nu(SO)$ stretching frequencies. The fragment ion $CpRu(PPh_3)(CO)S(O)_2S(O)_2^{+\cdot}$ was identified in the low resolution mass spectrum. The high resolution mass spectrum also gave a peak at m/e at 583.9453 which corresponds to $[CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}H]^{+\cdot}$; the ion $[CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}H]^{+\cdot}$ requires 583.9546 Da.



22 (4.25)

$CpRu(PPh_3)(CO)SSC_3H_7$ with 4.4 DMDO, and with H_2O added

The reaction of $CpRu(PPh_3)(CO)SSC_3H_7$ with 4.4 equivalents of DMDO in acetone/THF gave a yellow coloured solution which turned green when the solution was warmed above -20°C. Recrystallization of the crude residue from CH_2Cl_2/ether gave large pale yellow square crystals of $CpRu(PPh_3)(CO)S(O)_3H$,[32] which were identified by NMR, IR and elemental analysis (30% yield). The same reaction was repeated but with the addition of 5 equivalents of H_2O (Equation 4.26) and a white precipitate of $CpRu(PPh_3)(CO)S(O)_3H$ was formed, as identified by NMR.



(4.26)

$R = C_6H_5, C_3H_7$

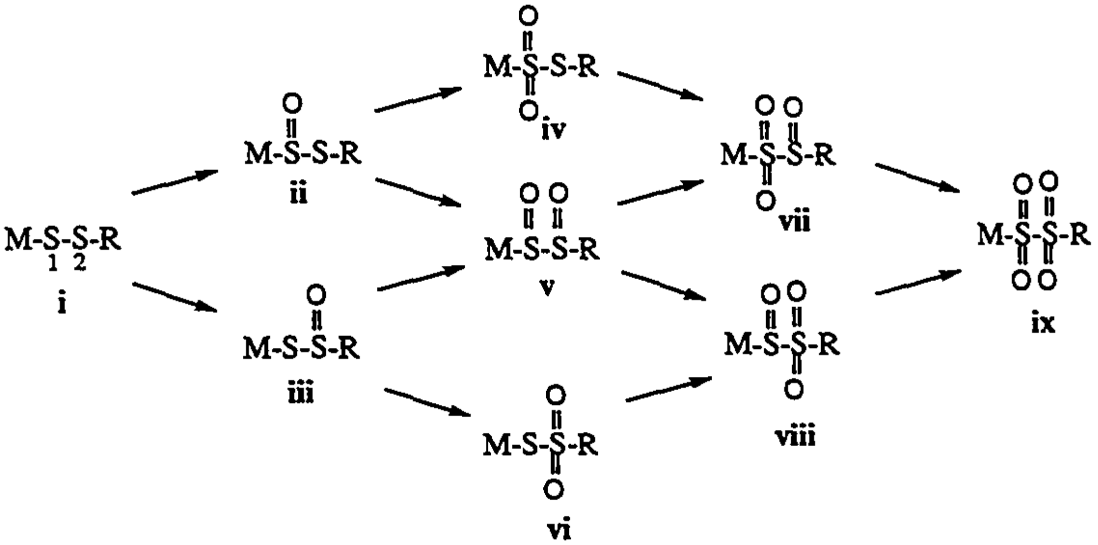
$CpRu(PPh_3)(CO)SS(O)CHMe_2$ with 3.3 DMDO

The reaction of 3.3 equivalents of DMDO with $CpRu(PPh_3)(CO)SS(O)CHMe_2$ gave a product which when recrystallized from acetone/hexanes gave $CpRu(PPh_3)(CO)S(O)_3H$. The same reaction done under similar conditions but recrystallized from THF/hexanes gave a yellow solid whose low resolution mass spectrum displayed a peak due to $CpRu(PPh_3)(CO)S(O)_2S(O)_2^{+\cdot}$, which is the result of the expected product, $CpRu(PPh_3)(CO)S(O)_2S(O)_2CHMe_2$ without the $CHMe_2$ group. In addition, the molecular ion, $[CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}H]^{+\cdot}$, was identified in the high resolution mass spectrum (m/e at 583.9443, $[CpRu(PPh_3)(CO)S(O)_2S(O)_2\text{-}H]^{+\cdot}$ requires 583.9446). Thus, $CpRu(CO)(PPh_3)S(O)_2S(O)_2CHMe_2$ is assigned as the product of the reaction of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ with 3.3 equivalents of DMDO. The same results were obtained from oxidation of the corresponding disulfane, $CpRu(PPh_3)(CO)SSCHMe_2$, with 4.4 equivalents of DMDO.

Discussion

The oxidation of a $CpRu(PPh_3)(CO)SSR$ and $CpRu(PPh_3)(CO)SS(O)R$ complexes with varying equivalents of DMDO gave several different oxidized compounds. Scheme 4.9 demonstrates the potential complexity in these reactions. Oxidation of a metallodisulfane **i** could occur at either the 1- and 2- sulfur atoms to give **ii** or **iii**, respectively. Stable examples of **iii** have been prepared,[26-28,67] but 1-oxodisulfanes **ii** are unknown. However, since compounds containing a MS(O)R ligand are rare and unstable,[27,68-70] while those of the type $MS(O)_2R$ are more stable,[27,36,68] it is possible that complexes of the type MS(O)SR will also be unstable. Continuing along these paths, oxidation of **ii** would lead to either **iv** or **v**. Complexes of the type **iv** are known: *trans*-$(PPh_3)_2Pt(phth)S(O)_2SR$ are stable while $CpRu(PPh_3)(CO)S(O)_2SR$ are unstable.[32] Complexes of the type **v** are expected to be unstable by analogy with the organic analogs, RS(O)S(O)R', which have only been characterized by low temperature NMR and have never been isolated.[71] On the other hand, oxidation of a 2-oxodisulfane **iii** can give either **v** or **vi**. Complexes of the type **vi** are known and are stable.[26] There are no known examples of transition metal complexes of structures **vii** or **viii**. Since a mixture of products was obtained in many of the reactions, it is possible that at least some of the oxidation occurred on the 1-sulfur atom giving unstable intermediates that decomposed. Thus, the target compound, $CpRu(PPh_3)(CO)S(O)_2S(O)_2R$, is at the end of a potentially complicated set of reactions.

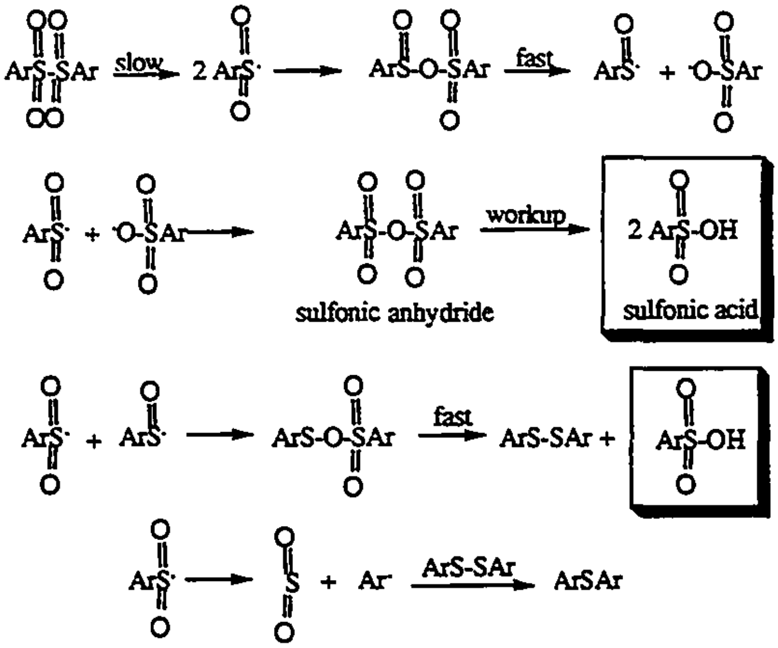
Scheme 4.9



Oxidations of $CpW(CO)_3SSR$ have been carried out with *m*-CPBA to give a mixture of compounds including $CpW(CO)_3SS(O)R$.[29] This is the only reference in the literature of oxidation of a disulfane ligand on one metal center, and the results parallel ours in the observed nonregioselectivity at the sulfur atoms.

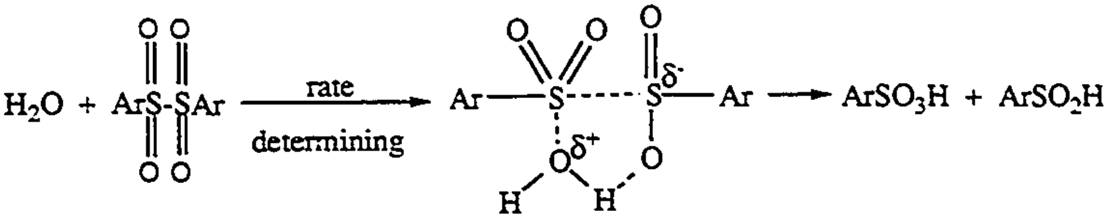
The organic alkyl and aryl analogs, α-disulfones, $RS(O)_2S(O)_2R$, are known and are a stable class of compounds[72] but the main byproduct in the both the synthesis and thermal decomposition of α-disulfones is RSO_3H.[25,72] Diaryl α-disulfone compounds are known to decompose via a radical mechanism[13,63] to give a sulfonic anhydride intermediate that can decompose further to give sulfonic acid as shown in Scheme 4.10. The sulfide and disulfide are also decomposition products.

Scheme 4.10

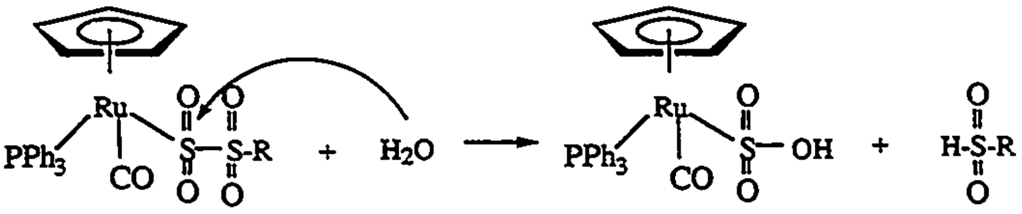


In addition, diaryl α-disulfone compounds react with H_2O via nucleophilic substitution at the sulfur to give the sulfonic acid and sulfinic acid derivatives. The rate determining step is proton transfer from the H_2O molecule to an oxygen from the neighbouring SO_2 group[23] (Scheme 4.11).

Scheme 4.11

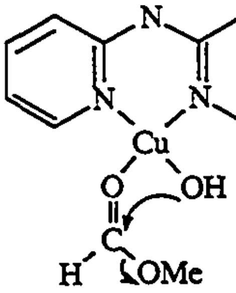


CpRu(PPh$_3$)(CO)S(O)$_3$H[32] is analogous to the sulfonic acid product described in Schemes 4.10 - 4.11. The tetraoxosulfano compounds, CpRu(PPh$_3$)(CO)S(O)$_2$S(O)$_2$R, are highly water sensitive and react to give CpRu(PPh$_3$)(CO)S(O)$_3$H[32] and R$_2$S$_2$. Since these are the only compounds which could be isolated from the reactions designed to give CpRu(PPh$_3$)(CO)S(O)$_2$S(O)$_2$R, these compounds may be unstable and decompose to CpRu(PPh$_3$)(CO)S(O)$_3$H. The product for R = C$_3$H$_7$, was the least stable, and decomposed above -20°C. Thus, the electron donating alkyl group appeared to destabilize the S(O)$_2$-S(O)$_2$ linkage to a greater extent than aryl groups. Oxidation of CpRu(PPh$_3$)(CO)SSR or CpRu(PPh$_3$)(CO)SS(O)R in the presence of H$_2$O resulted in only CpRu(PPh$_3$)(CO)S(O)$_3$H, which may have proceeded via nucleophilic attack from H$_2$O as illustrated in Equation 4.27.

 (4.27)

Despite the exhaustive precautions to exclude H$_2$O from the reactions, peaks due to H$_2$O appeared in many of the NMR spectra of the crude reaction products. Many of these NMR spectra also contained peaks due to HOAc that has been assigned from comparison of its NMR spectrum to that of the authentic sample (C$_6$D$_6$: Cp = 1.54 ppm, OH shift varies but is broad feature). In addition, the IR spectra of these same samples in toluene displayed a band at 1750 cm^{-1}, consistent with the position of an organic carboxylate stretching band.

The origin of the HOAc is unknown but it may be produced from the hydrolysis of methylacetate, MeOAc, a byproduct in the synthesis of DMDO.[50] MeOAc cannot be hydrolyzed under normal conditions to HOAc unless activated by a Lewis Acid. Recently, it has been reported[73] that $[(2,2'\text{-dipyridylamine})Cu(OH_2)_2]^{2+}$ will catalyze the hydrolysis of MeOAc to HOAc. The proposed mechanism involves precoordination of MeOAc to the copper center followed by intramolecular metal hydroxide attack on the MeOAc. Perhaps an unsaturated ruthenium species catalyzes the hydrolysis.



4.3 Conclusions

The reaction of $CpRu(CO)_2SH$ with $RS(O)_2Cl$ ($R = 4\text{-}C_6H_4Me$, C_6H_5) represents a facile new route to the complexes $CpRu(CO)_2SS(O)_2R$ which contain the rare $-SS(O)_2R$ ligand. The compounds $CpRu(CO)_2SS(O)_2R$ are exceptionally stable organometallic complexes. The complexes $CpRu(CO)_2SS(O)R$ ($R = 4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$) were also prepared via the established method of treating a M-SH with phthS(O)R. However, only $CpRu(CO)_2SS(O)CH_2C_6H_5$ was isolated because the complexes where $R = 4\text{-}C_6H_4Me$ and C_6H_5 spontaneously transfer oxygen to give $CpRu(CO)_2SSR$ and

$CpRu(CO)_2SS(O)_2R$. Both the preparative methods described above are non-oxidative. The compounds $CpRu(CO)_2SS(O)R$ react with PPh_3, losing sulfur and oxygen atoms and a CO ligand to give $CpRu(PPh_3)(CO)_2SR$, whereas $CpRu(CO)_2SS(O)_2R$ only undergoes ligand substitution when reacted with PPh_3 to give $CpRu(PPh_3)(CO)SS(O)_2R$.

Oxidation of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ by $NaIO_4$, a nucleophilic oxidant, gave a regioselective product, $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$. However, oxidation of $CpRu(PPh_3)(CO)SS(O)_yR$ with 1 or 2 ($y = 0$) and 1 ($y = 1$) equivalent of DMDO, an electrophilic oxidant, was not regioselective at the sulfur atoms. Thus, this is not a good route to complexes of the type $MSS(O)_yR$ ($y = 1$-2). This lack of selectivity suggests that DMDO cannot distinguish between the two different 1- and 2- sulfur atoms in $CpRu(PPh_3)(CO)SS(O)_yR$ ($y = 0, 1$). Perhaps the $CpRu(PPh_3)(CO)$ and R moieties do not affect the electron densities of the 1- and 2- sulfur atoms to the extent where they are chemically inequivalent and can be differentiated by DMDO.

The complexes $CpRu(PPh_3)(CO)S(O)_2S(O)_2R$ ($R = 4\text{-}C_6H_4Me$, $CHMe_2$, C_3H_7) are thought to be the initial products from oxidation of $CpRu(PPh_3)(CO)SS(O)_yR$ ($y = 0, 1$) with 4 and 3 equivalents of DMDO, respectively, but are very reactive and immediately react with trace amounts of H_2O to give $CpRu(PPh_3)(CO)S(O)_3H$ and R_2S_2. Although formation of $MS(O)_2S(O)_2R$ by an oxidative route seems to be successful, these complexes could not be isolated.

4.4 References

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Chapter 5.

Electrochemical Oxidation of $CpRu(CO)_2E$ (E = Cl, SH, SR, SSR, SS(O)R, $SS(O)_2R$)

5.1 Introduction

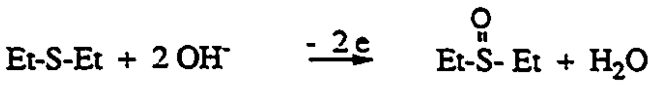
Electrochemical techniques have been used by organometallic chemists in the last fifteen years to obtain information about the redox properties of metal complexes. Many of these studies are directed towards gaining a deeper understanding of biological processes[1-6] involving redox-active metalloenzymes, as well as reactions involving complexes of industrial significance.[7,8] For example, the oxidation of Ni^{2+} to Ni^{3+} that is carried out by hydrogenases, has been modeled successfully by using nickel compounds with chelating thiolate and amine ligands.[9-12] In addition, electrochemical methods are complementary to other techniques used by chemists such as chemical oxidation or reduction,[13] UV-vis[6,8] and IR[14] spectroscopies, EPR,[2,15] and x-ray crystallography.[3,5]

Cyclic voltammetry (CV) is usually the electrochemical experiment of choice to supply information about the redox properties of a metal complex. The potential (E) at which an electron transfer to an electrode occurs is an indicator of electron density at the redox site. The potential can also indicate whether the process occurring in the cyclic voltammetry scan of an organometallic complex is metal or ligand based, by comparing potentials to those in standard electrochemical tables. The extent of electrochemical reversibility reflects kinetic limitations on the electron transfer process and can also point to the involvement of prior or post chemical reactions. Finally, the number of peaks in a cyclic voltammetry experiment is an indication of the complexity of the redox process.

There are some general reviews of the CV technique in the literature[16-18] in addition to reviews specific to organometallic chemistry.[19-21]

Although most of the organometallic literature is concerned with the redox properties of metal centers, there have also been reports of the redox properties of ligands coordinated to a metal. These are mostly for the reduction of pyridine[22] and the oxidation of thiolate ligands.[6,10,23,24] There are no reports of the cyclic voltammetry of transition metal disulfane ligands (or their oxidized derivatives) and overall, little work has addressed the oxidation of sulfur atoms coordinated to a metal center.

The electrochemistry of sulfur-containing organic compounds, such as sulfides and disulfides has been studied;[25] however, most of the experiments have been performed in aqueous solutions. It has been determined that the anodic oxidation of organic sulfides is irreversible, involves transfer of two electrons and the formation of sulfoxides.[26] As an example, the oxidation of diethyl sulfide is shown in Equation 5.1.



$$\text{Et-S-Et} + 2\,\text{OH}^- \xrightarrow{-2e} \text{Et-}\overset{\overset{\displaystyle O}{\|}}{\text{S}}\text{-Et} + H_2O \qquad (5.1)$$

In this chapter, cyclic voltammetry experiments were performed on the complexes $CpRu(CO)_2SS(O)_yR$ (y = 0-2) to study the oxidation of the different sulfur atoms in the disulfane, 2-oxodisulfane and 2-dioxodisulfane ligands. The chemical oxidation of these complexes (Chapter 4) turned out to be very complex. Electrochemical oxidation has the advantage in that there are no chemical byproducts from the oxidant to complicate the study. Since there are no published electrochemical studies of disulfane ligands and their oxidized counterparts, the cyclic voltammograms of $CpRu(CO)_2Cl$, $CpRu(CO)_2SH$ and $CpRu(CO)_2SR$ were also performed and the results used for comparison.

5.2 Results and Discussion

5.2.1 Initial Considerations

The conditions used to obtain well resolved cyclic voltammograms (CVs) will be briefly described. Initial cyclic voltammetry (CV) runs were performed using either a glassy carbon electrode (GCE) or a platinum electrode as the working electrode. Although both electrodes initially gave the same peak patterns in the cyclic voltammograms of the ruthenium-sulfur compounds, it has been reported that complexes containing sulfur tend to adsorb onto platinum electrodes.[7] Therefore, the GCE was chosen as the working electrode for all experiments. The CVs were performed at relatively slow scan rates (≤ 200 mV s^{-1}). CVs obtained at scan rates faster than 500 mV s^{-1} suffered from a large amount of noise and gave poor peak resolution. Experiments with fast scan speeds (> 500 mV s^{-1}) were performed to check for reversibility of the peaks. All peaks are reported relative to the ferrocene/ferrocinium (Fc/Fc^+) couple; a Ag/Ag^+ electrode served as the cell reference. Detailed experimental conditions are described in the Experimental Section.

Plots of 1) the absolute value of the current of the first oxidation peak versus the square root of the scan rate for the complexes $CpRu(CO)_2Cl$ and $CpRu(CO)_2S_xR$ ($x = 1, 2$; R = H, 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) and 2) E_p^{ox} (oxidation peak potential) versus log of sweep rate are given in Appendix 3 in Figures A.3.1 and A.3.2, respectively. The linear behavior of plots at scan speeds of 20, 100 and 200 mV s^{-1} in Figure A.3.1 suggest that the rate of oxidation is diffusion controlled, and a slope of 60 (± 20) mV/log(sweep rate) in Figure A.3.2 suggests that the electron transfer process is irreversible.[27,28]

5.2.2 $CpRu(CO)_2SH$ and $CpRu(CO)_2Cl$

In order to determine if ligand and/or metal oxidation occurred for the complexes $CpRu(CO)_2S_xO_yR$ ($x = 1, 2$; $y = 0$-2), CVs of $CpRu(CO)_2SH$ and $CpRu(CO)_2Cl$ were performed. If the redox process is ligand-based (sulfur and chlorine, respectively) then these two compounds should show large differences in electrochemical behavior.

The cyclic voltammogram of $CpRu(CO)_2SH$ at the scan speed of 20 mV s^{-1} in the potential range -1.6 to 1.2 V displays two irreversible oxidation waves, at 0.26 and 0.76 V (Figure 5.1 and Table 5.1). Both oxidation peaks are present when scanning initially in the positive or negative direction, regardless of the initial potential (-0.40 V, 0.30 V, 1.0 V). The first oxidation peak remains irreversible when scanning in the potential range 0.00 to 0.50 V at a scan rate of 500 mV s^{-1}. The same oxidation peaks appeared at scan rates of 100 and 200 mV s^{-1} in the potential range of -0.2 to 1.3 V. Since both oxidation peaks are irreversible, these CVs indicate that the oxidized species is either unstable and it undergoes chemical reaction before the subsequent reduction can occur or that the putative reduction process is extremely slow. To confirm that the oxidation peaks (0.26 V, 0.76V) were due to the ligand-based electron transfer, it was noted that the electrochemical potentials were at substantially more positive potentials than expected for Ru^{2+}/Ru^{3+} oxidation values given in electrochemical tables (-0.65 V).[29]

$CpRu(CO)_2Cl$ undergoes a single irreversible oxidation at 1.15 V at a scan rate of 20 mV s^{-1} in the potential range -1.7 to 1.3 V (Figure 5.2, Table 5.1). There was no corresponding reduction peak when scanning to -1.7 V. No reduction peak was observed even at 500 mV s^{-1}. As stated for $CpRu(CO)_2SH$, these two facts suggest that either the oxidized species is unstable and undergoes subsequent chemistry before a reduction process can occur or that the reduction process is extremely slow. The potential of the oxidation peak does not change with varying scan speeds.

The single oxidation peak in the CV of $CpRu(CO)_2Cl$ (1.15 V) appeared at a higher potential than the $CpRu(CO)_2SH$ (0.26, 0.76V) oxidation peaks. If the oxidation were due to the Ru^{2+}/Ru^{3+} couple, oxidation peaks at a similar potential might be expected. The oxidation for $CpRu(CO)_2Cl$ occurs at 0.89 V more positive than the first oxidation peak of

Table 5.1 Potentials obtained from cyclicvoltammograms for $CpRu(CO)_2E$ (E = Cl, SH, S-4-C_6H_4Me, SC_6H_5, $SCH_2C_6H_5$). [a]

Compound	20 mV s^{-1}		100 mV s^{-1}		200 mV s^{-1}		500 mV s^{-1}	
	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}
$CpRu(CO)_2Cl$	1.15	-	1.18	-	1.16	-		
$CpRu(CO)_2SH$	0.26 0.76	-	0.31 0.81	-	0.34 0.86	-		
$CpRu(CO)_2S$-4-C_6H_4Me	0.24 1.02 1.22	-1.23 ^{w} 1.12 ^{w}	0.27 1.00 $^{w, sh}$ 1.25	-0.34 -1.34 ^{w} 1.08 ^{w}	0.14 ^{w} 0.29 0.99 $^{w, sh}$ 1.26 $^{w, sh}$	-0.37 -1.06 ^{w} -1.62 ^{w}	0.15 ^{w} 0.34 1.02 $^{w, sh}$	-0.41 -1.07 ^{w} -1.79 ^{w}
$CpRu(CO)_2SC_6H_5$	0.31	-0.17 -0.88 ^{w}	0.32	-0.26 1.18 ^{w}	0.36	-0.28 -1.20 ^{w}	0.14 ^{w} 0.40	-0.34 -1.28
$CpRu(CO)_2SCH_2C_6H_5$	0.29	-0.61 ^{w}	0.30	-0.66	0.34	-0.71	0.39	-0.74

[a] All potentials were measured in THF, 0.1 M $[Bu_4N][PF_6]$ verses Fc/Fc^+, GCE with Ag/Ag^+ reference.

^{br} broad peak, ^{sh} shoulder, ^{w} small peak

Figure 5.1 Cyclic voltammogram of a THF solution of $CpRu(CO)_2Cl$ at a GCE, 0.001 M in complex and 0.1 M in $[Bu_4N][PF_6]$, at a sweep rate of 20 mV s^{-1}. Potentials are referenced to Fc/Fc^+. Initial potential is 0.00 V and the initial direction of the scan is positive as indicated by the direction of the arrow.

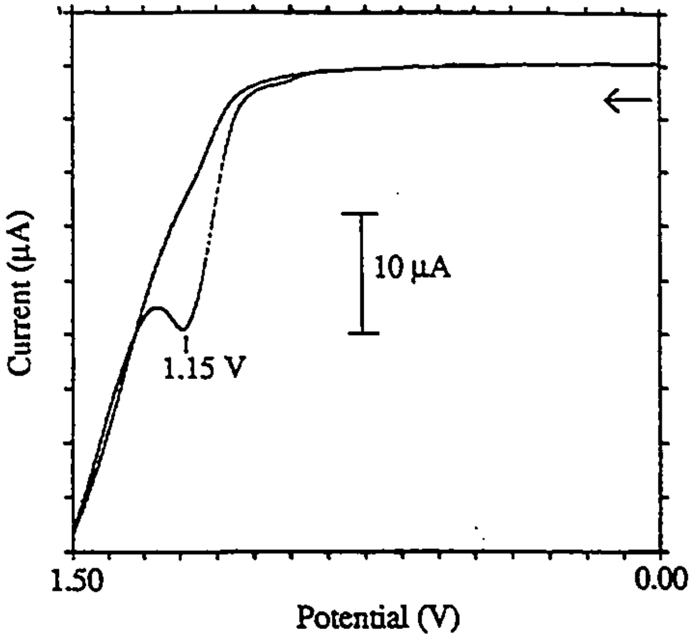
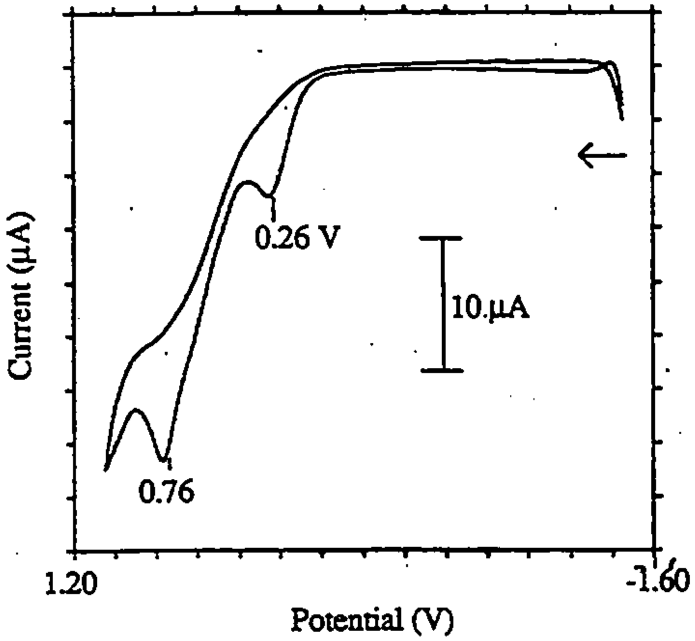


Figure 5.2 Cyclic voltammogram of a THF solution of $CpRu(CO)_2SH$ at a GCE, 0.001 M in complex and 0.1 M in $[Bu_4N][PF_6]$, at a sweep rate of 20 mV s^{-1}. Potentials are referenced to Fc/Fc^+. Initial potential is -1.60 V and the initial direction of the scan is positive as indicated by the direction of the arrow.



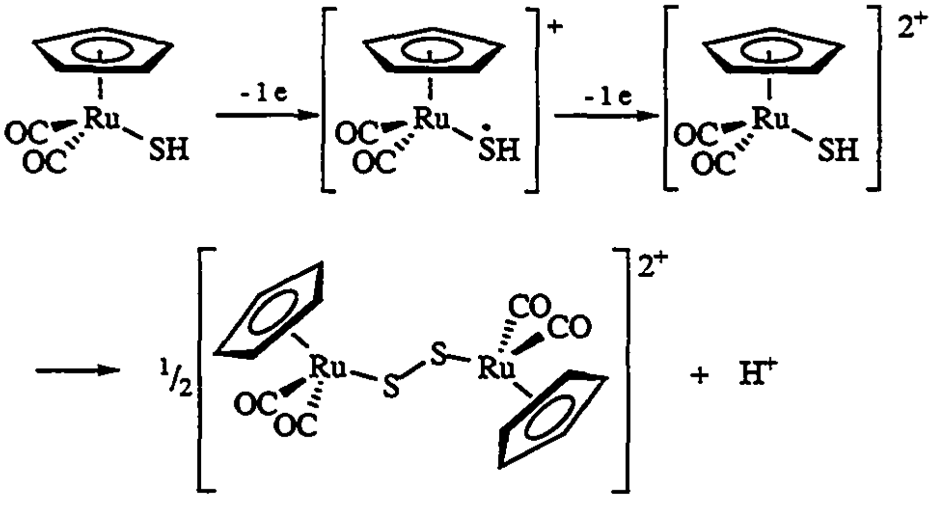
$CpRu(CO)_2SH$. This suggests that the oxidation peaks of the latter are sulfur-based and that the latter is more electron rich and easier to oxidize than the former, as expected.

There have been other electrochemical studies of similar compounds, namely, $CpRu(PPh_3)_2SH$ and $CpRu(PPh_3)_2Cl$.[13] The former complex undergoes two irreversible oxidation waves at 0.17 (vs. Ag/AgCl, (0.36 vs. Fc/Fc^+)) and 0.35 V (vs. Ag/AgCl, (0.53 V vs. Fc/Fc^+)) in CH_2Cl_2. Detailed electrochemical studies (coulometry) determined that the net oxidation involves two electrons and that the products of the oxidation were a proton and the disulfane bridged dinuclear complex, $(\mu\text{-}S_2)[CpRu(PPh_3)_2]^{2+}$ (Equation 5.2).

$$CpRu(PPh_3)_2SH \longrightarrow {}^1/_2\,(\mu\text{-}S_2)[CpRu(PPh_3)_2]_2^{2+} + H^+ + 2\,e \qquad (5.2)$$

Analogous to this work, the presence of two peaks in the CV of our complex, $CpRu(CO)_2SH$, may suggest that a similar process is occurring giving $(\mu\text{-}S_2)[CpRu(CO)_2]^{2+}$ as the product (Scheme 5.1).

Scheme 5.1



It is expected that $CpRu(CO)_2SH$ would be more difficult to oxidize than $CpRu(PPh_3)_2SH$ since two σ-donor PPh_3 ligands have been replaced by two CO π-accepting ligands, making the former complex more electron poor. This would be reflected in higher oxidation potentials for the former. However, this intuitive analysis may not be completely correct as the first oxidation potential of $CpRu(CO)_2SH$ was slightly lower than for $CpRu(PPh_3)_2SH$ (0.26 vs. 0.36 V). However, the difference for the first potentials (0.10 V) is relatively small and may reflect the effect of performing the experiments in different solvents (THF in this work vs. CH_2Cl_2[13]).

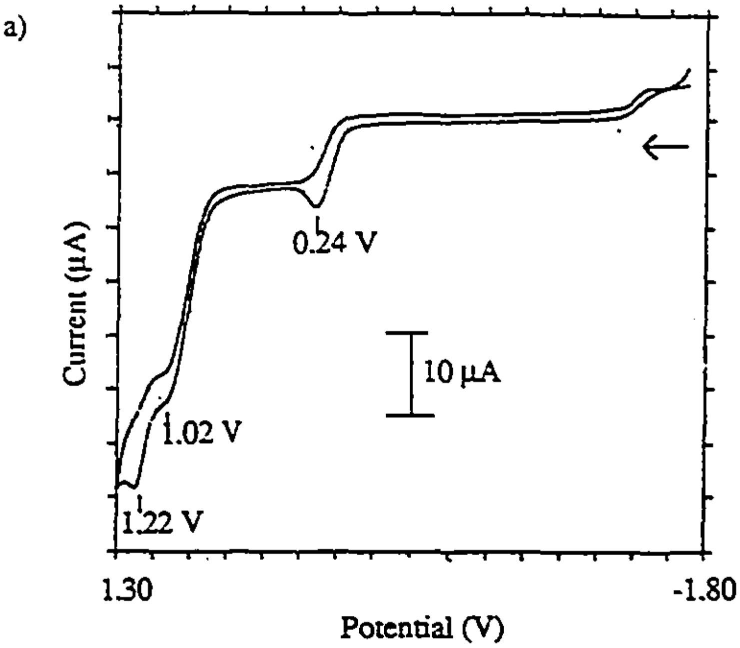
A different way of looking at the potential data that is relatively independent of experimental details is to look at the potential difference between the first and second oxidation peaks (ΔE_p^{ox}), for each complex. ΔE_p^{ox} is 0.50 V for $CpRu(CO)_2SH$ and 0.17 V for $CpRu(PPh_3)_2SH$. Thus, in a relative sense it is much more difficult to remove the second electron from $CpRu(CO)_2SH$, than for the bisphosphine substituted product, as expected from ligand bonding properties.

The comparison of the potential of the irreversible oxidation peak of $CpRu(PPh_3)_2Cl$ at 0.650 (vs. Ag/AgCl, (0.83 V vs. Fc/Fc^+))[13] to that of $CpRu(CO)_2Cl$ (1.15 V vs. Fc/Fc^+) also illustrates that the latter is more difficult to oxidize, as expected.

5.2.2 $CpRu(CO)_2SR$

The electrochemistry of the thiolate complexes, $CpRu(CO)_2SR$, was examined to determine the effect of replacing the SH ligand with SR, and to compare the results with those reported in the literature for other thiolate ligands.[6,10,12,23,30] Thus, the CVs of $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) in the potential range -1.80 and 1.25 V were examined. The cyclic voltammograms for $CpRu(CO)_2SC_6H_5$ and $CpRu(CO)_2SCH_2C_6H_5$ are similar and will be discussed together, while those of

Figure 5.3 Cyclic voltammograms of a THF solution of CpRu(CO)$_2$S-4-C$_6$H$_4$Me at a GCE, 0.001 M in complex and 0.1 M in [Bu$_4$N][PF$_6$], at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.30 V; b) 200 mV s^{-1} and initial potential is -1.80 V. Potentials are referenced to Fc/Fc$^+$ and the initial directions of the scans are positive as indicated by the direction of the arrows.



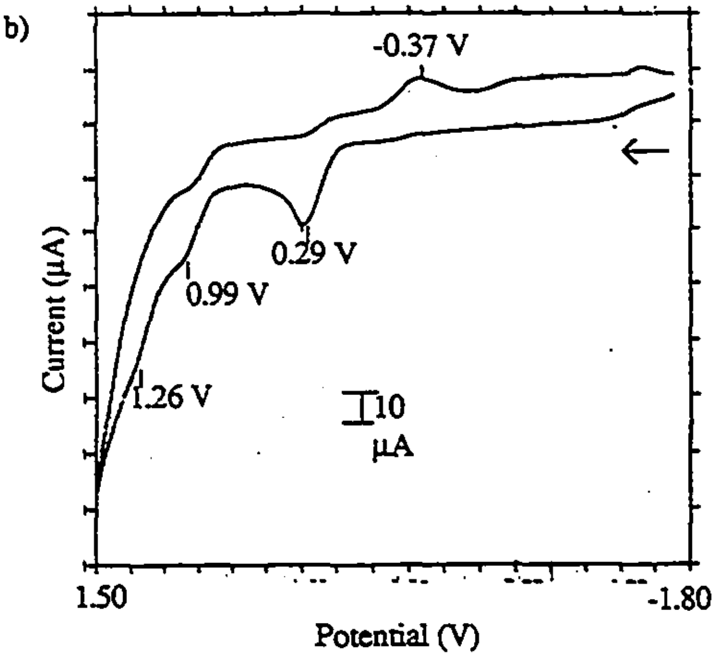


Figure 5.4 Cyclic voltammograms of a THF solution of CpRu(CO)$_2$SC$_6$H$_5$ at a GCE, 0.001 M in complex and 0.1 M in Et$_4$N][PF$_6$], at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.26 V; b) 200 mV s^{-1} and initial potential is -1.50 V. Potentials are referenced to Fc/Fc$^+$ and the initial directions of the scans are positive as indicated by the direction of the arrows.

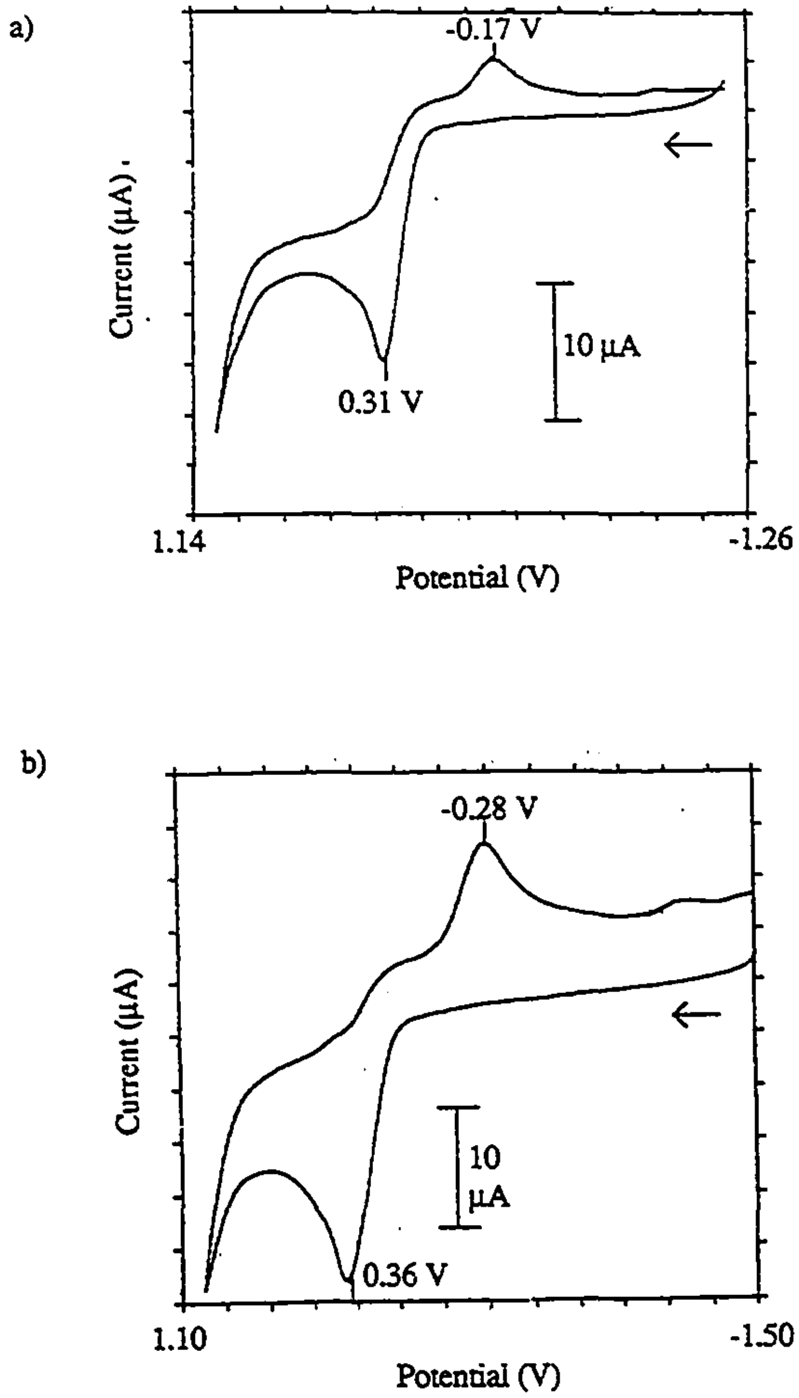
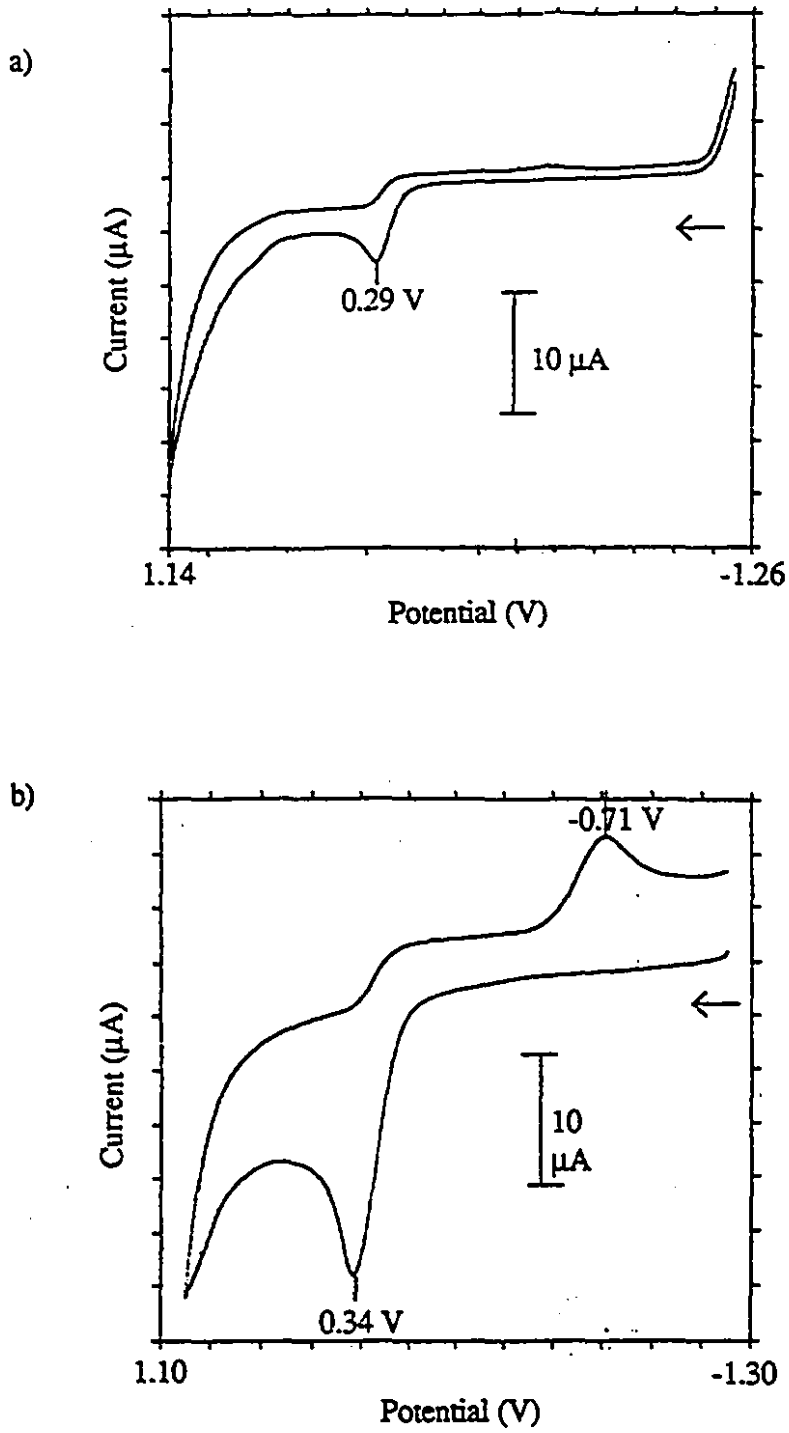


Figure 5.5 Cyclic voltammograms of a THF solution of CpRu(CO)$_2$SCH$_2$C$_6$H$_5$ at a GCE, 0.001 M in complex and 0.1 M in [Bu$_4$N][PF$_6$], at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.26 V; b) 200 mV s^{-1} and initial potential is -1.26 V. Potentials are referenced to Fc/Fc$^+$ and the initial directions of the scans are positive as indicated by the direction of the arrows.



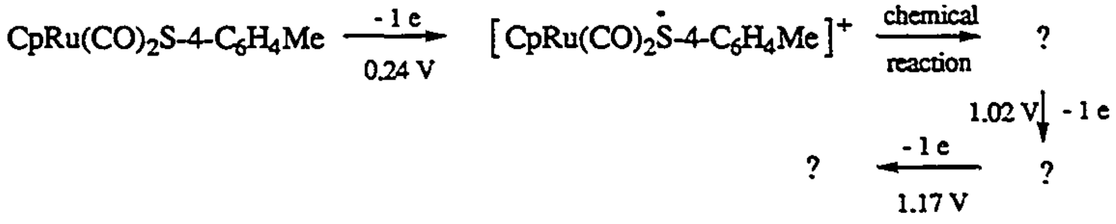
$CpRu(CO)_2S$-4-C_6H_4Me will be discussed separately. The CVs of $CpRu(CO)_2SR$ obtained at 20 and 200 mV s^{-1} are shown in Figures 5.3 - 5.5.

The cyclic voltammograms of $CpRu(CO)_2SC_6H_5$ and $CpRu(CO)_2SCH_2C_6H_5$ at 20 mV s^{-1} both display one irreversible oxidation peak at 0.31 and 0.29 V, respectively. Oxidation peak potentials obtained at sweep rates of 20, 100, 200 and 500 mV s^{-1} are given in Table 5.1 and show that even at higher sweep rates, no corresponding reduction wave is observed. This implies that either the oxidation product must be short-lived and reacts almost immediately to form another species before subsequent reduction can occur, or the reverse reaction involving electron transfer back into the oxidized species is too slow to be observed.

By contrast, the CV of $CpRu(CO)_2S$-4-C_6H_4Me at the sweep rate of 20 mV s^{-1} displays two irreversible oxidations at 0.24, 1.02 and one quasireversible couple at 1.17 V. The irreversible oxidation peak at 1.02 V is small. This same pattern is observed in the CV run at 100 mV s^{-1}. However, at 200 mV s^{-1}, the latter two oxidations peaks (0.99, 1.26 V) are significantly smaller than in the CVs obtained at slower sweep rates. Thus, the second and third oxidation peaks may be due to a new species formed from the unstable oxidized species and, at faster sweep rates, the oxidized species does not have time to react to form new products. Therefore it is not possible to observe further oxidation peaks. No reduction peak linked to this oxidation peak was observed even at sweep rates up to 1000 mV s^{-1}.

There is not a large change in $E_p{}^{ox}$ for the different R groups in CVs for $CpRu(CO)_2SR$. Moreover, the $\Delta E_p{}^{ox}$ is not large as one changes the ligand from -SH to -SR, implying that the R group does not have a large affect on the ease of oxidation. The significance of this result pertains to studies of the Claus Process. Since the ease of transferring an electron from both $CpRu(CO)_2SH$ and $CpRu(CO)_2SR$ complexes is similar, the stable complexes $CpRu(CO)_2SR$ may be studied as substitutes for the reactive complex $CpRu(CO)_2SH$. However, since the peak pattern for R = 4-C_6H_4Me is different than for R = C_6H_5 and $CH_2C_6H_5$, the R group may have an effect on the stability of the oxidized species formed, the former being the least stable. Thus, the second and third oxidation peaks due to $CpRu(CO)_2S$-4-C_6H_4Me may be a result of the instability of the first oxidized species formed reacting quickly to give another species which undergoes two subsequent oxidations (Scheme 5.2).

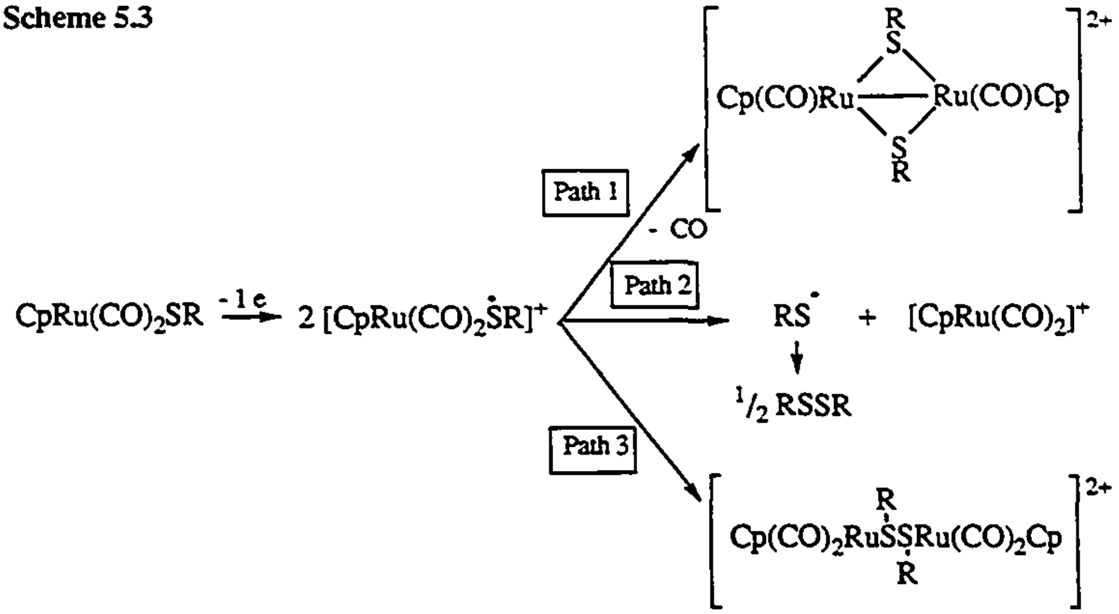
Scheme 5.2



The CVs of our thiolate complexes conform to literature analogs. First of all, it has been reported that sulfur-ligand oxidation is irreversible and many of the CVs of thiolates indicate that the R group on the thiolate ligand does not affect the oxidation potential or the follow-on chemistry, unless it is sterically hindering.[10,23] For example, [Ni(pdmt)(SR)]- (pdmt = pyridine-2,6-dimethanthiolate; R = Et, C_6H_5) undergoes only one irreversible oxidation at -0.08 V (vs. saturated calomel electrode (SCE), (0.05 V vs. Fc/Fc^+)) for R = Et and 0.01 V (vs. SCE, (0.14 V vs. Fc/Fc^+)) for R = C_6H_5. These values, and the relatively small ΔE_p^{ox} of 0.09 V [6] parallels that of our systems where ΔE_p^{ox} for R = 4-C_6H_4Me, C_6H_5 and $CH_2C_6H_5$ is 0.07 V.

The work done by others may shed some light onto the fate of an oxidized species, $[CpRu(CO)_2S^{\cdot}R]^+$. Three possibilities following the one-electron oxidation of mononuclear thiolates have been proposed and are shown with our complex as an example (Scheme 5.3):[23] 1) metal-metal coupling with loss of a CO ligand leading to thiolate bridged dimers, 2) homolytic cleavage of the M-S bond to give a short lived alkyl-thiyl radical which could recombine to give the disulfide and a unsaturated metal fragment and 3) formation of a sulfur-sulfur bond which bridges two metal atoms.

Scheme 5.3



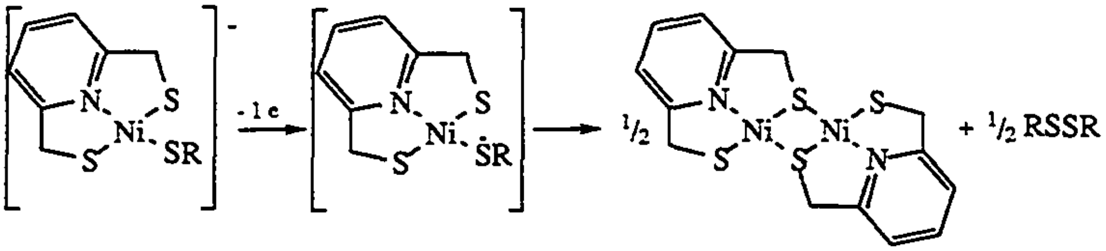
There are examples in the literature for all three paths and some of these examples will be briefly presented. An example for the first path has been observed in the irreversible one electron oxidation of the trigonal-bipyramidal thiolate anion $PhSFe(CO)_4^-$ which gave the $[PhSFe(CO)_4]^{\cdot}$ radical which rapidly lost a CO ligand and dimerized to give $(PhSFe(CO)_3)_2$ (Scheme 5.4).[31]

Scheme 5.4

$$[PhSFe(CO)_4]^- \xrightarrow{-1e} [PhSFe(CO)_4]^{\cdot} \xrightarrow{-CO} [PhSFe(CO)_3]^{\cdot} \xrightarrow{-CO} {}^1/_2\,(PhSFe(CO)_3)_2$$

An example of the second path is the nickel thiolate complex $[Ni(pdmt)(SR)]^-$ (pdmt = pyridine-2,6-dimethanthiolate; R = Et, C_6H_5) which loses a thiyl radical to give a nickel dimer as shown in Scheme 5.5.[6] In addition, the complexes $RSCr(CO)_5^-$ (R = Et, Ph)[23] undergo one electron oxidation to give $(RSSR)Cr(CO)_5$ resulting from the coupling of two thiyl radicals (Scheme 5.5).

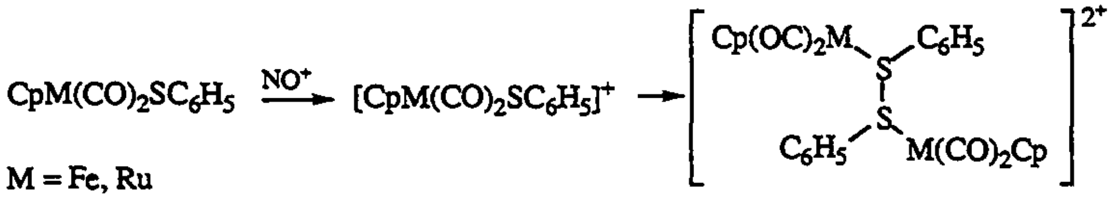
Scheme 5.5



$$[RSCr(CO)_5]^- \longrightarrow [R\dot{S}Cr(CO)_5] \longrightarrow RS\cdot + Cr(CO)_5 \xrightarrow{+RS\cdot} (RSSR)Cr(CO)_5$$

An example of the third path is the one electron chemical oxidation of $CpM(CO)_2SC_6H_5$ ($M = Fe^{32}$, Ru^{33}) with NO^+ which results in a cation which undergoes S-S coupling to give $[(CpM(CO)_2)_2(\mu\text{-}RSSR)]^{2+}$ ($R = C_6H_5$) (Scheme 5.6).

Scheme 5.6



$$CpM(CO)_2SC_6H_5 \xrightarrow{NO^+} [CpM(CO)_2SC_6H_5]^+ \longrightarrow \left[\begin{array}{c} Cp(OC)_2M\text{-}S(C_6H_5)\text{-}S(C_6H_5)\text{-}M(CO)_2Cp \end{array} \right]^{2+}$$

M = Fe, Ru

Applying these possibilities to our system, the most likely path may be the third since $[(CpRu(CO)_2)_2(\mu\text{-}RSSR)]^{2+}$ is known.

5.2.2 $CpRu(CO)_2SSR$

Given the foregoing analysis of the electrochemical properties of the relatively simple complexes $CpRu(CO)_2SR$ ($R = H$, $4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$), the CVs of the

Table 5.2 Potentials obtained from cyclic voltammograms for $CpRu(CO)_2SSR$ (R = $4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$). [a]

Compound	20 mV s^{-1}		100 mV s^{-1}		200 mV s^{-1}		500 mV s^{-1}	
	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}
$CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$	0.25 0.67^{w} 1.05	-	0.28 $0.71^{w, sh}$ 1.12	$-0.85^{w, sh}$ $-1.08^{w, br}$ $-1.30^{w, br}$	0.30 $0.72^{w, sh}$ 1.21	$-0.72^{w, br}$ -1.18^{br} -1.46^{br}	0.33 $0.79^{w, sh}$	$-0.78^{w, br}$ -1.22^{br} $-1.49^{w, br}$
$CpRu(CO)_2SSC_6H_5$	0.29 0.72^{w} 1.11	-	0.32 0.73^{w} 1.18	-0.81^{w} -1.19^{w} -1.44^{w}	0.35 0.75^{w}	-0.83^{w} -1.19^{w} -1.41^{w}	0.41	-0.84^{w} -1.22^{w} -1.48^{w}
$CpRu(CO)_2SSCH_2C_6H_5$	0.20 0.68^{w} 1.06	-	0.25 1.11^{sh}	-0.74^{w} -1.20^{w}	0.25	-0.74^{w} -1.08^{w}	0.32	-

[a] All potentials were measured in THF, 0.1 M $[Bu_4N][PF_6]$ verses F_c/F_c^+, GCE with Ag/Ag^+ reference.

[br] broad peak

[sh] shoulder

[w] small peak

Figure 5.6 Cyclic voltammograms of a THF solution of CpRu(CO)$_2$SS-4-C$_6$H$_4$Me at a GCE, 0.001 M in complex and 0.1 M in [Bu$_4$N][PF$_6$], at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.77 V; b) 200 mV s^{-1} and initial potential is -1.78 V. Potentials are referenced to Fc/Fc$^+$ and the initial directions of the scans are positive as indicated by the direction of the arrows.

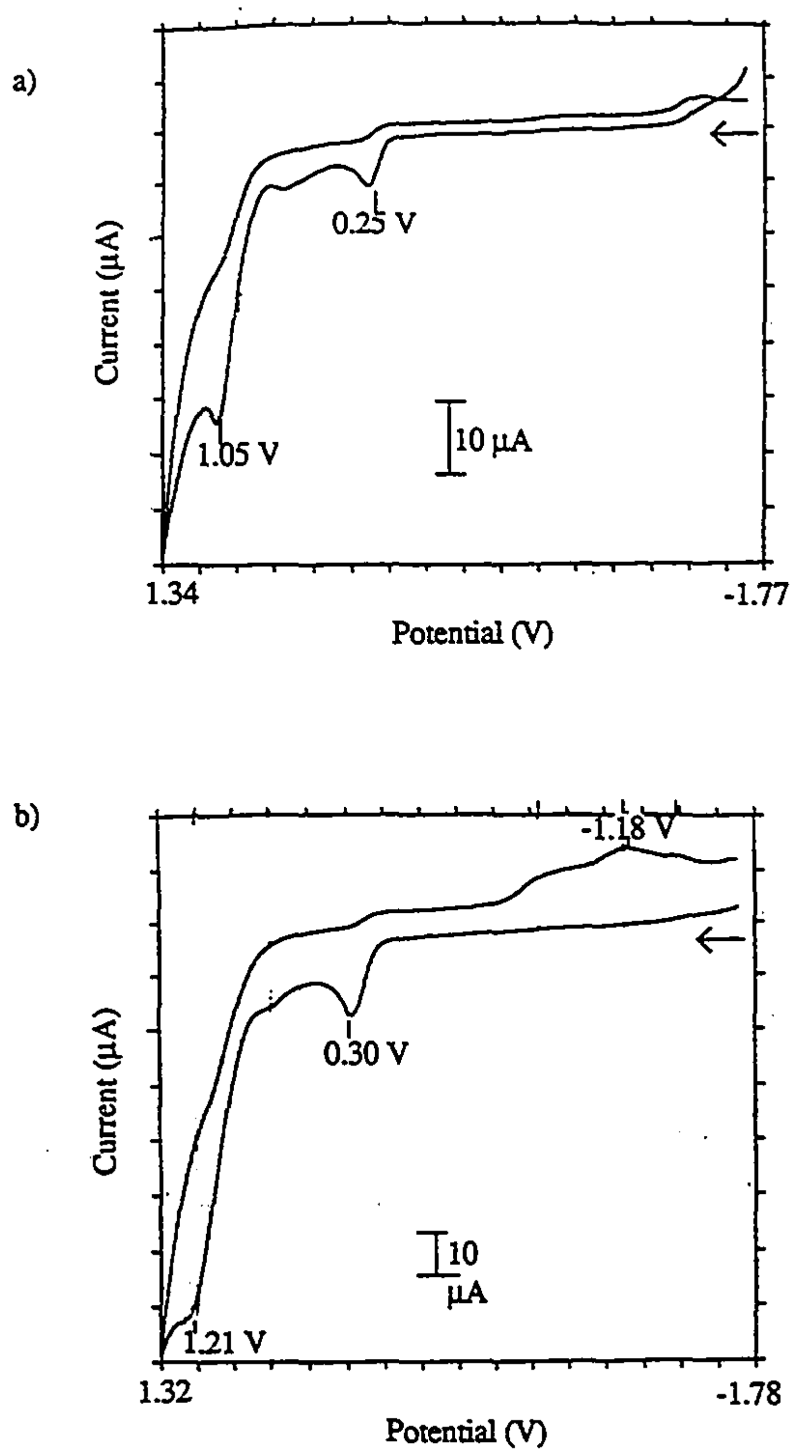
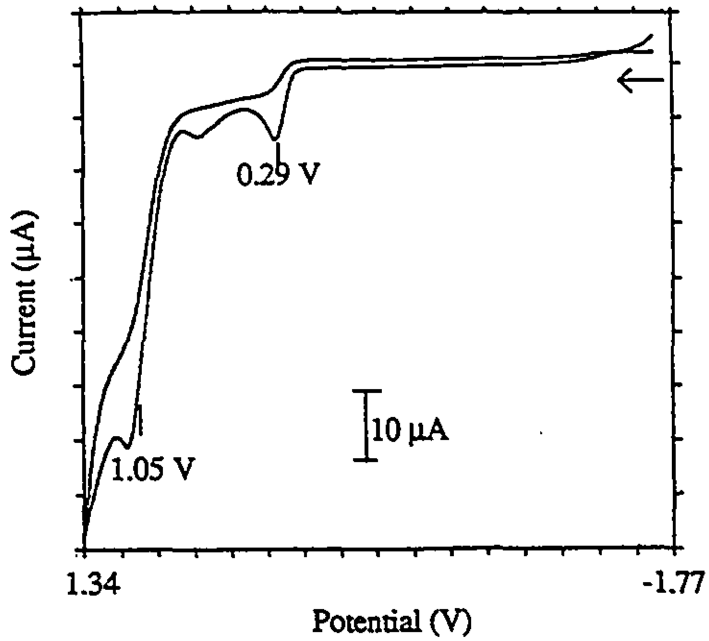


Figure 5.7 Cyclic voltammograms of a THF solution of $CpRu(CO)_2SSC_6H_5$ at a GCE, 0.001 M in complex and 0.1 M in $[Bu_4N][PF_6]$, at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.77 V; b) 200 mV s^{-1} and initial potential is -1.78 V. Potentials are referenced to Fc/Fc^+ and the initial directions of the scans are positive as indicated by the direction of the arrows.

a)



b)

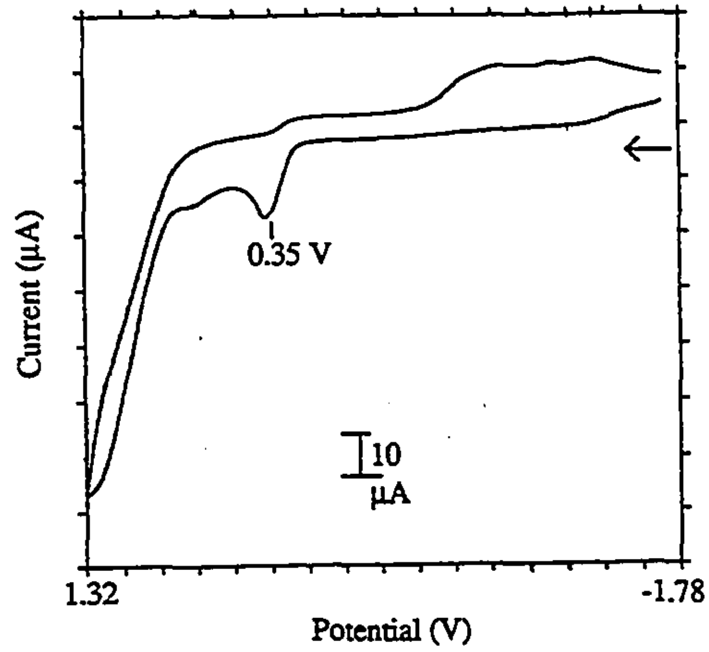
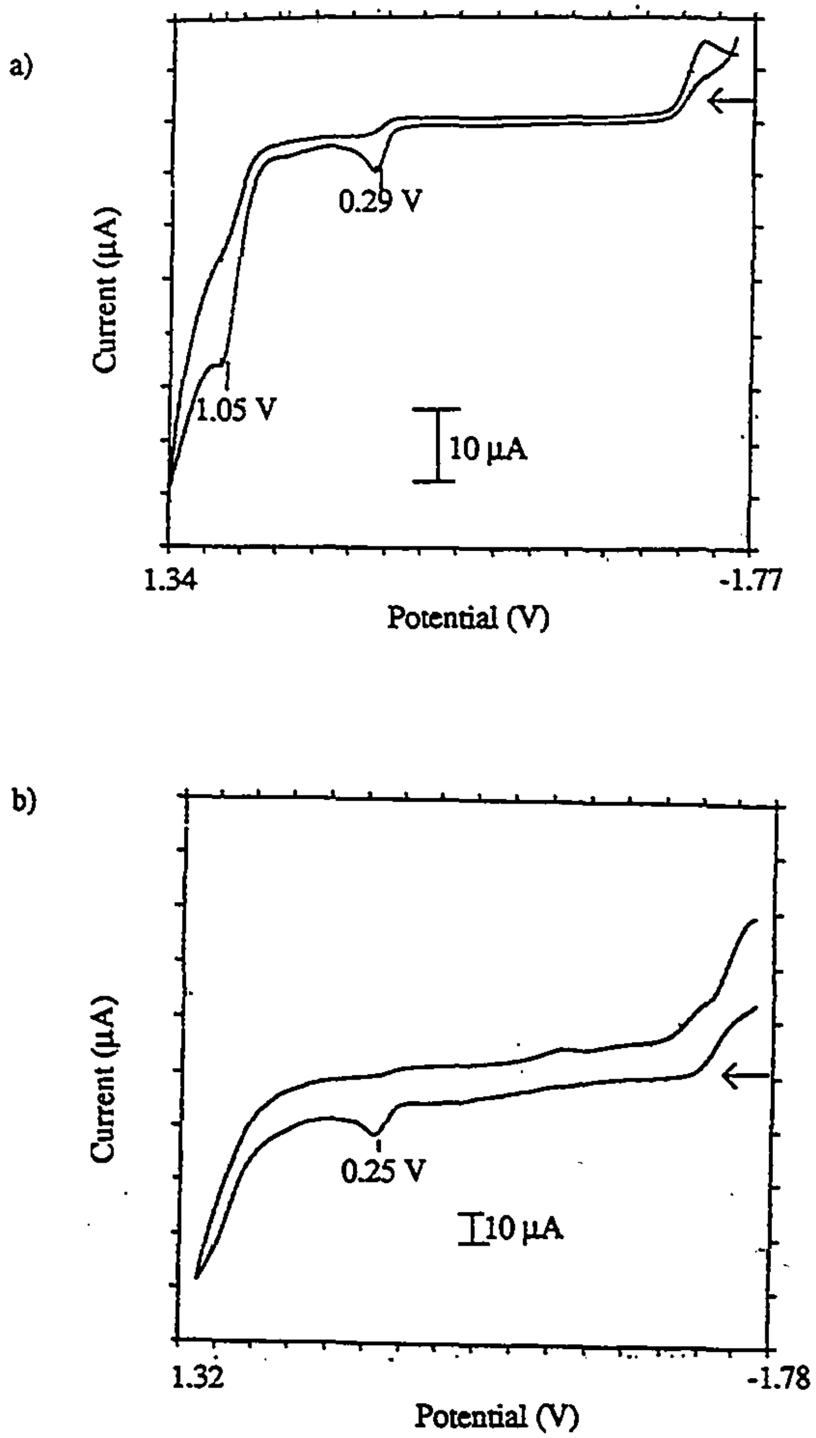


Figure 5.8 Cyclic voltammograms of a THF solution of $CpRu(CO)_2SSCH_2C_6H_5$ at a GCE, 0.001 M in complex and 0.1 M in $[Bu_4N][PF_6]$, at a sweep rate of a) 20 mV s^{-1} and initial potential is -1.77 V; b) 200 mV s^{-1} and initial potential is -1.78 V. Potentials are referenced to Fc/Fc^+ and the initial directions of the scans are positive as indicated by the direction of the arrows.



more complicated disulfane complexes, $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$), were performed. The CVs of all three $CpRu(CO)_2SSR$ complexes displayed three anodic waves corresponding to irreversible oxidations at similar potentials in the potential range -1.77 and 1.34 V (Table 5.2) and their CVs are shown in Figures 5.6-5.8, respectively. The first oxidation behaviour of $CpRu(CO)_2SSR$ seems to be relatively independent of the R group; therefore, CVs of $CpRu(CO)_2SS$-4-C_6H_4Me will be discussed as representative of the complexes $CpRu(CO)_2SSR$. Differences noted in the CVs for the complexes R = C_6H_5 and $CH_2C_6H_5$ will be discussed below.

The cyclic voltammogram of $CpRu(CO)_2SS$-4-C_6H_4Me at 20 mV s^{-1} displayed three irreversible oxidation peaks at 0.25, 0.67 and 1.05 V, respectively. The magnitude of the current of the first and third oxidation peaks (5.6, 26 μA, respectively) was much greater than the second oxidation peak (2.6 μA). None of the peaks were reversible at scan rates up to 1000 mV s^{-1} in the potential ranges 0.00 to 0.50 V, 0.40 to 0.85 V and 0.85 to 1.3 V. Similar CVs were obtained at sweep rates of 100 mV s^{-1} although the CV of $CpRu(CO)_2SSCH_2C_6H_5$ displayed only two irreversible oxidation peaks at 0.25 and 1.11 V, and did not have an oxidation peak that corresponded to the second oxidation , observed for the other two complexes. At higher scan rates the first oxidation peak was observed although the second and third peaks were not observed in all cases (Table 5.2). The absence of peaks at faster sweep rates seems to indicate that the second and third oxidation peaks may be due to oxidation of a new species formed from subsequent chemistry. Thus, at faster sweep rates there is insufficient time to give the new species which is subsequently oxidized.

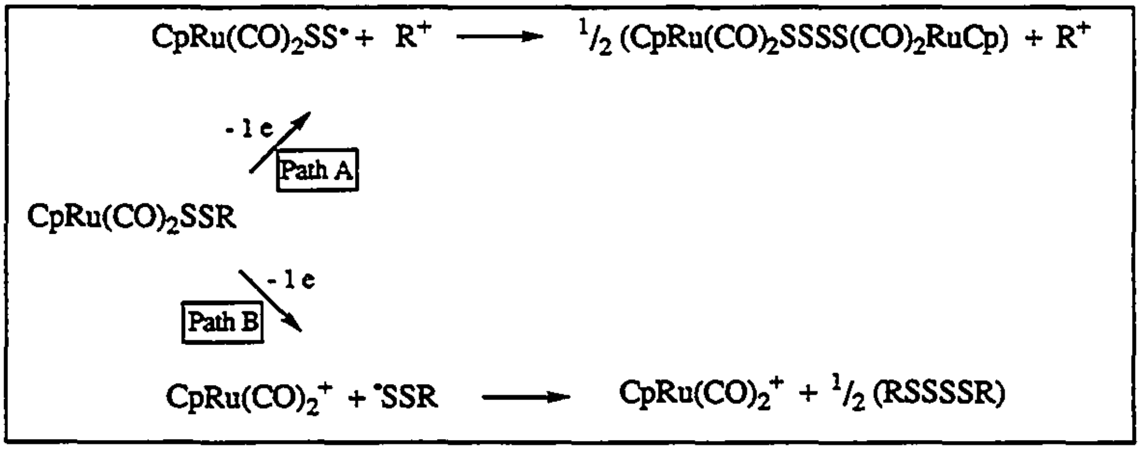
Comparison of the results from the CV experiments for $CpRu(CO)_2SSR$ and $CpRu(CO)_2SR$ reveal that the potentials of the first oxidation of both complexes are similar. This illustrates that changing the ligand from SR to SSR does not affect the removal of the first electron. This is significant because it implies that this electron may originate from the same atom or a similar orbital in both cases (disulfane and thiolate complexes). Since it has been decided that the first electron from $CpRu(CO)_2SR$ was removed from the ruthenium-coordinated sulfur atom, the first electron removed from $CpRu(CO)_2SSR$ may also be from the sulfur bonded to the ruthenium atom although this can not be confirmed at this stage. This would imply that the ruthenium-coordinated sulfur atom is more electron rich than the sulfur atom bonded to the R group. This result also suggests that this ruthenium-coordinated sulfur atom of the disulfane ligand may possess similar chemical behavior to that of the thiolate sulfur atom.

There are more oxidation peaks in the CVs of $CpRu(CO)_2SSR$ than of $CpRu(CO)_2SR$. These subsequent oxidations may be due to oxidations of products formed from follow-on chemistry. Thus, the species formed from the first oxidation ($[CpRu(CO)_2S^{\cdot}SR]^+$ or $[CpRu(CO)_2SS^{\cdot}R]^+$) may be more reactive than $[CpRu(CO)_2S^{\cdot}R]^+$.

These are the first reported electrochemical studies of disulfane ligands coordinated to a transition metal and can only be compared to the electrochemistry of the symmetrical disulfides.

Scheme 5.7

$$\mathrm{Me_3CSSCMe_3} \xrightarrow{-1\,e} \mathrm{Me_3CS\dot{S}} + \mathrm{Me_3C^+} \longrightarrow {}^1/_2\,(\mathrm{Me_3CSSSSCMe_3}) + \mathrm{Me_3C^+}$$



The disulfide $(CMe_3)_2S_2$ underwent a single one electron irreversible oxidation at 1.3 V (vs. SCE, MeCN (1.43 V vs. Fc/Fc^+) to give $Me_3CSS^{\cdot}$ and Me_3C^+, resulting from S-CMe_3 cleavage (Scheme 5.7).[34] $Me_3CSS^{\cdot}$ dimerizes to $(Me_3CSS)_2$ while Me_3C^+ is unstable and undergoes further chemistry. Thus, if our compounds behaved similarly, the reaction may go by either Path A or Path B in Scheme 5.7 to give $(CpRu(CO)_2SS)_2$ or $CpRu(CO)_2^+$, respectively. It is not known which path would be preferred but neither gives a stable cation (R^+ or $CpRu(CO)_2^+$). However, since the trisulfane dinuclear complex $(\mu\text{-}S_3)(CpRu(CO)_2)_2$ has been reported (Chapter 2), Path A leading to $(\mu\text{-}S_4)(CpRu(CO)_2)_2$ may be more likely.

In contrast to $(CMe_3)_2S_2$, the relatively sterically unhindered diphenyl and dimethyl disulfides ($(C_6H_5)_2S_2$ and Me_2S_2) undergo one electron irreversible oxidations at 1.34 (vs. Ag/Ag^+, MeCN, (0.94 vs. Fc/Fc^+)) and 1.11 V (vs. Ag/Ag^+, MeCN, (0.71 vs. Fc/Fc^+)), respectively.[35] The resulting radical decomposes and is trapped by the acetonitrile molecule as $[RSN{=}C^+Me]$ (Scheme 5.8) consistent with S-S bond cleavage. If this was the fate of our disulfane radical, then perhaps the disulfane bridged species and disulfide would be formed as shown in Scheme 5.8. Since our complexes, $CpRu(CO)_2SSR$, are not as sterically hindered as $(CMe_3)_2S_2$, our complexes may behave more in the fashion of R_2S_2, where R is sterically undemanding.

Scheme 5.8

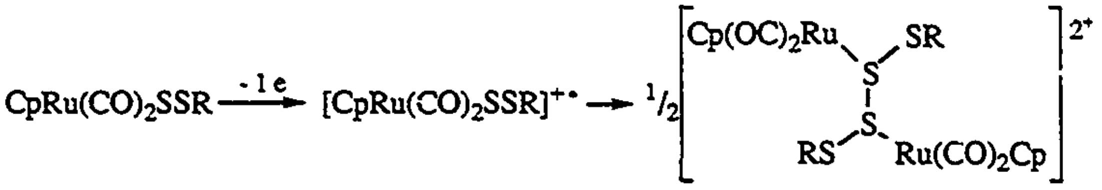
$$\mathrm{RSSR} \xrightarrow{-1e} [\mathrm{RS\dot{S}R}]^+ \xrightarrow{\mathrm{MeCN}} \mathrm{RS\text{-}N{=}C^+Me}$$

$$\boxed{\begin{array}{l} \mathrm{CpRu(CO)_2SSR} \xrightarrow{-1e} [\mathrm{CpRu(CO)_2SSR}]^{+\cdot} \longrightarrow \\ \qquad\qquad 1/2\,\{\,(\mathrm{CpRu(CO)_2SS(CO)_2RuCp})^{2+} + \mathrm{RSSR}\,\} \end{array}}$$

It is interesting to note that the potential of the oxidation for the organic disulfides, RSSR, (1.43 , 0.94 and 0.71 V for R = CMe_3, C_6H_5, and Me, respectively) is higher than observed for the $CpRu(CO)_2SSR$ complexes (0.25, 0.29 and 0.20 V for R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$, respectively). This implies that the organic compounds are more difficult to oxidize than the disulfane complexes which may be expected based on the high chemical reactivity of $CpRu(CO)_2SSR$. For example our MSSR complexes readily extrude sulfur whereas organic disulfides so not extrude sulfur.

There is an alternative fate for oxidized disulfane species. Perhaps coupling of the 1-sulfur atoms (coordinated to the ruthenium) occurs without loss of [SR] to give a dinuclear species similar to that described in Scheme 5.6 and shown in Scheme 5.9. Although the paths in Schemes, 5.7, 5.8 and 5.9 are all reasonable routes which our disulfane complexes might follow after one electron oxidation, it is not possible to determine which is route species of the type $[CpRu(CO)_2SSR]^{\cdot +}$ would prefer from our experiments.

Scheme 5.9



5.2.3 $CpRu(CO)_2SS(O)R$ and $CpRu(CO)_2SS(O)_2R$

It has been shown that changing from the thiolato to the disulfano ligand has little effect on the first oxidation potential of the complexes, indicating that the electron might be taken from a similar chemical environment. The effect on the first oxidation potential of switching to the 2-oxodisulfane ligand, -SS(O)R, can be examined. The CVs of

Table 5.3 Potentials obtained from cyclic voltammograms for $CpRu(CO)_2SS(O)_yR$ ($y = 1,2$; $R = 4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$). [a]

Compound	20 mV s^{-1}		100 mV s^{-1}		200 mV s^{-1}		500 mV s^{-1}	
	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}
$CpRu(CO)_2SS(O)\text{-}4\text{-}C_6H_4Me$	br	-	br	-1.20 [w] -1.47 [w]	br	-1.23 [w] -1.57 [w]	br	-1.37 [w] -1.56 [w]
$CpRu(CO)_2SS(O)C_6H_5$	br	-	br	-0.88 [w] -1.58 [w]	br	-1.05 [w] -1.43 [w]	br	-1.13 [w] -1.37 [w]
$CpRu(CO)_2SS(O)CH_2C_6H_5$	br	-1.56	br	-1.19 [w] -1.43 [w]	br	-1.16 [w] -1.47 [w]	br	-0.92 [w] -1.43 [w]
$CpRu(CO)_2SS(O)_2\text{-}4\text{-}C_6H_4Me$	br	-	br	-0.88 [w] -1.58 [w]	br	-0.89 [w] -1.17 [w] -1.45 [w]	br	-0.98 [w] -1.22 [w] -1.50 [w]
$CpRu(CO)_2SS(O)_2C_6H_5$	br	-	br	0.15 w -0.92 w	br	0.15 w -0.92 w	br	0.13 [w] -0.96 [w]

[a] All potentials were measured in THF, 0.1 M $[Bu_4N][PF_6]$ verses Fc/Fc$^+$, GCE with Ag/Ag$^+$ reference.

[br] No oxidation peak was detectable but the existence of a reduction peak necessitates that oxidation occured. Therefore, the peak must be extremely broad.

[w] small peak

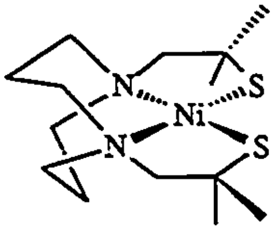
$CpRu(CO)_2SS(O)R$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) were obtained over a potential range -1.7 to 1.3 V at sweep rates of 20, 100, 200, 500 and 1000 mV s^{-1} and the results are displayed in Table 5.3 for sweep rates up to 500 mV s^{-1}. When R = 4-C_6H_4Me and C_6H_5, the samples used contained mixtures of $CpRu(CO)_2SS(O)R$ and $CpRu(CO)_2SS(O)_2R$ in the ratio of 9:1. Surprisingly, there were no oxidation peaks observed for any of the complexes regardless of the initial potential and the direction of the scan. This lack of reactivity of the 2-oxodisulfane compounds is surprising given their chemical reactivity. For example, these compounds undergo oxygen transfer reactions (Chapter 4). However, it was noted that after the oxidation scan, the reverse reduction scan for fast sweep rates contained peaks that were not present in reduction scans prior to the oxidation scan (Table 5.3). These cathodic peaks must arise from electron transfer to an oxidized species. These peaks grow in size at faster scan rates suggesting that at slower scan rates, there may be insufficient oxidized species present to react at a rate that can compete with diffusion away from the working electrode. The presence of the reduction peaks only after the oxidation scan implies that oxidation of $CpRu(CO)_2SS(O)R$ did occur. However, the oxidation must be a very slow process giving rise to broad peaks that cannot be discerned above background.

Thus, the change from the -SSR to the -SS(O)R ligand has a large effect on the first oxidation potential. It is extremely difficult to oxidize the latter. It is difficult to tell which sulfur is oxidized because the S(O) may influence to oxidation potential of the adjacent sulfur atom.

The large differences observed in the CVs resulting from changing from the 2-disulfane (well resolved peaks) to the 2-oxodisulfane ligand (broad peaks), prompted a careful investigation into the CVs of $CpRu(CO)_2SS(O)_2R$. The cyclic voltammograms of $CpRu(CO)_2SS(O)_2R$ (R = 4-C_6H_4Me, C_6H_5) in the potential range -1.7 and 1.3 V were electrochemically silent in the oxidation direction. This was not as surprising as was the case for $CpRu(CO)_2SS(O)R$ considering the chemical stability of the $MSS(O)_2R$

compounds (Chapter 4). However, on the reverse reduction scans, there were reduction peaks present that had not been present prior to the oxidation scan. This implies, as for the CpRu(CO)$_2$SS(O)R case, that oxidation does occur but it is very slow giving rise to a broad peak that cannot be observed.

These are the first reported electrochemical studies for complexes of the type MSS(O)R and MSS(O)$_2$R. No reports on the electrochemical oxidation of thiosulfinates (RSS(O)R') and thiosulfonates (RSS(O)$_2$R') were found in the literature. The work reported is only concerned with the electrochemical oxidation of organic disulfides in aqueous solvents to give thiosulfonates and thiosulfinates.[36,37] Thus, there are no organic or organometallic analogs with which we can compare our work. However, there are electrochemical studies of nickel complexes containing two chelating thiolate atoms.[9-11] The pertinent complexes are shown below.[10]



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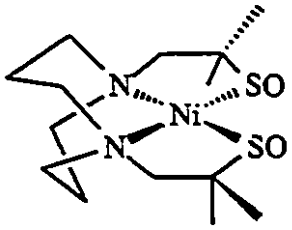

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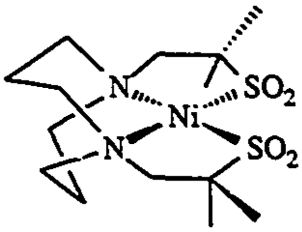

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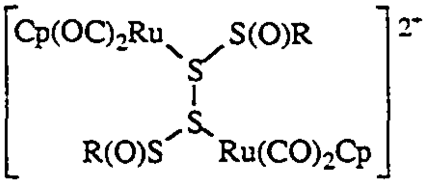
The CVs of these complexes each display two irreversible oxidation peaks. The first dithiolate complex (23) displayed two irreversible oxidation peaks at 0.26 V (vs. normal hydrogen electrode (NHE), MeCN, (-0.13 V vs. Fc/Fc$^+$)) and 1.07 V (vs. NHE, MeCN, (0.68 V vs. Fc/Fc$^+$)). The disulfoxide complex (24), gave a CV with two irreversible oxidation peaks at 0.29 V (vs. NHE, MeCN, (-0.11 V vs. Fc/Fc$^+$)) and 0.85 V (vs. NHE, MeCN, (0.45 V vs. Fc/Fc$^+$)). Thus 24 is slightly easier to oxidize than 23 in sharp contrast to our results. The disulfone complex (25), was the most difficult to oxidize with only one irreversible oxidation peak at 1.29 V (vs. NHE, MeCN, (0.89 V vs. Fc/Fc$^+$)).

In summary, ΔE_p^{ox} between the first oxidation peaks of 23 (with thiolate ligands) and 24 (with sulfoxide ligands) is very small (0.03 V) while the ΔE_p^{ox} between 23 and 25 is large (1.03 V). Thus, by analogy we might expect the E_p^{ox} of $CpRu(CO)_2SS(O)R$ at a similar potential as that of $CpRu(CO)_2SSR$, and E_p^{ox} of $CpRu(CO)_2SS(O)_2R$ to be at a much higher potential than that of $CpRu(CO)_2SSR$. Surprisingly, in our system the addition of even one oxygen atom to the sulfur atom bonded to R of $CpRu(CO)_2SSR$ causes a large change in the oxidation, making it impossible to determine E_p^{ox} for $CpRu(CO)_2SS(O)R$ (and for $CpRu(CO)_2SS(O)_2R$).

It is important to note that, as with the complexes $CpRu(PPh_3)SH$,[13] $[Ni(pdmt)(SR)]^-$ (pdmt = pyridine-2,6-dimethanthiolate; R = Et, C_6H_5)[6] and $[Cr(CO)_5SR]^-$ (R = Et, C_3H_7, CMe_3)[23], the oxidation of $CpRu(CO)_2SSR$ under our experimental conditions is expected to give a sulfur radical, and not a oxidized sulfur species $CpRu(CO)_2SS(O)R$. This statement is supported by examining the reduction peaks of the complexes $CpRu(CO)_2SS(O)_yR$ (y = 0-2) (Tables 5.1 - 5.3). If the species formed from the electrochemical oxidation contained an extra oxygen, the reduction peaks on the reverse scan in the CVs for $CpRu(CO)_2S_2(O)_yR$ (y = 0-2) should be the same. This is not the case. If the experiments were performed in water or if the sulfur-containing ligand was sterically restricted (as in the nickel complexes recently described),[10] then $CpRu(CO)_2SS(O)_yR$ species might be expected from electrochemical oxidation.

Although there is no precedent for the electrochemical oxidation of these types of complexes, one can speculate as to the fate of the oxidized species. Perhaps the $S-S(O)_y$ (y = 1, 2) bond remains intact after oxidation and gives species similar to **26** and **27.** Support for this lies in the fact that none of the reduction peaks on the reverse scans of the complexes occur at the same potential. The species produced after oxidation are evidently different for $CpRu(CO)_2SS(O)_yR$ (y = 1 or 2).



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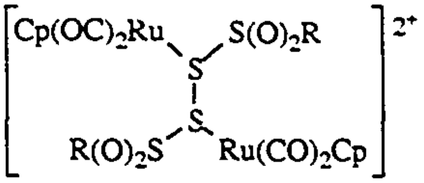

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5.2.5 Electrochemical Reduction of the $CpRu(CO)_2S_x(O)_yR$ Oxidation Product

In addition to the irreversible sulfur oxidation peaks observed in the CVs of $CpRu(CO)_2S_xO_yR$ ($x = 1,2$; $y = 0\text{-}2$; $R = 4\text{-}C_6H_4Me$, C_6H_5 $CH_2C_6H_5$), there were also reduction peaks observed in the CVs. For all complexes, starting from potentials of -0.20 V in the negative (reduction) direction, there were no reduction peaks down to -1.7 V. However, after oxidation to 1.3 V, there were subsequent reduction peaks that increased in current size at faster scan speeds. These peaks are listed in Tables 5.1 and 5.2. These peaks are attributed to species that were formed from follow-on chemistry of the oxidized species, and not due to the original $CpRu(CO)_2S_xO_yR$ species. However, based on the potentials of these reduction peaks alone, it is not possible to determine whether these redox processes are ligand or metal based.

5.3 Conclusions

This is the first electrochemical study of complexes of the type $MSS(O)_yR$ ($y = 0\text{-}2$). These experiments, where $CpRu(CO)_2S_x(O)_yR$ ($x = 1,2$; $y = 0\text{-}2$; $R = 4\text{-}C_6H_4Me$, C_6H_5 $CH_2C_6H_5$) was studied, provide insight into the relative electron density, or more specifically, the relative ease of removing the first electron from these complexes. These complexes undergo irreversible sulfur-based oxidation(s) in the potential range of -1.7 to 1.3 V (vs. Fc/Fc$^+$). The ease of removing the first electron seems to be only slightly dependent on the R group or the addition of a subsequent sulfur atom (from -SR to -SSR). In contrast, the addition of one or two oxygen atoms to the disulfane ligand substantially decreases the rate of oxidation.

The results of the CV studies suggest that the first electron from the disulfane complexes is removed from the sulfur atom nearest the metal atom; however, oxidation of the second atom cannot be ruled out based on these electrochemical experiments. A MSS(O)$_y$R (y = 0-2) system which undergoes relatively fast electron transfer giving well defined peaks is needed to determine the origin of the first electron.

These CV experiments do not include product analysis, and so the proposed mechanisms presented following oxidation are highly speculative. To determine the nature of the products, it is necessary to synthesize the proposed products and compare their electrochemical properties (peak potentials) to those of the products observed in the CVs. Thus, while the CV experiments have provided useful information about the relative ease of removing the first electron from CpRu(CO)$_2$SS(O)$_y$R (y = 0-2), specific information about the products or origin of the electron cannot be obtained.

The rapid and complex follow-up chemistry observed for the oxidized products in the CVs of CpRu(CO)$_2$S$_x$O$_y$R is reminiscent of the oxidation reactions described in Chapter 4.

5.4 References

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EXPERIMENTAL SECTION

General

All experiments were performed under a nitrogen atmosphere in schlenk tubes or three-necked flasks, unless otherwise stated. Standard inert-atmosphere techniques were used in all manipulations.[1] Hexanes and ether were distilled over sodium/benzophenone under N_2 before use. Tetrahydrofuran (THF) was distilled either over potassium or sodium/benzophenone under N_2 prior to use. Toluene was distilled over sodium under N_2. Carbon tetrachloride was distilled over phosphorous pentoxide under N_2 prior to use. Spectrograde acetone, spectrograde heptane, spectrograde acetonitrile and absolute ethanol were degassed by bubbling with nitrogen for 30 minutes prior use. Spectrograde acetonitrile was stored over 4 Å Molecular Sieves. Triethylamine was distilled prior to use. Deionized H_2O (18 MΩ·cm^{-1}) was obtained from a Milli-Q water system (Millopore; 3 bed ion-exchange/1 bed organic removal cartridge unit) connected to house-distilled H_2O.

1,8-bis(dimethylamino)naphlthalene (Proton Sponge®), methyllithium, C_6H_5SH, $C_6H_5CH_2SH$, $NaIO_4$ (10% w/w on silica), dioxone, S_8, $(4\text{-}C_6H_4Me)_2S_2$, $(C_6H_5)_2S_2$, $(C_6H_5CH_2)_2S_2$, $(4\text{-}MeC_6H_4)_2S_3$, $(C_6H_5)_2S_3$, $(C_6H_5CH_2)_2S_3$, galvinoxyl, 2,2-diphenyl-1-picrylhydrazyl hydrate and PPh_3 (all from Aldrich), $4\text{-}MeC_6H_4SH$ (Fairfield), $RuCl_3{\cdot}3H_2O$ and $Ru_3(CO)_{12}$ (Strem) were used as received. Tetrabutylammonium hexafluorophosphate ($[Bu_4N][PF_6]$) (Aldrich) was recrystallized once from ethanol. The compounds dimethyldioxirane (Me_2CO_2, DMDO);[2] $CpRu(PPh_3)(CO)SSR$ (R = $4\text{-}C_6H_4Me$, C_6H_5, $CHMe_2$, C_3H_7)[3]; $CpRu(PPh_3)(CO)SS(O)R$, where R = $4\text{-}C_6H_4Me$ and $CHMe_2$ [4]; phthSR (R = $4\text{-}C_6H_4Me$, $CHMe_2$; phth = phthalimide),[5] phthS(O)R (R = $4\text{-}C_6H_4Me$, $CH_2C_6H_5$, $CHMe_2$) were prepared according to published procedures.[6] The compounds phthSR (R = C_6H_5, $CH_2C_6H_5$), phthSS-4-C_6H_4Me were kindly prepared by Bernadette Soo Lum and Pierre Yves-Plouffe.

Solvents and other liquids were transferred by syringe or cannula. Filtrations were performed through Celite 1 under N_2 and the filtrates were reduced to dryness under vacuum (oil pump). The packing and elution of chromatography columns was performed under nitrogen with solvents that were deoxygenated. Activated alumina (80-120 mesh) (Anachemia) was deactivated to Grade 3 according to the literature procedure.[7] The bands from the chromatography columns were collected in round bottom flasks equipped with a N_2 inlet with N_2 gas flowing through the flask at a high rate. The bands were reduced to dryness under vacuum. Recrystallizations were done under nitrogen and the solutions were cooled at -16°C overnight or longer. Reactions involving H_2S were done using special precautions as described elsewhere.[3]

All IR spectra were recorded on a Bomem Michelson Model 100 Fourier transform infrared (FT-IR) spectrophotometer at 4 cm^{-1} resolution (deutrium triglyane sulfate (DTGS) detector). Solution spectra were recorded by using 0.1 mm path length NaCl cells. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a Varian XL-200 or a Varian Gemini spectrometer and all chemical shifts are in δ (ppm) units (±0.002 ppm) relative to tetramethylsilane (TMS) at 0 ppm. Gas-liquid chromatography (GLC) was performed on a Varian Model 3700 gas chromatograph. Low resolution (R = 700) mass spectra and fast atom bombardment (FAB) mass spectra were obtained on a KRATOS MS25RFA. The energy of electron ionization (EI) was 70 eV and chemical ionization (CI) spectra were measured using ammonia. Fast atom bombardment (FAB) mass spectra used nitrobenzyl alcohol (NBA) as the matrix and Xenon as the ionizing gas (7 kV). High resolution EI (R = 4000) mass spectra were measured under similar source conditions using either a scanning (SC) or peak matching (PM) technique. Elemental analyses were carried out by Canadian Microanalytical Service Ltd. (Delta, B.C.). Melting points were determined in grease-sealed capillary tubes under nitrogen using a Thomas Hoover capillary melting point apparatus and are uncorrected.

X-ray Structure Determination

X-ray structures were determined on a Rigaku AFC6S diffractometer using CuKα or MoKα graphite monochromated radiation. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The crystals chosen for x-ray structure determination were examined on a polarizing microscope to confirm that they were single and of appropriate size. The crystals were mounted in air on a glass fiber by placing the crystal on a glass microscope slide and bringing the glass fiber bearing a drop of epoxy cement on its tip up to the crystal until it just touched the crystal. After the epoxy cement had dried, the glass fiber was placed in a mound of sealing wax on top of a 1/8" brass pin. This pin was placed on an archless goniometer head The alignment was done by observing the center of the crystal and making sure that it remained centered as the crystal was automatically rotated in increments of 90°C. The program Search Routine provides starting cell parameters which were then converted to standard Delauney settings. Final cell parameters were obtained from a least squared refinement using the setting angles of 25 carefully centered reflections in the range of $33 < 2\theta < 35$ and $55 < 2\theta < 60$, using MoKα and CuKα radiation, respectively. Intensities were measured using the ω-2θ scan technique to a maximum 2θ value of 50° and 120°, using MoKα and CuKα radiation, respectively. The scan rate was chosen according to the average peak width of the 3 standards. Intensities of 3 representative reflections were measured every 150 reflections. Corrections to the data were made for Lorentz and polarization effects and decay. An empirical absorption correction was made using the program DIFABS.

The ruthenium atoms were found using the Patterson heavy atom method, and refinement and electron density difference syntheses revealed all of the other non-hydrogen atoms. The temperature factors of all non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated (C-H = 1.05 Å). Corrections were made for secondary extinction. Refinement was done on $|F_o|$ by full-matrix least squares, the weights used were based on counting statistics.

Sulfur Insertion and Exchange Reactions of $CpRu(CO)_2S_x(O)_yR$

All sulfur insertion and ligand exchange reactions were performed under similar conditions. In a typical experiment, the NMR tube was charged with 0.019 mmol of $CpRu(CO)_2S_x(O)_yR$ ($x = 1, 2$, $y = 0\text{-}2$; R = 4-C_6H_4Me, C_6H_5, and $CH_2C_6H_5$) and the desired amount of one or more of the reagents. The NMR tube was evacuated and refilled with N_2 twice, followed by the addition of 0.7 mL of C_6D_6 and some TMS. The NMR tube was sealed under vacuum, or under N_2 with a Teflon stopper or a grease-sealed stopper when CO or SO_2 gas were used. The experiments were performed at either 18 ± 2°C, 45 ± 2°C, or 67 ± 3°C. The latter two temperatures were obtained by placing the NMR tubes in a constant temperature oil bath. The reactions were monitored daily by ^1H NMR for at least 4 days, or until large amounts of precipitate appeared in the NMR tube. The NMR spectra were obtained using the absolute intensity mode and a minimum 15 second delay between pulses. The product distribution was measured by integration of the Cp peaks and alkyl peaks (if present). A table of the NMR data showing the Cp, R, and aromatic groups of all of the compounds observed in these experiments is at the end of the experimental section (Table E.1). Decomposition was monitored by integration of all the Cp peaks in the NMR spectrum compared to the integration of the TMS peak.

Cyclic Voltammetry

Cyclic voltammetry experiments were performed on a BAS 100B/W Electrochemical Workstation (Bioanalytical Systems Inc. (BAS), West Lafayette, IN). A glassy carbon electrode (GCE) with an area of 2.83 mm^2 (BAS) was used as the working electrode. The surface of the GCE was cleaned each day by polishing with microcloth pads and 0.3 μm and 0.05 μm alumina slurries (Buehler). Any residual polishing alumina was removed from the surface by sonication for 30 s in deionized water followed by rinsing with deionized water and acetone. Between voltammograms, the surface was repolished with 0.05 μM alumina, sonicated in deionized water followed by rinsing with deionized H_2O and acetone to provide a clean and reproducible surface. The quasi-reference electrode was a non-aqueous Ag/Ag^+ electrode (BAS) containing an internal solution of 1 mM $AgNO_3$ (BAS) and 0.1 M $[Bu_4N][PF_6]$ in acetonitrile ($AgNO_3$ is insoluble in THF). The solution in the reference electrode was separated from the bulk solution by a porous vycor tip. The auxiliary electrode was a platinum wire (Aldrich, 99.99%).

The electrochemical measurements were carried out in THF with $[Bu_4N][PF_6]$ as the supporting electrolyte (0.1M solution). The electrochemical cell consisted of a 10 or 25 mL Pyrex flask fitted with a Teflon disk with machined holes through which the electrodes and an argon feed could be inserted. A stream of argon was passed through the solution for 5 minutes prior to each experiment. The needle which was admitting the argon was then raised above the level of the solution to blanket the cell compartment during the electrochemical measurements. The cyclic voltammetry experiments were run with no stirring. The solution was stirred between successive cyclic voltammetric experiments to replenish the surface. The silver quasi-reference electrode was calibrated each day with the electrochemically reversible ferrocene/ferrocinium (Fc/Fc^+) couple run under the same experimental conditions as the ruthenium complexes. All potentials (E) are reported versus the Fc/Fc^+ couple. The error on the potentials is ± 0.01 V. Cyclic voltammograms were recorded at varying scan rates (between 0.020 V s^{-1} to 1 V s^{-1}). All experiments were run with *iR* compensation to compensate for the high resistivity of THF. The voltammograms of the ruthenium compounds were stored and a background voltammogram was run under identical conditions in a solution containing only the supporting electrolyte in THF. The resulting background-corrected voltammogram was used to obtain the potential (E) values for the ruthenium compounds. The cyclic voltammograms with the background (THF, $[Bu_4N][PF_6]$) are shown in Chapter 5.

Syntheses of Complexes

η^5-Cyclopentadienyl(dicarbonyl)thiolatoruthenium(II), $CpRu(CO)_2SH$ (3) and the organoruthenium sulfane (μ-S_3)($CpRu(CO)_2)_2$ (4)

Sodium metal (0.30 g, 1.3 mmole) was dissolved in degassed absolute ethanol (40 mL) and stirred for 10 minutes. A vigorous stream of H_2S was bubbled through the solution for 30 minutes. The solution was then purged with N_2 for 20 minutes and then evaporated to dryness under vacuum. THF (15 mL) and $CpRu(CO)_2Cl$ (0.500 g, 1.94 mmol) were added to give a bright yellow coloured slurry which became beige after 20 minutes. The slurry was stirred for 3 days and then reduced to dryness. The residue was extracted with toluene (2 x 20 mL) and the extracts were filtered, and the combined dark brown coloured filtrates were reduced to dryness under vacuum. The resulting dark brown oil was dissolved in benzene (4 mL) and placed on a chromatography column (1.5 cm x 20 cm). Elution with benzene gave a yellow band which was collected and reduced to dryness. Recrystallization from THF/hexanes gave analytically pure $CpRu(CO)_2SH$ as a bright yellow solid (0.426 g, 85%). mp. = decomposition starts at 56°C with formation of H_2S, melting at 63°C

IR(cyclohexane): ν(CO) 1995 (br, s), 2043 (sh, s) cm^{-1}

^1H NMR (C_6D_6): -2.93 (s, 1H, S*H*), 4.37 (s, 5H, Cp)

High resolution mass spectrum (EI-SC), $M^{+\cdot}$ measured: 255.9130 Da; $C_7H_6O_2S^{102}Ru$ requires 255.9126 Da.

Elution of the column with 1:1 THF/benzene gave a red band which was reduced to dryness under vacuum and recrystallized from ether/hexanes overnight to give dark burgundy microcrystals. The NMR spectrum of these crystals dissolved in C_6D_6 showed 2 Cp peaks in a ratio of 49:1 at 4.82 and 4.62 due to (μ-S_3)($CpRu(CO)_2)_2$ and an unknown complex, respectively (0.040 g, 8%). mp.= 120-122°C

IR(toluene): ν(CO) 1969 (br. s), 2024 (d, s) cm^{-1}

^{1}H NMR (C_6D_6) (μ-S_3)($CpRu(CO)_2)_2$: 4.82 (s, Cp)

FAB-MS, (m/z, rel. int., assignment) 541, 4.6% ,M$^+$: 509, 2.9%, M$^+$ - S; 477, .3, M$^+$ - 2S

Preparation of $CpRu(CO)_2SR$

η^5-Cyclopentadienyl(dicarbonyl)-4-methylbenzenethiolatoruthenium(II), $CpRu(CO)_2S$-4-C_6H_4Me (11a)

A flask equipped with a reflux condenser was charged with THF (65 mL) and cooled to -78°C (acetone/dry ice bath). Methyllithium (2.36 mL, 1.4 M in ether, 3.30 mmol) was added via syringe followed by 4-MeC_6H_4SH (0.410 g, 3.30 mmol). The cooling bath was removed and the solution was allowed to warm to room temperature (warm water bath) over 15 minutes. $CpRu(CO)_2Cl$ (0.500 g, 1.65 mmol) was added and the mixture was quickly brought to reflux (hot water bath) which was maintained for 15 minutes. The volume of the bright orange solution was immediately reduced under vacuum to 5 mL. Celite (10 mL) was then added, the mixture was reduced to dryness under vacuum, and the residue extracted with toluene (6 x 20 mL). The extracts were filtered through Alumina (2 cm) and the combined filtrates were reduced to dryness. Recrystallization of the residue from THF/hexanes gave large orange needles (0.485 g, 85 %). mp. = 78°C

IR(cyclohexane): ν(CO) 1990 (br, s), 2041 (sh, s) cm^{-1}

^{1}H NMR (C_6D_6): 2.11 (s, 3H, 4-C_6H_4-CH_3), 4.43 (s, 5H, Cp), 6.90 (d, 2H, $J_{(H-H)}$ = 8 Hz, *meta* H of 4-C_6H_4-CH_3), 7.69 (d, 2H, $J_{(H-H)}$ = 8 Hz, *ortho* H of 4-C_6H_4-CH_3)

High resolution mass spectrum (EI-PM), M$^{+\cdot}$ measured: 345.9589 Da; $C_{14}H_{12}O_2S^{102}Ru$ requires 345.9595 Da.

Anal. Calcd. for $C_{14}H_{12}O_2RuS_1$: 48.69%C, 3.50%H

Found: 48.61%C, 3.45%H

η^5-Cyclopentadienyl(dicarbonyl)phenylthiolatoruthenium(II), $CpRu(CO)_2S\text{-}C_6H_5$ (11b)

A flask equipped with a reflux condenser was charged with THF (40 mL) and cooled to -78°C (acetone/dry ice bath). Methyllithium (0.943 mL, 1.4 M in ether, 1.32 mmol) was added followed by C_6H_5SH (1.36 mL, 1.32 mmol), both via syringe. The cooling bath was removed and the solution was warmed to room temperature (warm water bath) over a period of 15 minutes. $CpRu(CO)_2Cl$ (0.200 g, 0.778 mmol) was added and the yellow coloured solution was quickly brought to reflux by means of a hot water bath for 15 minutes. The resulting bright orange solution was immediately concentrated to 5 mL under vacuum. Celite (10 mL) was added and the mixture was reduced to dryness and the residue extracted with toluene (3 x 20 mL). The extracts were filtered through Alumina (2 cm) and the combined filtrates were evaporated to dryness. Recrystallization from THF/hexanes gave bright yellow crystals of $CpRu(CO)_2C_6H_5$ (0.090 g, 36%). mp. = 98-101°C (literature: yield 31%, mp. = 100-101°C[7])

IR(toluene): ν(CO) 1987 (br, s), 2041 (sh, s) cm^{-1}.

IR(hexane): ν(CO) 1993 (s), 2043 (s) cm^{-1} (literature IR(hexane): ν(CO) 1992 (m), 2041 (m) cm^{-1}).[7]

^1H NMR (C_6D_6): 4.41 (s, 5H, Cp), 7.10 (m, 3H, *meta, para H* 's of C_6H_5), 7.73 (m, 2H, *ortho H*'s of C_6H_5)

^1H NMR ($CDCl_3$): 5.40 (s, 5H, Cp); 7.08 (m, 3H, *meta, para H* 's of C_6H_5); 7.47 (m, 2H, *ortho H*'s of C_6H_5) (literature: ^1H NMR ($CDCl_3$): 5.33 (s, 5H, Cp); 7.35 (m, 5H, C_6H_5)).[7]

High resolution mass spectrum (EI-PM), $M^{+\cdot}$ measured: 331.9447 Da; $C_{13}H_{10}O_2S^{102}Ru$ requires 331.9439 Da.

η^5-Cyclopentadienyl(dicarbonyl)benzylthiolatoruthenium(II), $CpRu(CO)_2S$-$CH_2C_6H_5$ (11c)

A flask was charged with THF (40 mL) and cooled to -78°C (acetone/dry ice bath). Methyllithium (0.943 mL, 1.4 M in ether, 1.32 mmol) was added followed by $C_6H_5CH_2SH$ (155 mL, 1.32 mmol), both via syringe. The cooling bath was removed and the mixture was warmed to room temperature (warm water bath) over the period of 10 minutes. $CpRu(CO)_2Cl$ (0.200 g, 0.777 mmol) was added and solution was quickly brought to reflux (hot water bath) which was maintained 15 minutes. The bright yellow solution was immediately reduced to 5 mL under vacuum and Celite (10 mL) was added. The mixture was reduced to dryness and the residue was extracted with toluene (2 x 20 mL) and THF (20 mL). The extracts were filtered through Alumina (2 cm) and the combined filtrates were reduced to dryness under vacuum. Washing with hexanes gave analytically pure orange oil (0.206 g, 90%). (literature yield 3% , mp. = 198-200°C[7])

IR(cyclohexane): ν(CO) 1985 (br, s), 2039 (s) cm^{-1}

IR(hexane): ν(CO) 1987 (br, s), 2041 (sh, s) cm^{-1} (literature IR(hexane): ν(CO) 1986 (s), 2038 (s) cm^{-1}).[7]

^1H NMR (C_6D_6): 3.61 (s, 2H, CH_2); 4.34 (s, 5H, Cp), 7.09 (m, 3H, *meta, para H* 's of C_6H_5), 7.40 (d of d, 2H, $J_{(H-H)}$ = 8 Hz, *ortho H*'s of C_6H_5)

High resolution mass spectrum (EI-PM), $M^{+\cdot}$ measured: 345.9598 Da; $C_{14}H_{12}O_2S^{102}Ru$ requires 345.9595 Da.

Preparation of $CpRu(CO)_2SSR$

η^5-Cyclopentadienyl(dicarbonyl)-4-methylbenzenedisulfanoruthenium(II), $CpRu(CO)_2SS$-4-C_6H_4Me (12a)

To a solution of $CpRu(CO)_2SH$ (0.312 g, 1.14 mmol) in THF (15 mL) was added phthS-4-C_6H_4Me (0.307 g, 1.14 mmol). The clear orange solution was stirred for 2 hours at room temperature, concentrated to 5 mL under vacuum, and placed on a chromatography column (2 cm x 30 cm). Elution with hexanes followed by benzene/hexanes (1:5) gave a yellow band which was collected and reduced to dryness to give a yellow/orange oil (crude yield = 75%). A light brown band remained on top of the column. Recrystallization from hexanes gave analytically pure $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ as a yellow crystalline solid (0.160 g, 35 %). mp. = 68°C

IR(cyclohexane): ν(CO) 1993 (br, s), 2043 (s) cm^{-1}

^1H NMR (C_6D_6): 2.06 (s, 3H, 4-C_6H_4-CH_3), 4.40 (s, 5H, Cp), 6.95 (d, 2H, $J_{(H\text{-}H)}$ = 8 Hz, *meta* H 's of 4-C_6H_4-CH_3), 7.76 (d, 2H, $J_{(H\text{-}H)}$ = 8 Hz, *ortho* H 's of 4-C_6H_4-CH_3)

High resolution mass spectrum (EI-PM), $M^{+\bullet}$ measured: 377.9314 Da; $C_{14}H_{12}O_2S_2{}^{102}Ru$ requires 377.9316 Da.

Anal. Calcd. for $C_{14}H_{12}O_2RuS_2$: 44.55%C, 3.20%H, 16.99%S

Found: 44.32%C, 3.19%H, 17.14%S

η^5-Cyclopentadienyl(dicarbonyl)phenyldisulfanoruthenium(II), $CpRu(CO)_2SSC_6H_5$ (12b)

To a solution of $CpRu(CO)_2SH$ (0.214 g, 0.813 mmol) in THF (10 mL) was added $phthSC_6H_5$ (0.212 g, 0.813 mmol). The solution was stirred for 40 minutes and then concentrated to 2 mL under vacuum. This was placed on a chromatography column (2 x 40 cm) and elution with hexanes followed by THF/hexanes (1:5) gave a yellow band which was concentrated to 15 mL and cooled to -16°C overnight. Bright shinny yellow flakes were collected (0.150 g, 50%). mp. = decomposition between 52 - 56°C, melting between 74 - 75°C

IR(cyclohexane): ν(CO) 1996 (br, s), 2043 (sh, s) cm^{-1};

^1H NMR (C_6D_6): 4.39 (s, 5H, Cp), 7.00 (t, 1H, *para* H of C_6H_5), 7.13 (m, 2H, *meta* H of C_6H_5); 7.82 (d, $J_{(H\text{-}H)}$ = 8 Hz, 2H, *ortho* H of C_6H_5)

High resolution mass spectrum (EI-PM), $M^{+\cdot}$ measured: 363.9169 Da: $C_{13}H_{10}O_2S^{102}Ru$ requires 363.9159 Da

Anal. Calcd. for $C_{13}H_{10}O_2RuS_2$: 42.97%C, 2.77%H, 17.64%S

Found: 42.88%C, 2.76%H, 17.88%S

η^5-Cyclopentadienyl(dicarbonyl)benzyldisulfanoruthenium(II),

$CpRu(CO)_2SSCH_2C_6H_5$ (12c)

A solution of $phthSCH_2C_6H_5$ (0.369 g, 1.37 mmol) in THF (15 mL) was added dropwise to a solution of $CpRu(CO)_2SH$ (0.336 g, 1.31 mmol) in THF (20 mL) over a period of 20 minutes. The resulting orange coloured solution was immediately reduced to 4 mL and placed on a chromatography column. Elution with hexanes followed by THF/hexanes gave a yellow band which was reduced in volume and cooled to -16°C. Removal of the mother liquors via a syringe gave an orange solid (0.160 g, 32 %) which was recrystallized from THF/hexanes to give large orange needles as the analytical sample (0.050 g, 10 %). mp. = 47°C

IR(cyclohexane): ν(CO) 1994 (d, s), 2038 (sh, s) cm^{-1}

^1H NMR (C_6D_6): 3.98 (s, 2H, CH_2); 4.43 (s, 5H, Cp), 7.07 (m, 3H, *meta, para H* 's of C_6H_5), 7.38 (d, $J_{(H-H)}$ = 8 Hz, 2H, *ortho H*'s of C_6H_5)

High resolution mass spectrum (EI-PM), $M^{+\cdot}$ measured: 377.9304 Da; $C_{14}H_{12}O_2S_2{}^{102}Ru$ requires 377.9317 Da.

Anal. Calcd. for $C_{14}H_{12}O_2RuS_2$: 44.55%C, 3.20%H

Found: 44.45%C, 3.27%H

η^5-Cyclopentadienyl(dicarbonyl)-2-propyldisulfanoatoruthenium(II),

$CpRu(CO)_2SSCHMe_2$ (12d)

To a solution of $CpRu(CO)_2SH$ (0.504 g, 1.97 mmol) in THF (30 mL) was added $phthSCHMe_2$ (0.413 g, 1.97 mmol). The solution was stirred for 7 hours and the resulting orange coloured solution was reduced to dryness under vacuum to give a red oil. This was dissolved in benzene (10 mL) and placed on a chromatography column (3 x 30 cm). Elution with hexanes (300 mL) was followed by elution with benzene/hexanes (1:1). This latter fraction was reduced to dryness, and a small amount was dissolved in C_6D_6. The NMR spectrum of this sample showed the presence of 1 set of peaks which were assigned to $CpRu(CO)_2SSCHMe_2$. Rerystallization of the oil in hexanes at -78°C resulted in an orange oil. The NMR spectrum in C_6D_6 of the oil which had been at -16°C for 1 week indicated mutiple Cp peaks. The most intense Cp peak was due to (μ-S_3)($CpRu(CO)_2)_2$ and peaks due to $(Me_2CH)_2S_2$ were also present. All attempts to obtain $CpRu(CO)_2SSCHMe_2$ as crystalline resulted in its decomposition.

IR(cyclohexane): ν(CO) 1987 (br, sh, s), 2034 (sh, s) cm^{-1}

^1H NMR (C_6D_6): 1.43 (d, $J_{(H\text{-}H)}$ = 7 Hz, 3H, CHMe_2), 3.00 (m, 1H, CHMe$_2$, 4.48 (s, 5H, Cp)

η^5-Cyclopentadienyl(dicarbonyl)-1-propyldisulfanoruthenium(II), $CpRu(CO)_2SSC_3H_7$ (12e)

To a solution of $CpRu(CO)_2SH$ (0.400g, 1.79 mmol) in THF (30 mL) was added dropwise via cannula a solution of phthSC_3H_7 (0.396 g, 1.79 mmol) in THF (30 mL). The solution immediately changed colour from brown to orange. The solution was stirred for 15 minutes and reduced to dryness under vacuum. The NMR spectrum of a sample of the solid dissolved in C_6D_6 showed 1 peak due to the Cp protons in addition to peaks due to the alkyl protons. The residue was extracted with toluene (5 x 10 mL) and the combined extracts were filtered and reduced to dryness under vacuum. The resulting oil was dissolved in THF (3 mL) and placed on a chromatography column (2 x 35 cm). Elution with hexanes followed by THF/hexanes (1:3) gave a yellow band which was reduced to dryness (98% yield). Recrystallization at -78°C gave a yellow powder. Upon removal of the mother liquors followed by warming to room temperature, the solid became an oil. The

NMR spectrum of the oil that was stored at -16°C for 3 days displayed peaks due to $CpRu(CO)_2SSC_3H_7$ in addition to many unknown peaks. The largest Cp peak was due to $(\mu\text{-}S_3)(CpRu(CO)_2)_2$.

^1H NMR (C_6D_6): 0.97 (t, $J_{(H\text{-}H)}$ = 7 Hz, 3H, $CH_2CH_2CH_3$); 1.86 (sextet, $J_{(H\text{-}H)}$ = 7 Hz, 2H, $CH_2CH_2CH_3$), 2.70 (t, $J_{(H\text{-}H)}$ = 7 Hz, 2H, $CH_2CH_2CH_3$), 4.50 (s, 5H,Cp)

Preparation of a $CpRu(CO)_2SSSR$

η^5-Cyclopentadienyl(dicarbonyl)-4-methylbenzenetrisulfanoruthenium(II), $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ (13a)

A solution of phthSS-4-C_6H_4Me (0.238 g, 0.788 mmol) in THF (10 mL) at -78°C (acetone/dry ice bath) was added dropwise via cannula to a solution of $CpRu(CO)_2SH$ (0.201 g, 0.788 mmol) in THF (20 mL) at -78°C over a period of 5 minutes. After stirring for 25 minutes at -78°C, a small aliquot of solution was removed from the mixture, reduced to dryness under vacuum, and the residue dissolved in C_6D_6. The NMR spectrum showed one set of peaks, assigned to $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$. The reaction mixture was reduced to dryness and extracted with toluene (2 x 20 mL). The combined extracts were filtered through Alumina (1 cm) and reduced to dryness under vacuum to give a red oil. The NMR spectrum of a sample of this oil dissolved in C_6D_6 showed 2 sets of peaks in the ratio of 9:1, due to $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ respectively. The oil was dissolved in THF (3 mL) and chromatographed on a column (1.5 cm x 20 cm). Elution with hexanes (150 mL) followed by THF/hexanes (1:4) gave a yellow band which was reduced to dryness. The NMR spectrum of the resulting orange oil in C_6D_6 showed the presence of $CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$ and $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$, in a ratio of 9:1 respectively. The oil decomposed at -16°C over prolonged periods of time to give a complex mixture of decomposition products including $CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$ and $(4\text{-}MeC_6H_4)_2S_2$, as identified by NMR.

IR(cyclohexane): ν(CO) 1993 (s), 2043 (s) cm^{-1}

^{1}H NMR (C_6D_6): 1.99 (s, 3H, C*H*$_3$), 4.53 (s, 5H, Cp), 6.88 (d, $J_{(H-H)}$ = 8.0 Hz, 2H, *meta* H of C_6H_4Me), 7.72 (d, $J_{(H-H)}$ = 6.2 Hz), 2H, *ortho* H of C_6H_4Me)

mass spectrum (CI), direct inlet, 200°C, (m/z, rel. int., assignment): 411, 1.4%, MH$^+$; 379, 12.0%, MH$^+$ - S; 347, 33.1%, MH$^+$ - 2S; 290 29.1%, MH$^+$ - 2CO - Cp; 246, 47.0%, MNH_3^+ - 2CO - SC_6H_4Me; 124, 100%, SC_6H_4Me

Preparation of $CpRu(CO)_2SS(O)_2R$

η^5-Cyclopentadienyl(dicarbonyl)-4-methylbenzene-2-dioxodisulfanoruthenium(II), $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me (19a)

To a solution of $CpRu(CO)_2SH$ (0.140 g, 0.549 mmol) in THF (15 ml) at 0°C (ice bath) was added via a cannula a solution of $ClS(O)_2$-4-C_6H_4Me (0.105 g, 0.549 mmol) in THF (10 ml) at 0°C and immediately afterwards 1,8-bis(dimethylamine)naphthalene (0.118 g, 0.549 mmol) was added. The solution turned bright red in colour and was stirred for 1 hour at 0°C. The volume was concentrated to 5 mL under vacuum (oil pump) and Celite (5 mL) was added. The mixture was reduced to dryness (oil pump), placed in a Soxhlet continuous extraction apparatus and extracted with ether (450 mL) for 2 hours. The resulting pale yellow coloured solution was reduced in volume under vacuum until it became turbid and then placed in the freezer at -16°C overnight to give bright orange crystals of $CpRu(CO)_2SS(O)_2$-4-C_6H_4Me. Concentration of the mother liquors under vacuum gave two additional crops of orange crystals (total yield = 0.119 g, 53%). mp. = decomposition starts at 96°C, melting between 118-120°C.

IR(toluene): ν(CO) 2002 (s), 2054 (s) cm^{-1}; ν(SO) 1079(m), 1132 (m) , 1276 (m) cm^{-1}

^{1}H NMR (C_6D_6): 1.85 (s, 3H, Me), 4.64 (s, 5H, Cp), 6.77 (d, $J_{(H-H)}$= 8 Hz, 2H, *meta H*'s of C_6H_4), 8.16 (d, $J_{(H-H)}$= 8 Hz, 2H, *ortho H*'s of C_6H_4)

High resolution mass spectrum (EI-PM), 150°C, $M^{+\cdot}$ measured: 409.9214 Da; $C_{14}H_{12}O_4S_2{}^{102}Ru$ requires 409.9206 Da

Anal. Calcd. for $C_{14}H_{12}O_4RuS_2$: 41.07%C, 2.95%H

Found: 41.04%C, 2.94%H

η^5-Cyclopentadienyl(dicarbonyl)phenyl-2-dioxodisulfanoruthenium(II), $CpRu(CO)_2SS(O)_2C_6H_5$ (19b)

To a solution of $CpRu(CO)_2SH$ (0.210 g, 0.824 mmol) in THF (30 mL) at 0°C (ice bath) was added $ClS(O)_2C_6H_5$ (0.105 mL, 0.824 mmol) by syringe and immediately afterward 1,8-bis(dimethylamine)naphthalene (0.177 g, 0.824 mmol) was added. An orange precipitate formed and the mixture was stirred for 40 minutes at 0°C. The reaction mixture was quickly filtered through Celite (2 cm) and activated Alumina (1 cm). A small aliquot of the filtrate was removed, reduced to dryness under vacuum, and dissolved in C_6D_6. Its NMR spectrum revealed peaks due to $CpRu(CO)_2SS(O)_2C_6H_5$, $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SC_6H_5$ in a ratio of 12:2:1 respectively. The filtrate was concentrated to 5 mL under vacuum, Celite (10 mL) was added, and the mixture was reduced to dryness. Continuous extraction of the mixture with a Soxhlet apparatus containing ether (200 mL) for 2 hours gave a yellow solution which was reduced in volume to 30 mL under vacuum and cooled at -16°C to give orange crystals of $CpRu(CO)_2SS(O)_2C_6H_5$ (0.073 g). Two further crops of crystals were obtained from the mother liquor (total yield = 0.145 g, 44%). mp. = decomposition starts at 88°C, melting between 123-124°C

IR(toluene): ν(CO) 2002 (s), 2054 (s) cm^{-1}; ν(SO) 1079 (m), 1132 (m), 1297 (w) cm^{-1}

^1H NMR (C_6D_6): 4.61 (s, 5H, Cp), 9.96 (m, 3H, *meta* and *para* *H*'s of C_6H_5), 8.22 (m, 2H, *ortho* *H*'s of C_6H_5)

High resolution mass spectrum (EI-PM), 130°C, $M^{+\cdot}$ measured: 395.9065 Da; $C_{13}H_{10}O_4S_2{}^{102}Ru$ requires 395.9058 Da

Anal. Calcd. for $C_{13}H_{10}O_4RuS_2$: 39.49%C, 2.55%H

Found: 38.98%C, 2.56%H

Preparation of $CpRu(CO)_2SS(O)R$

η^5-Cyclopentadienyl(dicarbonyl)-benzyl-2-oxodisulfanoruthenium(II), $CpRu(CO)_2SS(O)CH_2C_6H_5$ (20c)

To a solution of $CpRu(CO)_2SH$ (0.218 g, 0.848 mmol) in THF (20 mL) at -78°C (acetone/dry ice bath) was added dropwise via a cannula a solution of phth$S(O)CH_2C_6H_5$ (0.268 g, 0.940 mmol) in THF (25 mL) at -78°C over a period of 10 minutes. Stirring the reaction for 1 hour gave an orange coloured solution which contained 1 product as identified by NMR. The solution was concentrated to 10 mL under vacuum, Celite (10 mL) was added and the mixture was reduced to dryness. The residue was placed on a chromatography column (3 x 6 cm) and elution with hexanes (200 mL) followed by THF (80 mL) gave a yellow band which was reduced to dryness under vacuum to give a brown residue. This was extracted with toluene (20 mL) and the extracts were filtered through Celite, and the filtrate stripped to dryness. Recystallization from THF/hexanes gave long orange-brown needles (0.110 g, 31%). mp. = decomposition starts at 112°C, melting at 145°C

IR(cyclohexane): ν(CO) 2001 (s), 2049 (s) cm^{-1}

IR(toluene): ν(CO) 1992 (s), 2043 (s) cm^{-1}; ν(SO) 1030 (w) 1092 (m) cm^{-1}

^1H NMR (C_6D_6): 4.27 (s, 2H, $CH_2C_6H_5$); 4.63 (s, 5H, Cp), 7.07 (m, 3H, *meta, para H*'s of $CH_2C_6H_5$), 7.33 (d of d, $J_{(H\text{-}H)}$ = 8 Hz, 2H, *ortho H*'s of $CH_2C_6H_5$)

High resolution mass spectrum (EI-PM), $M^{+\cdot}$ measured: 393.9289 Da; $C_{14}H_{12}O_2S_2{}^{102}Ru$ requires 393.9265 Da.

Anal. Calcd. for $C_{14}H_{12}O_3RuS_2$: 42.74%C, 3.07%H

Found: 42.93%C, 3.04%H

Reaction of $CpRu(CO)_2SH$ + phthS(O)-4-C_6H_4Me

phthS(O)-4-C_6H_4Me (0.334 g, 1.17 mmol) was added to a yellow solution of $CpRu(CO)_2SH$ (0.320 g, 1.71 mmol) in THF (5 mL). The solution immediately became bright orange in colour. After stirring for 1 hour, a small aliquot of the solution was removed, reduced to dryness under vacuum and dissolved in C_6D_6. The NMR spectrum revealed 12 peaks in the Cp region, three of which corresponded to $CpRu(CO)_2SS(O)$-4-C_6H_5Me, $CpRu(CO)_2SS$-4-C_6H_5Me and $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me, accounting for 19%, 10% and 5% of the total intensity respectively. The reaction was stirred for an additional 2 hours and a small aliquot of the solution was once again removed from the reaction, reduced to dryness and dissolved in C_6D_6. The NMR spectrum of this sample showed 15 peaks in the Cp region. At this point, the solution was reduced in volume to 3 mL (vacuum pump), and placed on a chromatography column (1 x 50 cm). Elution with hexanes gave a bright yellow band which was collected and reduced to dryness under vacuum. The NMR spectrum of the residue indicated a mixture of $CpRu(CO)_2S$-4-C_6H_5Me, $CpRu(CO)_2SS$-4-C_6H_5Me and an unknown compound whose Cp peak appeared at 4.71 ppm, and did not have a corresponding peak due to Me protons, in the ratio of 2:1:2, respectively. The NMR spectrum also showed the presence of $(4\text{-}MeC_6H_5)_2S_2$ and two large unidentified peaks at 1.75 and 1.86 ppm. Concentration of this hexanes fraction under vacuum until cloudy gave a bright yellow solid whose NMR spectrum revealed peaks at 1.75, 1.86, and 4.71 ppm. This solid was discarded.

Subsequent elution of the column with THF/hexanes (1:1) gave a small bright yellow band containing $CpRu(CO)_2SS(O)$-4-C_6H_5Me, $CpRu(CO)_2S$-4-C_6H_5Me, $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me and $CpRu(CO)_2SS$-4-C_6H_5Me in the ratio of 2.5 : 1.5 : 1.5 : 1, respectively, as seen by its NMR spectrum. Recrystallization from THF/hexanes at -16°C gave an orange powder containing $CpRu(CO)_2SS(O)_2$-4-C_6H_5Me and $CpRu(CO)_2SS(O)$-4-C_6H_5Me in a ratio of 10:1. Concentration of the mother liquors under vacuum gave large orange rectangular crystals (0.025 g) containing $CpRu(CO)_2SS(O)$-4-

C_6H_4Me and $CpRu(CO)_2SS(O)_2C_6H_4Me$ in a ratio of 4:1. This sample was used for the ^1H NMR and mass spectra. A third crop of crystals was obtained from the mother liquors and it contained $CpRu(CO)_2SS(O)$-4-C_6H_4Me and $CpRu(CO)_2SS(O)_2C_6H_4Me$ in the ratio of 10:1 (0.007 g).

IR(cyclohexane): $CpRu(CO)_2SS(O)$-4-C_6H_4Me $\nu(CO)$ 1999 (s), 2045 (s) cm^{-1}; $\nu(SO)$ 1029 (w), 1250 (m) cm^{-1}

^1H NMR (C_6D_6) $CpRu(CO)_2SS(O)$-4-C_6H_4Me: 1.96 (s, 3H, 4-C_6H_4-CH_3), 4.70 (s, 5H, Cp), 6.91 (d, $J_{(H\text{-}H)}$ = 8Hz, 2H, *meta H* 's of 4-C_6H_4-CH_3), 7.86 (d, $J_{(H\text{-}H)}$ = 8Hz, 2H, *ortho H*'s of 4-C_6H_4-CH_3)

High resolution mass spectrum (EI-PM), 130°C, $CpRu(CO)_2SS(O)$-4-$C_6H_4Me^{+\cdot}$ measured: 393.9331 Da; $C_{14}H_{12}O_3S_2{}^{102}Ru$ requires 393.9265 Da; also observed: $CpRu(CO)_2SS(O)_2$-4-$C_6H_5Me^{+\cdot}$ measured: 409.9258 Da; $C_{14}H_{12}O_4S_2{}^{102}Ru$ requires 409.9214 Da; also observed: $CpRu(CO)_2S(O)_2$-4-$C_6H_5Me^{+\cdot}$ measured: 377.9474 Da; $C_{14}H_{12}O_4S_1{}^{102}Ru$ requires 377.9493 Da.

Reaction of $CpRu(CO)_2SH$ + $phthS(O)C_6H_5$

A solution of $phthS(O)C_6H_5$ (0.468 g, 1.72 mmol) in THF (40 mL) in a dropping funnel was added dropwise to a yellow solution of $CpRu(CO)_2SH$ (0.400 g, 1.56 mmol) in THF (40 mL) over 15 minutes. The solution immediately turned orange in colour and stirring was continued for 20 minutes. The solution was concentrated to 10 mL under vacuum, Celite (10 mL) was added and the mixture was reduced to dryness and extracted with toluene (2 x 20 mL). The combined extracts were filtered and the filtrate reduced to dryness under vacuum to give an orange oil. Recrystallization from THF/hexanes at -16°C for 1 day gave an orange oil. After 2 further days at -16°C, large yellow crystals (0.160 g) also appeared. The NMR spectrum of these crystals in C_6D_6 revealed a mixture of $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$, in the ratio of 19:1. Recrystallization of the orange oil from THF/hexanes gave an orange oil whose NMR spectrum in C_6D_6 revealed peaks due to $CpRu(CO)_2SS(O)_2C_6H_5$ and $CpRu(CO)_2SS(O)C_6H_5$, in the ratio of 1.2:1, in addition to 2 unknown compounds with Cp peaks at 5.21 and 5.28 ppm. This oil was discarded. Recrystallization of the yellow crystals from THF/hexanes gave a bright yellow solid containing $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ in the ratio of 9:1 (0.073 g, 13%). This sample was used for the spectroscopic analysis. Concentration of the mother liquors gave pale orange crystals containing $CpRu(CO)_2SS(O)C_6H_5$ and $CpRu(CO)_2SS(O)_2C_6H_5$ in the ratio of 5:1 (0.065 g, 11%).

IR(toluene): ν(CO) 1992 (s), 2042 (s) cm^{-1}; ν(SO) 1051 (m) cm^{-1}

IR(cyclohexane): ν(CO) 1999 (s), 2045 (s) cm^{-1}; ν(SO) 1040 (w), 1260 (m) cm^{-1}

^1H NMR (C_6D_6) $CpRu(CO)_2SS(O)C_6H_5$: 4.67 (s, 5H, Cp), 7.03 (m, 3H, *meta* and *para* *H* 's of C_6H_5), 7.89 (m, 2H, *ortho H*'s of C_6H_5)

High resolution mass spectrum (EI-SC), 120°C, $CpRu(CO)_2SS(O)C_6H_5^{+\cdot}$ measured: 379.9128 Da; $C_{13}H_{10}O_3S_2{}^{102}Ru$ requires 379.9108 Da; also observed: $CpRu(CO)_2SS(O)_2C_6H_5^{+\cdot}$ measured: 395.9055 Da; $C_{13}H_{10}O_4S_2{}^{102}Ru$ requires 395.9058 Da; also observed: $CpRu(CO)_2SSC_6H_5^{+\cdot}$ measured: 363.9178 Da; $C_{13}H_{10}O_4S_2{}^{102}Ru$ requires 363.9159 Da

Oxidation of $CpRu(PPh_3)(CO)SS(O)_yR$ (y = 0,1)

Reaction of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ + $NaIO_4$

To a yellow solution of $CpRu(PPh_3)(CO)SS(O)CHMe_2$ (0.210 g, 0.362 mmol) in THF (8 mL) was added sodium periodate (10% w/w supported on silica gel) (0.921 g, 0.471 mmol) and the resulting mixture was stirred for 30 hours. A small volume of the mixture was removed, reduced to dryness under vacuum and dissolved in C_6D_6. The NMR spectrum of this sample showed the presence of 1 peak due to Cp protons with corresponding peaks due to the alkyl protons. The light green mixture was filtered through

Celite (3 cm) and the Celite was washed with THF (2 x 8 mL). The combined filtrates were concentrated under vacuum to 5 mL and excess hexanes added to precipitate a solid. The mother liquors were removed with a syringe and the pale green solid was washed with hexanes (0.12 g, 55%). Recrystallization from THF/hexanes gave small light green needles. The NMR spectrum of the crystals revealed the presence of Cp peaks due to $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$ and an unknown in the ratio of 7:1 (0.065 g, 30%).

IR(C_6D_6): ν(CO) 1976 (s) cm^{-1}; ν(SO) 1106 (m), 1269 (w) cm^{-1}

IR(toluene): ν(CO) 1974 (s) cm^{-1}; ν(SO) 1081 (m), 1299 (w) cm^{-1}

IR(nujol): ν(CO) 1967 (s) cm^{-1}; ν(SO) 1090 (s), 1255 (s) cm^{-1}

^1H NMR (C_6D_6) $CpRu(PPh_3)(CO)SS(O)_2CHMe_2$: 1.43, 1.46 (d of d, $J_{(H\text{-}H)}$ = 3 Hz, 6H, CH*Me*$_2$), 3.35 (septet, 1H, C*H*Me$_2$), 4.82 (s, 5H, Cp), 7.00 (m, 9H, PPh_3), 7.45 (m, 6H, PPh_3); Unknown: 1.33, 1.41 (d of d, $J_{(H\text{-}H)}$ = 8 Hz, 6H, CH*Me*$_2$), 3.02 (m, 1H, C*H*Me$_2$), 4.91 (s, 5H, Cp), 7.00 (m, 9H, PPh_3), 7.53 (m, 6H, PPh_3)

High resolution mass spectrum (EI-PM), 230°C, $CpRu(PPh_3)(CO)SS(O)_2CHMe_2^{+\cdot}$ measured 596.0176 Da; $C_{27}H_{27}O_3P_1RuS_2$ requires 596.0208 Da

Reaction of $CpRu(PPh_3)(CO)SS(O)$-4-C_6H_4Me and 3.3 equivalents of DMDO

To a flask charged with $CpRu(PPh_3)(CO)SS(O)$-4-C_6H_4Me (0.059 g, 0.093 mmol) at -40°C (acetone/dry ice bath)was added dropwise via a syringe dimethyldioxirane (4.89 mL, 0.063M in acetone, 0.308 mmol) at -16°C. The solution was stirred for 20 minutes at -40°C. A small volume of the solution was removed by syringe, reduced to dryness, and dissolved in C_6D_6. The NMR spectrum of this sample revealed the presence of 2 compounds in the ratio of 5:1, with peaks due to Cp protons appearing at 4.68 and 4.59 ppm with corresponding Me peaks at 1.91 and 1.83 ppm respectively. After a total reaction time of 20 minutes, the solution was reduced to dryness and the residue was dissolved in toluene and excess hexanes was added. The solution was cooled to -78°C and a yellow solid precipitated. The mother liquors were discarded and the remaining yellow powder was washed with hexanes -78°C. The NMR spectrum of the yellow solid in C_6D_6 revealed the presence of 2 sets of peaks assigned to $CpRu(PPh_3)(CO)S(O)_2S(O)_2$-4-$C_6H_4Me$ and an unknown in the ratio of in a ratio of 7:1.

IR(nujol): ν(CO) 1955 (s) cm^{-1}; ν(SO) 1308 (m), 1262 (m) cm^{-1}

^1H NMR (C_6D_6) $CpRu(PPh_3)(CO)S(O)_2S(O)_2$-4-$C_6H_4Me$ 1.91 (s, 3H, Me). 4.67, (s, 5H, Cp), 6.72 (d $J_{(H-H)}$=7 Hz, 2H, *meta* H of 4-C_6H_4Me), 6.95 (m, 9H, PPh_3),4.48 (m, 6H, PPh_3), 7.68 (d $J_{(H-H)}$=7 Hz, 2H, *ortho* H of 4-C_6H_4Me); Unknown 1.83 (s, 3H,Me), 4.63 (s, 5H,Cp), 7.05 (m, 11 H, PPh_3, *meta* H of 4-C_6H_4Me), 7.18 (m, 6H, PPh_3), 8.10 (d $J_{(H-H)}$=8 Hz, 2H, *ortho* H of 4-C_6H_4Me);

High resolution mass spectrum (EI-PM), $CpRu(PPh_3)(CO)S(O)_2S(O)_2^{+\cdot}$ measured: 584.9426 Da; $C_{24}H_{20}O_5PS_2{}^{102}Ru$ requires 383.9546 Da.

Table E.1 ^1H NMR[a] Data for $CpRu(CO)_2E$ (E = SR, SSR, SSSR, SS(O)R, $SS(O)_2R$; R = $4\text{-}C_6H_4Me$, C_6H_5, $CH_2C_6H_5$).

No.	Compound	C_5H_5	$4\text{-}C_6H_4\underline{Me}$	C_6H_x
3	$CpRu(CO)_2SH$[b]	4.37		
4	$(\mu\text{-}S_3)(CpRu(CO)_2)$	4.82		
11a	$CpRu(CO)_2S\text{-}4\text{-}C_6H_4Me$	4.43	2.11	6.90[c], 7.69[c]
12a	$CpRu(CO)_2SS\text{-}4\text{-}C_6H_4Me$	4.40	2.06	6.95[c], 7.76[c]
13a	$CpRu(CO)_2SSS\text{-}4\text{-}C_6H_4Me$	4.53	1.99	6.88[c], 7.72[c]
20a	$CpRu(CO)_2SS(O)\text{-}4\text{-}C_6H_4Me$	4.70	1.96	6.91[c], 7.86[c]
19a	$CpRu(CO)_2SS(O)_2\text{-}4\text{-}C_6H_4Me$	4.64	1.85	6.77[c], 8.16[c]

[a] In C_6D_6 solution, reported in ppm.

[b] S$\underline{H}$ at -2.93 ppm.

[c] x = 2, doublet, $J_{(H\text{-}H)}$ = 8 Hz.; [d] x = 3, multiplet.

[e] x = 2, multiplet.

[f] x = 1, triplet.

[g] x = 2, doublet of doublets, $J_{(H\text{-}H)}$ = 8 Hz.

Table E.1 (continued)

No.	Compound	C_5H_5	$CH_2C_6H_5$	C_6H_x
11b	$CpRu(CO)_2SC_6H_5$	4.41		7.10[d], 7.73[e]
12b	$CpRu(CO)_2SSC_6H_5$	4.39		7.00[f], 7,13[e], 7.82[c]
	$CpRu(CO)_2SSSC_6H_5$	4.49		?
20b	$CpRu(CO)_2SS(O)C_6H_5$	4.67		7.03[d], 7.89[e]
19b	$CpRu(CO)_2SS(O)_2C_6H_5$	4.61		6.96[d], 8.22[e]
11c	$CpRu(CO)_2SCH_2C_6H_5$	4.34	3.61	7.09[d], 7.40[g]
12c	$CpRu(CO)_2SSCH_2C_6H_5$	4.43	3.98	7.07[d], 7.38[e]
	$CpRu(CO)_2SSSCH_2C_6H_5$	4.57	3.35	?
20c	$CpRu(CO)_2SS(O)CH_2C_6H_5$	4.63	4.27	7.07[d], 7.33[g]

[a] In C_6D_6 solution, reported in ppm.

[b] S$\underline{H}$ at -2.93 ppm.

[c] x = 2, doublet, $J_{(H\text{-}H)}$ = 8 Hz.

[d] x = 3, multiplet.; [e] x = 2, multiplet.

[f] x = 1, triplet.

[g] x = 2, doublet of doublets, $J_{(H\text{-}H)}$ = 8 Hz.

Table E.2 IR stretching frequencies for CpRu(L)(CO)E (L = PPh_3, E = $SS(O)_2CHMe_2$, $S(O)_2S(O)_2$4-C_6H_4Me; E = SR, SSR, SSSR, SS(O)R, $SS(O)_2R$, R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$).

CpRu(L)(CO)E			$\nu(CO)$[d] (cm^{-1})	$\nu(SO)$ (cm^{-1})
L	**E**	**R**		
CO	SR	H	1995, 2043 [a]	
		4-C_6H_4Me	1990, 2041 [a]	
		C_6H_5	1992, 2041 [a]	
		$CH_2C_6H_5$	1985, 2039 [a]	
		$SS(CO)_2RuCp$	1969, 2024 [b]	
CO	SSR	4-C_6H_4Me	1993, 2043 [a]	
		C_6H_5	1996, 2043 [a]	
		$CH_2C_6H_5$	1994, 2038[a]	
		$CHMe_2$	1987, 2034[a]	
CO	SSSR	4-C_6H_4Me	1993, 2043 [a]	
CO	SS(O)R	4-C_6H_4Me	1999, 2045 [a]	1129 [e], 1250 [f]
		C_6H_5	1999, 2045 [a]	1040 [e], 1260 [f]
		$CH_2C_6H_5$	2001, 2048[a]	1030 [e], 1292 [f]
CO	$SS(O)_2R$	4-C_6H_4Me	2002, 2054 [b]	1079 [f], 1132 [f], 1276 [f]
		R = C_6H_5	2002, 2054 [b]	1079 [f], 1132 [f], 1279 [e]
PPh_3	$SS(O)_2R$	$CHMe_2$	1974 [b]	1081 [f], 1299 [e]
PPh_3	$SS(O)_2S(O)_2R$	4-C_6H_4Me	1955 [c]	1153 [f], 1262 [f]

[a] cyclohexane

[b] toluene

[c] nujol

[d] all $\nu(CO)$ bands are strong in intensity

[e] weak intensity

[f] medium intensity

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CONTRIBUTION TO ORIGINAL KNOWLEDGE

1. Additional examples of an interesting and rare class of complexes containing S_xO_yR ligands, $CpRu(CO)_2ER$ (E = SS, SS(O), $SS(O)_2$) were prepared. The complexes $CpRu(CO)_2SS(O)_2R$ were prepared in reasonable yields by a novel route and has enabled chemical and the first studies of complexes of this type. The x-ray structure of $CpRu(CO)_2SS(O)_2C_6H_5$ was determined, only the second reported containing a $-SS(O)_2R$ ligand. The stability of the $-SS(O)_2R$ ligand in the presence of PPh_3 suggests that a $[MSSO_2]$ functionality is an unlikely route to [MSS], or catenation. The novel overall removal of SO from $CpRu(CO)_2SS(O)R$ by PPh_3 was observed. These two observations have important implications for the development of models for the Claus Process.

2. The demonstration of sulfur transfer in the complexes $CpRu(CO)_2SSR$ to give $CpRu(CO)_2S_xR$ (x = 1-3) and the insertion of a sulfur atom from added S_8 is unprecedented. The mechanism of the insertion appears to be complex. The reaction may be important as a possible route to the rarer higher metal polysulfano complexes, MS_xR ($x \geq 3$).

3. The thiolates $CpRu(CO)_2SR$ undergo novel sulfur atom insertion with S_8 to give higher sulfanes $CpRu(CO)_2S_xR$ (x = 2,3). An ionic route is proposed. The photoactivated ligand exchange observed between these thiolates and organic polysulfides R'_2S_y (y = 2,3) to give $CpRu(CO)_2S_xR'$ is also new. These phenomena are of particular interest when one remembers that the body contains many metal thiolate complexes and organic disulfides.

4. The first electrochemical studies of complexes of the type $CpRu(CO)_2ER$ (E = SS, SS(O), $SS(O)_2$) has demonstrated that these complexes undergo irreversible sulfur-

based oxidation. The potential of the first oxidation is independent of the R group or the presence of one or two sulfur atoms in the ligand, $E = S_x$ ($x = 1,2$). The rate of oxidation of $CpRu(CO)_2SS(O)_yR$ ($y = 1, 2$) is much slower than that for $E = S_x$ for reasons that are unknown.

5. It has been demonstrated that preparative oxidation reactions of $CpRu(PPh_3)(CO)SS(O)_yR$ ($y = 0,1$) are unlikely to be good routes to higher oxides unless more specific oxidants can be found. The higher oxides, particularly those with oxygen on the sulfur atom coordinated to the metal atom as in $CpRu(PPh_3)(CO)S(O)_2S(O)_2R$ are extremely moisture sensitive.

APPENDIX 1. Structural Analysis of $CpRu(CO)_2SS(O)_2C_6H_5$

Table A.1.1 Crystallographic Data for $CpRu(CO)_2SS(O)_2C_6H_5$.

Crystal Parameters

Formula: $C_{13}H_{10}O_4S_2Ru$
Crystal system: monoclinic
a = 10.143(2)Å
b = 11.318(2)Å
c = 13.259(2)Å
V = 1455.4(5)$Å^3$
δ_{calc} = 1.804 g cm^{-3}
Colour = yellow
Crystal size = 0.42 x 0.37 x 0.27 mm
Transmission factors = 0.87-1.38

Formula weight = 395.41
Space group = $P2_1/c$
$\alpha = 90°$
$\beta = 107.04°$
$\gamma = 90°$
Z = 4
μ(MoKα) = 13.39 cm^{-1}
Temperature = 19°C
λ = 0.71069Å

Data Collection and Structrure Refinement

Diffractometer: Rigaku AFC6S
Monochromator: graphite
Scan speed: 16°/min
Quadrant collected: h, k, ±l
Reflections collected: 2867
Least-squared method: full matrix
Absorption Correction: yes
Parameters refined: 182
R = 0.035
Goodness of fit = 1.28

Radiation: MoKα
Scan method: ω-2φ
Data limits: $4 < 2\varphi < 50$
Friedel pairs collected: no
Unique data: 2709
Data ($I > 3.0\sigma(I)$): 1856
Data/parameter ratio = 10.20
R_w = 0.039

$$R = \Sigma [\, |F_o| - |F_c| \,] / \Sigma |F_o|$$

$$R_w = [\, \Sigma w (|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2}, \text{ where } w = 1 / \sigma^2 (|F_o|)$$

$$\text{Goodness of fit} = [\, \Sigma w (|F_o| - |F_c|)^2 / (N_{obs} - N_{parm}) \,]^{1/2}$$

Table A.1.2 Atom cordinates, x,y,z and B_{iso} (Å^2) for $CpRu(CO)_2SS(O)_2C_6H_5$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Ru	0.12107(04)	0.26248(04)	0.06256(03)	2.56(2)
S(1)	-0.05633(15)	0.36366(12)	-0.06796(12)	3.21(6)
S(2)	-0.21519(13)	0.24612(12)	-0.10842(11)	2.95(5)
O(1)	-0.2660(04)	0.2205(04)	-0.0198(03)	4.6(2)
O(2)	-0.1844(04)	0.1456(03)	-0.1647(03)	4.0(2)
O(3)	0.3348(05)	0.3737(05)	-0.0250(04)	7.1(3)
O(4)	0.1236(05)	0.0430(04)	-0.0661(04)	5.5(2)
C(1)	0.1556(07)	0.1574(05)	0.2082(05)	4.0(3)
C(2)	0.0215(06)	0.2041(05)	0.1829(05)	3.7(3)
C(3)	0.0325(07)	0.3276(06)	0.1896(05)	3.9(3)
C(4)	0.1715(07)	0.3583(05)	0.2170(05)	3.8(3)
C(5)	0.2481(06)	0.2515(06)	0.2280(04)	3.9(2)
C(6)	0.2522(06)	0.3319(06)	0.0065(05)	4.0(3)
C(7)	0.1171(06)	0.1275(05)	-0.0212(05)	3.5(3)
C(8)	-0.3412(05)	0.3335(05)	-0.1996(04)	2.6(2)
C(9)	-0.3582(06)	0.3226(05)	-0.3066(05)	3.3(2)
C(10)	-0.4535(06)	0.3941(06)	-0.3765(05)	4.3(3)
C(11)	-0.5282(07)	0.4748(06)	-0.3393(06)	4.6(3)
C(12)	-0.5113(06)	0.4846(05)	-0.2331(05)	4.0(3)
C(13)	-0.4165(06)	0.4129(05)	-0.1614(05)	3.7(2)

B_{iso} is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table A.1.3 Anisotropic thermal factors for CpRu$(CO)_2SS(O)_2C_6H_5$. U(i,j) values (Å^2). E.S.Ds refer to the last digit printed.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.0323(02)	0.0336(03)	0.0316(02)	-0.0002(02)	0.0095(02)	0.0016(02)
S(1)	0.0394(08)	0.0319(08)	0.0446(09)	-0.0054(06)	0.0027(06)	0.0085(06)
S(2)	0.0343(07)	0.0342(08)	0.0419(08)	-0.0034(06)	0.0084(06)	0.0064(07)
O(1)	0.050(02)	0.072(03)	0.052(03)	-0.007(02)	0.016(02)	0.023(02)
O(2)	0.043(02)	0.036(02)	0.066(03)	0.003(02)	0.004(02)	-0.003(02)
O(3)	0.083(04)	0.124(05)	0.078(04)	-0.053(04)	0.051(03)	-0.027(03)
O(4)	0.097(04)	0.047(03)	0.064(03)	0.014(03)	0.023(03)	-0.010(02)
C(1)	0.066(04)	0.044(04)	0.044(04)	0.006(03)	0.019(03)	0.011(03)
C(2)	0.053(04)	0.053(04)	0.041(04)	-0.011(03)	0.020(03)	0.002(03)
C(3)	0.060(04)	0.050(04)	0.043(04)	0.015(03)	0.024(03)	0.003(03)
C(4)	0.062(04)	0.046(04)	0.036(04)	-0.011(03)	0.016(03)	-0.007(03)
C(5)	0.047(03)	0.061(04)	0.037(03)	0.000(03)	0.004(03)	0.006(03)
C(6)	0.048(04)	0.062(04)	0.041(04	-0.010(03)	0.014(03)	-0.011(03)
C(7)	0.046(04)	0.039(03)	0.048(04)	0.008(03)	0.015(03)	0.006(03)
C(8)	0.025(03)	0.031(03)	0.041(03)	-0.002(02)	0.007(02)	-0.000(03)
C(9)	0.037(03)	0.042(03)	0.048(04)	0.003(03	0.015(03)	0.006(03)
C(10)	0.056(04)	0.065(04)	0.041(04)	0.010(03)	0.013(03)	0.012(03)
C(11)	0.045(04)	0.058(04)	0.068(05)	0.012(03	0.013(04)	0.020(04)
C(12)	0.037(03)	0.045(04)	0.074(05)	0.009(03)	0.022(03)	-0.000(03)
C(13)	0.044(03)	0.048(04)	0.046(04)	-0.002(03)	0.012(03)	-0.003(03)

Anisotropic Temperature Factors are of the form:

$$\text{Temp} = -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})$$

Table A.1.4 Selected bond lengths (Å) and angles(°) for $CpRu(CO)_2SS(O)_2C_6H_5$. E.S.Ds refer to last digit printed.

Ru-S(1)	2.391(2)	O(4)-C(7)	1.139(7)
Ru-C(1)	2.206(6)	C(1)-C(2)	1.405(8)
Ru-C(2)	2.225(6)	C(1)-C(5)	1.392(8)
Ru-C(3)	2.252(6)	C(2)-C(3)	1.403(8)
Ru-C(4)	2.240(6)	C(3)-C(4)	1.393(8)
Ru-C(5)	2.198(5)	C(4)-C(5)	1.421(8)
Ru-C(6)	1.876(7)	C(8)-C(9)	1.384(7)
Ru-C(7)	1.882(6)	C(8)-C(13)	1.369(8)
S(1)-S(2)	2.037(2)	C(9)-C(10)	1.388(8)
S(2)-O(1)	1.444(4)	C(10)-C(11)	1.368(9)
S(2)-O(2)	1.444(4)	C(11)-C(12)	1.373(9)
S(2)-C(8)	1.780(5)	C(12)-C(13)	1.397(8)
O(3)-C(6)	1.142(7)		

S(1)-Ru-C(1)	141.7(2)	S(1)-S(2)-O(2)	112.1(2)
S(1)-Ru-C(2)	104.9(2)	S(1)-S(2)-C(8)	99.9(2)
S(1)-Ru-C(3)	90.2(2)	O(1)-S(2)-O(2)	116.5(3)
S(1)-Ru-C(4)	110.6(2)	O(1)-S(2)-C(8)	107.9(3)
S(1)-Ru-C(5)	147.8(2)	O(2)-S(2)-C(8)	107.9(2)
S(1)-Ru-C(6)	89.0(2)	Ru-C(1)-C(2)	72.2(3)
S(1)-Ru-C(7)	94.6(2)	Ru-C(1)-C(5)	71.2(3)
C(1)-Ru-C(2)	37.0(2)	C(2)-C(1)-C(5)	108.0(5)
C(1)-Ru-C(3)	61.2(2)	Ru-C(2)-C(1)	70.8(3)
C(1)-Ru-C(4)	61.7(2)	Ru-C(2)-C(3)	72.8(4)
C(1)-Ru-C(5)	36.8(2)	C(1)-C(2)-C(3)	107.8(5)
C(1)-Ru-C(6)	128.6(3)	Ru-C(3)-C(2)	70.7(4)
C(1)-Ru-C(7)	92.8(2)	Ru-C(3)-C(4)	71.5(3)
C(2)-Ru-C(3)	36.5(2)	C(2)-C(3)-C(4)	108.7(6)
C(2)-Ru-C(4)	61.2(2)	Ru-C(4)-C(3)	72.4(4)
C(2)-Ru-C(5)	61.6(2)	Ru-C(4)-C(5)	69.7(3)
C(2)-Ru-C(6)	158.8(2)	C(3)-C(4)-C(5)	107.2(5)
C(2)-Ru-C(7)	104.3(2)	Ru-C(5)-C(1)	71.9(3)
C(3)-Ru-C(4)	36.1(2)	Ru-C(5)-C(4)	72.9(3)
C(3)-Ru-C(5)	61.2(2)	C(1)-C(5)-C(4)	108.3(5)
C(3)-Ru-C(6)	130.1(3)	Ru-C(6)-O(3)	178.1(6)
C(3)-Ru-C(7)	139.7(3)	Ru-C(7)-O(4)	174.7(5)
C(4)-Ru-C(5)	37.3(2)	S(2)-C(8)-C(9)	119.7(4)
C(4)-Ru-C(6)	99.3(2)	S(2)-C(8)-C(13)	118.7(4)
C(4)-Ru-C(7)	153.1(2)	C(9)-C(8)-C(13)	121.6(5)
C(5)-Ru-C(6)	98.2(2)	C(8)-C(9)-C(10)	119.1(5)
C(5)-Ru-C(7)	116.6(2)	C(9)-C(10)-C(11)	120.0(6)
C(6)-Ru-C(7)	90.0(3)	C(10)-C(11)-C(12)	120.6(6)
Ru-S(1)-S(2)	104.31(7)	C(11)-C(12)-C(13)	120.4(6)
S(1)-S(2)-O(1)	111.1(2)	C(8)-C(13)-C(12)	118.5(6)

APPENDIX 2. Structural Analysis of $CpRu(CO)_2SS(O)C_6H_5$

Table A.2.1 Crystallographic Data for $CpRu(CO)_2SS(O)C_6H_5$.

Crystal Parameters

Formula: $C_{13}H_{10}O_3S_2Ru$
Crystal system: monoclinic
a = 6.700(1)Å
b = 28. 492(5)Å
c = 7.466(1)Å
V = 1409.6(4)$Å^3$
δ_{calc} = 1.788 g cm^{-3}
Colour = yellow
Crystal size = 0.62 x 0.15 x 0.12 mm
Transmission factors = 0.79-1.55

Formula weight = 379.41
Space group = $P2_1/n$
$\alpha = 90°$
$\beta = 98.51°$
$\gamma = 90°$
Z = 4
μ(CuKα) = 119.7 cm^{-1}
Temperature = 21°C
λ = 1.54178Å

Data Collection and Structrue Refinement

Diffractometer: Rigaku AFC6S
Monochromator: graphite
Scan speed: 16°/min
Quadrant colleced: h, k, ±l
Reflections collected: 2428
Least-squared method: full matrix
Absorption Correction: yes
Parameters refined: 173
R = 0.047
Goodness of fit = 1.42

Radiation: CuKα
Scan method: ω-2φ
Data limits: $4 < 2\varphi < 120$
Friedel pair collected: no
Unique data: 2176
Data ($I > 3.0\sigma(I)$): 1299
Data/parameter ratio = 7.51
R_w = 0.049

$R = \Sigma [\, |F_o| - |F_c| \,] / \Sigma |F_o|$

$R_w = [\, \Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$

Goodness of fit = $[\, \Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parm})\,]^{1/2}$

Table A.2.2 Atom cordinates, x,y,z and B_{iso} ($Å^2$) for $CpRu(CO)_2SS(O)C_6H_5$. E.S.Ds. refer to the last digit printed.

atom	x	y	z	B_{iso}
Ru	0.09794(14)	0.08518(03)	0.18252(12)	3.62(4
S(1)	-0.1006(05)	0.07291(10)	-0.1071(04)	5.4(2)
S(2)	-0.0368(06)	0.12228(11)	-0.2902(04)	6.1(2)
O(1)	0.1840(14)	0.1272(03)	-0.2914(11)	6.9(5)
O(2)	-0.1349(13)	0.1702(03)	0.2754(10)	5.4(4)
O(3)	-0.1787(13)	0.0216(03)	0.3513(13)	7.0(5)
C(1)	0.397(02)	0.1168(04)	0.170(02)	6.4(8)
C(2)	0.386(02)	0.0783(07)	0.071(02)	6.9(8)
C(3)	0.366(02)	0.0396(05)	0.175(03)	8(1)
C(4)	0.365(02)	0.0577(07)	0.356(03)	8(1)
C(5)	0.389(02)	0.1046(06)	0.346(02)	6.1(8)
C(6)	-0.053(02)	0.1381(04)	0.2322(14)	3.9(5)
C(7)	-0.079(02)	0.0463(04)	0.279(02)	4.9(6)
C(8)	-0.113(02)	0.1758(04)	-0.1890(15)	4.6(5)
C(9)	-0.309(02)	0.1834(05)	-0.168(02)	5.3(7)
C(10)	-0.354(02)	0.2266(05)	-0.096(02)	5.7(7)
C(11)	-0.214(02)	0.2611(04)	-0.055(02)	5.9(7)
C(12)	-0.024(02)	0.2525(05)	-0.083(02)	6.2(7)
C(13)	0.034(02)	0.2096(05)	-0.148(02)	5.6(7)

B_{iso} is the arithmetic mean of the principal axes of the thermal ellipsoid.

Table A.2.3 Anisotropic thermal factors for $CpRu(CO)_2SS(O)C_6H_5$.
U(i,j) values (Å^2). E.S.Ds refer to the last digit printed.

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.0446(05)	0.0454(04)	0.0481(05)	-0.0006(05)	0.0088(04)	0.0014(05)
S(1)	0.086(03)	0.057(02)	0.061(02)	-0.015(02)	0.002(02)	-0.0100(14)
S(2)	0.111(03)	0.081(02)	0.043(02)	-0.008(02)	0.020(02)	-0.007(02)
O(1)	0.098(08)	0.100(07)	0.076(06)	0.007(05)	0.052(06)	-0.002(05)
O(2)	0.081(07)	0.066(05)	0.054(06)	0.022(05)	0.000(05)	0.005(04)
O(3)	0.055(07)	0.086(06)	0.127(08)	0.003(05)	0.018(06)	0.046(06)
C(1)	0.060(10)	0.071(09)	0.109(13)	-0.011(08)	0.012(09)	0.014(09)
C(2)	0.059(10)	0.120(13)	0.090(11)	0.005(10)	0.030(08)	-0.024(11)
C(3)	0.045(10)	0.061(10)	0.21(02)	0.017(08)	0.009(12)	-0.033(12)
C(4)	0.043(10)	0.131(14)	0.13(02)	0.018(10)	0.014(10)	0.072(13)
C(5)	0.054(09)	0.107(11)	0.069(11)	-0.002(09)	0.002(08)	-0.008(09)
C(6)	0.040(07)	0.061(07)	0.044(07)	-0.003(06)	0.001(06)	0.009(06)
C(7)	0.034(08)	0.062(07)	0.088(10)	0.003(06)	0.006(07)	0.006(07)
C(8)	0.084(10)	0.056(06)	0.035(06)	-0.008(08)	0.006(06)	0.002(06)
C(9)	0.057(10)	0.075(09)	0.062(09)	-0.018(07)	-0.014(07)	0.013(07)
C(10)	0.065(10)	0.083(10)	0.061(09)	0.005(08)	-0.010(07)	0.013(08)
C(11)	0.085(12)	0.063(08)	0.073(10)	-0.002(08)	-0.004(09)	0.009(07)
C(12)	0.083(12)	0.086(10)	0.062(09)	-0.027(09)	0.004(08)	-0.002(08)
C(13)	0.073(10)	0.076(09)	0.070(09)	-0.012(08)	0.028(08)	-0.001(07)

Anisotropic Temperature Factors are of the form:

$$\text{Temp} = -2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})$$

Table A.2.4 Selected bond lengths (Å) and angles(°) for $\mathrm{CpRu(CO)_2SS(O)C_6H_5}$. E.S.Ds refer to last digit printed.

Ru-S(1)	2.391(3)	O(3)-C(7)	1.16(1)
Ru-C(1)	2.21(1)	C(1)-C(2)	1.32(2)
Ru-C(2)	2.22(1)	C(1)-C(5)	1.36(2)
Ru-C(3)	2.23(1)	C(2)-C(3)	1.36(2)
Ru-C(4)	2.20(1)	C(3) -C(4)	1.45(2)
Ru-C(5)	2.21(1)	C(4)-C(5)	1.35(2)
Ru -C(6)	1.88(1)	C(8)-C(9)	1.37(2)
Ru -C(7)	1.84(1)	C(8)-C(13)	1.38(2)
S(1)-S(2)	2.050(4)	C(9)-C(10)	1.39(2)
S(2) -O(1)	1.488(9)	C(10)-C(11)	1.36(2)
S(2)-C(8)	1.81(1)	C(11)-C(12)	1.35(2)
O(2)-C(6	1.14(1)	C(12)-C(13)	1.39(2)

S(1)-Ru-C(1)	114.1(5)	S(1)-S(2)-O(1)	111.9(4)
S(1)-Ru-C(2)	92.7(4)	S(1)-S(2)-C(8)	101.6(4)
S(1) -Ru-C(3)	103.6(6)	O(1)-S(2)-C(8)	105.4(6)
S(1)-Ru -C(4)	141.1(6)	Ru-C(1)-C(2)	73.1(8)
S(1)-Ru-C(5)	149.6(4)	Ru-C(1) -C(5)	72.1(8)
S(1)-Ru-C(6)	93.0(3)	C(2)-C(1)-C(5)	109(1)
S(1)-Ru-C(7)	87.7(4)	Ru-C(2)-C(1)	72.2(8)
C(1)-Ru-C(2)	34.7(5)	Ru-C(2)-C(3)	72.4(8)
C(1)-Ru -C(3)	59.8(5)	C(1)-C(2)-C(3)	111(1)
C(1)-Ru-C(4)	60.2(5)	Ru-C(3) -C(2)	71.9(8)
C(1)-Ru-C(5)	35.9(5)	Ru-C(3)-C(4)	69.7(8)
C(1)-Ru-C(6)	101.4(5)	C(2)-C(3)-C(4)	105(1)
C(1)-Ru-C(7)	154.1(5)	Ru-C(4)-C(3)	72.0(9)
C(2)-Ru-C(3)	35.7(5)	Ru-C(4)-C(5)	72.8(9)
C(2)-Ru-C(4)	60.7(6)	C(3)-C(4)-C(5)	106(1)
C(2)-Ru -C(5)	58.9(5)	Ru-C(5)-C(1)	72.0(9)
C(2)-Ru-C(6)	131.8(6)	Ru-C(5)-C(4)	71.6(9)
C(2)-Ru-C(7)	137.5(6)	C(1) -C(5)-C(4)	109(1)
C(3)-Ru-C(4)	38.3(6)	Ru-C(6)-O(2)	175(1)
C(3)-Ru-C(5)	60.7(5)	Ru-C(7)-O(3)	175(1)
C(3)-Ru-C(6)	158.7(5)	S(2)-C(8)-C(9)	121(1)
C(3)-Ru-C(7)	103.2(6)	S(2)-C(8)- C(13)	117(1)
C(4)-Ru-C(5)	35.6(5)	C(9)-C(8)-C(13)	122(1)
C(4)-Ru-C(6)	125.7(7)	C(8)-C(9)-C(10)	117(1)
C(4)-Ru-C(7)	94.1(5)	C(9)-C(10)-C(11)	123(1)
C(5)-Ru-C(6)	98.4(5)	C(10)-C(11)-C(12)	118(1)
C(5)-Ru-C(7)	120.1(6)	C(11)-C(12)-C(13)	122(1)
C(6) -Ru-C(7)	90.6(5)	C(8)-C(13)-C(12)	118(1)
Ru-S(1)-S(2)	111.1(2)		

APPENDIX 3. Plots verifying diffusion controlled processes.

Figure A.3.1 Plots of current verses the square root of scan speed ($\nu^{1/2}$):
a) $CpRu(CO)_2E$ (E = Cl, SH); b) $CpRu(CO)_2SR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$);
c) $CpRu(CO)_2SSR$ (R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$).

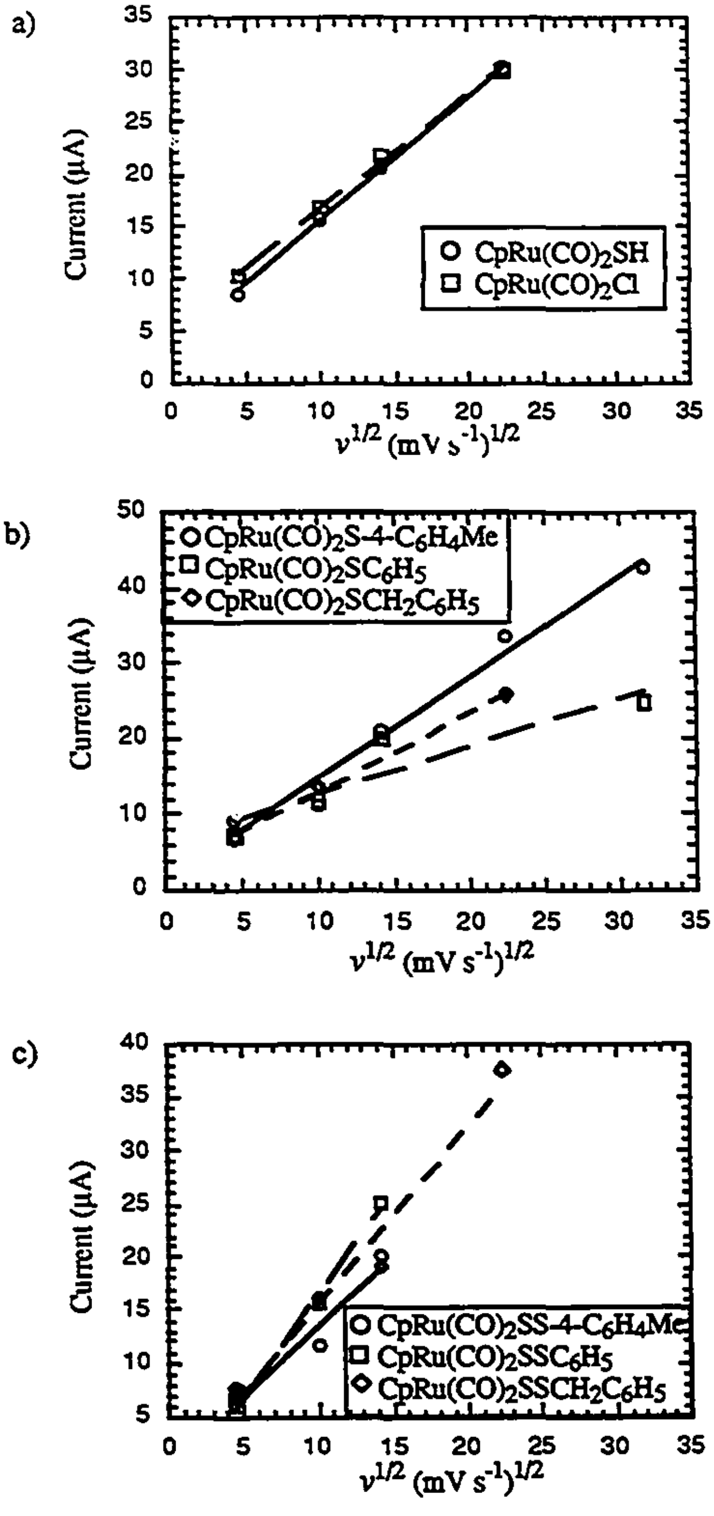
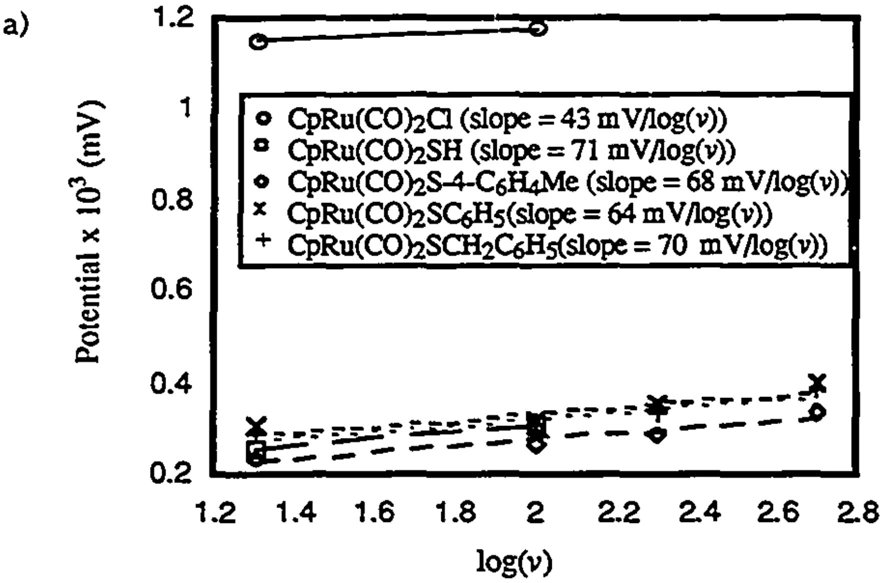
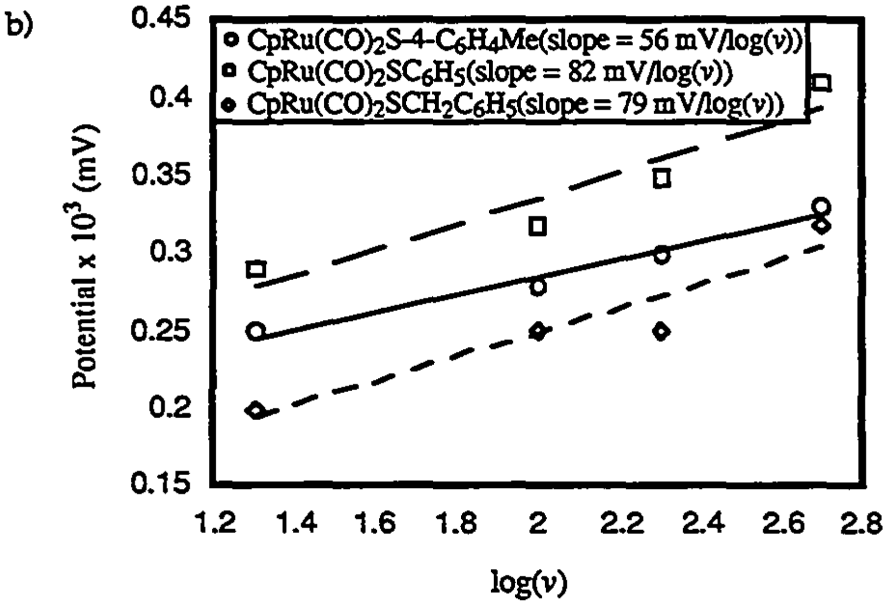


Figure A.3.2 Dependence of the peak oxidation potential for a) $CpRu(CO)_2E$ (E = Cl, SH, SR; R = 4-C_6H_4Me, C_6H_5, $CH_2C_6H_5$) and b) $CpRu(CO)_2SSR$ on the logarithm of the sweep rate.





APPENDIX 4.

Reprint of *Journal of Organometallic Chemistry* Article.

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The preparation of the mixed thiolato–isocyanide complexes *cis*- and *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(SR)(CNR')$: the structure of *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CNCMe_3)$

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Abstract

Treatment of the thiolato complexes $CpW(CO)_2(PPh_3)(SR)$, as a mixture of *cis* and *trans* isomers, with isocyanides gave *cis*- and *trans*-$CpW(CO)_2(SR)(CNR')$, where R = $CHMe_2$ or 4-C_6H_4Me, and R′ = CMe_3 or 2,6-$C_6H_3Me_2$. The *cis* isomer of the thiolato complex was preferentially consumed before the *trans* isomer. The structure of *trans*-$CpW(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CNCMe_3)$ was determined by X-ray crystallography: $P2_1/a$: $a = 12.242(4)$, $b = 17.592(5)$, $c = 18.728(8)$ Å, $\beta = 92.01(3)°$; $V = 4030.8(2)$ Å^3; $Z = 2$.

Keywords: Tungsten; Thiolate; Isocyanide; Substitution; Cyclopentadienyl; Crystal structure

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1. Introduction

Complexes of the type *cis*- and *trans*-$CpW(CO)_2(PPh_3)(SR)$, where R = alkyl or aryl, lose PPh_3 in solution to form the unsaturated 16-electron intermediate "$CpW(CO)_2SR$" [1]. Heating a solution of a mixture of *cis*-and *trans*-$CpW(CO)_2(PPh_3)SCHMe_2$ led to sequential loss of first PPh_3 and then one CO ligand to give the dimers $[CpW(CO)_2SCHMe_2]_2$ and $[CpW(CO)SCHMe_2]_2$ respectively [2]. The starting thiolato complexes easily add CO to give the tricarbonyls $CpW(CO)_3SR$. Treatment with CS_2 leads to insertion into the W–S bond to give the thioxanthates $CpW(CO)_2S_2CSR$. The mechanism of the latter reaction probably involves dissociation of PPh_3, followed by coordination of CS_2 and then insertion [1].

Isocyanides are very versatile ligands [3,4] and they undergo insertion reactions with metal–carbon σ bonds [5]. The factors which affect such reactions include the steric congestion in the coordination sphere of the metal upon coordination of the isocyanide [6], the nucleophilicity of the migrating atoms or group [7] and the electrophilicity of the coordinated isocyanide [8]. It became of interest to test the reactivity of the thiolato tungsten complexes above with isocyanides to see whether coordination and/or insertion would occur. There are a few examples of insertion by isocyanides into metal–heteroatom bonds namely M–N [9] and M–O [10]. Examples of complexes containing a three-membered M–C–S moiety, which might possibly form via insertion of an isocyanide into a metal thiolate, have been prepared via addition of the HS^- anion to a coordinated isocyanide [11]. Finally insertion of isocyanides into activated carbon–sulfur bonds (C–S) in organic systems have been reported [12]. Therefore a complex of the type $CpW(CO)_2(SR)(CNR')$ has many attributes that might lead to insertion of the isocyanide into the metal–sulfur bond.

2. Results and discussion

Treatment of solutions of mixtures of *cis*- and *trans*-$CpW(CO)_2(PPh_3)SR$, as obtained from methods previously described [1], with isocyanides gave the products of substitution of the PPh_3 ligand, namely $CpW(CO)_2(SR)CNR'$, where R = $CHMe_2$ or 4-C_6H_4Me and R′ = CMe_3 or 2,6-$C_6H_3Me_2$. The crude yields, as obtained from alumina columns, were high (greater than 83%)

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and the compounds were quite pure by NMR. The isolated yields were considerably reduced owing to high solubility in the recrystallizing solvents.

The compounds were formed as a mixture of *cis* and *trans* isomers as revealed by their NMR spectra which showed complete sets of peaks for each isomer. The ratios of isomers (see Section 3) were determined by integration of the NMR spectra and were invariant at all stages of the work-up. The peaks due to the isomers containing the $SCHMe_2$ ligand were assigned on the basis of the pattern of the Me resonances. These appear as a doublet of doublets in the *cis* isomer consistent with their diastereotopic environment while they appear as simple doublets in the *trans* isomers. It was not possible, on the basis of the room temperature ^1H NMR spectra, to assign the peaks to the isomers of the two other complexes which contained the S-4-C_6H_4Me ligand. No evidence was detected for separation of the isomers during the work-up which included chromatography on alumina. Crystallization of all four products gave only one type of crystal for each when examined under the microscope. No further effort was made to separate the isomers. Earlier attempts to separate the isomers of the starting complexes CpW-$(CO)_2(PPh_3)$SR were unsuccessful because they equilibrate in solution [1]. The solution IR spectra of the complexes in the ν(CO) and ν(CN) regions were consistent with their formulation and are given in Section 3.

The reactions were monitored by ^1H NMR spectroscopy which demonstrated that the *cis* isomer of the starting complexes was consumed first before the *trans* isomer reacted. The peaks due to the *cis* and *trans* isomers of the products appeared and grew in intensity at the same rate. This observation is consistent with a dissociative mechanism whereby the greater congestion in the *cis* isomers leads to steric acceleration of their rates of reaction. No evidence for possible insertion reactions was detected. A solution of $CpW(CO)_2$(S-4-$C_6H_4Me)CNCMe_3$ in $CDCl_3$ was treated with a slight excess of ligand and its NMR spectrum revealed strong peaks due to the coordinated and free ligands, consistent with very slow ligand exchange on the NMR time scale.

Recrystallization of $CpW(CO)_2$(S-4-$C_6H_4Me)CNCMe_3$ from hexanes gave red crystals, one of which was chosen at random and its structure determined. It proved to be the *trans* isomer. There were two very similar independent molecules in the unit cell; only one (molecule A) is depicted in Fig. 1. Crystal data and atomic coordinates are given in Tables 1 and 2 respectively. The structure is of the classic piano-stool type with the bulky $CNCMe_3$ and S-4-C_6H_4Me groups at extreme range; the latter bent downwards away from the Cp ring. The W–S bond length of 2.501(3) Å is very similar to that observed for $CpW(CO)_3SS$-4-C_6H_4Me (2.506(2) Å) [13] but much longer than that in CpW(η^2-$C_4(CF_3)_4CNMe_3)(SCHMe_2)CNCMe_3$ (2.374(3) Å) [14]. The thiolato and isocyanide ligands are adjacent in this complex owing to the bulky fulvalene ligand. The W–$CNCMe_3$ bond length in our complex is 2.079(12) Å and in the fulvalene complex it is 2.017(9) Å.

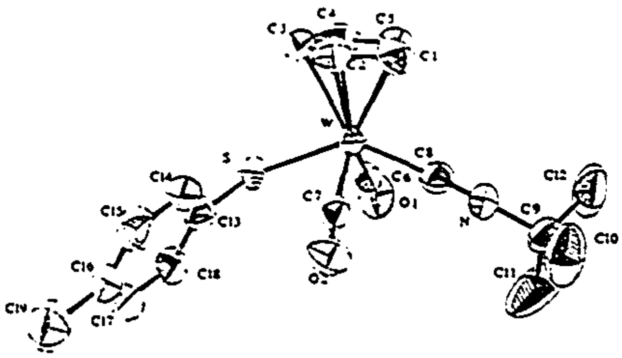

Fig. 1. ORTEP view of *trans*-$CpW(CO)_2$(S-4-$C_6H_4Me)(CNCMe_3)$ (molecule A). Selected bond lengths (Å) and angles (°) are as follows: W–Cp(average), 2.332 (12); W–S, 2.501 (3); W–C(6), 1.990 (13); W–C(7), 1.976 (11); W–C(8), 2.079 (12); S–W–C(8), 138.4 (3); W–S–C(13), 114.6(4); W–C(8)–N, 176.1 (10); C(8)–N–C(9), 176.1 (12).

A sample of the red crystals of *trans*-$CpW(CO)_2$(S-4-$C_6H_4Me)CNCMe_3$ was dissolved in $CDCl_3$ at −60°C. The solution was immediately inserted into the probe of the NMR instrument at room temperature and its spectrum taken. This initial spectrum showed only one set of peaks presumably due to the *trans* isomer (Cp, 5.60 ppm). After 2 min, the peaks due to the *cis* isomer began to appear and, after a further 8 min, equilibrium had been reached. The inability to separate the isomers of any of the isocyanide complexes is consistent with the rapid attainment of equi-

Table 1
X-ray crystallographic data for *trans*-$CpW(CO)_2$(S-4-$C_6H_4Me)(CNCMe_3)$

Chemical formula	$C_{19}H_{21}NO_2SW$
Formula weight	511.28
Space group	$P2_1/a$
a	12.242 (4) Å
b	17.592 (5) Å
c	18.728 (8) Å
β	92.01 (3)°
V	4030.8 (24) Å
Z	2
T	22°C
λ	0.70930 Å^3
ρ_{calc}	1.685 g cm^{-3}
μ(Mo Kα)	59.6 cm^{-1}
Transmission factors	0.14–0.29
R [1]	0.037
R_w [2]	0.026

[1] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[2] $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2
Positional parameters and isotropic thermal parameters for *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$CH$_3$)(CNC(CH$_3$)$_3$) where B_{eq} is the mean of the principal axes on the thermal ellipsoid

	x	y	z	B_{eq} (Å^2)
W	0.03325(4)	0.80443(3)	0.45683(3)	3.62(3)
S	−0.1191(3)	0.88656(17)	0.49786(20)	4.41(18)
O(1)	−0.1391(7)	0.8065(5)	0.3293(4)	7.0(6)
O(2)	−0.0512(7)	0.6928(5)	0.5719(4)	5.8(5)
N	0.0604(9)	0.6391(5)	0.3868(6)	5.4(6)
C(1)	0.2205(9)	0.7968(7)	0.4674(7)	5.2(8)
C(2)	0.1918(10)	0.8363(6)	0.5258(7)	4.8(7)
C(3)	0.1433(10)	0.9065(7)	0.4998(7)	5.7(8)
C(4)	0.1420(10)	0.9067(7)	0.4268(8)	6.2(9)
C(5)	0.1952(10)	0.8389(7)	0.4064(8)	5.9(9)
C(6)	−0.0780(9)	0.8043(6)	0.3768(6)	4.5(7)
C(7)	−0.0249(10)	0.7355(6)	0.5296(6)	3.9(6)
C(8)	0.0531(9)	0.6986(7)	0.4097(6)	4.1(6)
C(9)	0.0617(11)	0.5635(6)	0.3569(7)	4.8(8)
C(10)	0.1049(15)	0.5094(8)	0.4106(8)	9.6(12)
C(11)	−0.0475(15)	0.5439(9)	0.3345(13)	14.8(16)
C(12)	0.1339(15)	0.5660(7)	0.2968(8)	9.5(11)
C(13)	−0.1592(10)	0.8684(6)	0.5874(7)	4.1(7)
C(14)	−0.0836(10)	0.8589(7)	0.6442(8)	5.3(8)
C(15)	−0.1209(11)	0.8486(7)	0.7127(7)	5.8(8)
C(16)	−0.2281(11)	0.8451(6)	0.7254(7)	5.1(7)
C(17)	−0.3010(10)	0.8538(7)	0.6701(8)	6.0(8)
C(18)	−0.2674(9)	0.8648(6)	0.6003(7)	4.5(7)
C(19)	−0.2641(14)	0.8310(7)	0.8015(8)	7.9(10)
W′	1.06084(4)	0.69323(3)	1.06880(3)	3.53(3)
S′	0.9040(3)	0.60800(18)	1.03443(19)	4.47(18)
O(1′)	0.9625(7)	0.7960(5)	0.9467(4)	5.6(5)
O(2′)	0.9028(7)	0.7003(5)	1.1968(5)	6.9(6)
N′	1.0908(9)	0.8619(5)	1.1314(6)	5.8(7)
C(1′)	1.1666(10)	0.5896(6)	1.0281(7)	4.7(7)
C(2′)	1.1726(11)	0.5923(6)	1.1041(7)	5.0(8)
C(3′)	1.2247(10)	0.6600(7)	1.1230(7)	5.1(7)
C(4′)	1.2469(9)	0.7004(7)	1.0599(7)	4.9(7)
C(5′)	1.2112(9)	0.6548(6)	1.0013(7)	4.5(7)
C(6′)	0.9956(10)	0.7573(7)	0.9964(7)	4.7(7)
C(7′)	0.9574(9)	0.6974(7)	1.1481(7)	4.8(7)
C(8′)	1.0844(9)	0.8001(7)	1.1097(7)	4.6(7)
C(9′)	1.0919(11)	0.9383(6)	1.1611(7)	5.6(8)
C(10′)	0.9977(14)	0.9450(8)	1.2074(10)	10.0(12)
C(11′)	1.1951(13)	0.9467(7)	1.2024(9)	8.4(10)
C(12′)	1.0760(18)	0.9941(8)	1.1002(9)	12.2(15)
C(13′)	0.8568(9)	0.6201(6)	0.9433(6)	3.7(6)
C(14′)	0.7494(9)	0.6204(6)	0.9274(7)	4.3(7)
C(15′)	0.7057(10)	0.6254(7)	0.8600(7)	5.5(8)
C(16′)	0.7727(11)	0.6288(7)	0.8028(7)	5.6(7)
C(17′)	0.8857(11)	0.6258(7)	0.8164(7)	5.6(8)
C(18′)	0.9278(10)	0.6209(7)	0.8857(8)	5.2(8)
C(19′)	0.7320(12)	0.6351(7)	0.7255(8)	7.3(9)

librium of the isomers of *trans*-CpW(CO)$_2$(S-4-C$_6$H$_4$-Me)CNCMe$_3$.

3. Experimental section

All reactions were performed in 100 ml three-necked flasks equipped with a nitrogen inlet. Standard inert-atmosphere techniques were used in all manipulations [1,2]. Flasks charged with solids were evacuated twice and filled with nitrogen. Solvents were transferred by syringe. Filtrations were performed under nitrogen, and filtrates were reduced to dryness under vacuum (oil pump). The packing and elution of chromatography columns were performed under nitrogen with solvents which were deoxygenated. Activated alumina (80–200 mesh) was purchased from Anachemia. Recrystallizations were done under nitrogen in three-necked flasks using distilled solvents and were stored at −16°C overnight or longer. The mother liquors were removed via a cannula and the crystals washed with cold hexanes and dried overnight under vacuum. Hexanes were refluxed over sodium metal and benzophenone, and dichloromethane was refluxed over P$_2$O$_5$ under nitrogen. The compounds 2,6-dimethylphenylisocyanide (CN-2,6-C$_6$H$_3$Me$_2$) (Fluka, AG) and *tert*-butylisocyanide (CNCMe$_3$) (Aldrich) were used as purchased. The tungsten thiolates *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)SR, where R = CHMe$_2$ and 4-C$_6$H$_4$Me were prepared according to published procedures [1].

All IR spectra were recorded on a BOMEM Michelson model 100 Fourier transform IR spectrophotometer at 4 cm^{-1} resolution (deuterium triglyane sulfate (DTGS) detector). Solution spectra were recorded by using NaCl cells of 0.1 mm path length. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian XL-200 spectrometer and all chemical shifts are in δ (ppm) units (±0.002 ppm) relative to tetramethylsilane (TMS) at 0 ppm. Elemental analyses were carried out by Spang Microanalytical Laboratories, Eagle Harbour, MI. Melting points were determined in grease-sealed capillary tubes under nitrogen using a Thomas Hoover capillary melting-point (m.p.) apparatus and are uncorrected.

3.1. η^5-Cyclopentadienyl(dicarbonyl)(2-propylthiolato)-(2,6-dimethylphenylisocyanide)tungsten(II), CpW(CO)$_2$-(SCHMe$_2$)(CN-2,6-C$_6$H$_4$Me$_2$)

A three-necked flask was charged with *cis*- and *trans*-CpW(CO)$_2$(PPh$_3$)(SCHMe$_2$) (0.33 g, 0.51 mmol) and CH$_2$Cl$_2$ (40 ml). A solution of CN-2,6-C$_6$H$_3$Me$_2$ (0.08 g, 0.61 mmol) in CH$_2$Cl$_2$ (10 ml) was transferred by cannula to a dropping funnel and added dropwise to the above solution over a period of 30 min. The solution was stirred for 16 h, after which it was reduced to dryness by vacuum pump. The residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and chromatographed on alumina (2.5 × 20 cm). Eluting with hexanes to remove PPh$_3$ followed by 1:1 CH$_2$Cl$_2$: hexanes gave an orange band which contained the product (crude yield, 85%). A brown residue remained at the top of the column. The orange band was reduced to dryness by rotary evaporation and crystallized from hexanes

(−16°C) to give a red solid (0.044 g; 17%; m.p. 90–92°C).

^{1}H NMR ($CDCl_3$): *cis* 7.10 (m, 3H, $C_6H_3Me_2$); 5.62 (s, 5H, Cp); 2.76 (septet, 1H, $CHMe_2$, J(H–H) = 6.6 Hz); 2.45 (s, 6H, $C_6H_3Me_2$); 1.20, 1.33 (dd, 6H, $CHMe_2$); *trans* 7.13 (m, 3H, $C_6H_3Me_2$); 5.48 (s, 5H, Cp); 2.74 (septet, H, $CHMe_2$, J(H–H) = 6.6 Hz); 2.40 (s, 6H, $C_6H_3Me_2$); 1.28 (d, 6H $CHMe_2$); *cis*:*trans*, 1:1.5. IR (cyclohexane): ν(CO) 1904 (s), 1952 (sh, s); ν(CN) 2092 (s) cm^{-1}. Anal. Found: C, 44.73; H, 4.01; N, 2.81; S, 6.20. $C_{19}H_{21}N_1O_2S_1W_1$ calc.: C, 44.63; H, 4.14; N, 2.74; S, 6.27%.

3.2. η^5-Cyclopentadienyl(dicarbonyl)(2-propylthiolato)(tert-butylisocyanide)tungsten(II), $CpW(CO)_2(SCHMe_2)(CNCMe_3)$

As above, *cis*- and *trans*-$CpW(CO)_2(PPh_3)(SCHMe_2)$ (0.35 g, 0.56 mmol) in CH_2Cl_2 (30 ml) was treated with $CNCMe_3$ (0.75 ml, 0.65 mmol) added dropwise via a gas-tight syringe and the solution was stirred for 23 h. The yellow residue obtained from the chromatography column (crude yield, 92%) was crystallized from hexanes to give an orange solid (0.061 g; 32%) and then recrystallized from hexanes to give a light-yellow crystalline solid (0.041 g; 16%; m.p. 68–70%).

^{1}H NMR ($CDCl_3$): *cis* 5.52 (s, 5H, Cp); 2.69 (septet, 1H, $CHMe_2$, J(H–H) = 6.8 Hz); 1.20, 1.27 (dd, 6H, $CHMe_2$); 1.51 (s, 9H, $CNCMe_3$); *trans* 5.32 (s, 5H, Cp); 2.69 (septet, H, $CHMe_2$, J(H–H) = 6.8 Hz); 1.24 (d, 6H, $CHMe_2$); 1.57 (s, 9H, $CNCMe_3$); *cis*:*trans*, 1:1.4. IR (cyclohexane): ν(CO) 1898 (sh, s), 1952 (sh, s); ν(CN) 2119 (s) cm^{-1}. Anal. Found: C, 38.77; H, 4.58; N, 2.96; S, 6.86. $C_{15}H_{21}N_1O_2S_1W_1$ calc.: C, 38.98; H, 4.57; N, 3.02; S, 6.92.

3.3. η^5-Cyclopentadienyl(dicarbonyl)(4-methylphenylthiolato)(2,6-dimethylphenylisocyanide)tungsten(II), $CpW(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CN\text{-}2,6\text{-}C_6H_3Me_2)$

As above, *cis* and *trans*-$CpW(CO)_2(PPh_3)(S\text{-}4\text{-}C_6H_4Me)$ (0.23 g, 0.33 mmol) in CH_2Cl_2 (25 ml) was treated with $CN\text{-}2,6\text{-}C_6H_3Me_2$ (0.06 g, 0.40 mmol) in CH_2Cl_2 (10 ml), added dropwise, and the solution was stirred for 23 h. During this time, the color changed from orange to bright red. The orange residue from the chromatography (crude yield, 83%) was crystallized from hexanes to give red crystals (0.055 g; 30%: m.p. 96–98°C).

^{1}H NMR ($CDCl_3$): isomer A 7.13, 7.33 (m, 3H, $CNC_6H_3Me_2$); 6.87 (m, 4H, SC_6H_4Me); 5.66 (s, 5H, Cp); 2.21 (s, 3H, SC_6H_4Me); 2.34 (s, 6H, $CNC_6H_3Me_2$); isomer B 7.09, 7.30 (m, 3H, $CNC_6H_3Me_2$); 6.97 (m, 4H, SC_6H_4Me); 5.53 (s, 5H, Cp); 2.28 (s, 3H, SC_6H_4Me); 2.66 (s, 6H, $CNC_6H_3Me_2$); ratio of isomers, 1:1.1. IR (cyclohexane): ν(CO) 1912 (s), 1960 (sh, s); ν(CN) 2092 (s) cm^{-1}. Anal. Found: C, 49.20; H, 3.79; N, 2.43; S, 5.73. $C_{23}H_{21}N_1O_2S_1W_1$ calcd.: C, 49.39; H, 3.78; N, 2.50; S, 5.73%.

3.4. η^5-Cyclopentadienyl(dicarbonyl)(4-methylphenylthiolato)(tert-butylisocyanide)tungsten(II), $CpW(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CNCMe_3)$

As above, *cis*- and *trans*-$CpW(CO)_2(PPh_3)(S\text{-}4\text{-}C_6H_4Me)$ (0.21 g, 0.31 mmol) in CH_2Cl_2 (30 ml) was treated with $CNCMe_3$ (0.50 ml, 0.44 mmol) for 17 h. During this time, the color changed from orange to red. The orange residue obtained from the chromatography (crude yield, 89%) was crystallized from hexanes to give orange–red crystals as thin plates (0.095 g; 60%, m.p. 89–92°C).

^{1}H NMR ($CDCl_3$): *trans* 6.94 (AB quartet, 4H, SC_6H_4Me, J(H–H) = 4.9 Hz); 5.60 (s, 5H, Cp); 2.27 (s, 3H, SC_6H_4Me); 1.32 (s, 9H, $CNCMe_3$); *cis* 7.27 (AB quartet, 4H, SC_6H_4Me), J(H–H) = 7.9 Hz); 5.38 (s, 5H, Cp); 2.25 (s, 3H, SC_6H_4Me); 1.57 (s, 9H, $CNCMe_3$); ratio of isomers, 1:1.2. IR (cyclohexane): ν(CO) 1904 (sh, s), 1961 (s); ν(CN) 2135 (sh, s) cm^{-1}. Anal. Found: C, 44.59; H, 4.29; N, 2.67; S, 6.10. $C_{19}H_{21}N_1O_2S_1W_1$ calc.: C, 44.63; H, 4.14; N 2.74; S, 6.27%.

3.5. X-ray structure determination

Table 1 contains the crystal parameters for *trans*-$CpW(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CNCMe_3)$. Single crystals suitable for crystallographic studies were obtained by recrystallization from hexanes. A red crystal was glued with epoxy in a thin-walled glass capillary. Cell dimensions were obtained from 25 reflections with 2θ in the range 30.00–35.00°. A total of 5552 reflections were collected using the ω–2θ scan technique, where $2\theta < 50°$ on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation ($-13 \leq h \leq 13$; $0 \leq k \leq 18$; $0 \leq l \leq 20$); of these, 5256 were unique (merging $R = 2.6\%$) and 3012 having $I > 2.5\sigma$ were used in the final cycle of full-matrix least-squares refinement. The intensities of three representative reflections remained constant throughout data collection. An absorption correction was made from four ψ scans. The structure was solved by direct methods followed by a difference Fourier technique. An extinction correction was made. Anisotropic thermal parameters were used for all non-hydrogen atoms. All hydrogen atoms were added in calculated positions. All computing was performed using the NRCVAX system of programs [15].

4. Supplementary material available

An ORTEP drawing of molecule A′ of *trans*-$CpW(CO)_2(S\text{-}4\text{-}C_6H_4Me)(CNCMe_3)$, a full-length table of crystallographic data, a table of anisotropic temperature parameters, a table of bond lengths and angles, a table of hydrogen atom coordinates, and a table of observed and calculated structure factors are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Any request should be accompanied by the full literature citation for this communication.

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