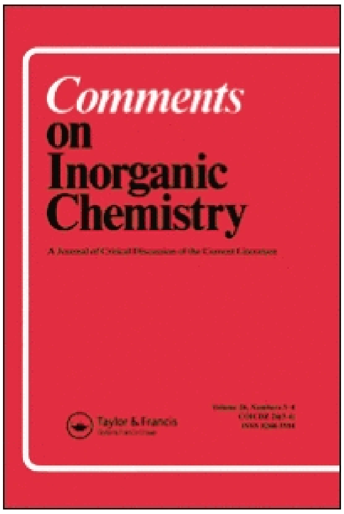

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A Framework for the Classification of Organosulfur Transition Metal Complexes

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A Framework for the Classification of Organosulfur Transition Metal Complexes

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More than 500 publications on the synthesis and reactivity of organosulphur transition metal complexes have appeared, but no coherent picture of the relations between the various compounds or their synthesis has emerged yet. A framework, based on simple formal conversions of thiocarbonyl and carbon disulfide complexes and the derived compound types, is now presented. The ten classes of compounds are obtained by various types of reactions of which alkylation, protonation, hydride addition, deprotonation, sulfur insertion and fragmentation are the most important.

Key Words: *organosulfur compounds, sulfur-containing metal complexes*

INTRODUCTION

The versatility of sulfur as the heteratom in hetero-organic ligands (combined with the ingenuity and luck of synthetic chemists) has been the source of the diversity of organosulfur ligands that exist. Various reviews have dealt with specific types of compounds[1] but a full picture of organosulfur coordination chemistry is still lacking.

As a first step towards providing some insight into the field as a whole, we created a simple scheme according to which a large number of organosulfur complexes can be organized, and also identified some of the methods by which the ligands in these compounds are produced.

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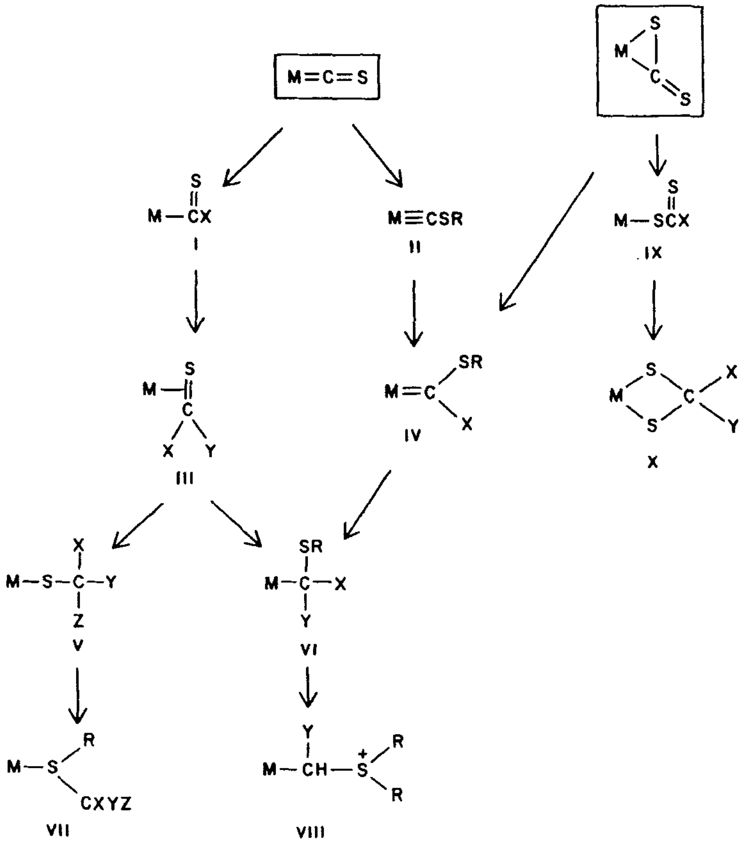
If only the carbon and sulfur atoms coordinated to the metal, and their α (and sometimes β) substituents are considered, ten basic structural types can be identified (Scheme I, Table I). Starting from coordinated CS or CS_2, the simplest organosulfur ligands, each type of ligand is related to the next by the addition of H, R or SR.

In some cases these formal progressions represent the outcome of actual reactions: H can be added either as H^+ or H^-, R as R^+, R^- or as an acetylene (sometimes combined with insertion of CO), and SR can be added either in electrophilic or nucleophilic form



SCHEME I

TABLE I

Basic types of metal coordinated organosulfur ligands
(see Scheme I).

Type	X	Y	Name
I.1	H		Thioformyl
I.2	R		Thioacyl
I.3	SR		Organodithiocarboxyl
II	(R)		Thiocarbyne
III.1	H	H	Thioformaldehyde
III.2	H	R	Thioaldehyde
III.3	H	SR	Organodithioformate
III.4	R	R	Thioketone, thioketene
III.5	R	SR	Dithioester
III.6	SR	SR	Di-organo trithiocarbonate
IV.1	H		Thiocarbene
IV.2	R		Organo(thio)carbene
IV.3	SR		Dithiocarbene
V	H,R	H,R	Thiolate (Z = H,R)
VI	H,R,SR		(Organothio)alkyl
VII	H,R	H,R	Thioether (Z = H,R)
VIII	(H)	H,R	Sulfonium
IX	H,R		Dithiocarboxylate
X	H	H	
X	R	R	Dithiolate
X	SR	SR	

(SR^+ or SR^-). Reactions involving H or SR groups can also occur in the direction opposite to that shown in Scheme I. These addition and elimination reactions constitute conversions between different structural types of organosulfur ligands already coordinated to a metal.

One also has to consider those organosulfur ligands which, although they can belong to any of the structural types in Scheme I, do not start out as modifiable coordinated organosulfur precursors, but either as organometallic complexes to which sulfur (as S or S^{2-}) is added, or as metal sulfides to which an organic fragment is added, or, alternatively, as organosulfur compounds that fragment in the coordination sphere of the metal through the scission of C–S bonds.

Variants of the last source are organosulfur compounds that retain their original frames, but in which the electron density is redistributed, as in the formal conversion of C–S double bonds to single bonds (sometimes with concomitant migration of hydrogen) which, for instance, occurs during certain orthometallation reactions. One also encounters compounds like diazomethane and 1,2,3-thiadiazoles that eliminate N_2 to produce reactive organic or organosulfur fragments.

Reactions in which ligands coordinate to the metal without being modified in any way (usually as sulfur-donor Lewis bases) and ion exchange reactions will not be considered in this review although many of the complexes produced may, of course, be accommodated in the scheme.

Although one will also come across complex, multi-step synthetic procedures, these can usually be broken down into combinations of the simple reactions which comprise the main routes leading to organosulfur complexes. These routes can be summarized as follows:

1. Modification of an existing organosulfur ligand by addition or elimination of H, R or SR.
2. Incorporation of S into an organometallic complex.
3. Addition of an organic reagent to a metal sulfide.
4. (a) Fragmentation of an organosulfur compound in the presence of a metal complex.
   (b) Electron redistribution in an organosulfur compound.
5. Coordination of an unmodified ligand.

Rather than attempting to cover the whole body of available literature, the examples cited in this review serve to illustrate structural types and main synthetic routes. A more comprehensive review of organometallic organosulfur and organoselenium complexes has been published.[2]

The "missing" types in the scheme, like $M{\equiv}CSH$ (II), MSC(X)(Y)Z (X, Y or Z = SR) (V) and MC(X)(Y)SH (VI), indicate types of compounds that have not been prepared yet.

A major obstacle in trying to obtain a comprehensive view of organosulfur coordination chemistry is the lack of generalization. In only a few reactions has the metal been varied and variation of ligands is usually restricted to changing the substituents on phosphine ligands or exchanging CO and CNR. Unfortunately, in the quest for novelty, the "mopping-up" work required to fully recognize and understand patterns in reactivity is usually neglected, or, in instances where negative results are obtained, not reported.

STRUCTURAL TYPES OF ORGANOSULFUR COMPLEXES

I.1 Thioformyl, $[\mathrm{M\{C(S)H\}}]$

The only stable thioformyl complexes mentioned in the literature are osmium compounds like $[\mathrm{Os\{C(S)H\}Cl(CO)_2(PPh_3)_2}]$, formed via the internal transfer of hydride to CS by treating $[\mathrm{OsH(Cl)(CS)(PPh_3)_3}]$ with CO,[3] and $[\mathrm{Os_3(CO)_9\{\mu_3\text{-}C(S)H\}(\mu\text{-}H)}]$, formed by hydride abstraction from the thioformaldehyde complex, $[\mathrm{Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}SCH_2)}]$.[4]

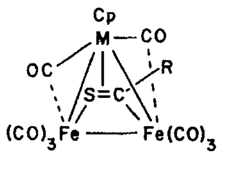
I.2 Thioacyl, $[\mathrm{M\{C(S)R\}}]$

In a simple modification reaction, the thioketene ligand in $[\mathrm{Fe_2(CO)_6}\{\mu\text{-}\mathrm{S{=}C{=}CR_2}\text{–}\mu S, \mu C^1\}]$ ($\mathrm{R_2 = Me_2C(CH_2)_3CMe_2}$) adds $\mathrm{H^-}$ to form the anionic thioacyl complex, $[\mathrm{Fe_2(CO)_6}\{\mu\text{-}\mathrm{C(S)CHR_2}\text{–}\mu C^1, \mu S\}]^-$.[5]

Internal transfer of an R group to CS occurs during the preparation of $[\mathrm{Os\{\eta^2\text{-}C(S)CPh{=}CHPh\}Cl(CO)(PPh_3)_2}]$ from $[\mathrm{Os(CPh{=}CHPh)Cl(CS)(PPh_3)_2}]$ and CO,[6] and of $[\mathrm{Os}\{\eta^2\text{-}\mathrm{C(S)C_6H_4Me}\text{-}p\}\mathrm{X(L)(PPh_3)_2}]$(X = Cl, Br, I, $\mathrm{O_2CCF_3}$; L = CO, $\mathrm{CNC_6H_4Me}$-*p*) when $[\mathrm{Os(C_6H_4Me}\text{-}p\mathrm{)X(L)(CS)(PPh_3)_2}]$ is heated.[7]

The metallacyclic compounds, $[\mathrm{Os\{C(S)CPh{=}CPh\}(CO)_2(PPh_3)_2}]$[6] and $[\mathrm{Os\{C(S)CH{=}CHCH{=}CH\}(CO)(PPh_3)_2}]$,[8] contain unsaturated R groups attached to CS and are obtained from the reaction of $[\mathrm{Os(CO)(CS)(PPh_3)_3}]$ with the acetylenes, $\mathrm{PhC{\equiv}CPh}$ and $\mathrm{HC{\equiv}CH}$.

Many thioacyl complexes have been prepared by the addition of S to carbyne ligands, for instance the monomeric $[\mathrm{Os}\{\eta^2\text{-}\mathrm{C(S)C_6H_4Me}\text{-}p\}\mathrm{Cl(CO)(PPh_3)_2}]$,[9] the dinuclear $[\mathrm{Fe(CO)_3}\{\mu\text{-}\mathrm{C(S)C_6H_4Me}\text{-}p\text{–}\mu C^1,\mu S\}\mathrm{ML(CO)_2}]$ (M = Mo, L = Cp; M = W; L = $\eta^5\text{–}\mathrm{C_5Me_5}$) and the trinuclear complex, 1 (M = Mo, R = $\mathrm{C_6H_4Me}$-*p*; M = W, R = Me).[10]



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Fragmentation of ligands of the type, $S{=}C(SR^1)OR^2$ (R^1 = Me, CH_2Ph; R^2 = cholestanyl, cholesteryl, menthyl and others) occurs in the presence of $[Fe_2(CO)_9]$ and leads to complexes with the general structure, $[Fe_2(CO)_6\{\mu\text{-}C(S)OR^2-\mu(C,S)\}(\mu\text{-}SR^1)]$. In the original publication these are described as carbene complexes on the basis of their ^{13}C NMR data.[11] Molybdenum complexes from $S{=}C(SR^1)R^2$ (R^1 = Et, $CH_2C_6H_4OMe\text{-}p$; R^2 = Me, CH_2Ph[12]; $R^1R^2 = (CH_2)_3$[13]) and $[(C_5H_4R)Mo(CO)_2]_2$ (R = H, Me) were reported.

I.3 Organodithiocarboxyl, [M{C(S)SR}]

A general method of preparing these ligands is the addition of R (as R^+ or an acetylene) to coordinated CS_2. Alkylation leads to complexes like $[Os\{\eta^2\text{-}C(S)SMe\}(CO)_2(PPh_3)_2]^+$, to Ru,[14] Fe[15] and W[16] complexes with similar ligands, and to the niobium complex, $[Cp_2NbBu\{\eta^2\text{-}C(S)SR\}]^+$ (R = Me, Et, Pr^i, CH_2CO_2Et).[17] Chelating vinyl–dithiocarboxyl complexes, $L_n\overline{M-C(S)SC(Z){=}C}(Z)$, are produced in the reaction between activated acetylenes ($ZC{\equiv}CZ$) and CS_2 complexes of Fe,[18] Rh[19] and Mo.[20]

The complex, $[CpFe\{C(S)SPh\}(CO)_2]$, was prepared from a thiocarbonyl complex to which PhS^- was added[21] and an anionic methyldithiocarboxyl intermediate forms when the dithioformate ligand in $[Fe_2(CO)_6\{\mu\text{-}S{=}CHSMe-\mu S^1,C,S^2\}]$ is deprotonated.[22]

The dialkyltrithiocarbonates, $S{=}C(SR^1)SR^2$ (R^1, R^2 = Me, CH_2–ferrocenyl), $S{=}\overline{CS(CH_2)_nS}$, (n = 2,3), and coordinated $S{=}C(SCH{=}CH_2)SMe$ fragment to the alkyldithiocarboxyl complexes, $[Fe_2(CO)_6\{\mu\text{-}C(S)SR^2-\mu(C,S^1)\}(\mu\text{-}SR^1)]$,[23] $[\overline{Pt\{C(S)\text{-}S(CH_2)_nS}\}(PPh_3)_2]$[24] and $[Fe_2(CO)_6\{\mu\text{-}C(S)SCH{=}CH_2-\mu(C,S^1)\}\text{-}(\mu\text{-}SMe)]$.[25]

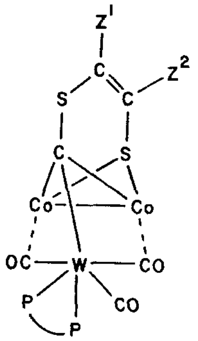
II. Thiocarbyne, [M(CSR)]

The addition of R, in the form of R^+, to thiocarbonyl ligands is a widely used method for the preparation of thiocarbyne complexes and has been reported for tungsten,[26] dimeric iron,[27] dinuclear mixed metal (Co, Mn; Rh, Mn[28] and Mn, Pt[29]) and trinuclear cobalt[30] complexes. Nucleophilic PhLi and MeLi (R^-) were used to convert $[CpWI(CO)(CS)PPh_3]$ and *trans*-$[HB(pz)_3WI(CO)_2CS]$ to thiocarbyne complexes (pz = 1-pyrazolyl).[31]

By deprotonating the thiocarbene complex, $[HB(pz)_3W(\eta^2\text{-}CHSMe)(CO)_2]^+$, H is eliminated to produce the thiocarbyne complex, $[HB(pz)_3W(CO)_2CSMe]$.[32]

Metal or sulfur centered anionic nucleophiles cause fragmentation of the dithiocarbene ligand in $[HB(pz)_3W(CO)_2\{\eta^2\text{-}C(SMe)SMe\}]^+$ to form the thiocarbyne complex $[HB(pz)_3W(CO)_2CSMe]$,[33] but in the case of the dimeric iron dithiocarbene complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)SPh\}]$, irradiation or heating is required to form the thiocarbyne and thiolate ligands in $[CpFe(CO)(\mu\text{-}CO)(\mu\text{-}CSMe)Fe(SPh)Cp]$.[34]

Further examples of dithiocarbenes that split into thiocarbyne and thiolate ligands were noted for **2**, obtained by treating $[W(CO)_3\{\overline{CSC(Z^1){=}C(Z^2)S}\}\widehat{L\,L}]$ (Z = H, CO_2Me, CF_3; $\widehat{L\,L}$ = dmpe, dppe) with $[Co_2(CO)_8]$[35] and a platinum complex reported by Ma *et al.*[36] (dmpe = dimethylphosphino ethane; dppe = diphenylphosphino ethane).



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III.1 Thioformaldehyde, $[M(S{=}CH_2)]$

The first thioformaldehyde complex to be reported, $[Os(CO)_2(PPh_3)_2(\eta^2\text{-}S{=}CH_2)]$, was prepared by Collins and Roper[3] by treating a thioformyl complex with H^-.

Several other starting materials have been used in the preparation of thioformaldehyde complexes, for example, $M{=}CH_2$ complexes like $[CpRe(CH_2)(NO)PPh_3]^+$,[37] $[OsCl(CH_2)(NO)(PPh_3)_2]$,[38]

$[Os_3(CO)_{10}(\mu\text{-}CH_2)]$[4] and $[Cp_2Ti(CH_2)PMe_3]$[39] that abstract sulfur from various sources, MCH_2I complexes of Rh,[40] and Co[41] that react with HS^- and bridging sulfides of Cr,[42] Mn[43] and W[44] that are converted to asymmetrically bridged thioformaldehyde complexes by reaction with CH_2N_2.

III.2 Thioaldehyde, $[M(S{=}CHR)]$

Reactions involving addition to or elimination of H from existing organosulfur ligands are represented by the catalytic hydrogenation of the thioketene ligand in $[CpRh(PPr^i_3)(\eta^2\text{-}S{=}C{=}CH_2)]$ which leads to the thioaldehyde complex, $[CpRh(PPr^i_3)(\eta^2\text{-}S{=}CHMe)]$,[40] protonation of the thioacyl complex, $[Fe_2(CO)_6\{\mu\text{-}C(S)CHR_2\text{-}\mu C^1,\mu S\}]^-$ ($R_2 = Me_2C(CH_2)_3CMe_2{}^5$, Section I.2), and the internal deprotonation of $[Cp_2Zr(Me)SCH_2R]$ (R = Me, Ph; in the presence of PMe_3) to form $[Cp_2Zr(\eta^2\text{-}S{=}CHR)PMe_3]$ with concomitant release of CH_4.[45]

Insertion of sulfur, originating from SCN^- or S_8, into the M=C bond of $[M(CHAr)(CO)_5]$ carbene complexes results in Cr and W thioaldehyde complexes, $[M(CO)_5S{=}CHAr]$ ($Ar = C_6H_4X\text{-}p$, X = OMe, H, CF_3, Me).[46] The unusual transfer of both a sulfur atom and a proton from the salt, $[H_2NEt_2][S_2CNEt_2]$, to the carbyne ligand in $[WCl(CR)(CO)_2(py)_2]$ (R = Me, Ph; py = pyridine), produces the thio-aldehyde complexes, $[W(S_2CNEt_2)(CO)(\eta^2\text{-}S{=}CHR)SCNEt_2]$.[47]

III.3 Alkyldithioformate, $[M(S{=}CHSR)]$

Alkyldithioformate ligands can be prepared by the addition of H^- to alkyldithiocarboxyl ligands, $-C(S)SR$, as in the preparation of the iron and niobium complexes, $[Fe(CO)(\eta^2\text{-}S{=}CHSMe)(PMe_3)_2L]$ (L = CO, PMe_3)[48] and $[Cp_2NbBu(\eta^2\text{-}S{=}CHSR)]$ (R = Me, Et, Pr^i, CH_2CO_2Et).[17]

In an alternative method the tungsten alkyldithioformate complexes, $[W(CO)_3(\eta^2\text{-}S{=}CHSR)dppe]$ (R = Me, Et, CH_2Ph) were synthesized by alkylating the dithiocarboxylate complex, $[W\{SC(S)H\}(CO)_3dppe]^-$ (type IX).[49]

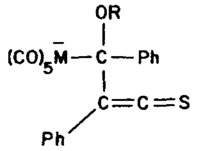
III.4 Thioketone, $[M(S{=}CR_2)]$ and Thioketene, $[M(S{=}C{=}CR_2)]$

The only preparative reaction for thioketone and thioketene ligands that occurs in the coordination sphere of the metal is the insertion of S into the M=C bond of diarylcarbene and vinylidene complexes. H. Fischer reports a number of thioketone complexes, $[W(CO)_5\{S{=}CPh(C_6H_4X\text{-}p)\}]$ (X = H, Me, OMe, Br, CF_3) prepared according to this method by utilizing either S_8[50] or an organic isothiocyanate, RN=C=S (R = Me, Et, Ph)[51] as sources of sulfur. The thioketene complexes, $[CpRh(PPr^{i}_{3})(\eta^2\text{-}S{=}C{=}CHR)]$ (R = H, Me, Ph) are produced by treating the vinylidene complexes, $[CpRh(C{=}CHR)PPr^{i}_{3}]$ with S_8.[52]

During the reaction of $[Mn_2(CO)_{10}]$ with diaryl thioketones of the type, $S{=}C(C_6H_4NR_2\text{-}p)_2$ (R = Me, Et), the organosulfur compound is orthometallated, but the C=S double bond is retained and the ligand is still regarded as a thioketone.[53] (See also Section V.)

III.5 Dithioester, $[M\{S{=}C(SR)R\}]$

Only one method for the preparation of dithio-ester ligands in the coordination sphere of metals has been reported yet, but normally, in iron carbonyl[54,55] or molybdenum[12] complexes, for instance, the ligands coordinate with their original structures intact.



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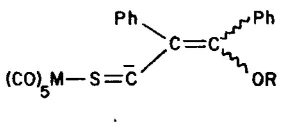
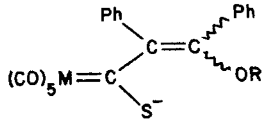


3a



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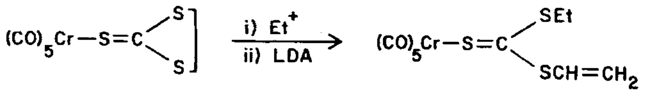
The thioketene adduct, **3** (M = Cr, W; R = Me, Et) obtained from the reaction between the thioacetylene anion $PhC{\equiv}CS^-$ and a Fischer carbene complex, serves as a synthon either for an anionic thioacyl ligand, as in **3a**, or for an anionic vinyl thiocarbene ligand (see Section IV.2), depending on the electrophile added. By adding RSSR the dithio-ester complexes, $[M(CO)_5\{S{=}C(SR^1)C(Ph)\text{-}$

$=C(OR^2)Ph]$ (M = Cr, W; R^1 = Me, Et, Ph; R^2 = Me, Et) are obtained,[56] and when S_8, followed by an acid, is added, the heterocyclic dithio-ester complexes, $[M(CO)_5\{S{=}\overline{CSSC(Ph){=}C}Ph\}]$ (M = Cr, W) form (with elimination of OR^2).[57]

III.6 Dialkyltrithiocarbonate, $[M\{S{=}C(SR)_2\}]$

A reaction in which the metal plays a role during the construction of the ligand is that between thiirane, $\overline{SCH_2CHR}$ (R = H, Me) and the CS_2 complex, $[W(CO)_3(\eta^2\text{-}CS_2)\overset{\frown}{L\,L}]$ ($\overset{\frown}{L\,L}$ = dppe, dmpe, 1,2-$C_6H_4(PPh_2)_2$) resulting in the cyclic dialkyltrithiocarbonate ligand in $[W(CO_3)(\eta^2\text{-}S\overline{CSCH_2CHRS})\overset{\frown}{L\,L}]$.[16]

Dialkyl trithiocarbonates in polymetallic systems usually coordinate as S donor ligands with their original structures intact. In two closely related reactions involving coordinated ethylene trithiocarbonate, deprotonation causes the ligand to rearrange and form new dialkyl trithiocarbonate ligands[58,25] (**4** and **5**):



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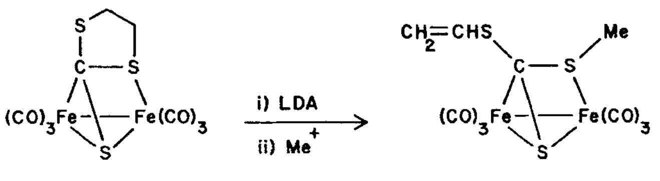

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IV.1 Thiocarbene, [M(CHSR)]

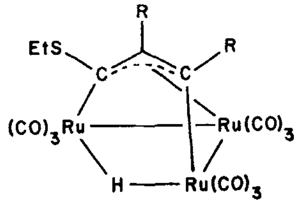
The synthetic procedures for thiocarbene complexes mainly involve modifications of existing organosulfur ligands by the addition or elimination of H, R or SR. The thiocarbyne complex, $[HB(pz)_3W(CO)_2CSMe]$ is protonated to generate the carbene complex, $[HB(pz)_3W(\eta^2\text{-}CHSMe)(CO)_2]^+$,[32] whereas $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CSR)]^+$ (R = CH_2Ph, Me, $CH_2{=}CHCH_2$) reacts with H^- to produce $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHSR)]$.[34]

An alkyl group is added to the thioformyl ligand in $[Os\{C(S)H\}Cl(CO)_2(PPh_3)_2]$ to form $[OsCl(CHSMe)(CO)_2(PPh_3)_2]^+$,[3] whereas SR is eliminated from the alkyl complexes, $[CpFe\{CH(SMe)_2\}(CO)L]$ (L = CO, PPh_3, $P(OPh)_3$),[59] $[CpFe(CH_2SPh)(CO)_2]$[60] and $[HB(pz)_3W(CO)_2\{\eta^2\text{-}CH(SMe)SEt\}]$[61] by reacting with Ph_3C^+ to lead to the thiocarbene complexes $[CpFe(CO)(CHSMe)L]^+$ (unstable), $[CpFe(CO)_2CHSPh]^+$ and $[HB(pz)_3W(CO)_2(\eta^2\text{-}CHSR)]^+$ (R = Me, Et), respectively.

IV.2 Organo(thio)carbene, [M{C(SR)R}]

Both thiocarbonyl and thioacyl complexes yield thiocarbene complexes upon alkylation. The complexes, $[CpMI\{C(SMe)Me\}PPh_3]^+$, M = Rh, Ir[62] and $[Ir(C_6F_5)I_2\{C(SMe)Me\}(PPh_3)_2]$[63] are obtained by alkylating the thiocarbonyl complexes, $[CpM(CS)PPh_3]$ and $[Ir(C_6F_5)(CS)(PPh_3)_2]$, and thioacyl complexes, [M{C(S)R}], lead to the organothiocarbene complexes, $[OsCl\{\eta^2\text{-}C(SMe)C_6H_4\text{-}Me\text{-}p\}(CNC_6H_4Me\text{-}p)(PPh_3)_2]^+$,[7] $[Os\{C(SMe)CPh{=}CPh\}(CO)_2(PPh_3)_2]^+$,[6] $[Os\{C(SR)CH{=}CHCH{=}CH\}(CO)_2(PPh_3)_2]^+$ and $[OsX\{C(SR)CH{=}CHCH{=}CH\}(CO)(PPh_3)_2]$ (R = H, Me; X = Cl, I).[8] Although the authors describe the last two complexes as metallabenzenes they can, in effect, be regarded as alkylthiocarbene complexes. The compounds with R = H are rare examples of mercaptocarbene complexes, [M{C(SH)R}].

The thiocarbyne complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CSMe)]^+$, is converted to an alkyl thiocarbene complex, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)CH_2Ph\}]$ by reacting with nucleophilic $PhCH_2^-$,[34] and in the complex, **6**, prepared by adding an alkyne to the triply bridged CSEt ligand in $[Ru_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CSEt)]$,[64] a vinyl(thio)carbene is present in a less obvious form as one of the contributing structures, $EtS{-}\ddot{C}{-}C(R){=}CR{-}\mu C^1, \mu C^3$, of the allyl sulfide ligand.



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The carbyne complexes, $[CpW(CR)(CO)_2]$ ($R = C_6H_4Me$-*p*), require electrophilic SMe^+ to form the compounds $[CpW\{\eta^2\text{-}C(SMe)R\}(CO)_2]^+$.[65]

By the addition of H_2S or MeSH to the $C{=}CH_2$ bond of the vinylidene complex, $[CpFe(C{=}CH_2)(CO)PPh_3]^+$, the mercaptocarbene (R = H) or alkyl(thio)carbene (R = Me) complexes $[CpFe\{C(SR)Me\}(CO)PPh_3]^+$ can be prepared.[66] A vinylidene complex, $[CpFe(C{=}CH_2)(CO)_2]^+$, has been suggested as the intermediate in the reaction between $[CpFe\{C(O)Me\}(CO)_2]$ and $(CF_3SO_2)_2O$. Further reaction with RSH (R = Me, Ph) leads to the methyl(thio)carbene complexes $[CpFe\{C(SR)Me\}(CO)_2]^+$.[60]

Starting out from adduct **3** (Section III.5) and by adding the alkylating agent, $[Et_3O][BF_4]$ or MeI as electrophiles, the adduct operates as a synthon for **3b** and the vinyl(thio)carbene complexes $[M\{C(SR^1)C(Ph){=}C(OR^2)Ph\}(CO)_5]$, (M = Cr, W; R^1, R^2 = Me, Et) are produced.[56] When Se_8 is added, followed by an acid, the heterocyclic thiocarbene ligand in $[W\{\overline{CSSeC(Ph){=}CPh}\}(CO)_5]$ is obtained.[57]

IV.3 Dithiocarbene, $[M\{C(SR)_2\}]$

Many procedures for the synthesis of dithiocarbene complexes have been covered in the review by Angelici *et al.*[1c] and will be mentioned only briefly. These include alkylation of alkyldithiocarboxyl complexes, $[M\{C(S)SR\}]$, alkylation of CS_2 complexes, and addition of activated acetylenes to coordinated CS_2 to give $[M\{\overline{CSC(Z){=}C(Z)S}\}]$ complexes. The last reaction type, usually applied to Fe complexes, has been extended to include Mn[67] and W[35] complexes and a proposed Rh intermediate.[68]

Thiocarbonyl complexes were converted into dithiocarbene complexes by successive treatment with RS^- and R^+.[1c] When ethylene sulfide is added to the thiocarbonyl complex, $[CpFe(CO)_2(CS)]^+$, the cylic dithiocarbene complex, $[CpFe(CO)_2(\overline{CSCH_2CH_2S})]^+$ results.[69] This can, in a sense, be regarded as the simultaneous addition of RS and R, a reaction reminiscent of the preparation of a dialkyl trithiocarbonate ligand from a CS_2 complex and a thiirane (Section III.6).

A method used for the first time only recently is the addition of SR to a thiocarbyne ligand. Doyle and Angelici, and Schroeder *et al.* made use of electrophilic MeS^+ and nucleophilic RS^- in their preparation of $[HB(pz)_3W(CO)_2\{\eta^2\text{-}C(SMe)SMe\}]^+$[33] and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(SMe)SR\}]$ (R = Me, Ph, CH_2Ph),[34] respectively.

The alkyl complex, $[CpFe\{C(SMe)_3\}(CO)_2]$, loses SMe and $[CpFe\{C(SMe)_2SR\}(CO)_2]$ loses SMe or SPh upon reaction with acids to form $[CpFe(CO)_2\{C(SMe)_2\}]^+$ and $[CpFe(CO)_2\{C(SMe)SR\}]^+$ or $[CpFe(CO)_2\{C(SMe)_2\}]$, respectively.[70] The suggested equilibrium between the alkyl complex, $[CpFe\{\eta^2\text{-}C(SMe)(SMe)_2\}CO]$, and the dithiocarbene–thiolate complex, $[CpFe(SMe)(CO)\{C(SMe)_2\}]$, also involves dissociation of SMe from the alkyl ligand,[71] but in this case the thiolate ligand is retained in the coordination sphere of the metal. A similar type of equilibrium for $Li[C(SPh)_3]$ has been discussed in Ref. 2.

Dialkyl trithiocarbonates may be desulfurized in the presence of metal complexes, and compounds like $[Fe_3(CO)_8(\overline{CSCH{=}CHS})(\mu_3\text{-}S)_2]$[72] and $[Fe_3(CO)_9(\mu_3\text{-}\overline{CSCH_2CH_2S}\text{-}\mu C^1,S^1)(\mu_3\text{-}S)]$[73] resulted from the reaction of $\overline{S{=}CSCH{=}CHS}$ and $[Cr(CO)_5(S{=}\overline{CSCH_2CH_2S})]$ with $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$.

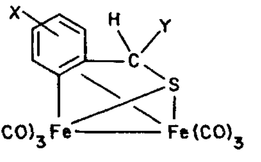
The dinuclear mixed metal complexes, $[Cp(CO)M^1(\mu\text{-}CO)\{\mu\text{-}C(SR)\overline{SR\}M^2}(CO)L]$, ($M^1$ = Fe, Ru; M^2 = Co, Fe; L = CO, NO; R = Me; RR = $(CH_2)_n$, n = 2,3) were obtained by reacting $[CpM^1(CO)\{C(SR)_2\}NCMe]^+$ with $[Co(CO)_4]^-$ or $[Fe(CO)_3NO]^-$.[74] This is in contrast with reactions discussed in Section II where treatment of a tungsten dithiocarbene complex with anionic metallic nucleophiles caused the ligand to split into thiocarbyne and thiolate fragments.

V. Thiolate

Although the method of preparing thiolate complexes by a reaction between a metal complex and HSR to give $[M_2(CO)_6(\mu\text{-}SR)_2]$ (M = Fe, Co; R = Et, Ph),[75] for instance, is still widely used, other methods have become known since. No attempt will be made to give a complete list of reactions leading to thiolate ligands and examples will be selected where patterns have begun to emerge.

Many complexes of type III, ($[M\{S{=}C(X)Y\}]$; X, Y = H or R), add H by protonation, reaction with H^-, or insertion into an

M–H bond to form thiolate ligands. The thioformaldehyde ligand, $S{=}CH_2$, is protonated to give methylthiolate in Co,[41] Rh[40] and Os[3] complexes or treated with hydride in a rhenium complex reported by Buhro *et al.*[37]



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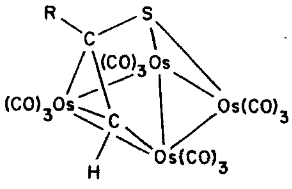
Thiolate ligands like that in **7** form via orthometallation of thioketones, $S{=}CR_2$, containing aryl substituents. A proton from the aryl ring is transferred to the $C{=}S$ carbon and the double bond changes to a single bond; X can be H, OMe, NMe_2, CF_3 or Br and Y C_6H_4H-*p*, OMe or OPr^i.[76,77]

In the ruthenium complex, $[Ru_2(CO)_6(\mu\text{-}\eta^2\text{-}S{=}C{=}CR_2\text{-}\mu S, C^1)_2]$ (R_2 = $Me_2C(CH_2)_3CMe_2$), the $C{=}S$ carbon of one ligand is protonated and then the other reacts with hydride to give the two enethiolate ligands in $[Ru_2(CO)_6(\mu\text{-}SCH{=}CR_2)_2]$.[78]

Insertion of $C{=}S$ into M–H bonds occurs when the thiolate complexes, $[Cp_2ZrCl(SCHR^1_2)]$,[79] $[Os_3(\mu\text{-}H)(\mu\text{-}SCHPh_2)(CO)_9(L)]$ (L = $S{=}CPh_2$,[80] CO[81]) and $[Cp_2Nb(SCH{=}CR^2_2)(\eta^2\text{-}S{=}C{=}CR^2_2)]$[82] are prepared from metal hydride complexes and the thioketone and thioketene ligands, $S{=}CR^1_2$ (thiocamphor, adamantanethione, or R^1 = C_6H_4X with X = H, Me, OMe), $S{=}CPh_2$ and $S{=}C{=}CR^2_2$ (R^2_2 = $Me_2C(CH_2)_3CMe_2$, Bu^t_2), respectively.

In a different type of reaction, unsaturated organic compounds add to metal sulfides, or M–SH compounds under basic conditions to form various thiolate ligands. Dithiolene ligands, $-SC(Z){=}C(Z)\text{-}S-$, are usually prepared by the addition of an acetylene to such a metal complex and can be found in a variety of monomeric and dimeric complexes.[2] Seyferth and his group showed that $[Fe_2(CO)_6(\mu\text{-}SH)_2]$ added activated olefins or acetylenes under basic conditions to form 1:2 adducts, $[Fe_2(CO)_6(\mu\text{-}SR)_2]$ or 1:1 adducts, $[Fe_2(CO)_6(\mu\text{-}SC_nS\text{-}\mu S,\mu S^2)]$ in which SC_nS can be a one, two or three carbon atom bridge, depending on the olefin (or acetylene) and the way it is substituted.[83] Ethene can add to $[Fe_2(CO)_6(\mu\text{-}S)_2]$ to produce $[Fe_2(CO)_6(\mu\text{-}SCH_2CH_2S\text{-}\mu S^1,\mu S^2)]$.[84]

The formation of $-SC(R){=}C(R)-$ ligands is less straightforward and the simplest reaction involves the addition of an acetylene, $RC{\equiv}CH$ (R = Ph, CO_2Me), to the sulfide complex, $[Os_4(CO)_{12}(\mu_3\text{-}S)]$, to form **8**.[85] A similar ligand originates in the reaction between $[Fe_3(CO)_9(\mu\text{-}Cl)(\mu_3\text{-}SBu^t)]$ and $PhC{\equiv}CH$ and **9** (R^1 = Ph, R^2 = H) results.[86]



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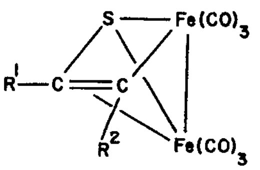

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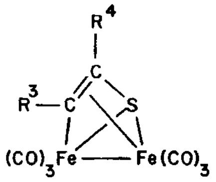
Although the reaction of $[CpFe(CO)\{C(CF_3){=}C(SMe)CF_3\}]_2$[*2Fe-S*] with $[Fe_3(CO)_{12}]$ does not resemble the previous one, a product also having structure **9** (R^1 = R^2 = CF_3) is obtained.[87] Related ligands (but bonded differently) were generated by the decomposition of 1,2,3-thiadiazoles in the presence of $[Fe_2(CO)_9]$ to form **10** (R^3, R^4 = H, Me, Bu^t, Ph, or $C_6H_4Bu^t\text{-}p$).[88,89] The ligand in $[(C_5Me_5)_2\overline{ZrSC(R){=}C}R]$ (R = Et, Ph, $C_6H_4Me\text{-}p$), obtained from $[C_5Me_5)_2Zr(S)L]$ (L = py, $4\text{-}Bu^t\text{-}py$), when treated with $RC{\equiv}CR$,[90] has the same basic structure but acts as a $2e^-$ donor in the monomeric complex.



10

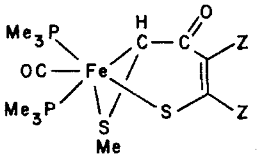
The remaining group of reactions that generate thiolate ligands involves scission of C–S bonds in organosulfur compounds. In a diverse set of compounds containing a $=C-SR$ grouping, with SR α to a double bond, the C–SR bond is broken and the SR binds as a thiolate ligand. We have seen this in the formation of thioacyl and μ-SR ligands from $S{=}C(SR^1)OR^2$ and $S{=}C(SR^1)R^2$ (Section I.2), alkyl dithiocarboxyl and μ-SR ligands from dialkyl trithiocarbonates, S=C(SR^1)SR^2 (Section I.3), and thiocarbyne and thiolate ligands from dithiocarbene complexes, [M=C(SR^1)SR^2] (Section II).

A similar type of behaviour occurs in organosulfur compounds with a R_2C=CH–SR arrangement. Stone and his co-workers were the first to report the fragmentation of simple vinyl sulfides, CH_2=CH–SR, to σ, π bonded olefin and μ-thiolate ligands in dinuclear iron complexes.[91] Further examples include the reaction of PhSCH=CH_2 with $[Os_3(CO)_{10}(NCMe)_2]$ to give $[Os_3(CO)_{10}(\mu\text{-}SPh)(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]$,[92] reaction of benzothiophene and other thiophenes with $[Fe_3(CO)_{12}]$ to give benzothiaferrole, thiaferrole and ferrole complexes,[93] the reaction between tetrathiafulvalene and $[Fe(CO)_5]$[94] and release of SMe from cyclo-octatetra-enylmethyl sulfide.[95] Other bonding modes occur in monomeric thiolate compounds derived from thiophene.[96–98] Various heterocyclic compounds containing two sulfur atoms were noted to fragment in such a way that a 1,n-dithiolate ligand is released which coordinates as $\mu\text{-}S(CH_2)_nS\text{-}\mu S^1,\mu S^2$ in $Fe_2(CO)_6$ complexes.[2]

It has been observed that alkyl ligands containing SR substituents, $[M\{C(X)Y\}_nSR]$, sometimes convert to thiolate ligands as has been reported for the thermally induced transformation of, e.g., $[HB(pz)_3W\{\eta^2\text{-}C(SMe)(SEt)SMe\}(CO)_2]$ to $[HB(pz)_3W(SMe)(SR^1)CSR^2]$ (R^1 = Me, Et; R^2 = Et, Me),[99] of $[Cp_2Zr(Ph)\{CH(SMe)SiMe_3\}]$ to $[Cp_2Zr\{CH(SiMe_3)Ph\}(SMe)]$, and of $[Cp_2Zr\{CH(SPh)Ph\}_2]$ to $[Cp_2Zr(SPh)_2]$, but which does not occur for $[Cp_2ZrR\{CH(SMe)SiMe_3\}]$ (R = Me, CH_2Ph).[100] Earlier, Taube and Steinborn noted the conversion of nickel and titanium CH_2SPh complexes to SPh complexes,[101] and King and Bisnette produced $[CpFe(SMe)(CO)_2]$ from $[CpFe\{(CH_2)_nSMe\}(CO)_2]$ (n = 2,3), by photolysis.[102] The equilibrium between $[CpFe(CO)\{\eta^2\text{-}C(SMe)(SMe)_2\}]$ and $[CpFe(SMe)(CO)\{C(SMe)_2\}]$, mentioned in Section IV.3, also involves this type of rearrangement.

VI. (Organothio)alkyl, [M{C(SR)(X)Y}]
(X,Y = H,R or SR)

In a number of cases type VI complexes were prepared by the alkylation of type III complexes, [M{S=C(X)Y}], or by the addition of H, R or SR to the thiocarbene complexes of type IV, [M{C(SR)X}] (X = H, SR). The conversion of thioformaldehyde ligands, S=CH_2, to $-CH_2SMe$ ligands by alkylation has been noted for Co,[41] Rh,[40] and Os[3] complexes. The thioaldehyde complex, [$Cp_2Zr(PMe_3)${η^2-S=CHMe}], is changed into a (methylthio)ethyl complex, [Cp_2ZrI{η^2-CH(SMe)Me}] by alkylation,[45] whereas the thioketene ligand in [CpRh(PPr^i_3)(η^2-S=C=CHR)](R = H, Me, Ph) becomes η^2-C(SMe)=CH_2,[52] formally a type VI ligand, $C(SR)R_2$, with R_2 = =CH_2. The η^3-coordinated dithioester ligand in [$W(CO)_3(PPr^i_3)$(η^3-S=C(SMe)Me}] is alkylated to give the η^2-bis-1,1-(methylthio)ethyl ligand in [WI{η^2-C(SMe)Me(SMe)}-(PPr^i_3)].[103] In a more complicated reaction, addition of an activated acetylene causes formal insertion of C=C–CO into the C=S bond of the methyl dithioformate complex, [$Fe(CO)_2$(η^2-S=CHSMe)$(PMe_3)_2$], to give the metallocyclic compound, **11** (Z = CO_2Me, CO_2Et),[104] containing a η^2-CH(SMe)R (as well as an –SR) ligand.



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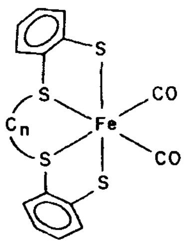
Anionic nucleophiles, X^-, usually are required to react at carbene carbon atoms and produce type VI complexes as is seen in the preparation of tungsten and iron complexes with –CH(SR)X (X = H, SR) and $-C(SR)_2X$ (X = H, R, SR) ligands from thiocarbene, [M(CHSR)], and dithiocarbene complexes, [M{$C(SR)_2$}], respectively.[31,32,59,71,105,106] Compounds like [$HC(pz)_3W${η^2-CH(SMe)(SBu^t)}$(CO)_2$]$^+$ and [CpFe{$C(SMe)_2$-(SPh)}$(CO)_2$] have been reported. The alkyl(thio)carbene complex, [CpW{η^2-C(SMe)Me}$(CO)_2$]$^+$, however, reacts with electrophiles like H^+ to form the type VI complex, [CpW{η^2-CH(SMe)Me}{$OC(O)CF_3$}$(CO)_2$]$^+$.[107] The vinylidene complex, [CpRu{C=$C(SMe)_2$}$(PMe_3)_2$]$^+$ also adds electrophilic H^+ or SMe^+ and rearranges to form [CpRu{η^2-C(SMe)=C(SMe)R}$(PMe_3)_2$]$^{2+}$ (R = H, SMe).[108]

By reacting with diazomethane, CH_2 is inserted into the M–SR bonds of $[Au\{\mu\text{-}SP(Ph)_2CH_2\}_2Hg]$ to give the (alkylthio)alkyl ligands in $[Au\{\mu\text{-}CH_2SP(Ph)_2CH_2\}_2Hg]$,[109] whereas substituted diazomethanes, $N_2CR^1R^2$ (R^2 = H, CO_2Me; R^2 = H, CO_2Me, CO_2Et), react at an M–SR bond of the dithiolene complexes, $[CpCoSC(Z^1){=}C(Z^2)S]$(Z^1 = H, CO_2Me; Z^2 = CO_2Me), to give $[CpCo\{CR^1R^2\}SC(Z^1){=}C(Z^2)S]$.[110]

VII. Thioether, $[M(SR_2)]$

By skillfully employing a simple reaction like alkylation, Sellmann and his co-workers were able to prepare a series of multidentate thiolate–thioether ligands and crown thioethers. The starting material, $[Fe(SC_6H_4\text{-}o\text{-}S)_2(CO)_2]^{2-}$, is used with alkylating agents, XC_nX, to form complexes like **12**, with both thiolate and thioether-type S donors in the ligand. Some alkylating agents that have been utilized are $BrCH_2CH_2Br$,[111] CH_2I_2, $Br(CH_2)_nBr$ (n = 3–8,12), $ClCH_2C(O)CH_2Cl$[112] and Me_2CBr_2.[113] Complexes of Mo,[113] Ru,[114,115] and Cr[116] with ligands related to that in **12** were also prepared. The macrocyclic thioether ligand in **13** could be liberated by treating the complex with acid.[117]



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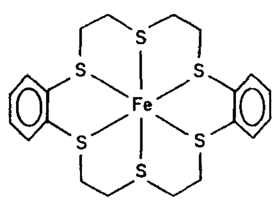
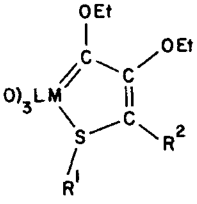


13

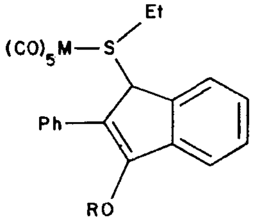
When acetylenes insert into M–SR bonds, vinyl thioether ligands, $-C(R){=}C(R)SR$, which coordinate through the sulfur to give four membered chelates, $[M\text{–}S(R)C(R){=}CR]$, result. Further insertion of CO or another molecule of acetylene leads to larger chelate rings. The reaction has been observed mainly for carbonyl and cyclopentadienyl complexes of Mn, Fe, Co, Mo, Ru, W and Fe.[118-126]

Some unusual thioether ligands are made by carbonyl insertion and rearrangement reactions in metal carbonyl complexes. When the alkyl or aryl thiocarbene complex, $[CpW\{\eta^2\text{-}C(SMe)R\}(CO)_2]$ (R = C_6H_4Me-*p*), reacts with PMe_3, coupling of CO and rearrangement produce the η^3-thioether ligand in $[CpW(CO)(PMe_3)\{\eta^2\text{-}S(Me)C(R){=}C{=}O\}]$.[127] A similar ligand, $S(Et)C(SiPh_3){=}C{=}O$, forms when the carbene complex, $[W(CO)_5\{C(SEt)SiPh_3\}]$, is heated above 0 °C.[128] A double carbonylation occurs when the α-deprotonated organosulfur compounds $Li[CH(SR^1)R^2]$ react with $[M(CO)_6]$ to give **14** (M = Cr, W; L = CO; R^1 = Me, Ph; R^2 = Ph, SPh; R^1R^2 = $(CH_2)_3S$,[129] CH_2SCH_2S; R^1 = Me; R^2 = S(O)Me, SMe[130]) upon subsequent alkylation. Products like **14** (M = Cr or W; L = CNBu^t, $P(OMe)_3$, $P(OPh)_3$, PPh_3, PMe_3) are obtained when the coordinated thioethers in $[M(CO)_5\{S(R^1)CH_2R^2\}]$ are deprotonated and alkylated in the presence of the ligands, L.[131]



14

The vinyl thiocarbene complexes, $[M\{C(SEt)C(Ph){=}C(Ph)OR\}(CO)_5]$ (M = Cr, W; R = Me, Et), rearrange spontaneously to the thioether complexes, **15**, in which the carbene ligand has been converted into an indenyl derivative.[56]



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VIII. Sulfonium, $[M(CH_2SR_2)]^+$

Sulfonium complexes are generally prepared by alkylating an (alkylthio)alkyl complex, $[M(CH_2SR)]$ (type VI), and complexes of Os[3] (like $[Os(CH_2SMe_2)Cl(CO)_2(PPh_3)_2]^+$), and of Pt,[132] Ni,[133] Fe and Mo[134] have been isolated.

Mononuclear, di- and trinuclear sulfonium complexes of rhenium were prepared from the carbene complex, $[CpRe(CH_2)(NO)PPh_3]^+$. Reaction with RSMe (R = Me, Ph) leads to the mononuclear compounds $[CpRe\{CH_2S(Me)R\}(NO)(PPh_3)]^+$; with $[CpRe(CH_2SMe)(NO)PPh_3]$ a dimer, $[MeS\{CH_2ReCp(NO)PPh_3\}_2]^+$, is obtained, and reaction with Na_2S gives a trinuclear product, $[S\{CH_2ReCp(NO)PPh_3\}_3]^+$.[135]

Unusual sulfonium type ligands are obtained when the thiocarbyne ligands in $[Rh_2(C_9H_7)_2W\{HB(pz)_3\}(\mu\text{-}CO)_3(\mu_3\text{-}CSMe)]$ and $[\{HB(pz)_3\}(CO)W(\mu\text{-}CO)(\mu\text{-}CSMe)Pt(\mu\text{-}CO)(\mu\text{-}CSMe)W(CO)\{HB(pz)_3\}]$ are alkylated to produce the corresponding cationic complexes with $\mu\text{-}CSMe_2^+$ ligands (only one CSMe ligand is alkylated in the second complex).[136]

IX. Dithiocarboxylate, $[M\{SC(S)X\}]$ (X = H, R)

The well-known method of preparing dithiocarboxylate complexes by insertion of CS_2 into M–H or M–R bonds has been reviewed extensively.[2,137] Recently two unusual η^2-η^3 isomeric types were found.[138]

Alternative methods were reported by Schenk and Schwietzke who treated coordinated CS_2 with H^- to produce $[W\{SC(S)H\}(CO)_3(dppe)]^-$[49] and by Busetto *et al.* who prepared $[CpFe\{\eta^2\text{-}SC(S)R\}CO]$ and $[M\{\eta^2\text{-}SC(S)R\}(CO)_4]$ (M = Mn, Re; R = Me, Ph) from the reaction between the acyl complexes, $[M\{C(O)R\}L_n]$ and P_4S_{10} or B_2S_3.[139]

Dithiocarboxylate complexes, $[CpM\{\eta^2\text{-}SC(S)R\}L_2]$ are obtained from the reaction of the carbyne complexes, $[CpM(CR)L_2]$ with sulfur atom donors: S_8 for M = Mo and W (R = CH_2Bu^t, C_6H_4Me-*p*; L = CO, $P(OMe)_3$),[140] and cyclohexenesulfide for M = W (R = Me; L = CO).[141]

X. 1,1-Dithiolate, [M{SC(S)(X)Y}] (X,Y = H,R or SR)[1g]

Carbon disulfide is reduced to a methylene dithiolate ligand in $[\{Os_3(\mu\text{-}H)(CO)_{10}\}_2(\mu\text{-}SCH_2S-\mu S^1,\mu S^2)]$ by reacting with two molecules of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[142] and a dimethyl dithiolate ligand is produced when $[CpCo(CO)PMe_3]$ reacts with CMe_2Br_2 and NaSH to give $[CpCo\{SC(S)Me_2\}PMe_3]$.[41]

The ligand, 1,3-dithiolane-2-thione, added S and changed into a bridging dithiolate ligand, $S\overline{C(SCH_2CH_2S})S$, when $[Fe_2(CO)_6\{\mu S{=}\overline{CSCH_2CH_2S}\}]$ was heated. The complex, $[(CO)_3Fe\{\mu\text{-}S\overline{C(SCH_2CH_2S})S-\mu S^1, \mu S^4\}Fe(CO)_2(\overline{CSCH_2CH_2S})]$ formed.[143]

References

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