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Review

40 years of transition-metal thiocarbonyl chemistry and the related CSe and CTe compounds

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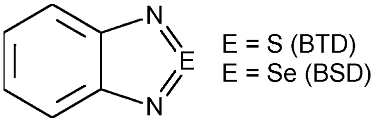
Contents

Abbreviations: bipy, 4,4′-bipyridyl; BTD, 2,1,3-benzothiadiazole; BSD, 2,1,3-benzoselenadiazole; bbzIm, 2-benzylbenzimidazolate; biphen, 4,5-dimethyl-9,10-dihydrophenanthren; bta, benzotriazolyl; DABCO, 1,4-diazabicyclo[2.2.2]octane; dppm, $Ph_2PCH_2PPh_2$; dpam, $Ph_2AsCH_2AsPh_2$; dppe, $Ph_2PCH_2CH_2PPh_2$; dmpe, $Me_2PCH_2CH_2PMe_2$; dpmb, 1,2-$C_6H_4(CH_2PPh_2)_2$; Fc, ferrocenyl; OEP, 2,3.7,8,12,13,17,18-octaetylporphinato; P∼O, (1,3-dioxan-2-ylmethyl)diphenylphosphine; pp′, $Ph_2PCH_2CH_2PMe_2$; PYAN, 1,2-bis(4-pyridyl)ethane; PYEN, 1,2-bis(4-pyridyl)ethylene; PYZ, pyrazine; th, thienyl; triphos, $(Ph_2PCH_2CH_2)_2PPh$; triphos-U, $MeC(CH_2PPh_2)_3$; TPP, 5,10,15,20-tetraphenylporphinato



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Abstract: This present review covers the development of the chemistry of transition metal complexes with the 10-electron systems CE (E = S, Se, Te). For thiocarbonyl complexes a comprehensive update starting from an earlier summary presented by Broadhurst in 1985 is given; seleo- and tellurocarbonyle compounds are completely reviewed. Priorities are set up on new pathways to these compounds and chemical reactions in which the title ligands are involved. Whereas the thiocarbonyl ligand exhibits a broad spectrum of bonding modes similar to carbonyl chemistry (terminal or various bridging modes), the higher homologues are limited to terminal coordination. On the basis of about 50 crystal structure analyses more insight into bonding parameters are now available. A further section is dedicated to theoretical calculations focused on the description of the electronic properties and bond energies mainly of coordinated CS. May this review simulate further investigation into this area of chemistry.

Keywords: Thiocarbonyl compounds; Selenocarbonyls; Tellurocarbonyls; Transition metals; CS coordination modes; Synthetic methods

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1. Introduction

More than 40 years have passed since Baird and Wilkinson synthesized the first thiocarbonyl complexes, *trans*-$RhX(CS)(PPh_3)_2$ (X = Cl, Br) [1]. Some years later related compounds followed with homologous terminal CSe [2,3] or CTe ligands [4], but till the present time their number is limited to only a few examples. A similar limitation is observed for compounds of the general type $M_m(CO)_n(CS)$. The first examples have been reported in 1973 with the group 6 series $M(CO)_5(CS)$ [5]; some years later followed the group 8 analogue $Fe(CO)_4(CS)$ from our group [6]. Similar derivatives of di- or oligonuclear compounds concentrate on $Mn_2(CO)_9(CS)$ and were described recently [7].

Furthermore, compounds with two and more CS groups are restricted to examples bonded to CpM fragments such as CpV, CpMn, CpFe, or CpCo or to compounds of the elements Os or Ir. One complex, $OsCl_2(CS)(CSe)(PPh_3)_2$, contains a terminal CS and a terminal CSe ligand in the same molecule [8]. The single complex with exclusively CS ligands at the metal, $Ni(CS)_4$, was reported to be very unstable [9].

Since the beginning of this chemistry the number of compounds with a CS ligand in a terminal or bridging positions has increased to about 200 spreading over the group 5 till group 11 elements. This is also the main field of carbonyl compounds with exception of few examples of group 4 and group 12 elements which have no relation to CS chemistry.

Compounds of the type L_nMCS, in which M represents a main group element, have not yet been reported; however, in the CO chemistry addition compound with group 13 elements are well known [10].

Previously the development of the transition metal thiocarbonyl chemistry and that of the related CSe and CTe compounds have been documented in some reviews [11–14]. A special compilation concerning all mononuclear complexes with the CpFe(CS) fragment has appeared in a Gmelin volume [15]; additional examples containing the substituted Cp ligand Cp*, e.g. the cation $[(Me_5C_5)Fe(CO)_2(CS)]^+$, have been prepared later [16] and are included here. Compounds with the Os(CS) fragment have similarly been described in a special Gmelin issue [17]. Compounds with Cp as ligand are summarized in [18].

Compounds containing the related selenocarbonyl and tellurocarbonyl ligand are restricted to those in which the ligand is bonded in a terminal manner; they are comprehensively reviewed here.

The scope of this review is the development of thiocarbonyl and related chemistry in the last years and is starting on from the results summarized in the review article of P.V. Broadhurst in 1985 [14]. Besides spectroscopic and structural properties of such complexes an important section is dedicated to reactions in which the CS ligand is involved. Furthermore, recent high level calculations could give us more information about the nature the metal to CS bond.

2. Mode of coordination

Similar to the carbonyl ligand the 10-electron molecule CS can coordinate to transition metals by different modes and based on the related structural chemistry of carbonyl compounds the arrangements **A**–**M** are possible with coordination of the CS ligand to 1, 2, 3, or 4 metals and donating 2, 4, or 6 electrons as depicted in Chart 1.

Bonding mode **A** comprises terminal bonding with a linear arrangement of the elements M, C, and S and in **B** the CS ligand bridges two metals symmetrically. In mode **C** the CS group coordinates nearly linear at one metal but with the carbon atom a semibridging interaction to a second metal is established. **D** is a combination of an end-on and a side-on bond. In **E** two end-on bonds are realized with an isothiocarbonyl structure. Compounds with mode **E** were prepared with soft or hard Lewis acids at both sites of the CS group. This is in contrast to the CO chemistry where similar O-coordination is known only with hard Lewis acids while the carbon atom bears a soft acid. In **F**, the CS ligand bridges a M_3 triangle in a μ_3 manner, and in **G** a bridging CS group coordinates to a further metal via the sulfur atom. The additional coordination via the orthogonal π-systems as depicted in **H** is only described for CO. The coordination to four metals is based on the further coordination of a μ_3 CS ligand to an isolated metal via the sulfur atom as in **I** or to a metal atom in a spiked triangle arrangement as in **K** via σ-sulfur interaction; in **L** the μ_3-CS group coordinates via the π-system as in some butterfly carbonyl cluster compounds. The coordination mode **M** is found in one iron cluster.

Similar to carbon monoxide the CS group is a variable electron donor system. Thus, in **A**, **B**, **C**, and **F** the CS ligand functions as a two-electron donor, whereas in **D**, **E**, **G**, **I**, **K** and **L** four electrons are shared with metal atoms. In **M** and **H** (CS example unknown) six electrons are involved with coordination to a transition metal.

The present review comprises only compounds in which the coordination modes **A**–**G** are operative dealing with group 6 to group 10 elements; no new examples of the earlier described modes **I**, **K**, **L**, and **M** were reported later. Up to now they are restricted to the compounds $[\{(\eta^5\text{-Cp})Co\}_3(\mu_3\text{-S})\{\mu_3\text{-CSCr(CO)}_5\}]$ (**I**) [19], $[Fe_4(CO)_{12}(CS)S]$ (**K**) [20], $[Os_4(CO)_{12}(CS)S]$ (**L**) [21], and $[Fe_5(CO)_{13}(CS)S_2]$ (**M**) [22] and are already summarized in [14].

Till the present time the coordination chemistry of the related CSe and CTe ligands is restricted to coordination mode **A**. It was confirmed, that the net electron withdrawing capacity of the chalcocarbonyl ligands increases as $CO < CS < CSe$ [23,24].

3. Synthetic routes

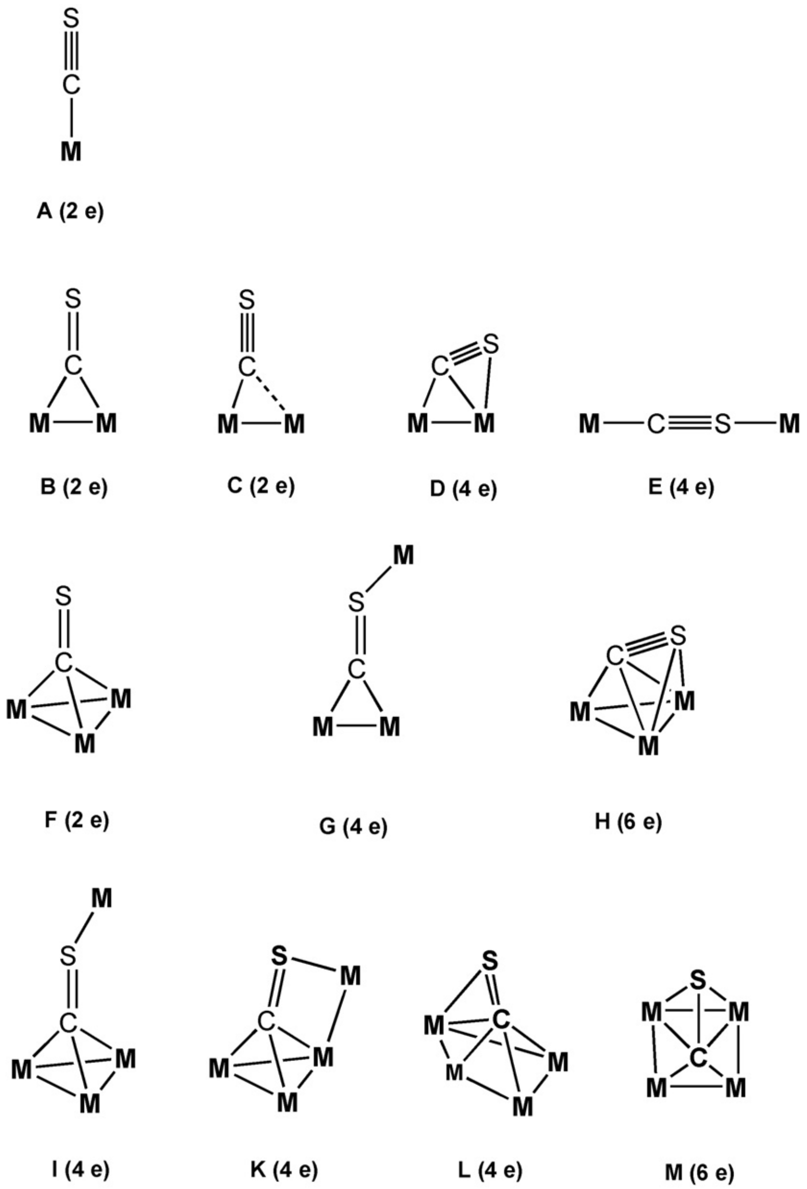
3.1. Compounds with terminal CS groups

The inherent instability of CS relative to the stable and isoelectronic CO does not allow a general synthetic pathway for transition metal complexes which only can be prepared by indirect routes. In principle, one can decide between four main methods for the introduction of a CS ligand:

- via Cl_2CS;
- modification of an η^2-bonded CS_2 derivative;
- modification of a σ-bonded C(S)R group;
- sulfurization of an existing metal to carbon bond.
- Other access.

Whereas the thiophosgene and the sulfurization methods are restricted to few examples, most of the compounds follow the CS_2 or the C(S)R route.

However, the majority of the new compounds reported in this review, are derived from other transition metal thiocarbonyl



A (2 e)
B (2 e)
C (2 e)
D (4 e)
E (4 e)
F (2 e)
G (4 e)
H (6 e)
I (4 e)
K (4 e)
L (4 e)
M (6 e)

Chart 1. Possible coordination modes **A**–**M** for the CS ligand; mode **H** is only restricted to carbonyl chemistry.

compounds and the CS ligand remains innocent and does not participate in the reaction.

3.1.1. *From thiophosgene*

The dehalogenation of thiophosgene by metalates (Eq. (1)) is the unique route to the few $M(CO)_x(CS)$ compounds containing no other ligands than CO and CS. For those compounds the common CS_2/phosphine route is inaccessible because of the nonexistence of the corresponding CS_2 compounds.

$$[L_nM]^{2-} + Cl_2CS \rightarrow L_nM(\mathbf{C{\equiv}S}) + 2Cl^- \qquad (1)$$

3.1.2. *Modification of a η^2-CS_2 derivative*

3.1.2.1. Desulfurization of an η^2-CS_2 ligand by phosphines. The most common route for the introduction of a terminal CS ligands follows the first preparation by Baird and Wilkinson [1] and is based on the desulfurization of an η^2-bonded CS_2 ligand with phosphines (Eq. (2)).

$$L_nM(\eta^2\text{-}CS_2) + PR_3 \rightarrow L_nM(\mathbf{C{\equiv}S}) + S{=}PR_3 \qquad (2)$$

3.1.2.2. Desulfurization of η^2-CS_2 by LiR. A desulfurization of *mer*-(dppe)$W(CO)_3(\eta^2\text{-}CS_2)$ by BuLi was reported by Schenk et al. (Eq. (3)). A nucleophilic attack at the bridging sulfur atom (thiophilic attack) instead of addition of the nucleophile to the carbon atom (to produce an η^1-S_2CR complex) was suggested. An intermediate formation of a metallodithiocarbonic acid ester of the type $[L_nMC(S)SR]^-$ was proposed, which, however, is too electron rich to be stable, finally decomposing into the thiocarbonyl compound and SR^-. This reaction can also be seen as the reverse of the nucleophilic attack of SR^- at a thiocarbonyl carbon atom, the equilibrium of the reaction

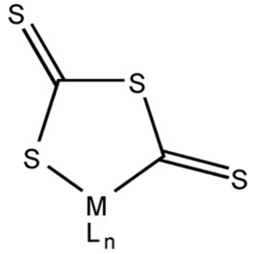


Chart 2.

$L_nM(C{\equiv}S) + SR^- \Leftrightarrow L_nMC(S)SR$, being on the left side [25].

$$L_nM(\eta^2\text{-}CS_2) + LiR \rightarrow L_nM(\mathbf{C{\equiv}S}) + LiSR \qquad (3)$$

3.1.2.3. Reductive elimination of SR from an η^2-C(S)SR group. Recently, the Dixneuf group has found a new route to a terminal CS ligand via reductive elimination of SR^- from a cationic η^2-CS_2R group (an alkylated η^2-bonded CS_2 complex) leading to new thiocarbonyl complexes of iron as shown in Eq. (4). Till the present time this reaction is restricted to $[(CO)_2(PR_3)_2Fe(\eta^2\text{-}CSSMe)]^+$ complexes [26–28]; in the case of R = Ph, elimination of SMe^- also occurs with PEt_3 or PBu_3 and the formation of SPR_3 and $[MePR_3]^+$ was suggested [26].

$$L_nM(\eta^2\text{-}C(S)SR) + Na/Hg \rightarrow L_nM(\mathbf{C{\equiv}S}) + SR^- \qquad (4)$$

3.1.2.4. Desulfurization of an intermediate η^2-CS_2 group. A metal assisted dismutation of CS_2 to CS and CS_3 (Eq. (7)) was observed in the reaction of $W(PMe_3)_2(CO)_3(NCMe)$ with CS_2 leading to the tungsten CS complex $W(PMe_3)_2(CO)_2(CS_3)(CS)$. In the first step the formation of an intermediate η^2-CS_2 complex was suggested which adds a second molecule of CS_2 to give the metalla heterocyclus shown in Chart 2 which splits into the ligands CS and CS_3 under formal oxidation of the metal [29].

$$L_nM(\eta^2\text{-}CS_2) + CS_2 \rightarrow L_nM(\mathbf{C{\equiv}S}) + \text{“}CS_3\text{''} \qquad (5)$$

3.1.2.5. Splitting of CS_2 by a carbyne complex. Splitting of CS_2 by a transition metal carbyne to produce a terminal CS group and a bridging thioacyl ligand (Eq. (6)) have also been reported [30]:

$$L_nRu{\equiv}CR + CS_2 \rightarrow L_n(\mathbf{C{\equiv}S})Ru{=}(\mu\text{-}S)CR \qquad (6)$$

3.1.2.6. Desulfurization of an intermediate μ-heteroallene group. One new synthetic route is based on the desulfurization of CS_2 complexes by other than phosphine compounds [31].

Splitting of coordinated E–C–E (E = S, Se) into μ-E bridged binuclear compounds containing a terminal CE ligand (Eq. (7)) is also reported [31]. Related to this procedure is the thermal decomposition of (μ-ECS) compounds (Eq. (8)) to give a terminal CS ligand [32]. CS cleavage of an intermediate η^1-coordinated CS_2 molecule and oxidative addition to a Pt_3 cluster with formation of an η^3-S ligand and a terminal CS group was also reported [33] (Eq. (9)). Similarly, dirhenium(III) thiocarbonyl compounds have been obtained from $Re_2X_4(dppm)_2$ or $Re_2X_4(dpam)_2$ and CS_2 via a two-electron redox process [34,35]; see also splitting of CS_2 into a μ^3-S and a terminal CS ligand by a trinuclear ruthenium cluster [36].

$$L_nM(\mu\text{-}ECE)ML_n \rightarrow L_nM(\mu\text{-}E)ML_n(\mathbf{C{\equiv}E}) \qquad (7)$$

$$L_nM(\mu\text{-}ECE)ML_n \rightarrow L_nMPt(\mathbf{C{\equiv}S}) + \ldots \qquad (8)$$

$$L_nRe_2 + CS_2 \rightarrow L_nRe_2(\mu\text{-}S)(\mathbf{C{\equiv}S}) \qquad (9)$$

3.1.3. Modification of a σ-bonded C(S)R group

3.1.3.1. Protonation of $M\text{-}C(S)NR_2$, M-C(S)OR, or M-C(S)SR. Another common route comprises the protonation of a thioalkoxy or thiocarbamoyl complex (Eq. (10)) leading to cationic thiocarbonyl species in the case of neutral starting materials.

$$L_nMC(S)NR_2 + HX \rightarrow [L_nM(\mathbf{C{\equiv}S})]^+X + HNR_2 \qquad (10)$$

Besides these methods some new access to thiocarbonyl compounds have been reported but which are in most cases restricted to special examples. They all represent slight variations of the methods shown above.

3.1.4. Sulfurization of an existing metal to carbon bond

3.1.4.1. Exchange of Cl^- by S^{2-}. The transformation of a dichlorocarbene ligand into a thiocarbonyl group described by Roper (Eq. (11)) has been restricted to some Os compounds [8].

$$L_nM{=}CCl_2 + H_2S \rightarrow L_nM(\mathbf{C{\equiv}S}) + 2HCl \qquad (11)$$

3.1.4.2. From a carbido complex. More recently, it could be shown that a carbido complex $Cl_2(PCy_3)_2RuC$ can take up a sulfur atom from elementary sulfur (⟨S⟩) to produce the related thiocarbonyl complex (Eq. (12)) [37].

$$L_nM{\equiv}C + \langle S\rangle \rightarrow L_nM(\mathbf{C{\equiv}S}) \qquad (12)$$

3.1.5. Other access

3.1.5.1. Reductive splitting of a M≡CSSC≡M group. Na/Hg reduction of $(ArRN)_3Mo{\equiv}CSSC{\equiv}Mo(NArR)_3$ generates the corresponding anionic thiocarbonyl complex (Eq. (13)). This compound is the first example where a thiocarbonyl ligand is bonded to a metal in a high oxidation state and the formulation of the compound with an anionic thiocarbyne ligand (M≡C–S) may be more relevant [38].

$$L_nM(C)SS(C)ML_n + Na/Hg \rightarrow 2[L_nM(\mathbf{C{\equiv}S})]^- \qquad (13)$$

3.1.5.2. From a dithiocarbamate $(S_2CNR_2)^-$. Novel sources without precedent are dithiocarbamates in the synthesis of rhenium thiocarbonyl complexes from formal Re^I and Re^{III} compounds containing phosphine ligands (Eq. (14)). An intermediate η^2-bonded S_2CNR_2 complex which is desulfurized with formation of SPR_3 and subsequent loss of $NaNR_2$ was suggested [39].

$$L_nM + S_2CNR_2^- \rightarrow L_nM(\mathbf{C{\equiv}S}) + NR_2^- + SPR_3 \qquad (14)$$

3.2. Compounds with CSe and CTe ligands

3.2.1. From a chlorocarbyne ligand and Na_2E

The CSe_2/PR_3 process similarly leads to the corresponding CSe compounds. However, this is not possible for CTe compounds according to the non-existence of CTe_2. Osmium CSe and CTe compounds are available following Eq. (11) starting with dichloro carbene compounds [8]. Transformation of a terminal bonded chlorocarbyne ligand into a chalcogene carbonyl compound with Na_2E (E = S, Se, Te) is also possible (Eq. (15)) [40].

$$\mathrm{L}_n\mathrm{M{\equiv}CCl} + \mathrm{Na_2E} \rightarrow [\mathrm{L}_n\mathrm{M}(\mathbf{C{\equiv}E})]^- \qquad (15)$$

3.2.2. From a terminal CS ligand

A four-step conversion of a terminal CS into a terminal CSe ligand is outlined in (Eq. (16)). This process involves nucleophilic attack of SeH^- at a cationic compound leading to neutral geometrical isomers η^2-CSSe and η^2-CSeS; the latter is alkylated to give the cationic η^2-CSeSMe complex which on treatment with HX produces the selenocarbonyl ligand [41].

$$\mathrm{L}_n\mathrm{M(C{\equiv}S)} + \langle\mathrm{Se}\rangle \rightarrow \mathrm{L}_n\mathrm{M}(\mathbf{C{\equiv}Se}) \qquad (16)$$

3.2.3. From a carbido complex

Treating of the anionic carbido complex $[(ArRN)_3Mo{\equiv}C]^-$ with elemental Se or Te generates the corresponding anionic seleno- or telluro carbonyl compounds (Eq. (17); see also Eq. (12), Section 3.1.4) [38].

$$[\mathrm{L}_n\mathrm{M(C)}]^- + \langle\mathrm{Se, Te}\rangle \rightarrow [\mathrm{L}_n\mathrm{M}(\mathbf{C{\equiv}Se}, \mathbf{Te})]^- \qquad (17)$$

3.3. Compounds with bridging CS groups

3.3.1. From terminal CS ligands

Preparative routes to compounds with bridging CS ligands are rare and concentrate on a few examples. The reduction of the cationic complex $[Cp^*(CO)_2Fe(CS)]^+$ ($Cp^* = C_5H_5$, C_5Me_5) leads to neutral bridging species (Eq. (18)). Small amounts of $Cp_2{}^*Fe_2(CO)_3(CS)$ and $Cp_2{}^*Fe_2(CO)_4$ were additionally formed [42,16]. In one case (Eq. (19)) the terminal CS ligand could be converted into a bridging one by replacing the monodentate PPh_3 by dppe [31].

$$\begin{aligned}&2[\mathrm{Cp^*(CO)_2Fe(CS)}]^+ + 2\mathrm{NaH}\\&\quad\rightarrow \mathrm{Cp_2{}^*Fe_2(CO)_2}(\mu\text{-}\mathbf{CS})_2 + 2\mathrm{Na}^+ + \mathrm{H_2} + 2\mathrm{CO}\end{aligned} \qquad (18)$$

$$\begin{aligned}&\mathrm{(dppe)Pt(\mu\text{-}Se)Pt(CS)(PPh_3)} + \mathrm{dppe}\\&\quad\rightarrow \mathrm{(dppe)Pt(\mu\text{-}Se)}(\mu\text{-}\mathbf{CS})\mathrm{Pt(dppe)}\end{aligned} \qquad (19)$$

$CpM(PR_3)(CS)$ (M = Co, Rh; $PR_3 = PMe_3, PMe_2Ph$) are sources for heterobimetallic compounds containing a μ-CS bridge of the type **B** by the reaction with compounds with a good leaving group such as THF (Eq. (20)) [43].

$$\mathrm{CpM(PR_3)(CS)} + \mathrm{CpMn(CO)_2THF} \xrightarrow[\mathrm{M=Co,\ Rh}]{} \mathrm{CpM(PR_3)}(\mu\text{-}\mathbf{CS})(\mu\text{-CO})\mathrm{Mn(CO)Cp} \qquad (20)$$

Ionic CS compounds lead to various types of bridging compounds. Thus, $[CpFe(CO)_2(CS)]^+$ generates type **B** compound with a carbonylate anion (Eq. (21)) [44]. Semibridging or side on bridging CS compounds have been obtained by reactions of the anionic CS complex $[HB(pz)_3(CO)_2W(CS)]^-$ with $ClAuPR_3$ [45] or with $[IndMo(CO)_2(MeCN)_2]^+$ [46], respectively.

$$\begin{aligned}&[\mathrm{CpFe(CO)_2(CS)}]^+ + [\mathrm{Mn(CO)_5}]^-\\&\quad\rightarrow \mathrm{CpFe(CO)}(\mu\text{-}\mathbf{CS})(\mu\text{-CO})\mathrm{Mn(CO)_4} + \mathrm{CO}\end{aligned} \qquad (21)$$

3.3.2. From the η^2-CS_2 ligand

A similar splitting in coordinated S and CS of an η^2-bonded CS_2 ligand according to Eq. (22) is also observed in the high yield synthesis of the trinuclear species $(PPh_3)(CO)_2FeCo_2Cp_2(\mu_3\text{-CS})(\mu_3\text{-S})$ [47,48].

$$\begin{aligned}&\mathrm{(PPh_3)_2Fe(CO)_2(\eta^2\text{-}CS_2)} + \mathrm{CpCo(PPh_3)_2}\\&\quad\rightarrow \mathrm{(PPh_3)(CO)_2FeCo_2Cp_2}(\boldsymbol{\mu}_\mathbf{3}\text{-}\mathbf{CS})(\mu_3\text{-S})\end{aligned} \qquad (22)$$

CS_2 can be reduced to a triply bridged CS ligand (type **F**) by $Cp_2Ni_2(\mu\text{-CO})_2$ with result of the 49 CVE Fischer-Palm compounds $Cp_3Ni_3(\mu_3\text{-CE})(\mu_3\text{-CE'})$ (E = O, S) [49].

Electron rich compounds with terminal CS groups may give end to end bridges of type **E** (Eq. (23)), and symmetrically bridged type **B** compounds similarly can be converted into type **I** products (Eq. (24)) using transition metal THF adducts. As THF adducts mainly serve $CpMn(CO)_2THF$ or $M(CO)_5THF$ (M = Cr, Mo, W).

$$\mathrm{L}_n\mathrm{M(C{\equiv}S)} + \mathrm{L}'_n\mathrm{M'(THF)} \rightarrow \mathrm{L}_n\mathrm{M{-}C{\equiv}S{-}M'L}'_n \qquad (23)$$

$$\mathrm{L}_n\mathrm{M(\mu\text{-}CS)ML}_n + \mathrm{L}'_n\mathrm{M'(THF)} \rightarrow \mathrm{L}_n\mathrm{M}(\mu_3\text{-}\mathbf{CSM'L'_\mathit{n}})\mathrm{ML}_n \qquad (24)$$

3.3.3. From 1,3-dithiole-2-thiones

The first time that a 1,3-dithiole-2-thione serves as a source for a bridging CS ligand by extrusion of CS via a binuclear transition metal complex (Eq. (25)); the resulting dithiolene is also coordinated to the complex bridging the two metals in an unsymmetrical manner [50].

$$\begin{aligned}&\mathrm{(RCS)_2CS} + \mathrm{L}_n\mathrm{M(\mu\text{-}CS)ML}_n\\&\quad\rightarrow \mathrm{L}_n\mathrm{M}(\boldsymbol{\mu}_\mathbf{2}\text{-}\mathbf{CS})\mathrm{ML}_n + \mathrm{(RC{=}S)_2}\end{aligned} \qquad (25)$$

4. New compounds

During the last 40 years a great number of new compounds has been prepared with various coordination modes of the CS ligand. A list of compounds including the ^{13}C shift and the IR absorption of the CS ligand are summarized in Table 1. In this section, all new thiocarbonyl compounds are numbered but those which have been prepared earlier and summarized in the first review in [14] and used as starting materials are not numbered or found in the following tables.

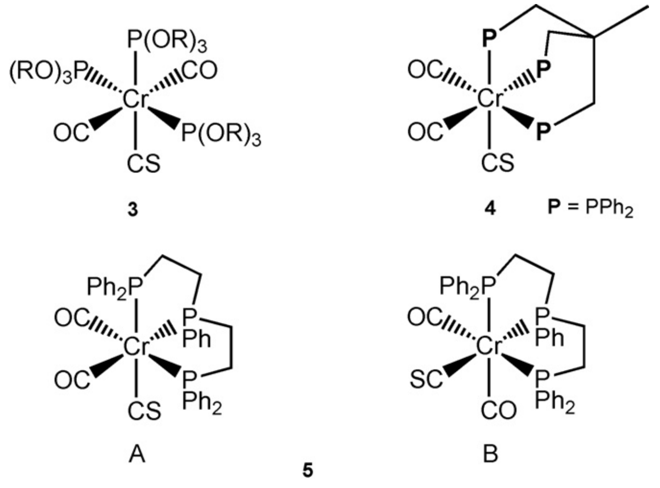


Chart 3.

4.1. Compounds with terminal CS ligands

4.1.1. Group 5 compounds (V, Nb, Ta)

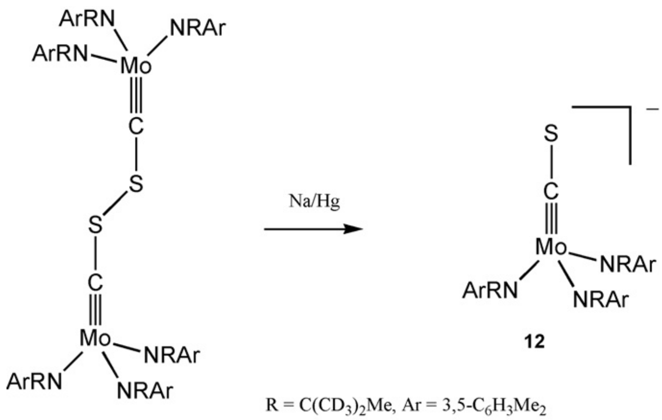
In this triad only the two vanadium compounds [CpV(CO)$_3$(CS)] (**1**) and [CpV(CO)$_2$(CS)$_2$] (**2**) containing terminal CS groups have been mentioned very early [51,52]; however, while reported in less available journals the compounds have not found entrance in subsequent reviews. To our knowledge, no additional activities in this area of chemistry could be recognized.

4.1.2. Group 6 compounds (Cr, Mo, W)

4.1.2.1. Cr. New CS compounds in this series were mainly obtained from chromium and tungsten. Recently, one thiocarbyne like compound of molybdenum has been prepared [38]. Earlier thiocarbonyl compounds of Mo are collected in the review of Broadhurst [14].

A mixture of *mer*, *trans*-Cr(CO)$_3$(CS){P(OPh)$_3$}$_2$ (**3**) and *cis*- and *trans*-Cr(CO)$_4$(CS){P(OPh)$_3$} (**6a**) have been obtained upon reacting (CO)$_5$Cr(CS) with P(OPh)$_3$; the products could be separated by column chromatography [53]. The similar reaction with PPh$_3$ and the substitution promoter Me$_3$NO yields a mixture of *cis* and *trans*-Cr(CO)$_4$(CS)(PPh$_3$) (**6b**) [54]. Three tertiary phosphite ligands or one tridentate phosphine ligand can be introduced to form Cr(CO)$_2$(CE){P(OR)$_3$}$_3$ compounds (E = S, Se; R = Me, Et, Bu-n, Ph) (the thiocarbonyl derivatives **3a–d**) by replacement of various arenes of the corresponding (η^6-arene)Cr(CO)$_2$(CE) complexes. The arene ligands can easier be replaced than CO in (CO)$_5$Cr(CE). The *mer*-product **3** was found to be the major isomer. Treatment of the arene complex with triphos-U gives **4** whereas with triphos an isomer mixture of **5** (*A*/*B* = 4/1 ratio) was obtained [23]. Conditions for the formation of *mer*-Cr(CO)$_2$(CS){P(OMe)$_3$}$_3$ (**3a**) from (η^6-PhCOOMe)Cr(CO)$_2$(CS) are described in [55]; the structures of **3–5** are depicted in Chart 3.

The earlier described complex (η^6-C$_6$Et$_6$)Cr(CO)$_2$(CS) was found to react with NOBF$_4$ to give [(η^6-C$_6$Et$_6$)Cr(CO)(CS)(NO)](BF$_4$) (**8**). The cation is equipped with four different ligands, but nothing is reported about chirality of this complex [56].



R = C(CD$_3$)$_2$Me, Ar = 3,5-C$_6$H$_3$Me$_2$

Scheme 1.

The CS$_2$/PPh$_3$ method upon irradiation leads to a compounds with the arene 4,5-dimethyl-9,10-dihydrophenanthrene. Starting with the related (η^6-arene)Cr(CO)$_3$ one CO is replaced to give (η^6-arene)Cr(CO)$_2$(CS) (**9**); the mixture of isomers (*exo* and *endo* epimers) could be separated by chromatography [57]. New (η^6-arene)Cr(CO)$_2$(CS) complexes **10** with fluor containing arenes for conformation studies [58] and with substituted benzene ligands (PhMe, PhOMe, C$_6$H$_3$Me$_3$) [59] have been prepared by standard methods.

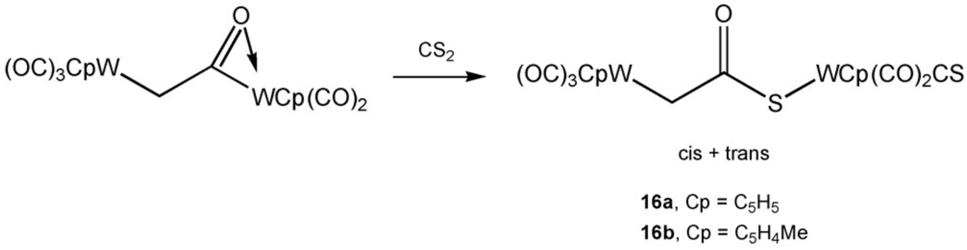
4.1.2.2. Mo. Reduction of the disulfide **Mo**CSSC**Mo** with Na/Hg cleaves the S–S bond with formation of the thiocarbonyl complex **11** which is converted into the ion separated salt **12** by addition of 12-crown-5 as shown in Scheme 1 [38]; its the first anionic complex with a CS ligand.

4.1.2.3. W. The neutral tungsten complex HC(pz)$_3$(CO)$_2$W(CS) (**15**) was obtained from (N(C$_4$H$_9$)$_4$)[IW(CO)$_4$(CS)] and HC(pz)$_3$ [60].

New tungsten compounds comprise some *mer*-(R$_2$PC$_2$H$_4$PR$_2$)W(CO)$_3$(CS) (**13**) species obtained by desulfurization of the corresponding η^2-CS$_2$ complexes [25] and the mixed trithiocarbonate thiocarbonyl compound W(PMe$_3$)$_2$(CO)$_2$(CS$_3$)(CS) (**14**) prepared by reaction of W(PMe$_3$)$_2$(CO)$_3$(NCEt) with CS$_2$ [29]. Cp(CO)$_3$WCH$_2$C(O)SWCp(CO)$_2$(CS) (**16a**) was obtained as a mixture of *cis* and *trans* isomers by the reaction of the O-coordinated ketene complex Cp(CO)$_3$W(μ-η^1:η^2-CH$_2$CO)WCp(CO)$_2$ with CS$_2$; the related compound with Cp′ = C$_5$H$_4$Me (**16b**) was prepared analogously (Scheme 2) [61].

4.1.3. Group 7 compounds (Mn, Re)

4.1.3.1. Mn. The first binuclear thiocarbonyl compound of manganese, Mn$_2$(CO)$_9$(CS) (**17**), could be obtained in low yield from NaMn(CO)$_5$ and thiophosgene. However, it could not be separated from Mn$_2$(CO)$_{10}$, also formed by this procedure. The ^{55}Mn NMR spectrum of **17** shows the presence of two isomers according to the CS group *cis* or *trans* to the Mn(CO)$_5$ group. Treatment of this mixture with Br$_2$



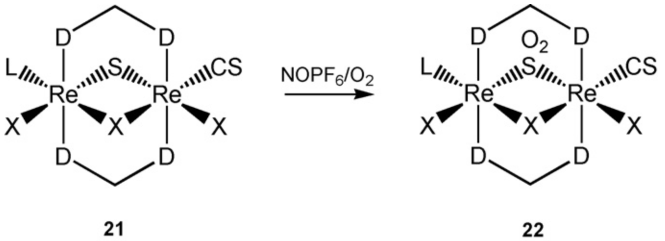
Scheme 2.

leads to a mixture of $Mn(CO)_4(CS)Br$ (**18**) and $Mn(CO)_5Br$ [7].

$C_5Me_5Mn(CO)(CS)(CNCF_3)$ (**19**) has been obtained from $C_5Me_5Mn(CO)$(*cis*-C_8H_{14})$(CNCF_3)$ and PPh_3 in CS_2 [62]. Irradiation of $Ph_3SnMn(CO)_3(C_5H_4N\text{-}2\text{-}CH{=}NPr\text{-}i)$ at 173 nm in CS_2 affords the photosubstitution product $Ph_3SnMn(CO)_2(C_5H_4N\text{-}2\text{-}CH{=}NPr\text{-}i)(\eta^2\text{-}CS_2)$ which on raising the temperature is probably converted into the thiocarbonyl complex $Ph_3SnMn(CO)_2(CS)(C_5H_4N\text{-}2\text{-}CH{=}NPr\text{-}i)$ (**20**) [63].

4.1.3.2. Re. A variety of neutral complexes of the type $Re_2(\mu\text{-}S)(\mu\text{-}X)X_3(CS)(\mu\text{-}D\text{–}D)_2$ (**21a–c**) have been obtained by reductive cleavage of CS_2 by the corresponding $Re_2X_4(D\text{–}D)$ compounds (D–D = dppm, dpam; X = Cl, Br); derivatization by reaction with $TlPF_6$ in the presence of various monodentate ligands L′ (L′ = nitriles, isonitriles, CO) give the cations $[Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(\mu\text{-}D\text{–}D)_2(L')]PF_6$ (**21d–o**); oxidation with $[Cp_2Fe]PF_6$ or $[NO]PF_6$ leads to the cations (**21p–q**) [34,35,64]. Oxidation with $NOPF_6/O_2$ leads to the related $\mu\text{-}SO_2$ compounds (**22**) as depicted in Scheme 3 [35,64,65]. The cationic μ-S and $\mu\text{-}SO_2$ species with L′ = CO can be reduced to the one- and two-electron reduction products $Re_2(\mu\text{-}S)(\mu\text{-}X)X_2(CS)(CO)(\mu\text{-}D\text{–}D)_2$ (**21r-s**) and $[Re_2(\mu\text{-}SO_2)(\mu\text{-}X)X_2(CS)(CO)(\mu\text{-}D\text{–}D)_2]^-$ (**22k–m**), respectively [64]. The individual compounds **21** and **22** are listed in Table 1.

The mononuclear species $Re(CS)(PMe_2Ph)_3(S_2CNEt_2)$ (**23**) and $Re(CS)(S_2CNEt_2)_3$ (**24**) have been obtained by a procedure according to Eq. (14) from $ReCl_3(Me_2PhP)_3$ and $NaEt_2dtc{\cdot}3H_2O$ [39].



D-D = dppm, dpam
X = Cl, Br
L = CO, nitriles, isonitriles, X

Scheme 3.

4.1.4. Group 8 compounds (Fe, Ru, Os)

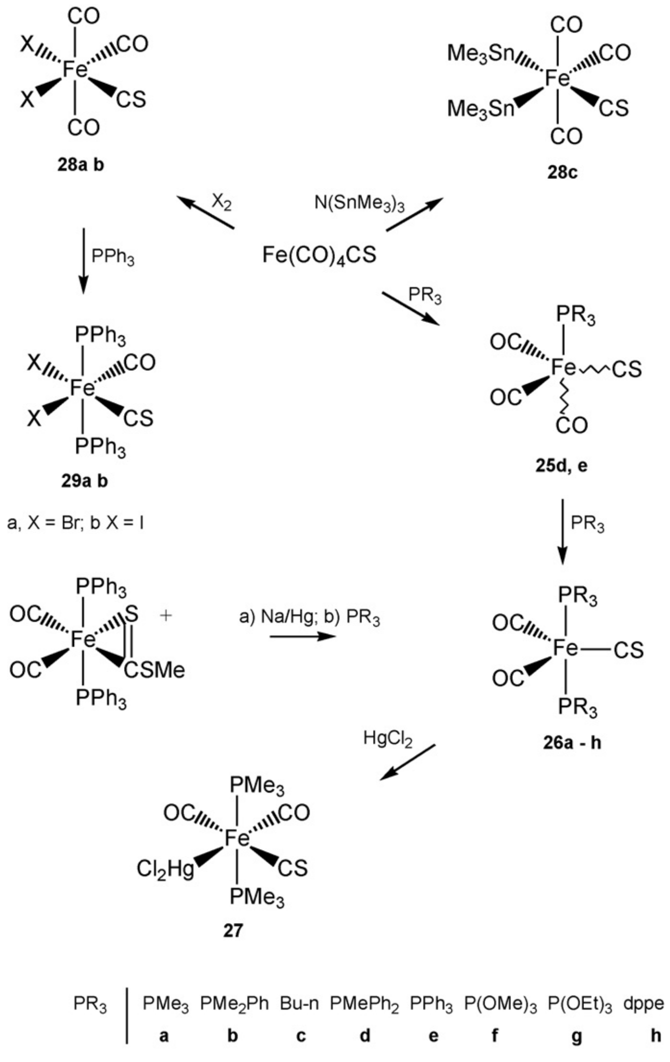
4.1.4.1. Fe. Substitution of carbon monoxide of $Fe(CO)_4(CS)$ by the phosphine ligands PPh_3 or PPh_2Me with the aid of Me_3NO leads to new compounds **25** and **26**. The presence of one PR_3 allows two isomers with the CS ligand either in the axial or the equatorial position [67]. Further disubstituted complexes **26**, however, are available with better yields by the reductive elimination route from $[(CO)_2(PR_3)_2Fe(\eta^2\text{-}CSSR)]^+$ according to Eq. (4) [26–28]. $(CO)_2(PPh_3)_2Fe(CS)$ (**26e**) was not obtained by this procedure but forms from the corresponding cation with PEt_3 or PBu_3 [26]. If the cationic compound $[(CO)_2(PMe_3)_2Fe(\eta^2\text{-}CSSR)]^+$ is similarly treated in the presence of dppe the thiocarbonyl complex **26i** is obtained in low yields.

In the case of L = PMe_3 the basicity of the iron center of **26a** is sufficient to give stable adducts with $HgCl_2$ resulting in the six-fold coordinated complex $(CO)_2(CS)(PMe_3)_2FeHgCl_2$ (**27**) [27]. An improved synthesis for **26e** and **26g** with R = Ph, (84% yield) and R = Et, (15%) involving the reaction of $(CO)_2\{P(OR)_3\}Fe(\eta^2\text{-}CS_2)$ with 2 mol PBu_3 is presented in [68].

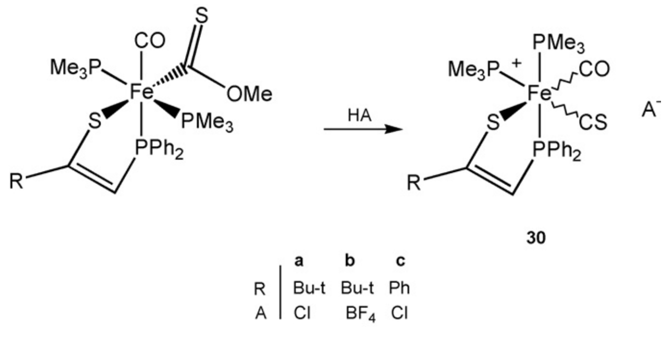
$Fe(CO)_4(CS)$ is starting material for the access to a variety of iron compounds with a terminal CS ligand as depicted in Scheme 4. Thus, oxidation with X_2 (X = Br, I) gives the octahedral compounds $FeX_2(CO)_3(CS)$ (**28a**, **b**); further reaction of **28a**, **b** with PPh_3 at low temperature replaces two CO groups to produce the corresponding $FeX_2(CO)(CS)(PPh_3)_2$ (**29a**, **b**) compounds [66]. In a similar oxidation process *fac*-$(CO)_3Fe(CS)(SnMe_3)_2$ (**28c**) could be generated by the reaction of $Fe(CO)_4(CS)$ with $N(SnMe_3)_3$ [69].

Protonation of $(PMe_3)_2(CO)Fe(PPh_2CH{=}C(R)S)(C(S)OMe)$ with HBF_4 or HCl leads to the cationic species **30** (R = Ph, Bu-t; A = Cl, BF_4), shown in Scheme 5, following also the procedure outlined in Eq. (10) [70].

The air stable complex **31** with a CS_2 group linking two iron atoms can be obtained in about 10% yield by irradiation of the metallacyclic precursor (Scheme 6); the other products have not been identified [71]. The cationic complex $[Cp^*Fe(CO)_2(CS)]BF_4$ ($Cp^* = C_5Me_5$) (**32**) was obtained following the procedure similar to that for the Cp derivative by acidification of $Cp^*Fe(CO)_2C(S)SMe$ with HBF_4; $Cp^*Fe(CO)_2(CS)C(O)OMe$ (**32a**) was prepared from **32** with NaOMe/MeOH [16]. Mononuclear compounds with the CpFe(CS) fragment from refs. [42,72] are summarized in a Gmelin volume and not further reviewed here [15].



Scheme 4.



Scheme 5.

New mono and binuclear six-coordinate complexes Fe(TPP)(CS)(L–L) (**33a–e**) and {Fe(TPP)(CS)}$_2$(L–L) (**33f–k**), respectively, were prepared by addition of the appropriate ligand to the five coordinate starting complex Fe(TPP)(CS) and studied by IR and electronic absorption spectra and others; mono and binuclear complexes are in a dynamic equilibrium [73].

The five-coordinate complex Fe(OEP)(CS) (**34**) was prepared from Fe(OEP)Cl/sodium amalgam and thiophosgene in THF; the related six-coordinate species **35a–e** were obtained from **34** and excess of the appropriate ligand (py, 1-MeIm, Pip, 4-CNPy and 4-NMe$_2$Py) in CH_3Cl/MeOH [74]. Further studies on **34** in the presence of various pyridine derivatives are described in [75].

4.1.4.2. Ru. The mononuclear complex **36** and the binuclear complexes **37** and **38** with terminal CS ligands were obtained by procedures following a modified PPh_3/CS_2 procedure (Eqs. (26)–(28)) [76].

$$\mathrm{RuH(CO)Cl(AsPh_3)_3 + CS_2} \rightarrow \mathrm{RuH(CO)(CS)Cl(AsPh_3)}\ (\mathbf{36}) \tag{26}$$

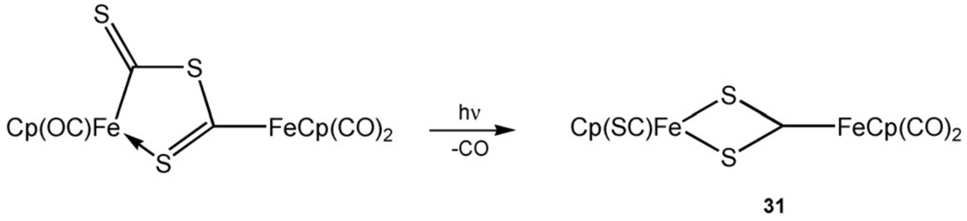
$$\mathrm{Ru(MeCN)_2Cl_2(PPh_3)_2 + PPh_3/CS_2} \rightarrow \mathrm{[Ru(CS)Cl(PPh_3)_2]_2(\mu\text{-}Cl)_2}\ (\mathbf{37}) \tag{27}$$

$$\mathrm{RuH(MeCOO)(PPh_3)_3 + CS_2} \rightarrow \mathrm{[Ru(CS)(MeCOO)(PPh_3)_2]_2(\mu\text{-}S)}\ (\mathbf{38}) \tag{28}$$

The stable and well characterized neutral ruthenium carbido complex $Cl_2(PCy_3)_2RuC$ takes up a sulfur atom from elementary sulfur to produce the related thiocarbonyl complex $Cl_2(PCy_3)_2Ru(CS)$ (**39**) according to the procedure outlined in Eq. (12) [37].

RuI_3 reacts with CS_2/PPh_3 to produce $RuI_2(CS)(PPh_3)_3$ (**41**) [77]. The bromide **40** was similarly prepared from $RuBr_2(Me_2SO)_3$; with CS_2 only $RuBr_2(CS)(Me_2SO)_2$ (**42**) was formed. However the $CS_2/AsPh_3$ system with $RuBr_2(Me_2SO)_3$ results in the formation of $RuBr_2(CS)(AsPh_3)_2(Me_2SO)$ (**43**) [78].

The dimeric species $[RuCl_2(CS)(PPh_3)_2]_2$ is cleaved by dithiolate ligands such as $EtOCS_2^-$ or the related anion $Ph_2PC(S)NPh^-$ to give the chelate complexes $Ru(Et_2dtc)_2(CS)(PPh_3)$ (**44**), $Ru(Etxant)_2(CS)(PPh_3)$ (**45**) or $Ru(Ph_2PCSNPh)_2(CS)(PPh_3)$ (**46**), respectively; a similar reaction between



Scheme 6.

$Ph_2PC(S)NPh^-$ and $RuCl_2(CO)(CS)(PPh_3)_2$ gives the monosubstitution product $RuCl(Ph_2PC(S)NPh)(CO)(CS)(PPh_3)$ (**47**) [79].

In the neutral complex, $RuClH(CS)(PPh_3)_3$ the Cl^- ion and one phosphine can be replaced by the S_2CPCy_3 ligand to give the cation $[RuH(CS)(PPh_3)_2(\eta^2\text{-}S_2CPCy_3)]^+$ (**48**) with the phosphine groups in *trans* position [80].

The cations $[(S_3)Ru(CS)X(PPh_3)]^+$ (**49a**, **b**) (X = H, Cl) were obtained from the reaction of the thiacrown ether 1,4,7-trithiacyclononane (S_3) with $Ru(CS)HCl(PPh_3)_3$ or $Ru(CS)(OH_2)Cl_2(PPh_3)_2$, respectively [81]; a similar procedure with $RuRCl(CS)(PPh_3)_2$ ($R = CO_2MeC{=}CHCO_2Me$) proceeds with loss of a chloride and a phosphine ligand to produce the thiacrown ether complex **49c**; with R = H, Ph migration of the olefin to the thiocarbonyl carbon atom occurs [82]; the complexes **49** are shown in Chart 4.

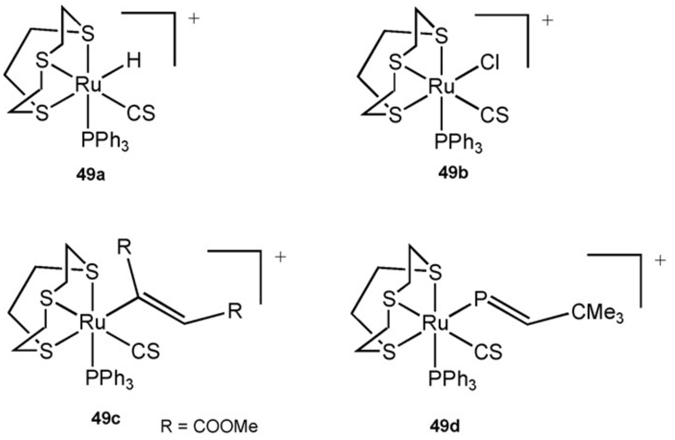
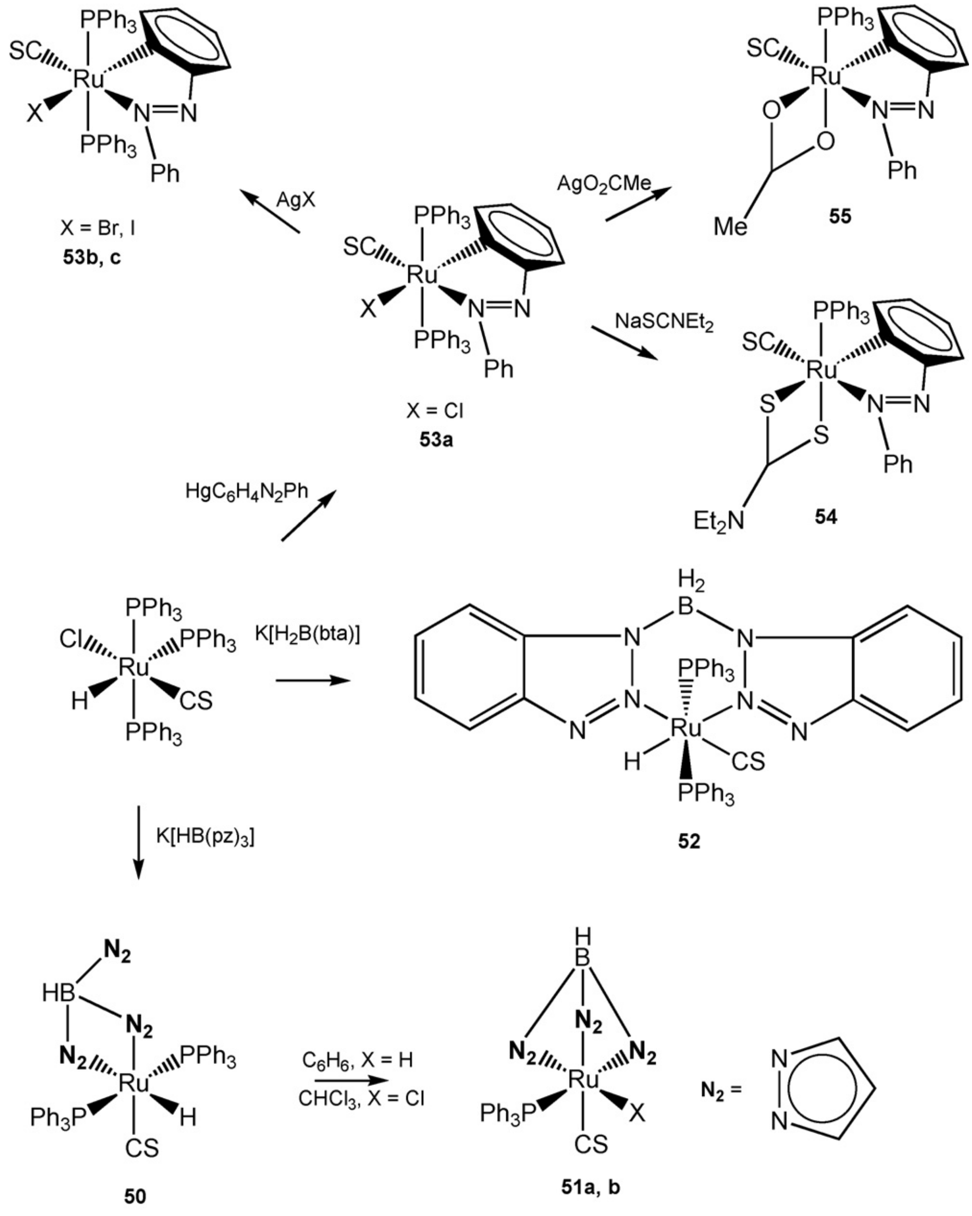
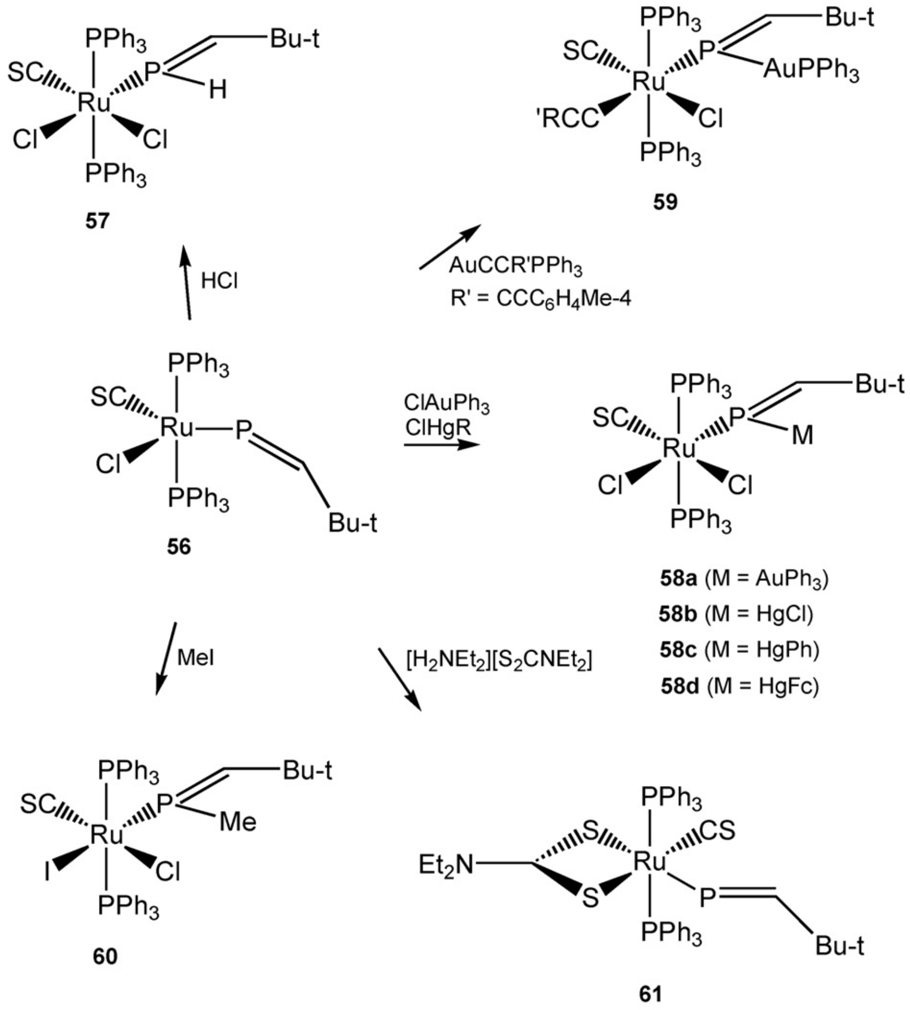


Chart 4.



Scheme 7.



Scheme 8.

The hydrido complex Ru(CS)HCl(PPh$_3$)$_3$ is starting material for further products. Thus, reaction with the anionic polydentate ligands K[HB(pz)$_3$] and K[H$_2$B(bta)$_2$] produces the η^3- and η^2-poly(azolyl)borate complexes **50**, **51a**, **b**, and **52** [83].

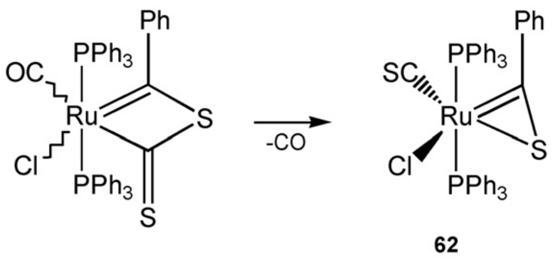
Treatment of Ru(CS)HCl(PPh$_3$)$_3$ with Hg(o-C$_6$H$_4$N = NC$_6$H$_5$) affords RuX(CS)(η^2*C,N*-*o*-C$_6$H$_4$N = NC$_6$H$_5$) **53a** (X = Cl). Chloride exchange with AgNO$_3$/NaBr or NaI generates **53b**, **c** (X = Br, I); with NaS$_2$CNEt$_2$ or AgOC(O)Me the substituted complexes **54** and **55**, respectively, are formed [84]; the chemistry of the Ru complexes is depicted in Scheme 7.

Ru(CS)HCl(PPh$_3$)$_3$ hydrometallates the phosphaalkyne P≡CBu-t to gives the five coordinate addition compound **56** [85]; addition of HCl or various gold and mercury halogen compounds to **56** produces the new phosphaalkene thiocarbonyl compounds **57** and **58a-d**, respectively [86,87]; addition of MeI to **56** leads to the phosphaalkene complex **60** [88] (Scheme 8). With the salt [N$_2$NEt$_2$][S$_2$CNEt$_2$] the complex **61** is obtained while the thiocrown ether (S$_3$) (see above) produces the cation **49d** (Chart 4) [85].

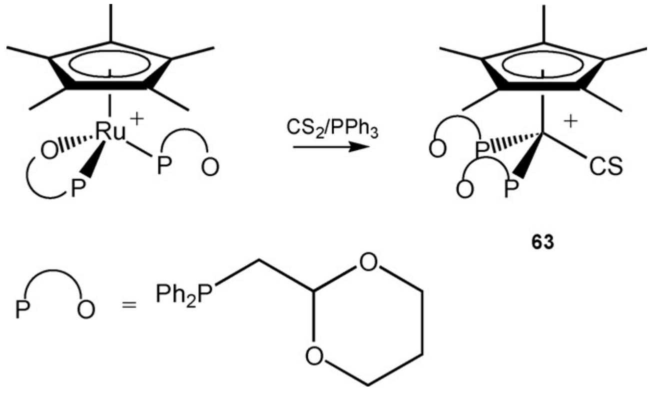
The preparation of Ru(CS)Cl(PPh$_3$)$_2$(η^2-SCPh) (**62**) from the carbyne complex Cl(CO)PPh$_3$)$_2$Ru≡CPh and CS$_2$ is reported. A mechanism with addition of CS$_2$ to the carbyne triple bond and formation of an intermediate 1-metalla,3-thiacyclobutene-1 as shown in Scheme 9 was proposed followed by splitting of the ring CS bond and arrangement to **62** [30].

The first ruthenium thiocarbonyl complex containing an η^5-bonded ligand was formed by the convenient CS$_2$/PPh$_3$ process which opens the Ru–O bond of the chelating P∼O ligand in the cationic complex [(C$_5$Me$_5$)Ru(μ-P∼O)(P∼O)]$^+$ to produce **63** according to Scheme 10 [89].

Addition of the catecholboranes HBR$_2$ such as **I** or **II** to MHCl(CS)(PPh$_3$)$_3$ leads to the corresponding five-coordinate species M(BR$_2$)Cl(CS)(PPh$_3$)$_2$ (**64**, **65**, M = Ru) with a metal



Scheme 9.



Scheme 10.

boron bond (Chart 5); the related Os compound **101** forms by reaction of **I** with $OsPhCl(CS)(PPh_3)_2$ splitting off benzene [90]. Similarly, treatment of $RuPhCl(CS)(PPh_3)_3$ with $HgPh_2$ leads to unsaturated $MPhCl(CS)(PPh_3)_2$ (**66**, M = Ru); the PPh_3 groups are probably in the axial position [30]. Treatment of $MHCl(CS)(PPh_3)_3$ (M = Ru, Os) or unsaturated $M(Ph)Cl(CS)(PPh_3)_2$ with $HSiMe_2Cl$ gives the corresponding $M(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (**67**, M = Ru) compounds; the Si–Cl bond is reactive and ethanolysis results in the formation of the related complexes $M(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**68**) [91].

$Ru(CS)HCl(PPh_3)_3$ [14] is the starting complex for a variety of new thiocarbonyl compound as shown in Scheme 11. Thus, it reacts with BTD or BSD to produce the compounds **72a** and **72b**, respectively. With diphenylacetylene it is converted into the complex **70.** Addition of $K[H_2B(pz)_2]$ replaces Cl^- and one PPh_3 group to give compound **69**. The phenyl analogue **66** reacts similarly with the pyrazolyl salt with formation of **73** [92].

CS_2 activation by the trinuclear Ru cluster $Ru_3(CO)_7(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}PCy_2)_2$ leads to the 50 CVE complex **74** as depicted in Scheme 12 [36].

The vinyl group in $Ru(CH{=}CH_2)Cl(CS)(PPh_3)_2$ (**70a**) is replaced by reacting with $TeCl_4$ to produce $Ru(TeCl_3)Cl(CS)(PPh_3)_2$ (**75**) [93].

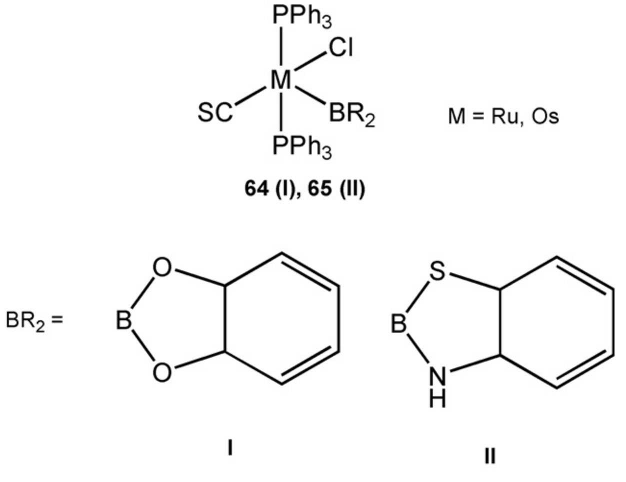


Chart 5.

With (TTP)M(CS)L complexes in the case of M = Ru the starting material (TTP)Ru(CS)(EtOH) (**76a**, TTP = tetra-*p*-tolylporphyrin) produces the isolable species **76b–p** with a couple of monodentate bases as summarized in Table 1 [94]. (TPP)Ru(CS)(CO) **77** (TPP = tetra-phenylporphyrin) was obtained in 90% yield by reacting (TPP)Ru(CO)(EtOH) with CS_2 in benzene [95].

4.1.4.3. Os. Scheme 13 shows that replacement of a phosphine or the carbonyl group of $Os(CO)(CS)(PPh_3)_3$ can lead to new thiocarbonyl compounds; see also some preparative procedures for osmium thiocarbonyl compounds in [96]. Thus, displacement of CO and one PPh_3 by PhCCPh results in the formation of $Os(CS)(PPh_3)_2(PhCCPh)$ (**78**) which is converted into the new thiocarbonyl complex **79** by HCl; CNR (R = *p*-tolyl) can be added to **79** to produce the six-coordinate complex $OsCl(\eta^1\text{-}CPh{=}CHPh)(CS)(CNR)(PPh_3)_2$ (**79a**). **78** is an example for a four-electron donor acetylene ligand allowing coordination number 4 [97]. However, C_2F_4 replaces a PPh_3 group of $Os(CO)(CS)(PPh_3)_3$ to give **80** [98]. Propyne reacts with $Os(CO)(CS)(PPh_3)_3$ to give a mixture of the oxidative addition product **81** and an osmabenzene (see Section 5) [99] and $P(NC_4H_4)_3$ replaces one PPh_3 group to give $Os(CO)(CS)(PPh_3)_2[P(NC_4H_4)_3]$ **83** [100]. The action of $Cd(CF_3)_2$ probably generates the difluor carbene containing thiocarbonyl complex $Os(CS)(CO)(CF_2)(PPh_3)_2$ (**82**) [101]. **78** is also the starting complex for the osmabenzofuranes **84–86** and the tethered osmabenzenes **87a** and **87b**, as shown in Scheme 14; the thiocarbonyl ligand remains "innocent" [102].

Starting from $OsCl_2(CS)(PPh_3)_3$ one phosphine group can be replaced to give $OsCl_2(CS)(PPh_3)_2L$ complexes. Benzoselenadiazole produces the orange complex **88** in good yield [103], while the action of $Hg(CCl_3)_2$ in the presence of PPh_3 gives the dichlorocarbene complex $OsCl_2(CCl_2)(CS)(PPh_3)_2$ **89** in 72% yield. **90** forms upon treatment the complex $OsCl_2(CCl_2)(CO)(PPh_3)_2$ with NaHS in methanol/benzene and **89** is the starting complex for **91** and **92** by treatment with H_2S or H_2Se, respectively, [8] for the $OsCl_2(CS)(PPh_3)_2L$ compounds, see Chart 6. The pentacoordinate complex $OsCl_2(CS)(PCy_3)_2$ (**93**) was prepared in 53% yield from $OsCl_2(CS)(PPh_3)_3$ upon phosphine exchange; the related iodide $OsI_2(CS)(PCy_3)_2$ (**94**) was obtained in 85% yield by reacting **93** with excess NaI in toluene [104].

A series of thiocarbonyl osmium compounds containing an "innocent" nitrosyl ligand are available according to Scheme 15. The iodide ligand in **95** is labile and can be abstracted with $AgClO_4$ in the presence of CO to give the cation **98**; the CO

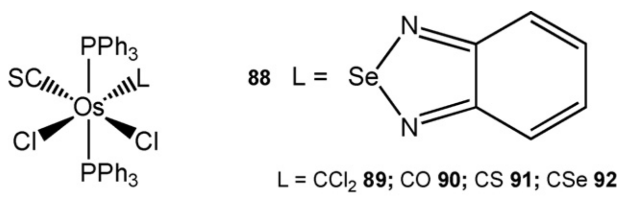
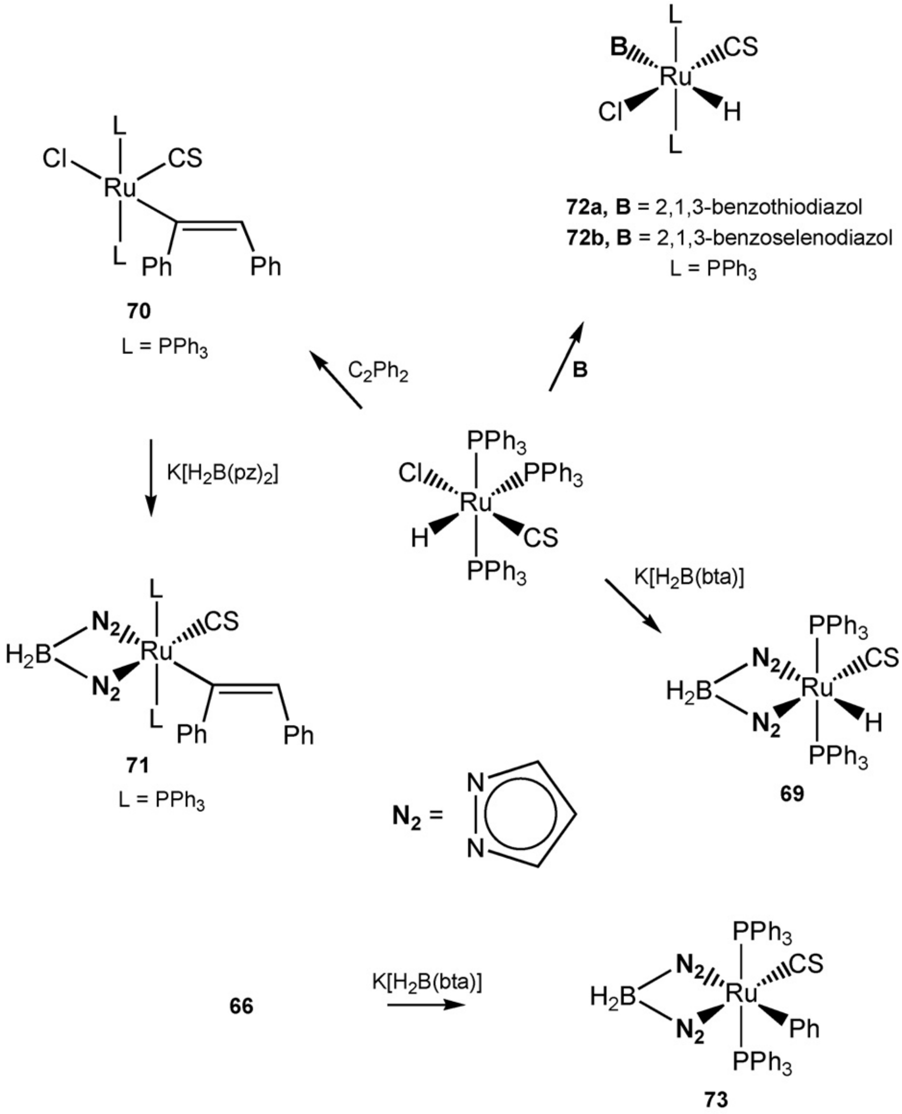


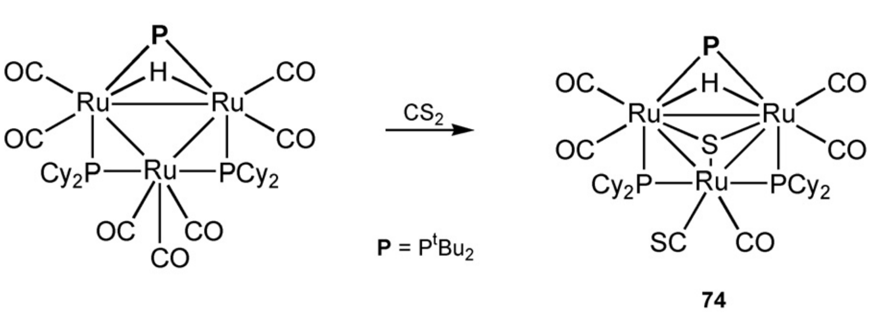
Chart 6.



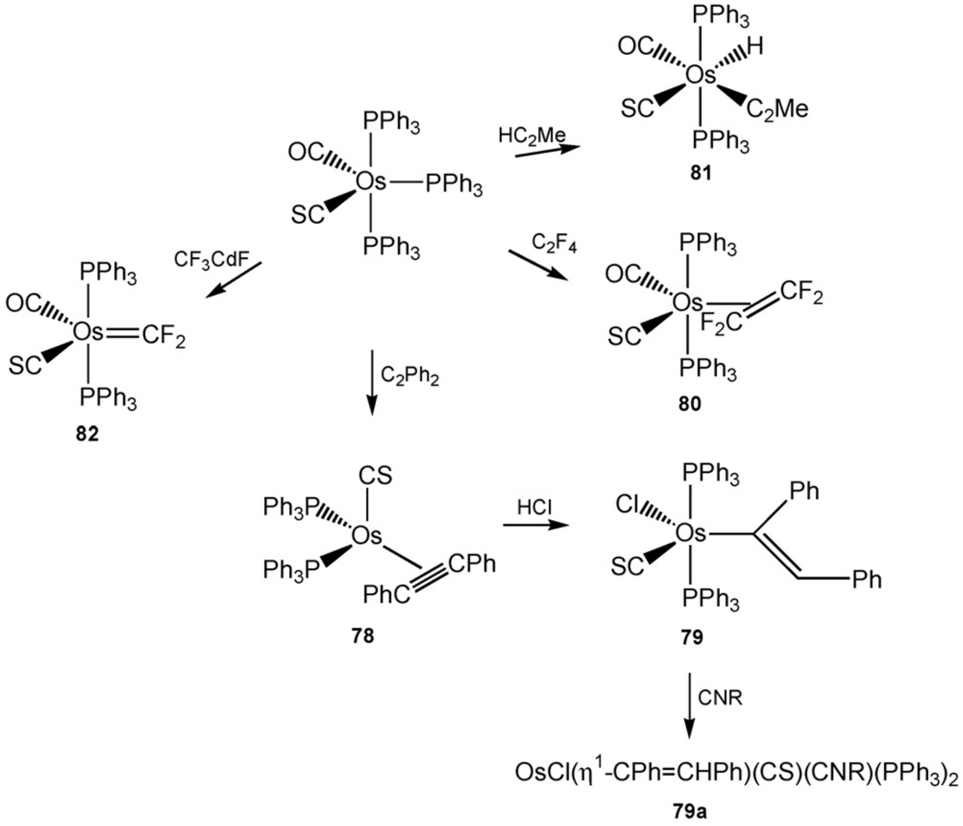
Scheme 11.

ligand is also labile and can be replaced by phosphine to give **99**. Reconversion to **95** is achieved by I^-. The lability of the iodide ligand in **95** can be used to prepare the corresponding chloride **96** or the hydridoselenide **97**, while oxidation with iodine produces the cation **100** (as the I_3 salt). The formation of **95** from a cationic η^2-CSSMe species was explained via an intermediate labile η^2-CTeS complex decomposing into elemental Te and the terminal thiocarbonyl ligand [105].

Related to the Ru complex **64** in Chart 5 the Os compound **101** forms by reaction of HBR_2 (**I**) with



Scheme 12.



Scheme 13.

OsPhCl(CS)(PPh$_3$)$_2$ splitting off benzene [90]. Similarly to the Ru complexes **67** and **68** treatment of OsHCl(CS)(PPh$_3$)$_3$ or unsaturated Os(Ph)Cl(CS)(PPh$_3$)$_2$ with HSiMe$_2$Cl gives the corresponding Os(SiMe$_2$Cl)Cl(CS)(PPh$_3$)$_2$ (**102**); the Si–Cl bond is reactive and ethanolysis results in the formation of Os(SiMe$_2$OEt)Cl(CS)(PPh$_3$)$_2$ (**103**) [91].

Some five-coordinate silatranylosmium(II) compounds were also mentioned. Thus, OsClPh(CS)(PPh$_3$)$_2$ (**104**) was reported to react with the silatrane HSi(OH$_2$CH$_2$)$_3$N to produce **105** under release of benzene; **105** can be alkylated with MeI at the nitrogen atom to give the iodide **106** as shown in Scheme 16 [106]. OsHCl(CS)(PPh$_3$)$_3$ is also the starting complex for compounds listed in Scheme 17. Thus, the salt **107** was obtained by reacting it with AgClO$_4$ in refluxing acetonitrile. Subsequent reaction with [NEt$_4$]Cl and BTD produces quantitatively the complex **108** which with 4-ethynyltoluene gives the complex **109** [107].

Within this group a series of new porphyrine thiocarbonyl compounds with the (Por)M fragments (M = Fe, Ru) have been prepared. Earlier reports from (Por)M(CS) compounds are available with M = Fe, Ru, Os [14]; selenocarbonyls concentrate on (TPP)Fe(CSe) [108].

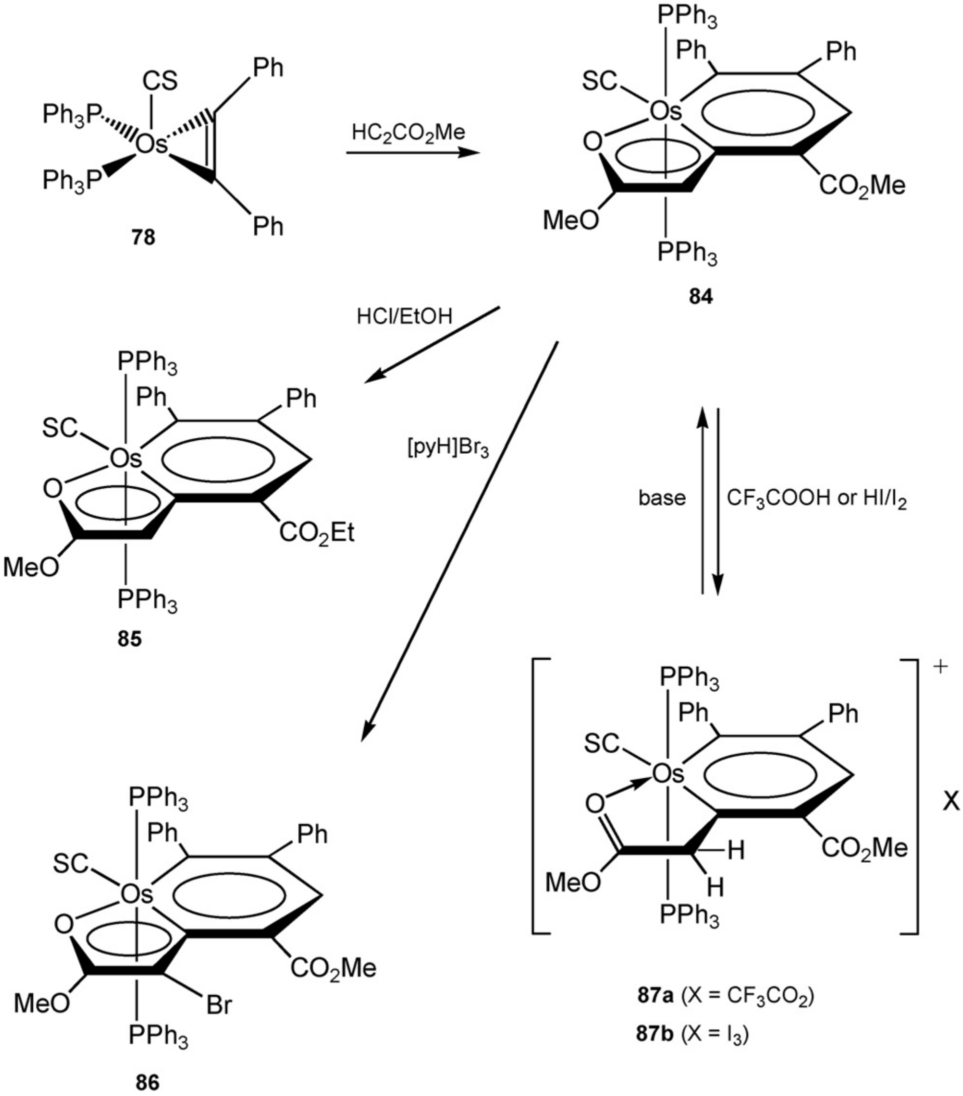
4.1.5. *Group 9 compounds (Co, Rh, Ir)*

4.1.5.1. Co. Some thiocarbonyl compounds of cobalt have been reported earlier [14], but further activities in this field are not known. New thiocarbonyl compounds concentrate on rhodium and iridium thiocarbonyl compounds.

4.1.5.2. Rh. The convenient PPh$_3$/CS$_2$ route converts the nitrosyl complex Rh(NO)(PPh$_3$)$_3$ (**110**) into Rh(CS)(NO)(PPh$_3$)$_2$ [109].

RhCl(CS)(PPh$_3$)$_2$ is the starting material for various other Rh complexes with a terminal CS group. With the “thiacrown” 1,4,7-trithiacyclononane ([9]aneS$_3$) in the presence of NaClO$_4$ the cationic compound [(S$_3$)Rh(CS)(PPh$_3$)]$^+$ (**111**) is generated [110]. The reaction with K[H$_2$B(bta)$_2$] produces the compound Rh(H$_2$B(bta)$_2$(CS)(PPh$_3$)$_2$ (**112**) [111] and the reaction with K[Fe(CO)$_3$(Si(OMe)$_3$(dppm)] leads to the orange binuclear complex Fe(CO)$_3$(Si(OMe)$_3$(μ-dppm)Rh(CS)(PPh$_3$) (**113**) as shown in Chart 7 [112]. A series of mononuclear and binuclear compounds **114–119** are mentioned in a short communication. Treatment of the starting compound with AgClO$_4$ and an imidazole ligand leads to the cationic compounds [Rh(HRIm)(CS)(PPh$_3$)$_2$]$^+$ (**116**) which can be deprotonated with KOH to the neutral trinuclear species **115**; however, trinuclear compounds of the type {Rh(μ-RIm)(CS)(PPh$_3$)}$_3$ (**114**) are available under elimination of one PPh$_3$ molecule by treating the complex directly with the corresponding imidazolate anions. Treatment of [Rh(CS)(PPh$_3$)$_2$(Me$_2$O)$_x$]$^+$ with the gold azolate complex Au(RIm)(PPh$_3$) produces the heterodinuclear complex [(PPh$_3$)$_2$(CS)Rh(μ-RIm)Au(PPh$_3$)]ClO$_4$ (**119**) [113].

4.1.5.3. Ir. Some new Ir compounds have been prepared. Thus, CpIr(CS)(PPh$_3$) upon protonation leads to the cationic species [CpIr(H)(CS)(PPh$_3$)]$^+$ (**120**) [114]. The chlorine atom



Scheme 14.

of $IrCl(CS)(PPh_3)_2$ can be exchanged by various pyrazolate and imidazolate anions to produce $Ir(bzIm)(CS)(PPh_3)_2$ (**121**) compounds [113].

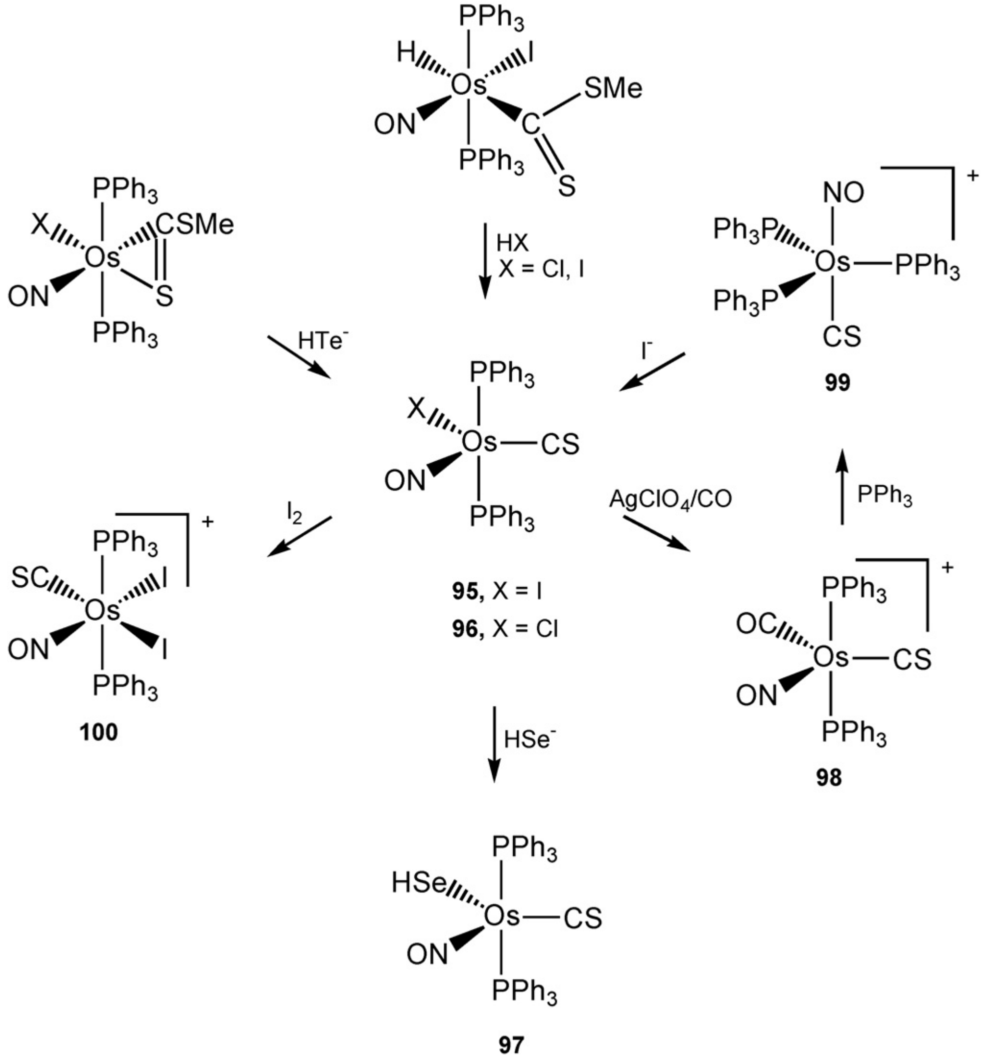
An improved synthesis (95% yield) of Vaska's thiocarbonyl analogue $IrCl(CS)(PPh_3)_2$ (**122**) from thermal decomposition of $IrHCl(C\{S\}SMe)(CO)(PPh_3)_2$ is published in [116,117]. The iodide **123** is available by halogen exchange which can be converted into **124** upon treatment with air; the O_2 uptake can be reversed on heating a solution under vacuum [118]. **122** as well as Vaska's compound can also be used as starting materials for further Ir(I) and Ir(III) thiocarbonyl compounds which form after various oxidative addition and subsequent reductive elimination steps (Scheme 18). The second CS ligand of the cationic compound **125** was obtained by oxidation of **126** as the triiodide **125a** and, by use of ICl, as the chloride **125b**. The ionic–covalent equilibrium between **126** and **127** (R = SPh) depends on the polarity of the solvent; in nonpolar or weakly polar solvents the neutral species predominates and in polar solvents the (alkylthio)thiocarbonyl ligand becomes bidentate. The pentacoordinate cationic complex **128** is formed either by reductive dehydrohalogenation of **129** in the presence of the isonitrile ($R = C_6H_3Me_2$-2,6) or from $IrCl(CS)(PPh_3)_2$ (**122**) with excess isonitrile [115].

4.1.6. Group 10 compounds (Ni, Pd, Pt)

Within the nickle triad only some new platinum complexes with terminal CS ligands were reported. From nickel no stable compounds with a terminal CS ligand is known as yet and to our knowledge the same is true for palladium compounds including bridging compounds.

The first mononuclear thio- and selenocarbonyl platinum complexes **130** (E = S) and **196** (E = Se) as shown in Chart 8 were obtained in the group of Werner by thermal decomposition of the corresponding (dpmb)Pt(μ-ECE)$Pt(PPh_3)_2$ complex at 40–70 °C in benzene or dichloromethane; a similar procedure with $Ph_3PPt(\mu\text{-}SCS)Pt(PPh_3)_2$ leads to $(PPh_3)_2Pt(CS)$ (**131**) [32].

Further binuclear PtCS compounds have been obtained by the same group via metal induced cleavage of coordinated CSE molecules (E = S, Se) according to Eq. (7). Thus, various



Scheme 15.

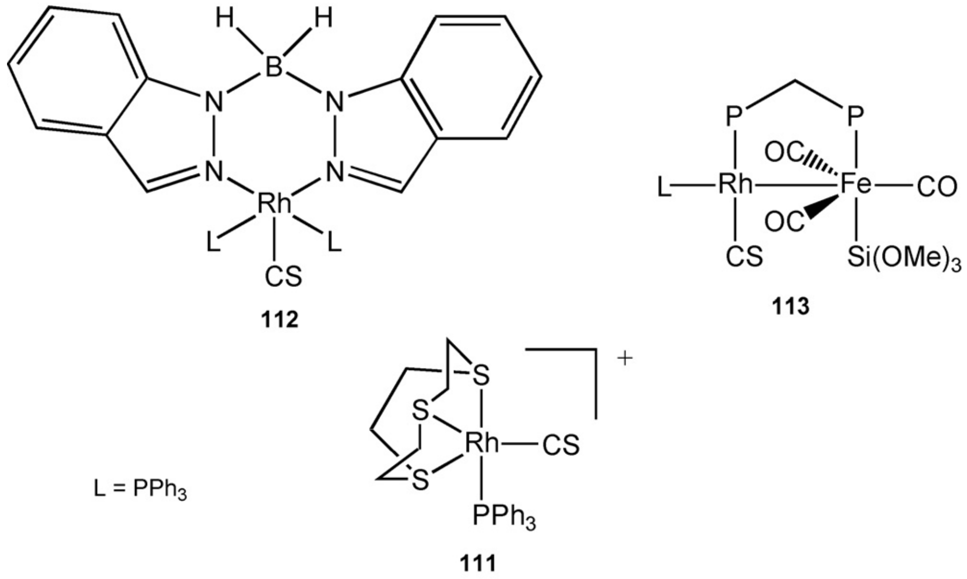
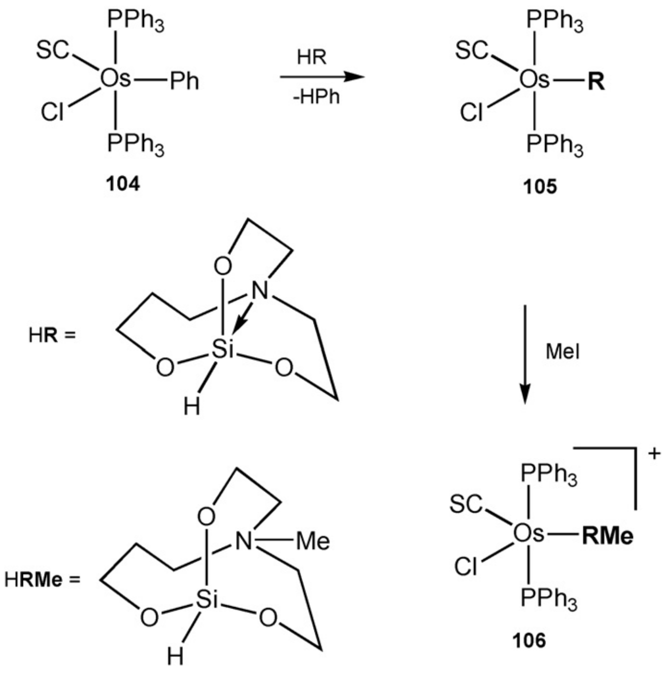
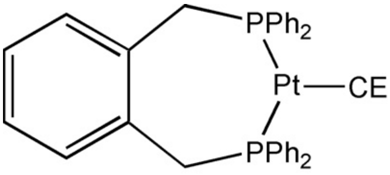


Chart 7.



Scheme 16.



130, E = S
196, E = Se

Chart 8.

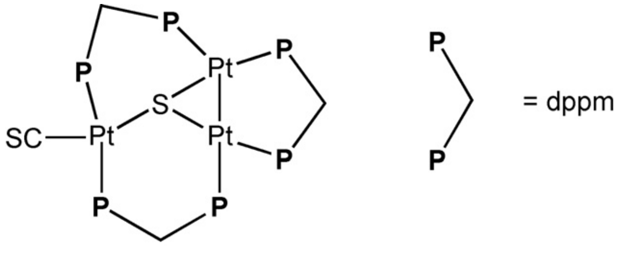


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Chart 9.

chelate (diphos)Pt(η^2-CEE′) compounds react with Pt(PPh$_3$)$_4$ or Pt(PPh$_3$)$_2$(C$_2$H$_4$) to produce the μ-E compounds **132a–d** (Scheme 19) [31,119,120]. The related (PPh$_3$)$_2$Pt(η^2-CEE′) gives complex **133**. A mechanism with formation of an intermediate μ-η^2-CSE complex in the first step which loses a further phosphine and CSE cleavage or the formation of an intermediate μ-η^3-CSE complex was proposed [31].

The Pt complex **134** in Chart 9 was reported by Puddephatt to be formed by reacting the coordinatively unsaturated complex [Pt$_3$(μ_3-CO)(μ-dppm)$_3$]$^{2+}$ with CS$_2$; an intermediate η^1-S=C=S adduct was postulated which undergoes an oxidative addition. A structure with only one Pt–Pt bond in the trinuclear cluster was deduced from spectroscopic properties [33].

4.1.7. Group 11 compounds (Cu, Ag, Au)

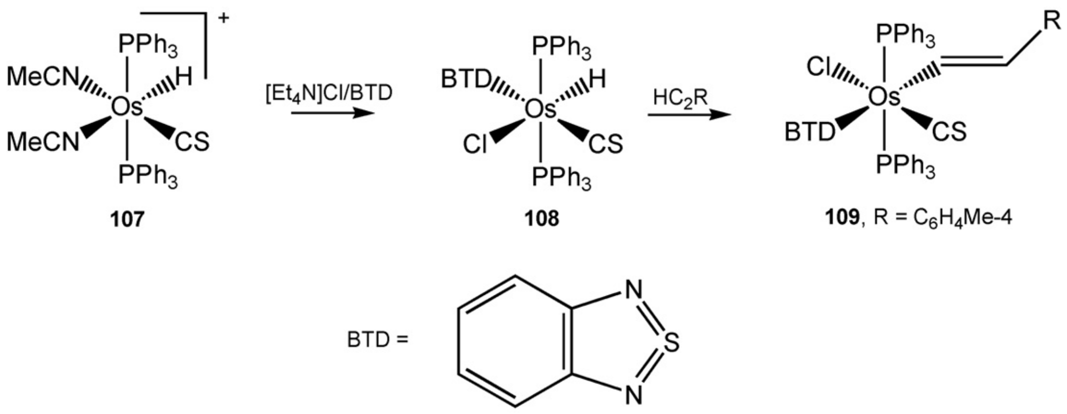
No isolable compounds with a terminal thiocarbonyl or other CE ligand of one of the group 11 elements is known till the present time. However, a semibridging interaction between Au and a CS group in the compounds HB(pz)$_3$(CO)$_2$(CS)WAuPR$_3$ (R = Me, Ph) has been reported (Table 1, Nos **166a** and **166b**) [45].

The species Au(CS), Au(CS)$_2$ and Au$_2$(CS) were established in solid argon matrix [121].

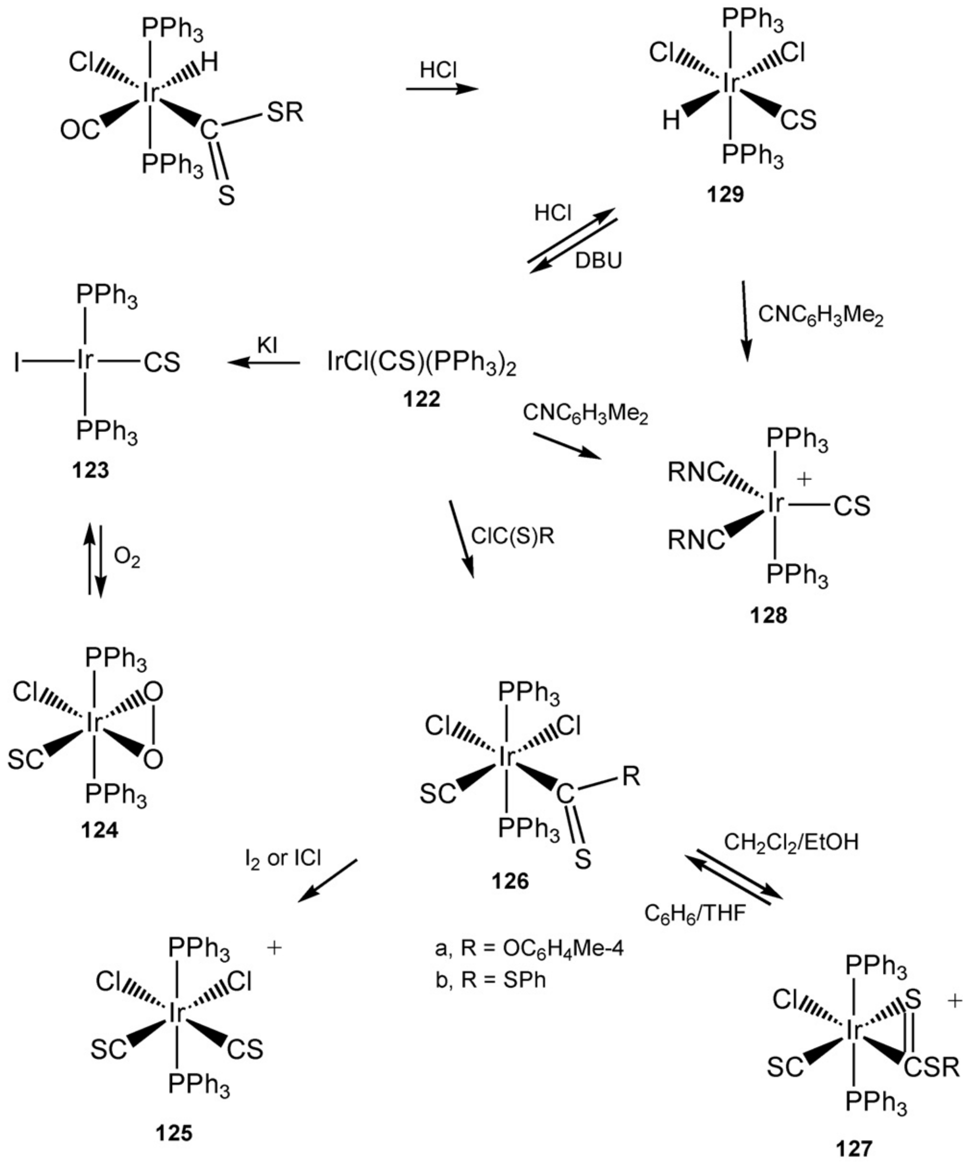
4.2. Compounds with bridging CS ligands

4.2.1. Bridging μ_2-CS

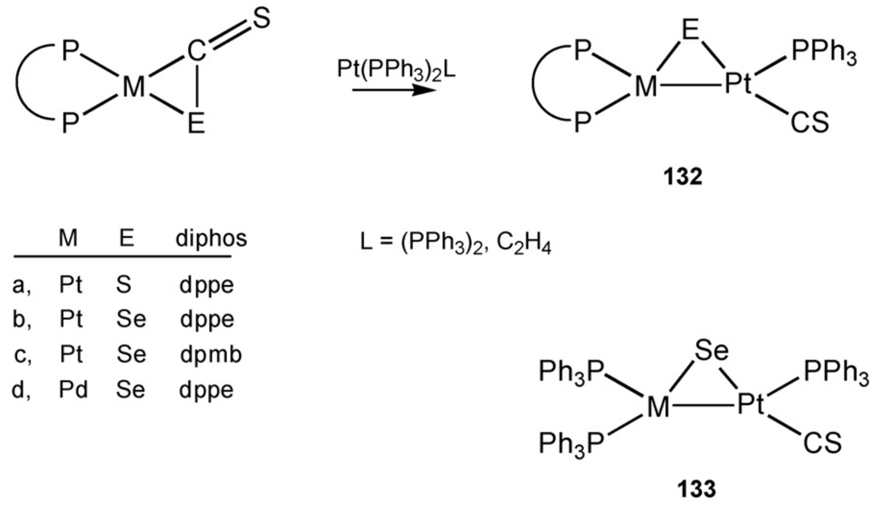
The dimeric compounds {Cp*Fe(CO)(CS)}$_2$ (Cp* = C$_5$H$_5$, **135a**; C$_5$Me$_5$, **135b**) were obtained by the group of Angelici as a mixture of the *cis*/*trans* isomers by reduction of [Cp*Fe(CO)$_2$(CS)]$^+$ with NaH; small amounts of {Cp*Fe(CO)$_2$}$_2$ and Cp$^*_2$Fe$_2$(CO)$_3$(CS) were also formed. The CS ligand always prefer the bridging position [16,42].



Scheme 17.



Scheme 18.



Scheme 19.

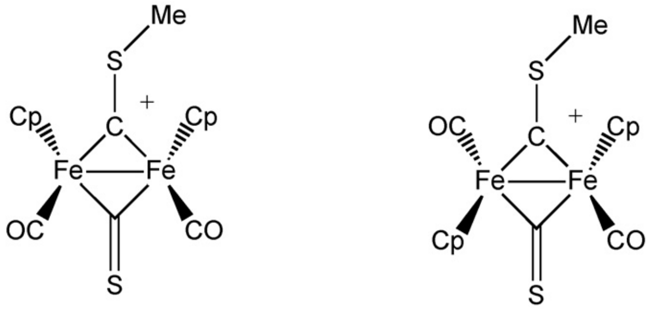


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Chart 10.

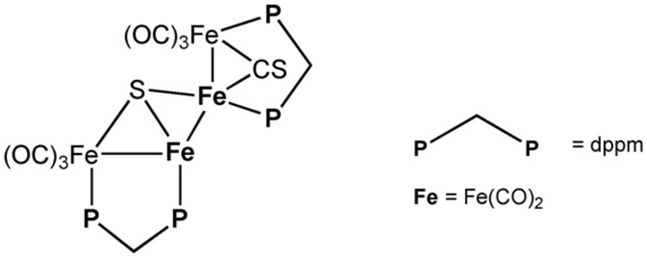

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Chart 11.

An extended chemistry is known with $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS)$ and $Cp_2Fe_2(CO)_2(\mu\text{-}CS)_2$ **135a**, the thiocarbonyl derivatives of *cis*/*trans*-$Cp_2Fe_2(CO)_4$. $Cp_2Fe_2(CO)_2(\mu\text{-}CS)(\mu\text{-}CH_2)$ **136** was obtained by reduction of **135a** with Raney Ni [16]. Alkylation of *cis*- and *trans*-$Cp_2Fe_2(CO)_2(\mu\text{-}CS)_2$ separated by chromatography with magic methyl leads to the cationic *cis* and *trans* complexes **137** shown in Chart 10 [42]. The lack of isomerization of **137** in solution was interpreted as a consequence of the higher bond order of the Fe-(μ-CS) interaction [122].

Busetto et al. reported about different reaction routes of the cationic species **137** with nucleophiles by modification of the μ-carbyne ligand. The reaction of both the *cis* and the *trans* isomer with NCO^- causes insertion into the CS bond of the μ-bridging carbyne ligand to give **138**. Subsequent treatment of the insertion product **138** with hard acids occurs at different nucleophilic centers; H^+ prefers the nitrogen atom to give **139** while Me^+ adds at the sulfur atom of the bridging CS group to produce the related cationic complexes (Scheme 20 and reactions of **138** in Scheme 36) [123,124].

CN^- or H^- only add at the bridging carbyne carbon atom of **137** to produce new thiocarbonyl complexes **140** with μ-carbene ligands [122].

The μ-C(SMe)X group acts as an S-donor and is able to replace a terminal CO group with formation of **141** with an η^2-bonded bridging carbene ligand; the action of NCMe gives **142** (Scheme 21) [122]. On the other hand, 2-thienyllithium (Lith) mainly undergoes Cp addition to form an η^4-C_5H_5th ligand in complex **144**; a CO attack occurs to a minor extend with formation of **143** with a C(O)th ligand [125]; the reactions are summarized in Scheme 21. The complex **137** (as the SO_3CF_3 salt) is also the starting material for the preparation of the following complexes, Thus, **145** is obtained with Me_2dt while acetonitrile with two equivalents of Me_3NO produces **146**. Complex **147** forms upon irradiation of **145** or from **146** with Me_2dt in acetone [126].

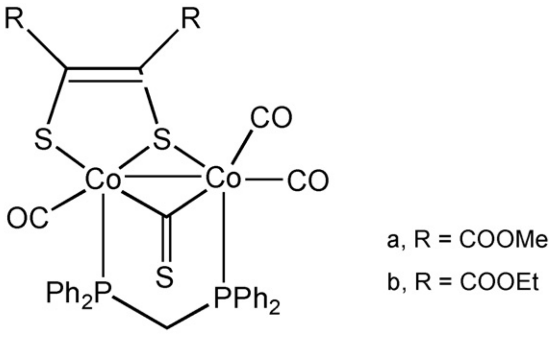

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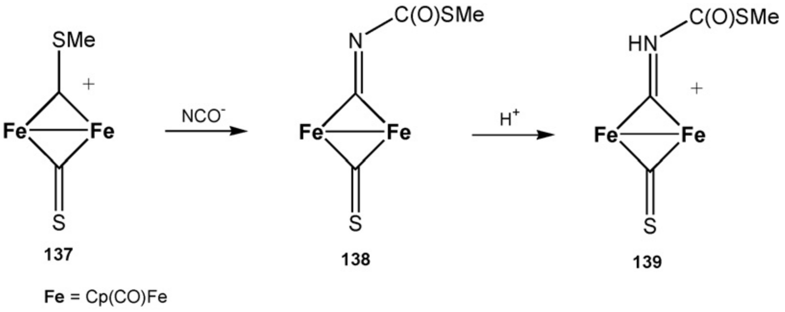
Chart 12.

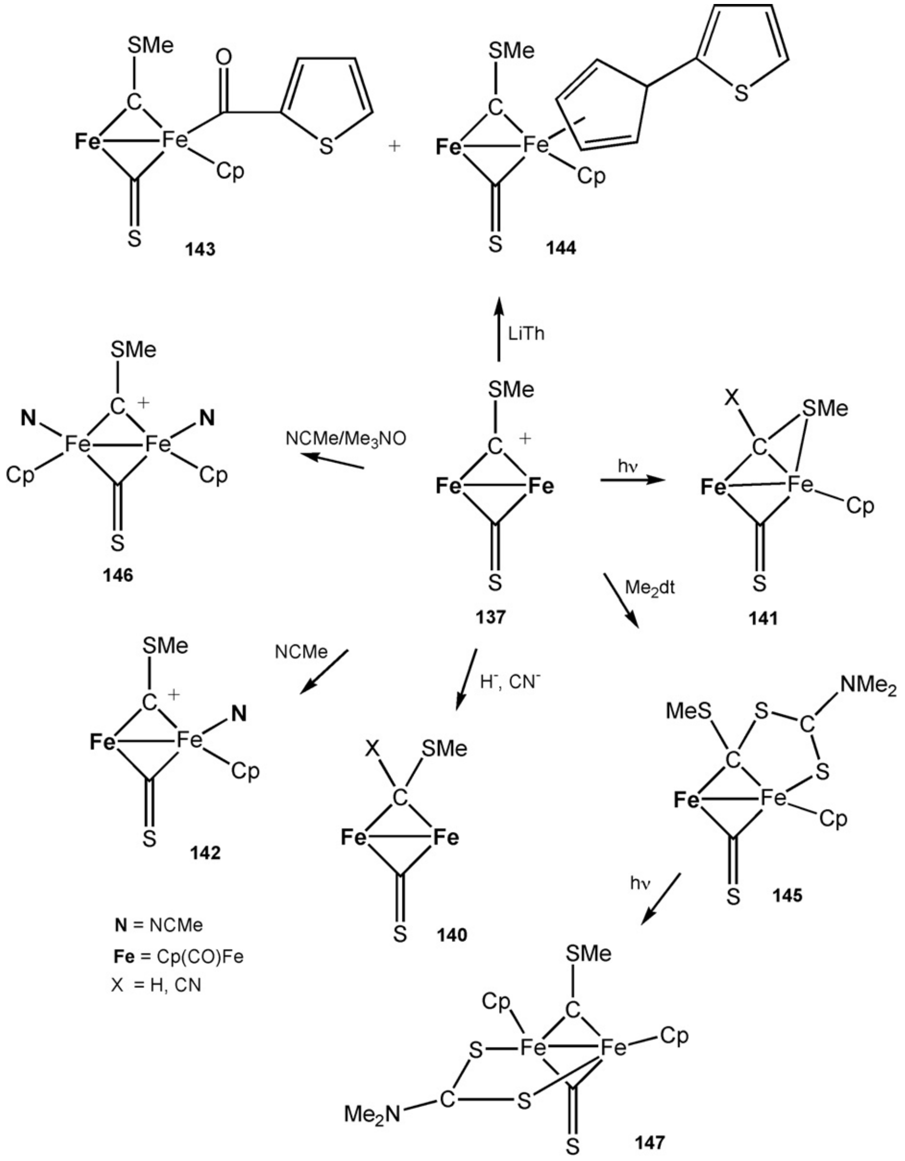
The reaction of CS_2 with the $Fe_2(CO)_9$ derivative $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}dppm)$ leads to carbon–sulfur bond scission to produce $Fe_4(CO)_{10}(\mu_3\text{-}S)(\mu\text{-}CS)(\mu\text{-}dppm)$ **148** for which a structure with a bridging CS ligand as shown in Chart 11 was suggested; the spectroscopic data indicate the formation of two isomers [127].

The binuclear cobalt complexes **149** ($R = CO_2Me$, **a**; CO_2Et, **b**) depicted in Chart 12 was obtained in about 40–60% yields by reacting the corresponding 1,3-dithiole-2-thiones with $Co_2(\mu\text{-}dppm)(CO)_6$ [50].

A symmetrically bridging CS ligand is also formed in the reaction of the diplatinum compound **132b** (the chelating ligand

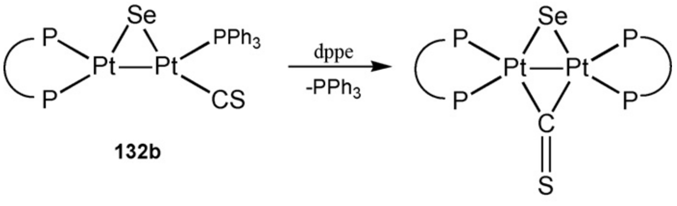


Scheme 20.



Scheme 21.

is dppe) containing a μ-Se ligand when reacted with dppe with result of **150** as shown in Scheme 22; however, treatment of similar compounds with a chelating ligand causes coupling of the bridging chalcogen with CS to produce a μ-ECS compound as shown in Section 5 (Scheme 33); the type of reaction seems to depend on the metal (Pt or Pd), the bridging chalcogen (Se or S), and the diphos ligand (dppe or dpmb) introduced [31].

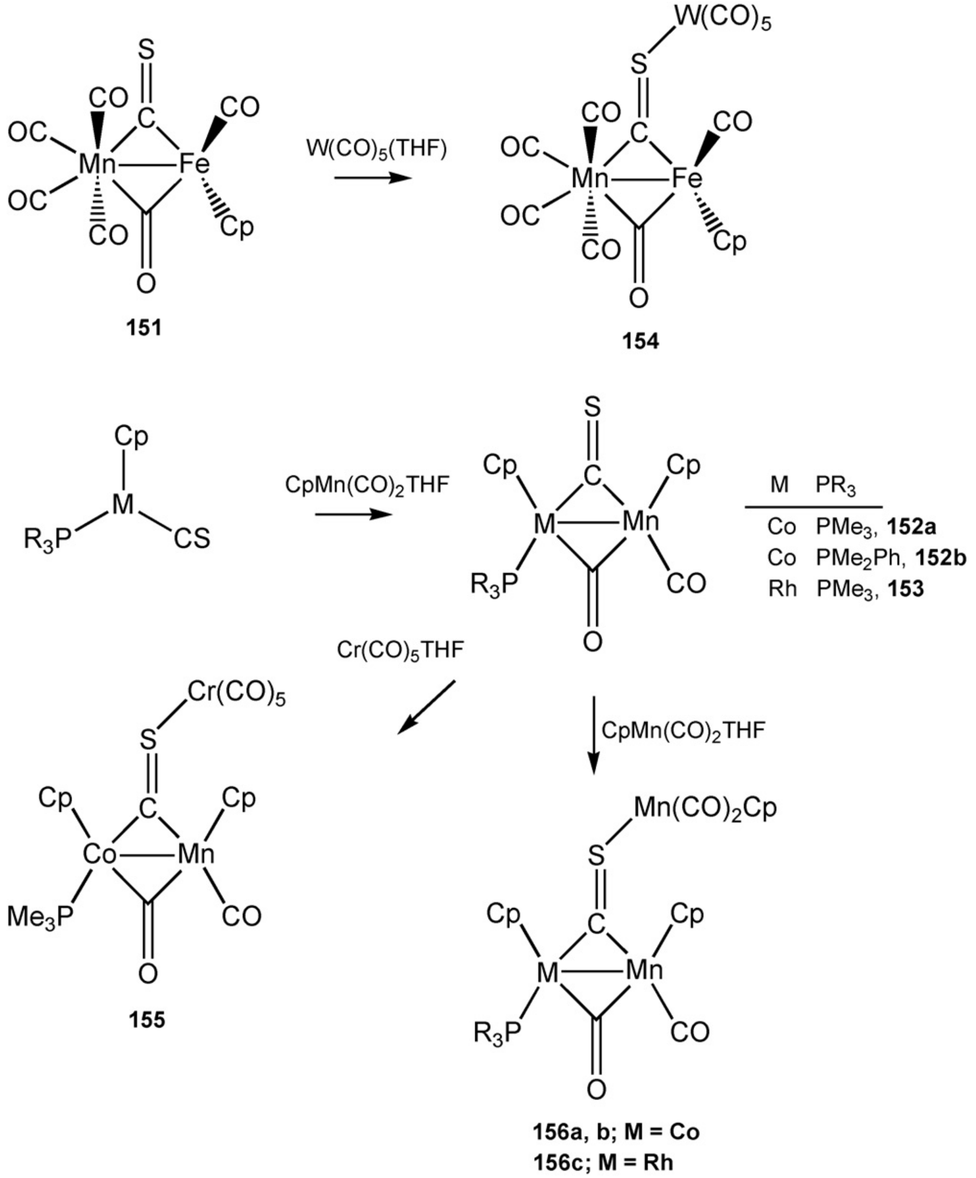


Scheme 22.

New heterodinuclear compounds with Fe–Mn, Co–Mn, Rh–Mn, W–Au, W–Mo bonds bridged by CS have been described by the groups of Werner and Busetto and shown in Scheme 23. Thus, a bridging CS group have been obtained from $[CpFe(CO)_2(CS)]^+$ and $[Mn(CO)_5]^-$ to give Cp(CO)Fe(μ-CO)(μ-CS)$Mn(CO)_4$ (**151**) [44] and from CpM(CS)(PR_3) and $CpMn(CO)_2$(THF) with result of Cp(PR_3)M(μ-CO)(μ-CS)Mn(CO)Cp; (M = Co, **152a**, **b**; M = Rh, **153**) [43]. Both types of compounds contain a symmetrical bridging CS group along with a bridging CO group. As shown from earlier results, the bridging CS group is more nucleophilic and is able to add 16-electron fragments.

4.2.2. *μ_3-CS (**F** and **G**)*

Thus, further reaction of **151** with $W(CO)_5$THF leads to **154** [44] and the compounds **152** and **153** similarly can be converted into the type **G** compounds **155** and **156**, respectively (Scheme 23) [43].

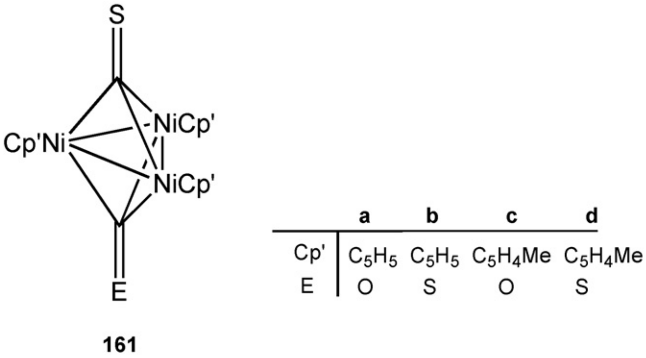


Scheme 23.

The thiophilic Ag^+ cation or $HgCl_2$ can also coordinate to the bridging CS group. Thus, $Cp_2Fe_2(CO)_3(CS)$ and $Cp_2Fe(CO)_2(CS)_2$ react with $AgBF_4$ to give $[\{Cp_2Fe_2(CO)_3(CS)\}_3Ag]BF_4$ (**157**) and $[Cp_2Fe_2(CO)_3(CS)_2Ag]BF_4$ (**158**), the latter probably being polymeric [16]. Similarly, the type **G** compound $Cp_2Fe_2(CO)_2(CS)(CSHgCl_2)$ (**159**) is obtained from the dithiocarbonyl complex with $HgCl_2$ [42].

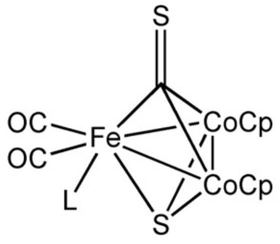
The new trinuclear Co cluster $(C_5Me_5)_3Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**160**) of type **F** has been obtained by reacting $(C_5Me_5)_3Co_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)$ with CS_2 at room temperature [128].

Thiocarbonyl compounds of nickel are restricted to a few paramagnetic trinuclear species of the Fischer-Palm type with 49 electrons and with μ_3-bridging CS groups. The compounds $Ni_3Cp'_3(\mu_3\text{-}CS)(\mu_3\text{-}CE)$ (**161a–d**), shown in Chart 13, have been obtained in about 10–30% yield by reacting the corresponding $Ni_2Cp'_2(\mu_2\text{-}CO)_2$ with CS_2 at reflux temperature; the compounds could be separated by chromatography [49].



	a	b	c	d
Cp'	C_5H_5	C_5H_5	C_5H_4Me	C_5H_4Me
E	O	S	O	S

Chart 13.



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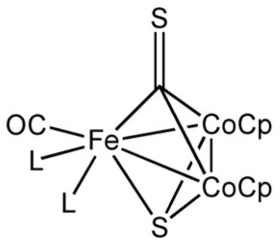

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a, L = PPh_3
b, L = $P(OMe)_3$
c, L = $P(OPh)_3$
d, L = $P(Bu^n)_3$
e, L = CNMe
f, L = CNMes
g, L = 2,6-$Cl_2C_6H_3NC$

e, L = CNMe
f, L = CNMes
g, L = 2,6-$Cl_2C_6H_3NC$

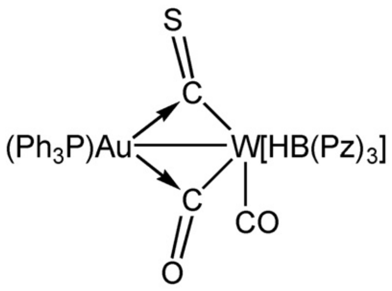
Chart 14.

A series of heterotrinuclear compounds with a Fe–Co–Co triangle and a μ_3-CS ligand has been prepared and summarized in Chart 14. The 48-electron cluster **162** forms upon the reaction of $Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)$ with the appropriate $Cp^*Co(PPh_3)_2$ ($Cp^* = C_5H_4Me$) [48]. The related compounds **163a** with the Cp ligand were similarly prepared; the PPh_3 group in **163a** can be replaced by other phosphines to produce the compounds **163b–d**. Addition of isonitriles to **163a** gives the complexes **163e**–**g** [47,48,129]. Further addition of isonitriles gives the disubstituted products **164e–g**; with CO the related starting complexes **163** are recovered. Addition of PPh_3 to **163g** replaces one CNR group to give the mixed substitution product **165** [129].

4.2.3. Other bridging modes

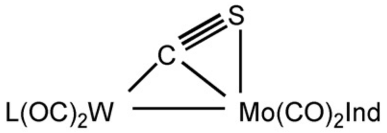
*4.2.3.1. Semibridging CS (**C**).* Reaction of the anionic species $[HB(pz)_3Cr(CO)_2(CS)]^-$ with $ClAuPR_3$ leads to $[HB(pz)_3](CO)_2(CS)WAuPR_3$, (**166**), the first examples of complexes containing a semibridging CO and a semibridging CS ligand (mode **C**) in the same molecule as shown in Chart 15; the crystal structure is described in Section 7 [45].

*4.2.3.2. Side on (**D**).* The only side-on bridge of type **D** (Chart 16) is realized in $[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2Ind$ (**167**) obtained from $[IndMo(CO)_2(MeCN)_2]BF_4$ and $[Bu_4N][HB(pz)_3](CO)_2W(CS)]$ [46].



166a, R = Me
166b, R = Ph

Chart 15.



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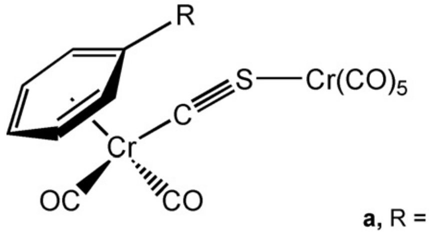
L = $HB(pz)_3$; Ind = $\eta_5\text{-}C_9H_7$

Chart 16.



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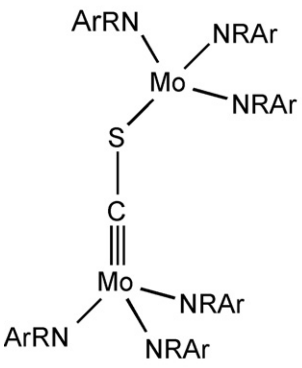
a, R = Me
b, R = OMe
c, R = Mes

Chart 17.

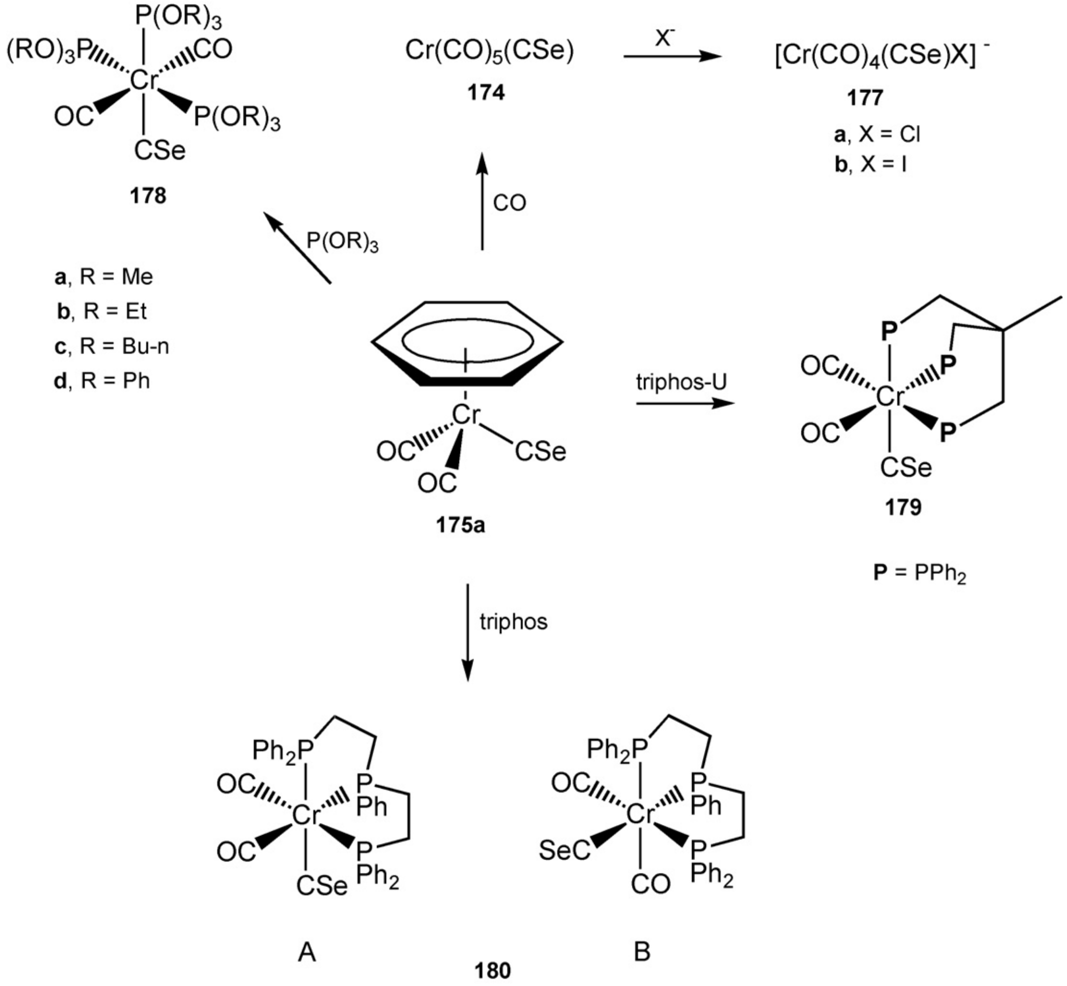
*4.2.3.3. End to end (**E**).* New compounds with one end to end bonded CS ligand of mode **E** have been obtained by replacement of the weakly coordinated THF ligand in $Cr(CO)_5THF$ by some $(\eta^6\text{-arene})(CO)_2Cr(CS)$ compounds; in the compounds **168** as η^6-arenes are used PhMe, PhOMe, and 1,3,5-$C_6H_3Me_3$ (Chart 17) [59]. The reaction with the anionic thiocarbonyl complex $[(HB(pz)_3)(CO)_2Mo(CS)]^-$ [14] with cationic organometal Lewis acids $[ML_n]^+$ leads to the corresponding $(HB(pz)_3)(CO)_2MoCSML_n$ compounds ($ML_n = CpFe(CO)_2$ **169**, $Re(CO)_5$ **170**, $CpRu(PPh_3)_2$ **171**); the cation $[(C_7H_7)Mo(CO)_3]^+$ loses CO to give $(HB(pz)_3)(CO)_2MoCSMo(CO)_2(C_7H_7)$ (**172**) [130].

Addition of CS_2 to $Mo(N\{R\}Ar)_3$ gives a 1:1 mixture of $[(\mu\text{-}CS)[Mo(N\{R\}Ar)_3]_2$ (**173**) (Chart 18) and $Mo(S)(N\{R\}Ar)_3$ in 42% yield [131].



173 R = $C(CD_3)_2Me$, Ar = 3,5-$C_6H_3Me_2$

Chart 18.



Scheme 24.

4.3. *Compounds with terminal CE (E = Se, Te) ligands*

4.3.1. *Compounds with Cr, Mo, W*

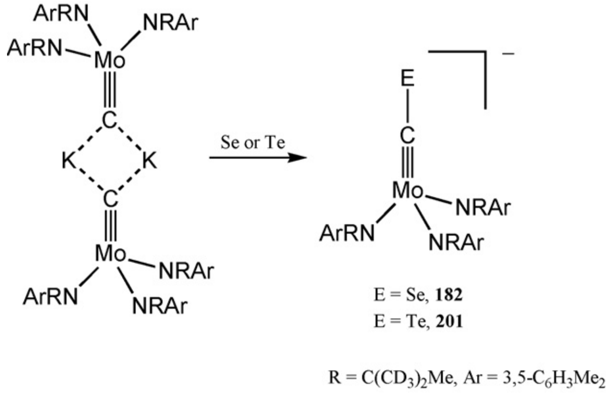
A series of selenocarbonyl compounds of chromium are collected in Scheme 24. The simplest selenocarbonyl complex, containing only CO and CSe as ligands, $Cr(CO)_5(CSe)$ (**174**), can not be prepared similar to its thiocarbonyl analogue. However, the selenocarbonyl complex (η^6-C_6H_6)$Cr(CO)_2(CSe)$ (**175**) is readily prepared in 45% yield by the CSe_2/PPh_3 route [132]; a similar procedure yields (η^6-C_6H_5COOMe)$Cr(CO)_2(CSe)$ (**176**) [2,133]. Treatment of this complex with excess CO under pressure produces $Cr(CO)_5(CSe)$ (**174**) in about 33% yield; this is the only access to this compound and the CSe ligand remains unchanged [132,134]. Halides replace the CO or the CSe ligand in **174** to give a mixture of the anions $[Cr(CO)_5X]^-$ and $[Cr(CO)_4(CSe)X]^-$ (X = Cl, **177a**; X = I, **177b**); thus, [PNP]Cl or Bu_4NI give 5/4 or 3/1 mixtures, respectively [132]. Three tertiary phosphite ligands or one tridentate phosphine ligand can be introduced to form $Cr(CO)_2(CE)[P(OR)_3]_3$ compounds (E = S, Se; R = Me, Et, Bu-n, Ph) by replacement of various arenes of the corresponding (η^6-arene)$Cr(CO)_2(CE)$ complexes **178**. The arene ligands can easier be replaced than CO in **174**. The *mer*-product **178** was found to be the major isomer. Treatment of the arene complex with triphos-U gives **179a** whereas with triphos an isomer mixture of **180** (*A*/*B* = 4/1 ratio; *A* consists of a pair of enantiomers) was obtained [23]. The related thiocarbonyl species are described in the previous section.

New Mo compounds of the type $[Mo(CO)_2(CE)(HB(3,5\text{-}Me_2C_3HN_2)_3)]^-$ with E = S, Se, Te have been prepared (E = Se, **181**; Te, **200**) according to Eq. (12) from the clorocarbyne complex $Mo(CO)_2(\equiv CCl)(HB(3,5\text{-}Me_2C_3HN_2)_3)$ by reacting with Na_2E [40]; the corresponding thiocarbonyl complex has already been reviewed in [14].

The dimeric anionic carbido complex {[**Mo**C]K}$_2$ takes up Se or Te to generate the corresponding seleno or tellurocarbonyl complex **182a**, **b** and **201** in 70 and 46% yield, respectively, as shown in Scheme 25 [38].

4.3.2. *Compounds with Mn, Re*

The compounds $CpM(CO)_2(CSe)$ with M = Mn, (**183**) and Re (**185**), and (η^5-C_5H_4Me)$Mn(CO)_2(CSe)$ (**184**) have been obtained via the CSe_2/PPh_3 route starting with the photochemically generated $CpM(CO)_2)THF$ complex [133]; a checked preparation of **183** is given in [135].



E = Se, **182**
E = Te, **201**

R = $C(CD_3)_2Me$, Ar = 3,5-$C_6H_3Me_2$

Scheme 25.

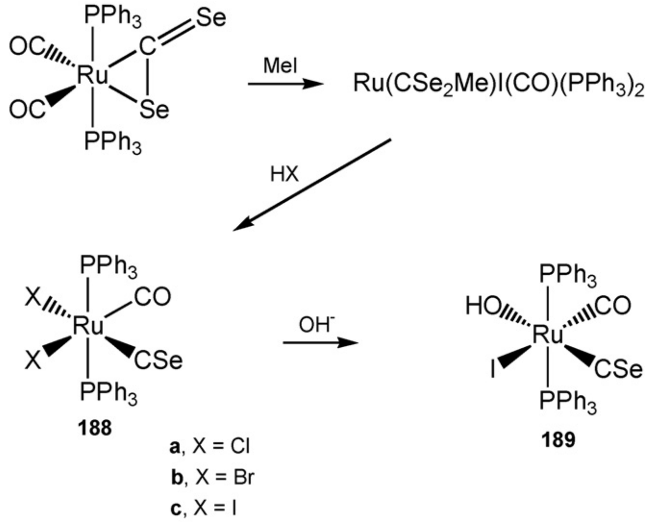
4.3.3. *Compounds with Fe, Ru, Os*

(TPP)Fe(CSe) (**186**) can be obtained by two different routes. It forms in about 50% yield by addition of catalytic amounts of $FeCl_2$ to an acetonitrile solution of Fe(TPP)(C(Cl)SeCH$_2$Ph) or by reduction of $PhCH_2SeCCl_3$ by Fe(TPP). Ethanol, *N*-methylimidazole, and pyridine give the six-coordinate compounds **186a–c** [108]. A further synthetic route to the compounds (TPP)Fe(CE) (E = S, Se **186**) has been described by Bottomley. It starts with (TPP)FeCl and reaction with thiophosgene-Na/Hg [136], or $C_6H_5CH_2SeCCl_3$–Na/Hg [137], respectively. The five-coordinate compounds (OEP)Fe(CE) (E = S, Se **187**) have similarly been obtained. Reaction of **187** with a series of nitrogenous bases produced exceptionally stable six-coordinate complexes which could be oxidized or reduced [75].

A series of selenocarbonyl compounds of ruthenium have been obtained by Roper et al. with $Ru(CO)_2(\eta^2\text{-}CSe_2)(PPh_3)_2$ as starting material. Thus, oxidative addition of MeI leads to the neutral diselenomethyl ester complex $Ru(CO)I(\eta^2\text{-}CSe_2Me)(PPh_3)_2$ which with the corresponding HX is slowly transferred into the air stable selenocarbonyl compounds $RuX_2(CO)(CSe)(PPh_3)_2$ (**188a–c**) with evolution of MeSeH as depicted in Scheme 26. The resulting iodide complex is hydrolyzed on alumina to give the hydroxide **189** [3].

An interesting four step conversion of a CS ligand into a CSe ligand was also reported by the same group. Thus, the Ru complex $RuCl_2(CSe)(CNR)(PPh_3)_2$ (**190**) is obtained from the reaction of $RuCl_2(\eta^2\text{-}CSeS)(CNR)(PPh_3)_2$ (originated from $RuCl_2(CS)(CNR)(PPh_3)_2$) with MeI, followed by HCl. With $AgClO_4$/CO **190** is converted into the cation $[RuCl(CSe)(CO)(CNR)(PPh_3)_2]^+$ (**191**) [41].

A series of osmium thio-, seleno-, and tellurocarbonyl compounds have been obtained by modification of a dichlorocarbene ligand (Eq. (11)) [4]. The dichlorocarbene complex $Cl_2Os(PPh_3)_2CO(CCl_2)$ is the starting complex to new seleno or tellurocarbonyl complexes as depicted in Scheme 27. The action of H_2E (E = S, Se, Te) converts the ligand CCl_2 into the corresponding CE with formation of the complexes **192** (E = Se) and **198a** (E = Te). For **193** with the CS and the CSe ligand in the same molecule, see the thiocarbonyl derivative **90**. The action of $AgClO_4$/CO on **198a** produces the cation **197** which with MeO/CO generates five-coordinate Os(0) complex **199**; the overall reactions are collected in Scheme 27 [8].



188

a, X = Cl
b, X = Br
c, X = I

189

Scheme 26.

4.3.4. *Compounds with Co, Rh, Ir*

A mixture of $CpCo(CSe)PMe_3$ (**194**, 19%) and $CpCo(CSe)PPh_3$ (**195**, low) was reported to be obtained by treatment of $CpCo(\eta^2\text{-}CSe_2)PMe_3$ with triphenyl phosphine [18,138].

4.3.5. *Compounds with Ni, Pd, Pt*

In this row, only the Pt selenocarbonyl complex **196** was reported and prepared analogously to the thiocarbonyl derivative **130** as depicted in Chart 8 [32].

4.4. *List of new compounds*

All compounds are collected here in the coordination modes **A**–**L** along with the ν(CE) vibrations and the ^{13}C NMR shifts of the appropriate CE carbon atom isolated since 1985. Table 1 contains all new type **A** compounds with a CS ligand. In Table 2, compounds with the various bridging modes of the CS ligand are collected. Tables 3 and 4 contain all compounds with terminal CSe and CTe ligands, respectively.

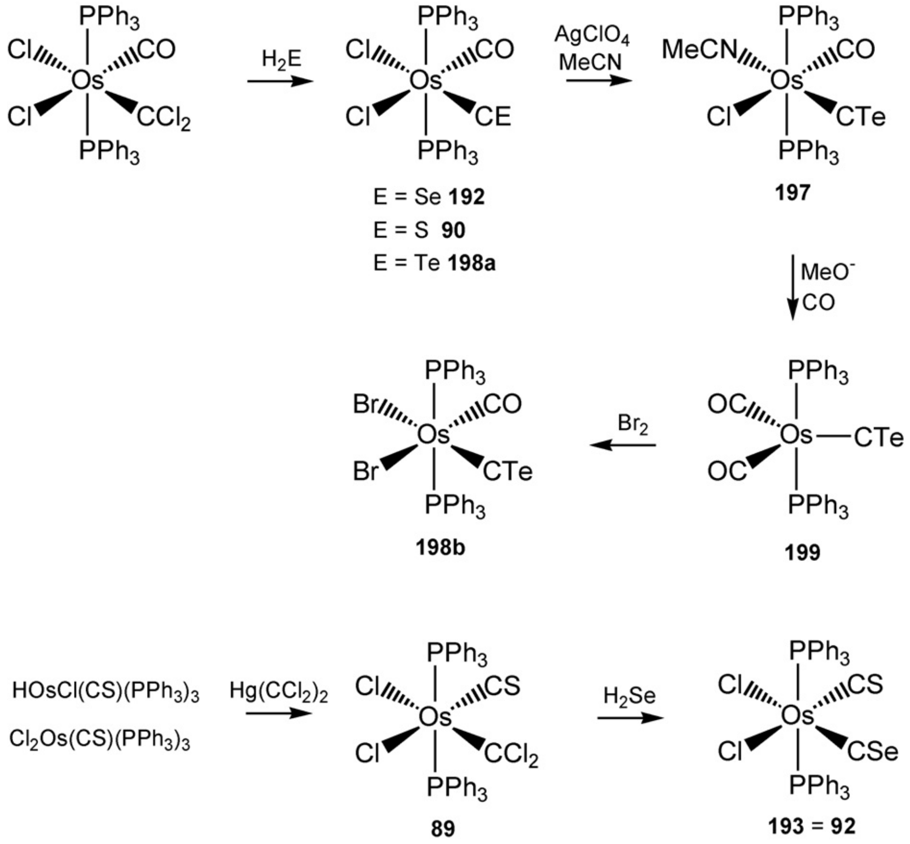
It is remarkable, that no new compounds with a terminal CS ligand have been reported from the elements Co, Ni, and Pd; examples from the latter two elements are still lacking.

4.4.1. *Compounds with terminal CS (type **A**)*

New compounds with a terminal CS group of type A are listed in Table 1 including IR absorptions and ^{13}C NMR shifts of the CS ligand if available.

4.4.2. *Compounds with bridging CS Groups (type **B**, **C**, **D**, **E**, **F**, **G**)*

New compounds with any type of bridging CS groups are listed in Table 2 including IR absorptions and ^{13}C NMR shifts of the CS ligand if available.



Scheme 27.

4.4.3. *Compounds with CSe and CTe groups*

All known compounds with terminal CSe and CTe ligands are listed in Tables 3 and 4, respectively, including IR absorptions and ^{13}C NMR shifts if available.

5. New chemical reactions

The chemistry of thiocarbonyl compounds can be divided into reactions involving the CS ligand and into reactions with retention of the CS group. However, this section is restricted to reactions in which the CS ligand is modified or removed. Reactions of thiocarbonyl complexes with retention of the CS ligand are only found in Section 4. To avoid confusion the new products derived from compounds with a CE ligand are numbered as **R–x**.

The chemistry of the seleno- or tellurocarbonyl complexes and the modification of these ligands are restricted to few examples.

5.1. *Reactions of the terminal bonded CS ligand*

The carbon atom of terminal CS groups exhibits electrophilic behavior, whereas the sulfur atom shows nucleophilic properties. The introduction of electron donating ligands into a molecule increases the nucleophilicity of the sulfur atom by decreasing the electrophilic properties of the carbon atom. In the few known compounds with only CO as additional ligands the sulfur atom is not nucleophilic enough and no adducts with electrophiles is observed.

5.1.1. *Nucleophilic behavior of the CS ligand*

As known from the carbonyl chemistry similarly the nucleophilicity of a CS group increases in the range CS < μ_2-CS < μ_3-CS. According to the soft nature of the sulfur atom electron deficient transition metal fragments can act as electrophilic agents with formation of stable complexes of the type **E** [59], **G** [16,43,44], and **I**. A correlation of the ν(CS) frequency and the nucleophilicity of the sulfur atom was suggested. A ν(CS) value well below 1230 cm^{-1} of terminal CS groups should make an adduct formation possible [59].

Methylation of HB(Pz)$_3$(CO)$_2$(CS)WAuPPh$_3$ (**166b**) with Me$_3$OBF$_4$ cleaves the W–Au bond to generate the terminal thiocarbyne complex HB(pz)$_3$(CO)$_2$W≡CSCH$_3$ [45]. The sulfur atom of the electron-rich insoluble complex HC(pz)$_3$(CO)$_2$W(CS) (**15**) is nucleophilic enough to be alkylated to give the cationic carbyne complex [HC(pz)$_3$(CO)$_2$W≡CSCH$_3$]$^+$ in good yield [60].

The binuclear platinum complex **132a** is able to take up two methyl groups the terminal CS group is transferred into a μ-bridging carbyne ligand to produce the salt **R-1** with loss of the platinum–platinum bond as depicted in Scheme 28 [119].

Compounds with end to end bonded CS groups such as **168** are available with some (η^6-arene)Cr(CO)$_2$(CS) com-

Table 1
Collection of compounds with terminal CS ligands, $\nu(CS)$ values, and ^{13}C NMR shifts of the CS ligand

Compound	$\nu(CS)$	^{13}C NMR	Ref.
$CpV(CO)_3(CS)$ (**1**)			[51,52]
$CpV(CO)_2(CS)_2$ (**2**)			[51,52]
$Cr(CO)_2(CS)L_3$			
L = $P(OMe)_3$ (**3a**)	1205	336.5	[55,23]
L = $P(OEt)_3$ (**3b**)	1193		[23]
L = $P(OBu\text{-}n)_3$ (**3c**)	1192		[23]
L = $P(OPh)_3$ (**3d**)	1220		[23]
$Cr(CO)_2(CS)$(triphos-U) (**4**)	1190		[23]
$Cr(CO)_2(CS)$(triphos) (**5**)	1191		[23]
$Cr(CO)_4(CS)L$			
L = *trans*-$P(OPh)_3$ (**6a**)	1256	336.3	[53]
L = *cis*-$P(OPh)_3$ (**6b**)	1256	333.6	[53]
L = *trans*-PPh_3 (**6c**)	1244	330.9	[54]
L = *cis*-PPh_3 (**6d**)	1244		[54]
mer, *trans*-$Cr(CO)_3(CS)\{P(OPh)_3\}_2$ (**7**)	1249	334.2	[53]
$[(\eta^6\text{-}C_6Et_6)Cr(CO)(NO)(CS)][BF_4]$ (**8**)	1300	351.5	[56]
$Cr(CO)_2(CS)(\eta^6$-biphen)[a] (**9**)	1210		[57]
$Cr(CO)_2(CS)(\eta^6\text{-}Ar)$			
Ar = PhMe (**10a**)	1205		[59,139]
	1230		
	1216		
Ar = PhOMe (**10b**)	1218		[59]
Ar = 1,3,5-$C_6H_3Me_3$ (**10c**)	1220		[59]
Ar = MeC_6H_4F-2 (**10d**)		346.80	[58]
Ar = PhF (**10e**)		346.85	[58]
Ar = PhCl (**10f**)	1223		[139]
$[(ArRN)_3Mo(CS)]Na$ (dimeric) (**11**)		292.4	[38]
$[(ArRN)_3Mo(CS)][Na(benzo\text{-}12\text{-}crown\text{-}4)_2]$ (**12**)			[38]
$W(CO)_3(CS)L_2]$			
L_2 = dppe (**13a**)	1212		[25]
L_2 = pp′ (**13b**)	1210		[25]
L_2 = dmpe (**13c**)	1203		[25]
$W(PMe_3)_2(CO)_2(CS_3)(CS)$ (**14**)	1228		[29]
$\{HC(pz)_3\}(CO)_2W(CS)$ (**15**)	1178		[60]
$Cp(CO)_3WCH_2C(O)SWCp(CO)_2(CS)$ (**16a**)	1593	343,7 *trans*; 330.2 *cis*	[61]
$Cp'(CO)_3WCH_2C(O)SWCp'(CO)_2(CS)$ (**16b**) ($Cp' = C_5H_4Me$)	1593	348.2 *trans*, 332.8 *cis*	[61]
$Mn_2(CO)_9(CS)$ (**17**)	1280, 1300		[7]
$Mn(CO)_4(CS)Br$ (**18**)	1320		[7]
$(C_5Me_5)Mn(CO)(CS)(CNCF_3)$ (**19**)	1273	341.7	[62]
$Ph_3SnMn(CO)_2(CS)(C_5H_4N\text{-}2\text{-}CH{=}NPr\text{-}i)$ (**20**)	1255		[63]
$Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_3(CS)(dpam)_2$ (**21a**)	1284		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_3(CS)(dppm)_2$ (**21b**)	1287		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ (**21c**)	1291		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(L)]PF_6$			
L = CNxyl (**21d**)	1308		[34]
L = CNBu-t (**21e**)	1310		[34]
L = NCtolyl (**21f**)	1312		[34]
L = NCMe (**21g**)	1312		[34]
L = NCEt (**21h**)	1309		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(dppm)_2(L)]PF_6$			
L = CNxyl (**21i**)	1308		[34]
L = NCtolyl (**21k**)	1308		[34]
L = NCEt (**21l**)	1315		[34]
L = NCMe (**21m**)	1314		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(dpam)_2(L)]PF_6$			
L = NCEt (**21n**)	1314		[35,34]
L = NCMe (**21o**)	1310		[34]

Table 1 (*Continued*)

Compound	ν(CS)	^{13}C NMR	Ref.
$[Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2]PF_6$ (**21p**)	1322		[34]
$[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_3(CS)(dppm)_2]PF_6$ (**21q**)	1316		[34]
$Re_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_2(CS)(dppm)_2(CO)]PF_6$ (**21r**)	1334		[64]
$[Re_2(\mu\text{-}S)(\mu\text{-}Br)Br_2(CS)(dppm)_2(CO)]PF_6$ (**21s**)	1330		[64]
$[Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2L]PF_6$			
L = CO (**22a**)	1338		[64]
L = NCMe (**22b**)	1328		[65]
L = NCEt (**22c**)	1328		[65]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(dppm)_2$ (**22d**)	1308		[35,65]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(dppm)_2$ (**22e**)			[35,65]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_3(CS)(\mu\text{-}dpam)_2$ (**22f**)	1306		[65]
$[Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dppm)_2(CO)]PF_6$ (**22g**)	1336		[64]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(CO)$ (**22h**)	1314		[64]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dppm)_2(CO)$ (**22i**)	1310		[64]
$[Cp_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(CO)]$ (**22k**)	1264		[64]
$[Cp_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Br)Br_2(CS)(\mu\text{-}dppm)_2(CO)]$ (**22l**)	1264		[64]
$[Cp_2Co][Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_3(CS)(\mu\text{-}dppm)_2]$ (**22m**)	1294		[65]
$Re_2(\mu\text{-}SO_2)(\mu\text{-}Cl)Cl_2(CS)(\mu\text{-}dppm)_2(NCMe)$ (**22n**)	1296		[65]
$Re(CS)(PMe_2Ph)_3(Et_2dtc)$ (**23**)	1178	277.8	[39]
$Re(CS)(Et_2dtc)_3$ (**24**)	1234	271.7	[39]
$Fe(CO)_3(CS)L$			
L = $PMePh_2$ (**25a**)	1265, 1292	325.89 (J_{CP} = 33.7 Hz)	[67]
L = PPh_3 (**25b**)	1272, 1299	326.53 (J_{CP} = 27.7 Hz)	[67]
$Fe(CO)_2(CS)L_2$			
L = PMe_3 (**26a**)	1215	324.6 (J_{CP} = 37 Hz)	[27]
L = PMe_2Ph (**26b**)			[27]
L = $P(Bu\text{-}n)_3$ (**26c**)			[27]
L = $PMePh_2$ (**26d**)	1228	322.82 (J_{CP} = 37.8 Hz)	[67]
L = PPh_3 (**26e**)	1235	324.28 (J_{CP} = 39 Hz)	[67,26]
L = $P(OMe)_3$ (**26f**)	1240		[28]
L = $P(OEt)_3$ (**26g**)	1245	318.0 (J_{CP} = 50 Hz)	[68]
L = $P(OPh)_3$ (**26h**)	1266	315.8 (J_{CP} = 54 Hz)	[68]
$Fe(CO)_2(CS)(dppe)$ (**26i**)	1235		[27]
$Fe(CO)_2(CS)(PMe_3)_2\text{-}HgCl_2$ (**27**)	1280		[27]
$Fe(CO)_3(CS)X_2$			
X = Br (**28a**)	1351		[66]
X = I (**28b**)	1347		[66]
X = $SnMe_3$ (**28c**)	1280	305.4	[69]
$Fe(CO)(CS)(PPh_3)_2X_2$			
X = Br (**29a**)	1294		[66]
X = I (**29b**)	1311		[66]
$[(PMe_3)_2Fe(CO)(CS)(SC(Bu){=}CHPPh_2)]X$			
X = BF_4 (**30a**)	1285		[70]
X = Cl (**30b**)	1280		[70]
$[(PMe_3)_2Fe(CO)(CS)(SC(Ph){=}CHPPh_2)]Cl$ (**30c**)	1275		[70]
$Cp(CS)Fe(\mu\text{-}S_2C)Fe(CO)_2Cp$ (**31**)	1263		[71]
$[Cp^*Fe(CO)_2(CS)]BF_4$ (**32**) ($Cp^* = C_5Me_5$)	1332	317.2	[16]
$Cp^*Fe(CO)(CS)(C(O)OMe)$ (**32a**) ($Cp^* = C_5Me_5$)	1292	329.4	[16]
Fe(TPP)(CS)(L–L)			
L–L = PYAN (**33a**)			[73]
L–L = PYEN (**33b**)			[73]
L–L = Bipy (**33c**)			[73]
L–L = DABCO (**33d**)			[73]
L–L = PYZ (**33e**)			[73]
{Fe(TPP)(CS)}$_2$(L–L)			
L–L = PYAN (**33f**)			[73]
L–L = PYEN (**33g**)			[73]
L–L = Bipy (**33h**)			[73]
L–L = DABCO (**33i**)			[73]

Table 1 (*Continued*)

Compound	ν(CS)	^{13}C NMR	Ref.
L–L = PYZ (**33k**)			[73]
Fe(OEP)(CS) (**34**)	1297		[75]
Fe(OEP)(CS)(L)			
L = py (**35a**)	1280		[74]
L = 1-MeIm (**35b**)	1272		[74]
L = pip (**35c**)	1280		[74]
L = 4-CNPy (**35d**)	1284		[74]
L = 4-NMe_2Py (**35e**)	1279		[74]
L = CH_3OH (**35f**)			[74]
$RuH(CS)Cl(PPh_3)_2(AsPh_3)_2$ (**36**)	1320		[76]
$[Ru(CS)Cl(PPh_3)_2]_2(\mu\text{-}Cl)_2$ (**37**)	1290		[76]
$[Ru(CS)(CH_3COO)(PPh_3)_2]_2(\mu\text{-}S)$ (**38**)	1290		[76]
$RuCl_2(CS)(PCy_3)_2$ (**39**)			[37]
$RuBr_2(CS)(PPh_3)_3$ (**40**)	1265		[78]
$RuI_2(CS)(PPh_3)_3$ (**41**)	1270		[77]
$RuBr_2(CS)(Me_2SO)_2$ (**42**)	1250		[78]
$RuBr_2(CS)(AsPh_3)_2(Me_2SO)$ (**43**)	1265		[78]
$Ru(Etdtc)_2(CS)(PPh_3)$ (**44**)	1275		[79]
$Ru(Etxant)_2(CS)(PPh_3)$ (**45**)	1290		[79]
$Ru(Ph_2PCSNPh)_2(CS)(PPh_3)$ (**46**)	1270		[79]
$RuCl(Ph_2PCSNPh)(CO)(CS)(PPh_3)$ (**47**)	1275		[79]
$[RuH(CS)(PPh_3)_2(\eta^2\text{-}S_2CPCy_3)]^+$ (**48**)	1267		[80]
$[(S_3)Ru(CS)(PPh_3)X]^+$[b]			
X = Cl (**49a**)	1298		[81]
X = H (**49b**)	1281		[81]
X = $C(CO_2Me){=}CHCO_2Me$ (**49c**)	1290		[82]
X = P=CHBu-t (**49d**)	1284		[85]
$RuH(CS)(PPh_3)_2(\eta^2\text{-}HB(pz)_3)$ (**50**)	1262	304.0 ($^2J_{CP}$ = 17.0 Hz)	[83]
$RuH(CS)(PPh_3)(\eta^3\text{-}HB(pz)_3)$ (**51a**)	1269	305.1 ($^2J_{CP}$ = 19.6 Hz)	[83]
$RuCl(CS)(PPh_3)(\eta^3\text{-}HB(pz)_3)$ (**51b**)	1290	307.9 ($^2J_{CP}$ = 17.8 Hz)	[83]
$RuH(CS)(PPh_3)_2(\eta^2\text{-}H_2B(bta)_2)$[c] (**52**)	1282	305.2 ($^2J_{CP}$ = 16.1 Hz)	[83]
$RuCl(CS)(\eta^2 C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ (**53a**)	1267	306.7 (J_{CP} = 15.6 Hz)	[84]
$RuBr(CS)(\eta^2 C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ (**53b**)	1268	306.9 (J_{CP} = 16.1 Hz)	[84]
$RuI(CS)(\eta^2 C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)_2$ (**53c**)	1276	307.6 (J_{CP} = 16.5 Hz)	[84]
$Ru(S_2CNEt_2)(CS)(\eta^2 C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)$ (**54**)	1275	303.2 (J_{CP} = 18.1 Hz)	[84]
$Ru(O_2CMe)Cl(CS)(\eta^2 C,N\text{-}o\text{-}C_6H_4N{=}NC_6H_5)(PPh_3)$ (**55**)	1271	292.2 (J_{CP} = 19.1 Hz)	[84]
$RuCl(CS)(PPh_3)_2C(R){=}CHR'$			see [82]
$RuCl(CS)(PPh_3)_2(P{=}CHBu\text{-}t)$ (**56**)	1267	297.7 ($^2J_{PC}$ = 15.2 Hz)	[86,85]
$RuCl_2(CS)(PPh_3)_2$[**P**]			
[**P**] = PH=CHBu-t (**57**)			[86]
[**P**] = $P(AuPPh_3){=}CHBu\text{-}t$ (**58a**)			[86]
[**P**] = P(HgCl)=CHBu-t (**58b**)			[86]
[**P**] = P(HgPh)=CHBu-t (**58c**)	1289		[87]
[**P**] = P(HgFc)=CHBu-t (**58d**)			[87]
$RuClR(CS)(PPh_3)_2P(AuPPh_3){=}CBu\text{-}t$ (**59**) R = $(C{\equiv}CC_6H_4Me\text{-}4)$			[86]
$RuICl(CS)(PPh_3)_2P(Me){=}CHBu\text{-}t$ (**60**)	1290	295.5	[88]
$Ru(S_2CNEt_2)(CS)(PPh_3)_2(P{=}CHBu\text{-}t)$ (**61**)	1252	305.4 ($^2J_{CP}$ = 12.7 Hz)	[85]
$Ru(CS)Cl(PPh_3)_2(\eta^2\text{-}SCPh)$ (**62**)			[30]
$[(C_5Me_5)Ru(P{\sim}O)_2(CS)]BPh_4$ (**63**)	1264	314.0	[89]
$RuCl(CS)(PPh_3)_2(BO_2C_6H_4)$ (**64**)	1292		[90]
$RuCl(CS)(PPh_3)_2(BSNHC_6H_4)$ (**65**)	1275		[90]
$Ru(Ph)Cl(CS)(PPh_3)_3$ (**66**)			[30]
$Ru(SiMe_2Cl)Cl(CS)(PPh_3)_2$ (**67**)	1271		[91]
$Ru(SiMe_2OEt)Cl(CS)(PPh_3)_2$ (**68**)	1276		[91]
$RuH(CS)(PPh_3)_2(\eta^2\text{-}H_2B(pz)_2)$ (**69**)	1264		[92]
$RuCl(CH{=}CH_2)(CS)(PPh_3)_2$ (**70a**)			[93]
$RuCl(CPh{=}CHPh)(CS)(PPh_3)_2$ (**70b**)			[92]
$Ru(CPh{=}CHPh)(CS)(PPh_3)_2(\eta^2\text{-}H_2B(pz)_2)$ (**71**)			[92]
$RuHCl(CS)(BTD)(PPh_3)_2$ (**72a**)	1266		[92]
$RuHCl(CS)(BSD)(PPh_3)_2$ (**72b**)	1266		[92]

Table 1 (*Continued*)

Compound	*ν*(CS)	^{13}C NMR	Ref.
Ru(Ph)(CS)(PPh$_3$)$_2$(η^2-H$_2$B(pz)$_2$) (**73**)	1265		[92]
Ru$_3$(CO)$_5$(CS)(μ-H)(μ-P^{t}Bu$_2$)(μ-PCy$_2$)$_2$(μ$_3$-S)] (**74**)	1262		[36]
RuCl(CS)(PPh$_3$)$_2$TeCl$_3$ (**75**)			[93]
(TTP)Ru(CS)L (TTP = tetra-*p*-tolylporphyrin)			
L = EtOH (**76a**)	1295		[94]
L = CN$^-$ (**76b**)	1249		[94]
L = imidazole (**76c**)	1274		[94]
L = benzimidazole (**76d**)	1275		[94]
L = MeCN (**76e**)	1277		[94]
L = pyr (**76f**)	1290		[94]
L = 4-Me-pyridine (**76g**)	1281		[94]
L = toluidine (**76h**)	1282		[94]
L = 4,3-phenylpropylpyr (**76i**)	1283		[94]
L = 3-Cl-pyr (**76k**)	1283		[94]
L = 4-Cl-pyr (**76l**)	1285		[94]
L = 2-Cl-pyr (**76m**)	1288		[94]
L = 1-Me-imidazole (**76n**)	1286		[94]
L = PPh$_3$ (**76o**)	1286		[94]
L = 5,5-dicyanoimidazole (**76p**)	1290		[94]
(TPP)Ru(CS)(CO) (TPP = tetraphenylporphyrin) (**77**)	1385		[95]
Os(CS)(PhCCPh)(PPh$_3$)$_2$ (**78**)	1250	270.0	[97]
OsCl(CS)(PPh$_3$)$_2$(η^1-PhC=CHPh) (**79**)	1300	261.8	[97]
OsCl(CS)(PPh$_3$)$_2$(η^1-PhC=CHPh)(NCR) (R = *p*-tolyl) (**79a**)	1285		[97]
Os(CS)(CO)(C$_2$F$_4$)(PPh$_3$)$_2$ (**80**)	1302		[98]
OsH(Cl)(CS)(C$_2$Me)(PPh$_3$)$_2$ (**81**)	1259		[99]
Os(CS)(CO)(CF$_2$)(PPh$_3$)$_2$ (**82**)			[101]
Os(CS)(CO)(PPh$_3$)$_2$[P(NC$_4$H$_4$)$_3$] (**83**)	1247		[100]
Os[C$_7$H$_2$O(OMe-7)(CO$_2$Me-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**84**)	1229	291.1	[102]
Os[C$_7$H$_2$O(OMe-7)(CO$_2$Et-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**85**)	1228	291.0	[102]
Os[C$_7$HO(OMe-7)(Br-6)(CO$_2$Me-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**86**)	1244		[102]
[Os[C$_5$H (CH$_2$CO$_2$Me-5)(CO$_2$Me-4) (Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$][CF$_3$CO$_2$] (**87a**)		294.8	[102]
[Os[C$_5$H (CH$_2$CO$_2$Me-5)(CO$_2$Me-4) (Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$]I$_3$ (**87b**)		294.4	[102]
OsCl$_2$(CS)(PPh$_3$)$_2$L			
L = BSD (**88**)	1279		[103]
L = CCl$_2$ (**89**)	1312		[8]
L = CO (**90**)	1315	258.7	[8]
L = CS (**91**)	1260, 1370		[8]
L = CSe (**92**)	1322, 1342		[8]
OsCl$_2$(CS)(PCy$_3$)$_2$ (**93**)		239.7	[104]
OsI$_2$(CS)(PCy$_3$)$_2$ (**94**)		241.1	[104]
Os(NO)(CS)(PPh$_3$)$_2$X			
X = I (**95**)	1258		[105]
X = Cl (**96**)	1279		[105]
X = SeH (**97**)	1260, 1270		[105]
[Os(NO)(CS)(PPh$_3$)$_2$L]ClO$_4$			
L = CO (**98**)	1295		[105]
L = PPh$_3$ (**99**)	1278		[105]
[OsI$_2$(NO)(CS)(PPh$_3$)$_2$]I$_3$ (**100**)	1370		[105]
OsCl(CS)(PPh$_3$)$_2$(BO$_2$C$_6$H$_4$) (**101**)	1302		[90]
OsCl(CS)(PPh$_3$)$_2$(SiMe$_2$Cl) (**102**)	1287		[91]
OsCl(CS)(PPh$_3$)$_2$(SiMe$_2$OEt) (**103**)	1283		[91]
OsCl(CS)(PPh$_3$)$_2$(Ph) (**104**)			[106]
OsCl(CS)(PPh$_3$)$_2$(Si(OCH$_2$CH$_2$)$_3$N) (**105**)			[106]
[OsCl(CS)(PPh$_3$)$_2$(Si(OCH$_2$CH$_2$)$_3$NMe)]I (**106**)			[106]
[OsH(CS)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ (**107**)			[107]
OsH(Cl)(CS)(BTD)(PPh$_3$)$_2$ (**108**)	1290		[107]
Os(CH=CHC$_6$H$_4$Me-4)Cl(CS)(BTD)(PPh$_3$)$_2$ (**109**)	1272		[107]
Rh(NO)(CS)(PPh$_3$)$_2$ (**110**)	1260		[109]
[(S$_3$)Rh(CS)(PPh$_3$)]ClO$_4$ (**111**)	1279	293.0[d]	[110]
Rh(H$_2$B(bta)$_2$(CS)(PPh$_3$)$_2$ (**112**)	1327		[111]
PPh$_3$Rh(CS)(μ-dppm)Fe(CO)$_3$Si(OMe$_3$)$_3$ (**113**)	1190		[112]

Table 1 (*Continued*)

Compound	ν(CS)	^{13}C NMR	Ref.
{Rh(μ-bzIm)(CS)(PPh$_3$)}$_3$ (**114**)	1310-1295		[113]
{Rh(μ-RIm)(CS)(PPh$_3$)}$_3$ (**115**)			[113]
[Rh(HRIm)(CS)(PPh$_3$)$_2$]ClO$_4$ (**116**)			[113]
Rh(bbzIm)(CS)(PPh$_3$)$_2$ (**117**)	1308		[113]
[Rh(HbbzIm)(CS)(PPh$_3$)$_2$]ClO$_4$ (**118**)			[113]
[(PPh$_3$)$_2$(CS)Rh(μ-RIm)Au(PPh$_3$)]ClO$_4$ (**119**)			[113]
[CpIr(H)(CS)(PPh$_3$)]CF$_3$SO$_3$ (**120**)	1372		[114]
Ir(bzIm)(CS)(PPh$_3$)$_2$ (**121**)	1320		[113]
IrCl(CS)(PPh$_3$)$_2$ (**122**)	1332		[116,117]
IrI(CS)(PPh$_3$)$_2$ (**123**)	1322	240.8	[118]
IrI(CS)(PPh$_3$)$_2$(O$_2$) (**124**)	1321	259.6 (J_{CP} = 9.1 Hz)	[118]
[IrCl$_2$(CS)$_2$(PPh$_3$)$_2$]X			
X = I$_3$ (**125a**)	1357, 1425		[115]
X = Cl (**125b**)	1369, 1438	232.4	[115]
IrCl$_2$(PPh$_3$)$_2$(CS)C(S)R			
R = OC$_6$H$_4$Me-4 (**126a**)	1365	244.9	[115]
R = SPh (**126b**)	1363	242.8	[115]
[IrCl(η^2-SCSPh)(CS)(PPh$_3$)$_2$]PF$_6$ (**127**)	1360	250.9	[115]
[Ir(CNC$_6$H$_3$Me-2,6)$_2$(CS)(PPh$_3$)$_2$]Cl (**128**)	1292	283.4	[115]
IrCl$_2$(PPh$_3$)$_2$(CS)H (**129**)	1358		[115]
Pt(CS)(dpmb) (**130**)	1305		[32]
Pt(CS)(PPh$_3$)$_2$ (**131**)	1305		[32]
(dppe)Pt(μ-S)Pt(CS)(PPh$_3$) (**132a**)	1305		[119,120,31]
(dppe)Pt(μ-Se)Pt(CS)(PPh$_3$) (**132b**)	1305		[120,31]
(dpmb)Pt(μ-Se)Pt(CS)(PPh$_3$) (**132c**)	1305		[120,31]
(dppe)Pd(μ-S)Pt(CS)(PPh$_3$) (**132d**)	1305		[120,31]
(PPh$_3$)$_2$Pt(μ-Se)Pt(CS)(PPh$_3$) (**133**)	1310		[31]
Pt$_3$(μ$_3$-S)(CS)(μ-dppm)$_3$ (**134**)	1376	250[e]	[33]

[a] biphen = 4,5-dimethyl-9,10-dihydrophenanthren.

[b] (S$_3$) = 1,4,7-trithiacyclononane.

[c] bta = benzotriazolyl.

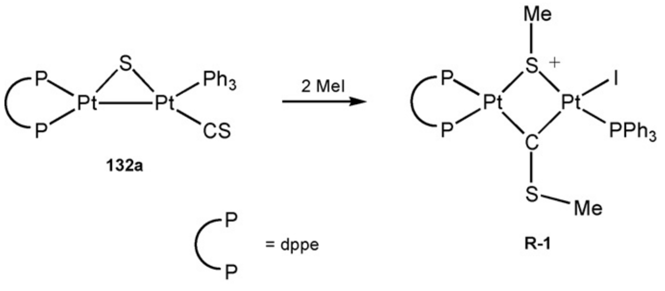
[d] ^1J(Rh,C) = 71.4 Hz.

[e] ^1J(Pt,C) = 1333 Hz.

pounds by reacting with (CO)$_5$Cr(THF) as shown in Table 2 and Chart 17 [59] and with the related anionic complex [(HB(pz)$_3$)(CO)$_2$Mo(CS)]$^-$ [130].

5.1.2. Electrophilic behavior of CS

Similar to the related cation with the Cp ligand, [Cp*Fe(CO)$_2$(CS)]$^+$ (**32**) adds a variety of nucleophiles at the thiocarbonyl carbon atom. However, MeO$^-$ attacks initially one CO carbon atom to give Cp*Fe(CO)(CS)C(O)OMe but migrates slowly to the thiocarbonyl carbon atom with result of Cp*Fe(CO)$_2$C(S)OMe [16]. See also earlier reports about the addition of nucleophiles summarized in [14].



Scheme 28.

5.1.3. Desulfurization reaction

An unusual and not previously observed desulfurization of a terminal bonded thiocarbonyl ligand takes place with P(NMe$_2$)$_3$ which is also a powerful desulfurization agent in organic chemistry.

The addition of P(NMe$_2$)$_3$ to a solution of Fe(CO)$_4$(CS) produces quantitatively S = P(NMe$_2$)$_3$ and undefined tarry materials. However, if it is taken care for a great excess of the phosphine during the reaction, the new mononuclear complex **R-2** [140] and the binuclear compounds **R-3** and **R-4** [141] could be isolated in low yields as depicted in Scheme 29. All compounds bear a new unusual chelating ligand composed of P(NMe$_2$)$_3$, CS, CO and an additional sulfur atom. The ligand can be considered as a betaine-like compound formally being formed from the addition of the unknown ylide (NMe$_2$)$_3$P = C = S at COS [140,141]. Desulfurization of Cl$_2$(PCy$_3$)$_2$Ru(CS) (**39**) with Mo(H)(η^2-Me$_2$CNAr)(N[*i*-Pr]Ar)$_2$ leads to the air stable carbido complex Cl$_2$(PCy$_3$)$_2$RuC (**R-5**) in about 55% yield [37]. Similarly, Cl$_2$Os(CS)(PCy$_3$)$_2$ (**93**) can be desulfurized with Ta(OSi-*t*-Bu$_3$)$_3$ to give the carbido complex Cl$_2$(PCy$_3$)$_2$OsC (**R-6**) in 90% yield. The related reaction with I$_2$Os(CS)(PCy$_3$)$_2$ (**94**) leads to an impure material containing the carbido complex I$_2$(PCy$_3$)$_2$OsC (**R-6b**) as the major product [104].

Table 2
Collection of compounds with various types of μ-CS ligands including ν(CS) values, and ^{13}C NMR shifts of the CS ligand

Compound	ν(CS)	δ ^{13}C	Ref.
Compounds of type **B**			
cis-$Cp_2Fe_2(CO)_2(\mu\text{-}CS)_2$ (**135a-*cis***)	1124		[42]
trans-$Cp_2Fe_2(CO)_2(\mu\text{-}CS)_2$ (**135a**-tr)	1131		[42]
cis-$Cp^*_2Fe_2(CO)_2(\mu\text{-}CS)_2$ (**135b-*cis***) ($Cp^* = C_5Me_5$)	1108	388.0	[16]
trans-$Cp^*_2Fe_2(CO)_2(\mu\text{-}CS)_2$ (**135b**-tr) ($Cp^* = C_5Me_5$)	1108	390.3	[16]
$Cp_2Fe_2(CO)_2(\mu\text{-}CS)(\mu\text{-}CH_2)$ (**136**)	1155, 1135		[16]
cis-$[Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(CO)_2]SO_3CF_3$ (**137**-*cis*)	1163	347.7	[123]
trans-$[Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(CO)_2]SO_3CF_3$ (**137**-tr)	1175	346.1	[123]
cis-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CNC(O)SMe)(CO)_2$ (**138**-*cis*)	1141	375.6	[123]
trans-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CNC(O)SMe)(CO)_2$ (**138**-tr)	1139	376.8	[123]
[*cis*-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CNHC(O)SMe)(CO)_2]SO_3CF_3$ (**139**-*cis*)	1173		[124]
cis-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}C(H)SMe)(CO)_2$ (**140a**-*cis*)	1113	382.2	[122]
trans-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}C(H)SMe)(CO)_2$ (**140a**-tr)		383.0	[122]
cis-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}C(CN)SMe)(CO)_2$ (**140b**-*cis*)	1146	370.0	[122]
trans-$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}C(CN)SMe)(CO)_2$ (**140b**-tr)	1138	370.6	[122]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}C(H)SMe)FeCp$ (**141a**)	1108	383.3	[122]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}C(CN)SMe)FeCp$ (**141b**)	1123	374.7	[122]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}CSMe)Fe(NCMe)Cp$ (**142**)			[122]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}CSMe)Fe(COth)Cp$[a] (**143**)	1139		[125]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}CSMe)Fe(CO)(\eta^4\text{-}C_5H_5th)$[a] (**144**)	1132	376.9	[125]
$Cp(CO)Fe(\mu\text{-}CS)(\mu\text{-}CSMe)FeSC(S)NMe_2Cp$ (**145**)	1107	393.4	[126]
$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(NCMe)_2]SO_3CF_3$ (**146**)		388.3	[126]
$Cp_2Fe_2(\mu\text{-}CS)(\mu\text{-}CSMe)(\mu\text{-}S_2CNMe_2)$ (**147**)	1118	397.7	[126]
$Fe_4(CO)_{10}(\mu_3\text{-}S)(\mu\text{-}CS)(\mu\text{-}dppm)_2$ (two isomers) (**148**)	1093, 1095		[127]
$Co_2(\mu\text{-}CS)(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-}dppm)$ $R = CO_2Me$ (**149a**)	1147	353.3 ($J_{PC} = 14$ Hz)	[50]
$Co_2(\mu\text{-}CS)(\mu\text{-}S_2C_2R_2)(CO)_3(\mu\text{-}dppm)$ $R = CO_2Et$ (**149b**)	1148	354.2 ($J_{PC} = 14$ Hz)	[50]
$(dppe)Pt(\mu\text{-}Se)(\mu\text{-}CS)Pt(dppe)$ (**150**)	1055		[31]
$Cp(CO)Fe(\mu\text{-}CO)(\mu\text{-}CS)Mn(CO)_4$ (**151**)	1127	376.32	[44]
$Cp(PMe_3)Co(\mu\text{-}CO)(\mu\text{-}CS)Mn(CO)Cp$ (**152a**)	1106		[43]
$Cp(PMe_2Ph)Co(\mu\text{-}CO)(\mu\text{-}CS)Mn(CO)Cp$ (**152b**)	1094		[43]
$Cp(PMe_3)Rh(\mu\text{-}CO)(\mu\text{-}CS)Mn(CO)Cp$ (**153**)	1102		[43]
Compounds of the type **C** with a semibridging CS group			
$[HB(pz)_3](CO)_2(CS)W\text{-}AuPMe_3$ (**166a**)		295.70	[45]
$[HB(pz)_3](CO)_2(CS)W\text{-}AuPPh_3$ (**166b**)		301.05	[45]
Compounds of the type **D** with a side-on bridging CS group			
$[HB(pz)_3](CO)_2W(\mu\text{-}CS)Mo(CO)_2Ind$ (**167**)		285.8	[46]
Compounds of the type **E** with end to end bridging CS group			
$Cr(CO)_2(\eta^6\text{-}PhMe)CSCr(CO)_5$ (**168a**)	1156		[59]
$Cr(CO)_2(\eta^6\text{-}PhOMe)CSCr(CO)_5$ (**168b**)	1140		[59]
$Cr(CO)_2(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)CSCr(CO)_5$ (**168c**)	1160		[59]
$(HB(pz)_3)(CO)_2MoCSMo(C_7H_7)(CO)_2$ (**169**)			[130]
$(HB(pz)_3)(CO)_2MoCSFeCp(CO)_2$ (**170**)			[130]
$(HB(pz)_3)(CO)_2MoCSRe(CO)_5$ (**171**)			[130]
$(HB(pz)_3)(CO)_2MoCSRuCp(PPh_3)_2$ (**172**)			[130]
$(Ar[R]N)_3MoCSMo(N[R]Ar)_3$ ($R = C(CD_3)_2Me$; $Ar = 3,5\text{-}C_6H_3Me_2$) (**173**)		293.5	[131]
Compounds with a type **F** triple μ_3 bridging CS group			
$(C_5Me_5)_2Co_3(\mu_3\text{-}CS)(\mu_3\text{-}S)$ (**160**)	1040, 1021		[128]
$Ni_3Cp_3(\mu_3\text{-}CS)(\mu_3\text{-}CO)$ (**161a**)	1135		[49]
$Ni_3Cp_3(\mu_3\text{-}CS)_2$ (**161b**)	1105		[49]
$Ni_3Cp'_3(\mu_3\text{-}CS)(\mu_3\text{-}CO)$ (**161c**)	1128		[49]
$Ni_3Cp'_3(\mu_3\text{-}CS)_2$ (**161d**)	1101		[49]
$(C_5H_4Me)_2Co_2Fe(CO)_2(PPh_3)(\mu_3\text{-}S)(\mu_3\text{-}CS)$ (**162**)			[48]
$Cp_2Co_2Fe(CO)_2(L)(\mu_3\text{-}S)(\mu_3\text{-}CS)$			[47,48]
$L = PPh_3$ (**163a**)	1020	355.5	[47,48,129]
$L = P(OMe)_3$ (**163b**)	1044		[48]
$L = P(OPh)_3$ (**163c**)	1047, 1072		[48]
$L = Bu_3{}^nP$ (**163d**)	1024	357.4 ($J_{PC} = 3.4$ Hz)	[129]
$L = MeNC$ (**163e**)	1054	358.0	[129]
$L = MesNC$ (**163f**)	1058	355.7	[129]
$L = 2,6\text{-}Cl_2\text{-}C_6H_3NC$ (**163g**)	1066	354.5	[129]
$Cp_2Co_2Fe(CO)(L)_2(\mu_3\text{-}S)(\mu_3\text{-}CS)$ (**164**)			[129]
$L = MeNC$ (**164e**)	1948		[129]

Table 2 (*Continued*)

Compound	ν(CS)	δ ^{13}C	Ref.
L = MesNC (**164f**)	1959	356.9	[129]
L = 2,6-Cl_2-C_6H_3NC (**164g**)	1964		[129]
L = 2,6-Cl_2-C_6H_3NC, PPh_3 (**165**)	1944	359.6	[129]
Compounds of the type **G** with a μ_3 bridging CS group			
Cp(CO)Fe(μ-CO)(μ-CSW$(CO)_5$)Mn$(CO)_4$ (**154**)	1053		[44]
Cp(PMe_3)Co(μ-CO)(μ-CSCr$(CO)_5$)Mn(CO)Cp (**155**)	1050		[43]
Cp(PMe_3)Co(μ-CO)(μ-CSMn(CO)Cp)Mn(CO)Cp (**156a**)	1050		[43]
Cp(PMe_2PH)Co(μ-CO)(μ-CSMn(CO)Cp)Mn(CO)Cp (**156b**)	1028		[43]
Cp(PMe_3)Rh(μ-CO)(μ-CSMn(CO)Cp)Mn(CO)Cp (**156c**)	1055		[43]
[$(Cp_2Fe_2(CO)_3(CS))_3$Ag]BF_4 (**157**)			[16]
[$Cp_2Fe_2(CO)_2(CS)_2$Ag]BF_4 (**158**)	1030		[16]
$Cp_2Fe_2(CO)_2$(μ-CS)(μ-CSHgCl_2) (**159**)	1018[b]		[42]

[a] th = 2-thienyl.

[b] ν(μ-CS) at 1177, 1168 cm^{-1}.

5.1.4. Conversion into a CSe complex

The conversion of the CS ligand in $RuCl_2(CS)(CNR)(PPh_3)_2$ in a CSe ligand in $RuCl_2(CSe)(CNR)(PPh_3)_2$ (**190**) in high yield via a four step mechanism with $RuCl_2(\eta^2\text{-CSeS})(CNR)(PPh_3)_2$ and $[RuCl_2(\eta^2\text{-CSeSMe})(CNR)(PPh_3)_2]^+$ as intermediates (see also preparation of **190**) was reported by Roper and co-workers [41].

Table 3
Collection of compounds with terminal CSe ligands, ν(CSe) values, and ^{13}C NMR shifts of the CSe ligand

$Cr(CO)_5(CSe)$ (**174**)	1077	360.7	[134,132]
η^6-$C_6H_6Cr(CO)_2(CSe)$ (**175**)	1061	363.7	[24,132]
(η^6-C_6H_5COOMe)$Cr(CO)_2(CSe)$ (**176**)	1071		[2,133]
[PNP][ClCr$(CO)_4$(CSe)] (**177a**)		359.4	[132]
[NBu_4][ICr$(CO)_4$(CSe)] (**177b**)			[132]
$Cr(CO)_2(CSe)L_3$			
L = $P(OMe)_3$ (**178a**)	1018	356.4 td	[23]
L = $P(OEt)_3$ (**178b**)	1016	354.8	[23]
L = P(OBu-n)$_3$ (**178c**)	1018		[23]
L = $P(OPh)_3$ (**178d**)	1023		[23]
$Cr(CO)_2$(CSe)(triphos-U) (**179**)	1031		[23]
$Cr(CO)_2$(CSe)(triphos) (**180**)	1037		[23]
[$Mo(CO)_2(CSe)(HB(3,5\text{-}Me_2C_3HN_2)_3)$]$^-$ (**181**)	1005		[40]
[$(ArRN)_3$Mo(CSe)][K(benzo-15-crown-5)$_2$] (**182a**)			[38]
[$(ArRN)_3$Mo(CSe)]K (dimeric) (**182b**)		271.9	[38]
$CpMn(CO)_2(CSe)$ (**183**)	1107	358.0	[2,133, 135]
(η^5-C_5H_4Me)$Mn(CO)_2(CSe)$ (**184**)	1106		[133]
$CpRe(CO)_2(CSe)$ (**185**)	1124		[133]
(TPP)Fe(CSe) (**186**)	1145		[108,137]
L = EtOH (**186a**)	1140		[108]
L = M-methylimidazole (**186b**)			[108]
L = Py (**186c**)			[108]
(OEP)Fe(CSe) (**187**)	1134		[75]
$RuCl_2(CO)(CSe)(PPh_3)_2$ (**188a**)	1125		[3]
$RuBr_2(CO)(CSe)(PPh_3)_2$ (**188b**)	1125		[3]
$RuI_2(CO)(CSe)(PPh_3)_2$ (**188c**)			
$RuI(OH)(CO)(CSe)(PPh_3)_2$ (**189**)	1137		[3]
$RuCl_2(CNR)(CSe)(PPh_3)_2$ (**190**)	1134		[41]
[$RuCl(CNR)(CO)(CSe)(PPh_3)_2$]$^+$ (**191**)	1135		[41]
$OsCl_2(CO)(CSe)(PPh_3)_2$ (**192**)	1156	278.8	[4,8]
$OsCl_2(CS)(CSe)(PPh_3)_2$ (**193 = 92**)	1130		[8]
$CpCo(CSe)PMe_3$ (**194**)	1128		[138,18]
$CpCo(CSe)PPh_3$ (**195**)	1130		[138]
Pt(CSe)(dpmb) (**196**)	1110		[32]

Table 4
Collection of compounds with terminal CTe ligands, ν(CTe) values, and ^{13}C NMR shifts of the CTe ligand

$OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2$ (**197**)	1048		[8]
$OsX_2(CO)(CTe)(PPh_3)_2$			
X = Cl (**198a**)	1046	297.7	[4,8]
X = Br (**198a**)			[101]
$Os(CO)_2(CTe)(PPh_3)_2$ (**199**)			[101]
[$Mo(CO)_2(CTe)(HB(3,5\text{-}Me_2C_3HN_2)_3)$]$^-$ (**200**)	951		[40]
[$(ArRN)_3$Mo(CTe)]K (dimeric) (**201**)		252.6	[38]

5.1.5. Cycloaddition reactions

A theoretical study concerning formation of metallabezenes is found in [142]. $Os(CS)(CO)(PPh_3)_3$ reacts with PhC≡CPh to give a 1:1 mixture of $Os(CS)(PPh_3)_2$(PhC≡CPh) (**78**) and the metallacyclus **R-7**. The complex **78** is an example for a four-electron donor acetylene ligand. It can be converted quantitatively into **R-7** by addition of CO [97]. Similarly, propyne gives a mixture of the oxidative addition product **81** and the osmabenzene **R-8** [99] as shown in Chart 19.

In Scheme 30, the results of the cycloaddition reactions between $IrCl(CS)(PPh_2)_2$ (**122**) and $IrI(CS)(PPh_2)_2$ (**123**) with various acetylenes are summarized. Thus, **123** and ethyne leads

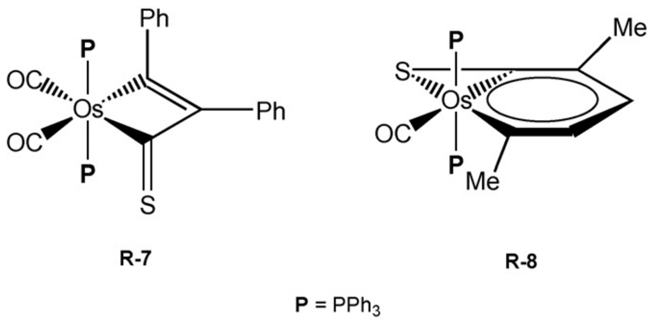
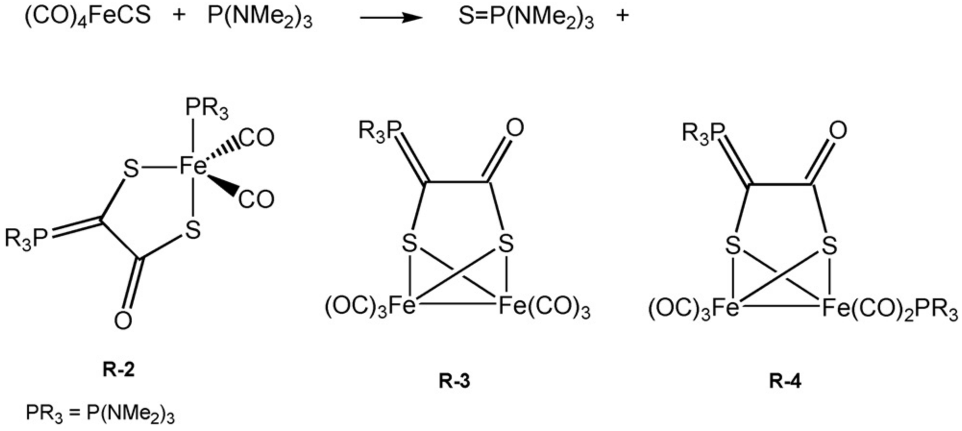


Chart 19.

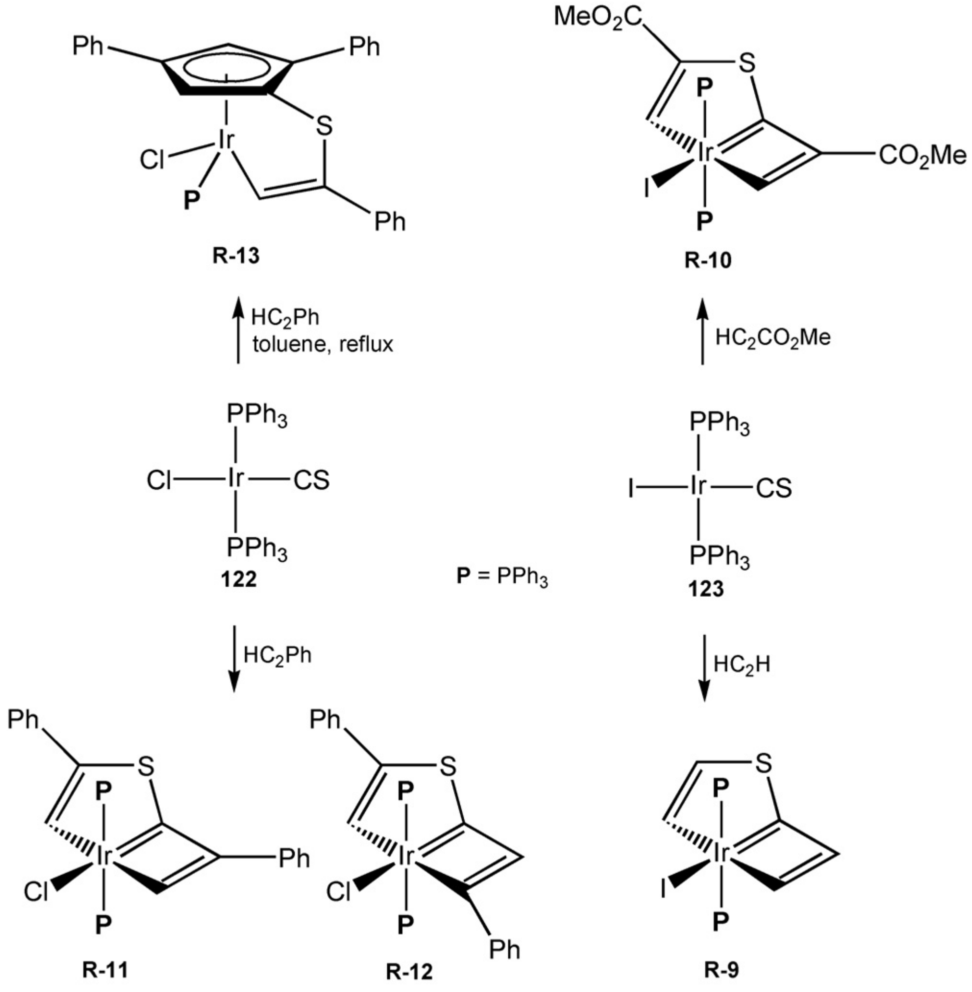


Scheme 29.

to the formation of the tethered iridabutadiene **R-9** in 56% yield. With HC≡CCO_2Me the related iridabutadiene **R-10** was obtained in about the same yield. If $IrCl(CS)(PPh_2)_2$ (**122)** was allowed to react with phenylacetylene in refluxing benzene an isomer mixture of the iridabutadiene **R-11** (major isomer) and **R-12** (minor isomer) was obtained. If the reaction was carried out at higher temperature in refluxing toluene the tethered cyclopentadienyl complex **R-13** was obtained in approximately 50% yield [118].

5.1.6. *Insertion into M–C bonds*

Organic groups are motivated to move from the metal to the thiocarbonyl carbon atom if CO or other soft ligands are introduced.



Scheme 30.

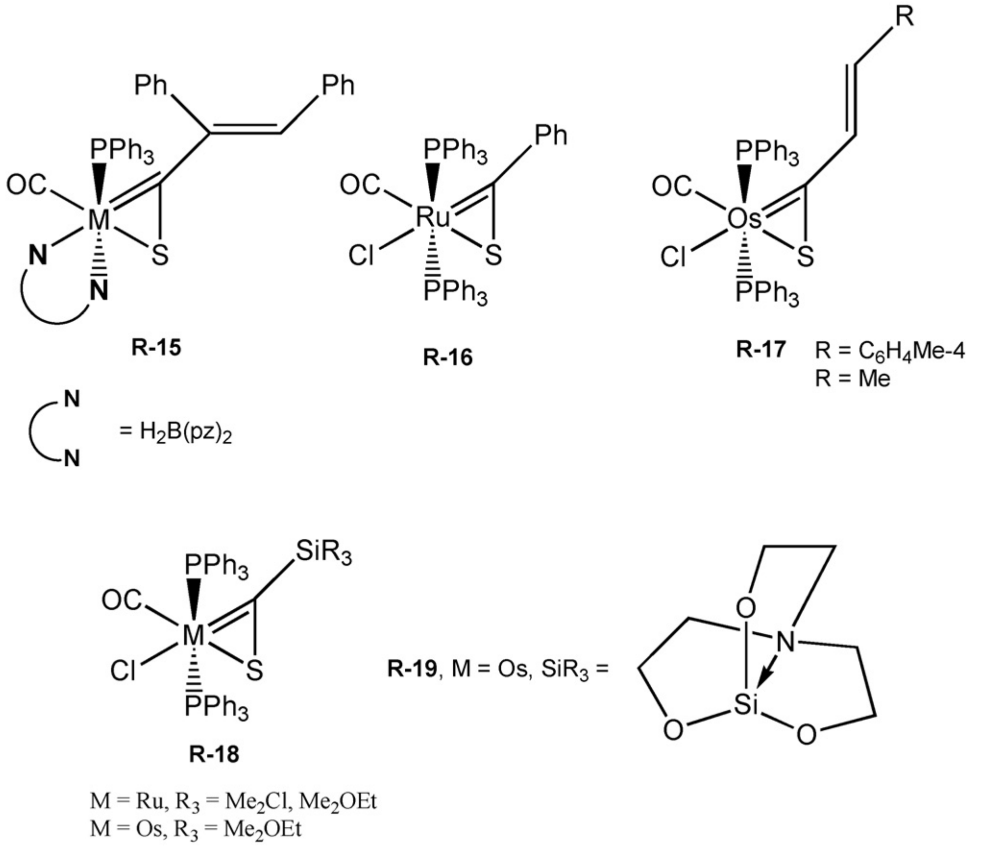
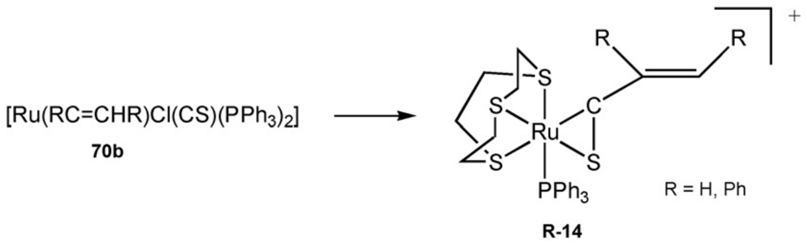


Chart 20.

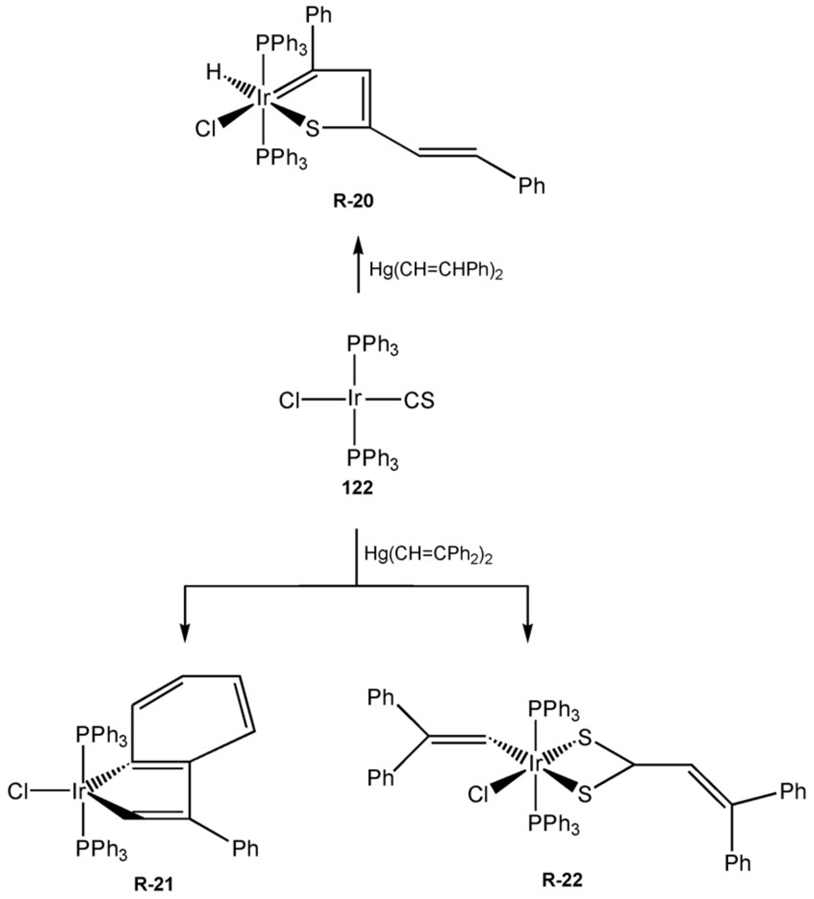
Thus, insertion of CS into a Ru–C-bond occurs, when Ru(CR=CHR)(Cl)(CS)(PPh$_3$)$_2$ (**70b**) is treated with the crown ether 1,4,7-trithiacyclononane to produce the cation **R-14** (Scheme 31) [82].

The introduction of CO in coordinatively unsaturated Ru and Os compounds causes vinyl, phenyl or silyl groups to migrate to the thiocarbonyl carbon atom to produce thioacyl or silathioacyl complexes, respectively; the resulting insertion products are shown in Chart 20. Thus, addition of CO to Ru(CPh=CHPh)(CS)(PPh$_3$)$_2$(H$_2$B(pz)$_2$) (**71**) generates the complex **R-15** [92]. Similarly, the phenyl (M = Ru; R = Ph) or vinyl (M = Os; R = CH=CHC$_6$H$_4$Me-4) group of MR(CS)Cl(PPh$_3$)$_2$ (**66**, Ru; **109**, Os) migrate under the influence of CO with formation of **R-16** and of **R-17**, respectively, containing η^2-bonded thiobenzoyl ligands [30,107] and the compounds M(SiR$_3$)Cl(CS)(PPh$_3$)$_2$ (M = Ru **67** and **68**; Os **102** and **103**; R = Cl, OEt) react with CO to give a series of the η^2-silathioacyl complexes **R-18**; a rapid formation of intermediate cationic species [M(SiMe$_2$R)Cl(CO)(CS)(PPh$_3$)$_2$]$^+$ was suggested [91]; a similar silatrane migration is found by reacting CO with Os(Si(OCH$_2$CH$_2$)$_3$)N)Cl(CS)(PPh$_3$)$_2$ (**105**) to produce **R-19** [106]. Addition of HCl to the thiocarbonyl complex **81** causes the CCMe group via an intermediate vinylidene complex to migrate to the thiocarbonyl carbon atom to give **R-17** (R = Me) [99]. The insertion of a thiocarbonyl ligand into an Os–B bond is mentioned in [143].

The 2-iridiathiophene complex **R-20** was obtained in 75% yield from the reaction between **122** and Hg(CH = CHPh)$_2$; oxidative addition products were postulated as intermediates. In contrast, Hg(CH = CPh$_2$)$_2$ and **122** produce a mixture of the 1-iridatiophene **R-21** and **R-22** in 20 and 8% yield, respectively, as depicted in Scheme 32 [116].



Scheme 31.



Scheme 32.

5.1.7. *E–CS coupling reactions*

In some binuclear Pt compounds with a μ-chalcogen ligand E = S, Se (**132a–d**) a recombination to a η^2-bridging CSE ligand within the coordination sphere of the metals can occur by addition of a chelating dppe or dpmb ligand to produce **R-23** as shown in Scheme 33 [31,119,120].

5.1.8. *Conversion into a thioaldehyde ligand*

Irradiation of the complex $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ leads to the loss of one CO group with oxidative addition of the ortho-CH bond of the phosphite ligand to give **R-24** with a thioaldehyde coordinating at the iron atom in an η^2-manner (Scheme 34) [144].

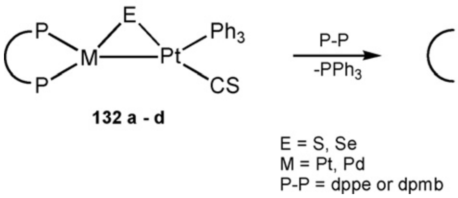
5.1.9. *Exchange reaction*

From ^{13}C NMR experiments it was found that a CS_2/CS exchange can occur from enriched FpC*(S)SFp and cationic $[Fp(CS)]^+$ to produce FpC(S)SFp and $[Fp(C^*S)]^+$ [72].

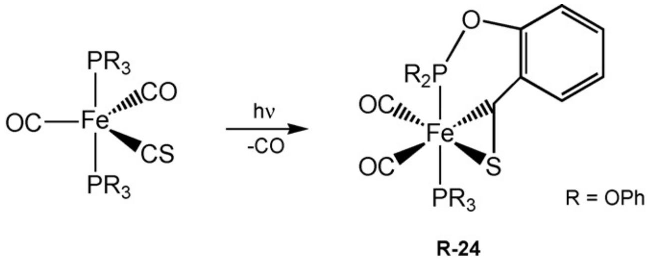
5.2. *Reactions of bridging CS ligands*

5.2.1. *with electrophiles*

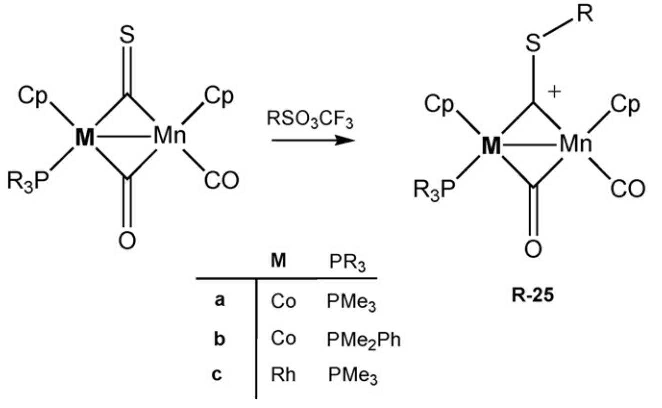
Reactions of bridging thiocarbonyl groups with various hard and soft electrophilic agents have also been reported earlier [14] and due to the stronger nucleophilic nature of the μ-CS sulfur atom with respect to the terminal bonded CS group the formation of μ-carbyne ligands is enhanced. Transition metal compounds containing weakly bonded ligands such as THF (e.g.



Scheme 33.



Scheme 34.



	M	PR₃
a	Co	PMe₃
b	Co	PMe₂Ph
c	Rh	PMe₃

Scheme 35.

(CO)$_5$Cr(THF) or CpMn(CO)$_2$(THF)) form compounds of the type **G**; new compounds of type **G** and **F** are summarized in Table 2 [43]. The thiophilic Ag$^+$ cation and HgCl$_2$ can also coordinate to the bridging CS group to produce compounds of type **G** [16,42].

Scheme 35 shows that alkylation transfers a bridging CS group into a μ-carbyne ligand upon reacting the heterobinuclear complexes **152–153** with MeSO$_3$CF$_3$ to produce a series of cationic species (**R-25**); as counterion act PF$_6$$^-$ [43].

However, if a molecule contains two bridging CS groups, only one can be reacted and if a μ-CO and μ-CS group is present in the same molecule, the sulfur atom is more nucleophilic than the oxygen atom. Further examples of S-alkylation with formation of the cationic compounds **R-26**, **R-27**, and **R-28** is shown in Scheme 36 [122–124].

5.2.2. *Other reactions*

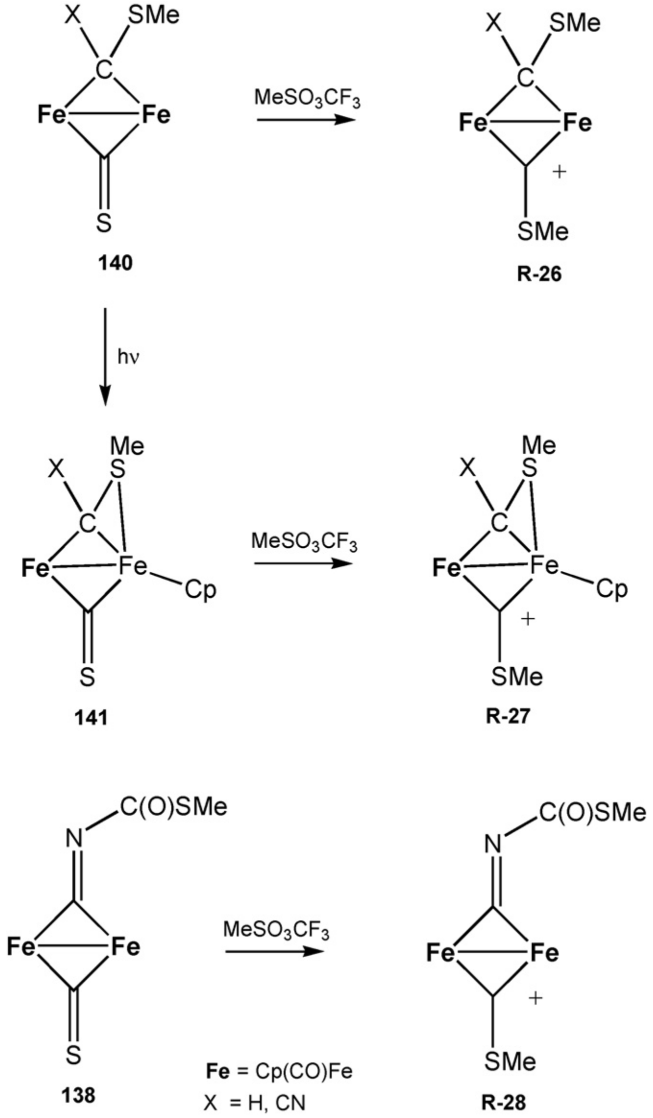
The first report of a desulfurization of a bridging thiocarbonyl ligand of the type **B** is shown in Scheme 37.

The bridging thiocarbonyl ligand of Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CS) and one of Cp$_2$Fe$_2$(CO)$_2$(μ-CS)$_2$ (**135**) can be converted into a bridging methylene group with Raney nickel; however the yields of the *cis/trans* isomer mixtures *A* and *B* of **R-29** are very low ranging from 11% to trace amounts [16].

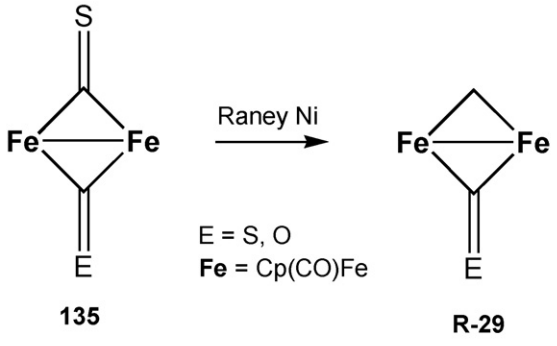
Conversion of a μ$_3$-CS ligand of Cp$_2$Co$_2$Fe(CO)$_2$(L)(μ$_3$-S)(μ$_3$-CS) (**163**) into a μ$_3$-carbyne ligand by treatment with MeI, MeSO$_3$CF$_3$, or EtSO$_3$CF$_3$ to give cationic species **R-30** is reported in [48] (Chart 21). Heating of Cp$_2$Co$_2$Fe(CO)$_2$(PPh$_3$)(μ$_3$-S)(μ$_3$-CS) with CS$_2$ converts it into the cluster **R-31** with an unusual C$_2$S$_3$ bridging ligand [145]; similar reaction occurs with the compounds Cp$_2$Co$_2$Fe(CO)(L^1)(L^2)(μ$_3$-S)(μ$_3$-CS) (**164**) [146].

5.3. *Elimination of the CS ligand*

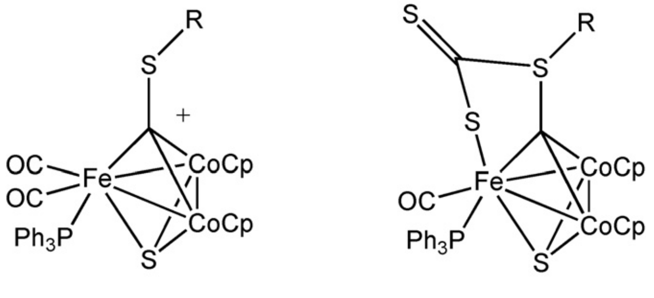
In the majority of reactions of thiocarbonyl compounds the coordinated CS ligand is either involved because of the more electrophilic character of the CS carbon atom, or it remains untouched in terms of the stronger metal carbon bond with respect to the metal CO bond. However, elimination of CS proceeds by reacting RuCl$_2$(CO)(CS)(PPh$_3$)$_2$ with the chelating ligands EtOCS$_2$$^-$ or Et$_2$NCS$_2$$^-$ (S,S) to produce the corresponding Ru(S,S)$_2$(CO)(PPh$_3$) compounds. A proceeding nucleophilic attack of the dithiolate ligand on the thiocarbonyl via an intermediate metallacycle (Chart 22) was supposed which decomposes with loss of CS [79]. The cation



Scheme 36.



Scheme 37.



R-30 **R-31**

Chart 21.

$[(S_3)Rh(CS)(PPh_3)]^+$ is oxidized by I_2 to give the CS-free cationic complex $[(S_3)Rh(PPh_3)I_2]^+$ [110].

Partial elimination of CS occurs also in some CpFe(CS) compounds [147] as summarized in the Gmelin volume concerning the CpFe(CS) chemistry [15].

5.4. *Reactions with retention of the CS Ligand*

A lot of reactions, such as substitution or redox reactions have been carried in which the CS ligand remains “innocent”. The preparation of those compounds is covered in Section 4 and is not discussed further. The same is true for compounds bearing innocent terminal CSe or CTe ligands.

Kinetic studies of the arene substitution reaction by phosphines of various $(\eta^6\text{-arene})Cr(CO)_2(CS)$ compounds and of $C_6H_6Cr(CO)_2(CSe)$ have been carried out. Compared to similar $(arene)Cr(CO)_3$ complexes, a dramatic increase in reactivity was found in the corresponding CS complexes and more pronounced in the CSe compound. The reactions are first order in both substrate and entering phosphine ligand. The increased reactivity results in a weaker bond between Cr and the arene caused by the better π acceptor capacity of the CS and CSe ligands [24].

5.5. *Reaction of compounds with CSe and CTe ligands*

Also a couple of compounds with terminal CSe or CTe ligands have been prepared, reports on modification of these ligands are rare and concentrate mainly on reactions with nucleophilic or electrophilic reagents.

In a short note, Roper has reported, that the cationic compound $[RuCl(CNR)(CO)(CSe)(PPh_3)_2]^+$ (**191**; R = *p*-tolyl) can be converted with SeH^- into $Ru(\eta^2\text{-}CSe_2)(CO)(CNR)(PPh_3)_2$ (**R-32**) constituting a novel access to an η^2-CSe_2 complex without use of free CSe_2 [41].

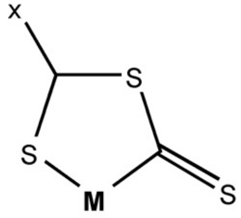
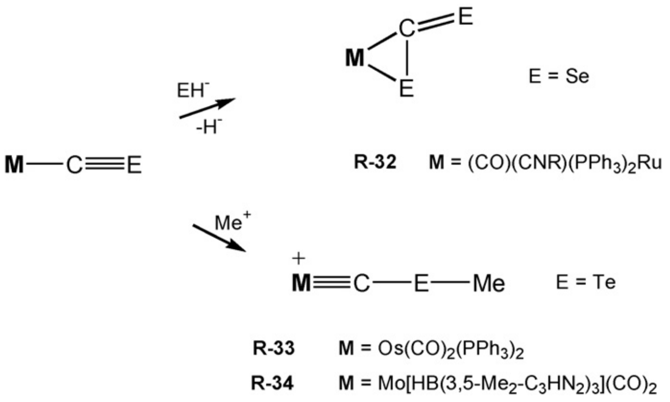


Chart 22.



R-32 M = $(CO)(CNR)(PPh_3)_2Ru$

R-33 M = $Os(CO)_2(PPh_3)_2$

R-34 M = $Mo[HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3](CO)_2$

Scheme 38.

The only known reaction of a terminal CTe ligand is the alkylation to produce the corresponding carbyne ligand. Thus, $Os(CO)_2(CTe)(PPh_3)_2$ (**199**) is transferred with MeI into the cationic carbyne complex $[Os(CO)_2(\equiv CTeMe)(PPh_3)_2]^+$ (**R-33**). The carbyne ligand is in the equatorial position [101]. The anionic compounds $[Mo(CO)_2(CTe)(HB(3,5\text{-}Me_2C_3HN_2)_3)]^-$ (**200**) is similarly transferred into the neutral carbyne compound $Mo(CO)_2(\equiv CTeMe)(HB(3,5\text{-}Me_2C_3HN_2)_3)$ (**R-34**) [40]; the reactions are summarized in Scheme 38.

6. Spectroscopic properties

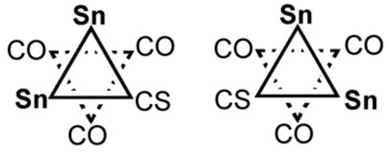
6.1. *IR spectroscopy*

All compounds show strong ν(CS) absorptions in the IR spectra. With few exceptions terminal CS groups absorb between 1180 and 1380 cm^{-1} and bridging CS groups (**B**) were found between 1050 and 1110 cm^{-1}. If the bridging CS group coordinates to a further metal center a shift of about 50 wave numbers to lower frequencies is observed; a similar shift is with terminal CS groups when coordinated to a further metal center (mode **G**).

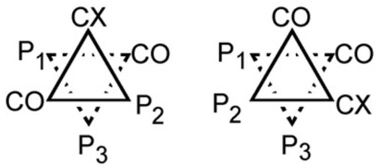
The pressure dependence of IR spectra of $Cr(CO)_5(CS)$ and $(\eta^6\text{-}C_6H_6)Cr(CO_2(CS)$ were studied for pressures at room temperature up to 25 and 30 kbar. High-pressure micro-Raman have been similar investigated in the low energy region (450–300 cm^{-1}) up to 25 kbar. In $Cr(CO)_5(CS)$ π-back donation is enhanced by increasing pressure for CS and *trans*-CO as indicated by a shift of the stretching bands to lower frequencies [148].

Absolute integrated IR intensities in CS_2 solution of $(\eta^6\text{-}C_6H_6)Cr(CO_2(CE)$ (E = O, S, Se) for the stretching modes have been determined. From the intensity results a decrease of the CrCX dipole moment and π-acceptor capacity as CSe > CS > CO was suggested [149].

An absolute integrated IR intensity study with $(arene)Cr(CO)_2(CS)$ compounds (arene = PhMe, PhCl, C_6H_6, $PhCO_2Me$) was also performed. Thus, the intensities of the CO and CS stretching bands were found to correlate well with the Hammett substituent parameters, σ^0 [139].



28c



7 (X = S),**178a**(E = Se)

Chart 23.

Vibrational spectra and potential constants of (η^6-Bz)Cr(CO)$_2$(CE) and (η^6-C$_6$H$_6$)Cr(CO)$_2$(CE) complexes (E = CO, CS, CSe) were determined in [150,151].

6.2. *NMR spectroscopy*

The low temperature NMR spectrum (−105 °C) of [(η^6-C$_6$Et$_6$)Cr(CO)(CS)(NO)]$^+$ shows all 18 carbon atoms of the hexaethylbenzene ligand differentiated. The ligand adopts the 1,2,5-proximal-2,4,6-distal arrangement. On lowering the temperature two separate rate processes are observed. The higher energy process ($\Delta G^* = 11.5$ kcal/mol) involves uncorrelated rotation of the ethyl groups. The lower activation energy ($\Delta G^* = 9.5$ kcal/mol) represents the barrier to tripod rotation [56].

The mechanism of arene displacement was studied. Thus, the formation of Cr(CO)$_2$(^{13}CO)$_3$(CS) from [(η^6-PhCO$_2$Me)Cr(CO)$_2$(CS) and ^{13}CO and no incorporation of a fourth ^{13}CO molecule establishes a non-dissociative pathway during *mer-fac* isomerization process [152].

The dynamic behavior of Fe(CO)$_3$(CS)(SnMe$_3$)$_2$ (**28c**) was studied by variable temperature multi nuclear NMR spectroscopy. A small temperature dependence of δ ^{13}C(CS) and δ ^{119}Sn values and the constant coupling constant ^2J(C$_{\text{CS}}$,Sn) values indicated that the CO equilibration occurs via a mechanism which keeps the relative position of the CS and Sn ligands unchanged, involving a rotation of the CO plane against the CSSn$_2$ plane via a trigonal prismatic pathway with rotation of the (CO)$_3$ plane versus the Sn$_2$C(S) plane (see Chart 23) [69].

2-D NOE ^{31}P NMR spectroscopy has shown that the isomerization process between the pure *mer*-isomer into the *fac*-isomer of the stereochemically nonrigid octahedral complex Cr(CO)$_2$(CX)(P(OMe)$_3$)$_3$ with X = S (**7**), Se (**178a**) proceeds intramolecularly via a trigonal prismatic pathway being the lowest energy path (Chart 23) [153,154].

Equimolar mixture of both (*exo* and *endo*) epimers of the chromium complex **9** with the arene ligand 4,5-dimethyl-9,10-dihydrophenanthrene (Chart 24) were obtained and configural assignments were based on CD and ^{1}H NMR spectra; the kinetics of the biphenyl flip around the biphenyl axis was determined [57].

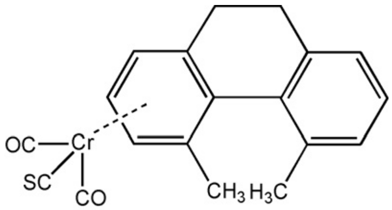


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Chart 24.

From a small downfield shift of the ring proton resonance in CpMn(CO)$_2$(CX) compounds in going from X = O to S, Se it was deduced that the CSe ligand is a better electron withdrawing group than both CO and CS. It was explained with less electron density on the metal and an increased ring π bond order resulting from a decrease in metal to ring d-π^* back bonding [133].

^{31}P chemical shift anisotropy in solid Cr(CO)$_4$(CS)(PPh$_3$) (*cis* and *trans*) was estimated at 293 K [54].

In the series of OsCl$_2$(CO)(CE)(PPh$_3$)$_2$ compounds all four possible derivatives have been prepared with E = O, S (**90**), Se (**192**), and Te (**198a**). In going down the periodic system a deshielding of the CE ^{13}C NMR shift occurs of about 20 ppm; for group16 elements shifts of 173 (O), 259 (S), 279 (Se), and 298 (Te) ppm were estimated [8].

The carbon-13 chemical shift anisotropies of the carbonyl and thiocarbonyl ligands in (C$_6$H$_6$)Cr(CO)$_3$ and (C$_6$H$_6$)Cr(CO)$_2$(CS) are estimated by solid state NMR at room temperature. The shift anisotropy of the CS group is much larger than that for carbonyls. The principal components, isotropic values, and anisotropies of the ^{13}C shielding tensors for both compounds are collected in a table [155].

In the ^{57}Mn NMR spectrum of Mn$_2$(CO)$_9$(CS) (**17**), the presence of two isomers with the CS group either *trans* to CO or to Mn(CO)$_5$, respectively, is indicated by two pairs of resonance signals (Isomer I: −2372, −2082 ppm; Isomer II: −2248, −2125 ppm) [7].

6.3. *UV/vis spectra*

The room temperature electronic spectra of Cr(CO)$_5$(CX) and (η^6-C$_6$H$_6$)Cr(CO)$_2$(CX) compounds (X = O, S, Se) support the order of increasing electron withdrawing capacity of the chalcocarbonyl ligands as CO < CS < CSe [156]

6.4. *PE spectroscopy*

Photoelectron spectroscopy studies of (CO)$_5$M(CS) and CpMn(CO)$_2$(CS) were mentioned earlier and comparison were made to the carbonyl analogues [14]. The He(I) PE of ArCr(CO)$_2$CX and Cr(CO)$_5$(CSe) (**174**) were also measured. For **174** all the ionization potentials are slightly lower than those of the CS analogue. The first ionization potentials of (η^6-C$_6$H$_6$)Cr(CO)$_2$CX (X = O, S, Se) were compared with those of the corresponding $Cr(CO)_5(CX)$ compounds; a significant electron transfer from the benzene ring in each case was found [157]. The He(I) PE spectrum of $(CO)_4Fe(CS)$ was measured. A comparison with that of $Fe(CO)_5$ shows, that the nature of the 3d orbitals is only slightly perturbed by replacing a CO ligand by CS. The first and the second IP are slightly lower. The sequence of the first two ionization potentials originating from the CS group have changed in comparison to the free ligand. The different isomers (CS in the equatorial or axial position) lead to identical potentials [158].

X-ray PE spectrum of $(Ph_3P)ClRuCl_3Ru(CS)(PPh_3)_2$ was measured and does not differs from that of the corresponding carbonyl complex [159].

6.5. *Mössbauer spectroscopy*

Mössbauer spectra were obtained for the five-coordinate complex Fe(OEP)(CS) (**34**) and for several six-coordinate Fe(OEP)(CS)L (**35a–e**). **34** exhibits a very small value for the isomer shift ($\delta_{Fe} = 0.08$ mm/s at 4.2 K and −0.03 mm/s at 293 K) and a large quadrupole splitting constant of 1.95 mm/s. In the six-coordinate complexes **35**, an increase of δ_{Fe} of about 0.14–0.19 mm/s occurs and the quadrupole splitting values drop down to 0.80–0.42 mm/s. It was suggested that the sixth ligand effect is primarily induced by changes in σ-bonding [74].

7. Photolysis

UV photolysis of $(CO)_5Cr(CSe)$ (**174**) has been performed. Irradiation of the compound with 254 and 366 nm in argon matrix at 20 K generates two isomers of $(CO)_4Cr(CSe)$, $Cr(CO)_6$ and CO. The two isomers are assigned square pyramidal geometries with the CSe group either in the axial (C_{4v} symmetry) or in the basal position (C_s symmetry). On irradiation with visible light, the starting material is regenerated [160].

Irradiation of $Rh(PPh_3)_2(CS)Cl$ at 452 nm in CH_2Cl_2 leads to metal-to-ligand charge transfer (MLCT) and initiates photooxidation to give finally $Rh(PPh_3)_2(CS)Cl_3$ as a stable photoproduct according to Eq. (29) [161].

$$Rh(PPh_3)_2(CS)Cl + 2CH_2Cl_2 \rightarrow Rh(PPh_3)_2(CS)Cl_3 + 2^{\bullet}CH_2Cl \qquad (29)$$

Photocatalytic dehydrogenation of cyclohexane is closely related to photodissocation of the CS ligand. As effective absorption band is the second lowest at $\lambda_{max} = 339$ nm. Thus, as active species the fragment $RhCl(PPh_3)_2$ was suggested [162].

8. Structural aspects

Crystal structural data of about 50 compounds containing terminal and various bridging CS groups are available at the present time. Structural data of CSe and CTe complexes are restricted to four and two examples, respectively.

On the bases of new studies and including earlier results concerning compounds with terminal bonded CS groups the C–S bond length is found to vary enormously ranging between about 136 and 160 pm and no correlation with the stretching frequencies could be detected. However, a realistic average value of 152 pm can be estimated. From present data the average C–E bond lengths for E = S, Se, Te increases approximately in the order 152, 168, 192 pm, respectively; in the special case of $OsCl_2(CO)(CE)(PPh_3)_2$ compounds with the CE ligand attached at the same fragment, the order is 148, 161, 192 pm and $\Delta(\nu)$ values of 13 cm^{-1} between S and Se and 32 cm^{-1} between Se and Te are found. The *trans* influence of the chalcocarbonyl ligands was found to increase in the order CO < CS ≤ CSe < CTe [8].

In going from coordination of the CS ligand to 1, 2 to 3 metals and on the bases of only few compounds the average CS bond length is in the order 152 (μ_1), 159 (μ_2), and 162 pm (μ_3) confirming an increase of π-back donation with increasing number of metals to be bridged.

The crystal structure of Cp(CO)Fe(μ-CO)(μ-CS)$Mn(CO)_4$ is remarkable because the related carbonyl compound $Cp(CO)_2FeMn(CO)_5$ contains only terminal CO groups; the preference of the CS group going into a bridging position seems to be a general feature [44].

The crystal structure of (η^6-PhMe)$Cr(CO)_2CSCr(CO)_5$ (**168a**) with a CrCSCr arrangement of coordination mode **E** is the first example of an end to end bonded thiocarbonyl ligand. The most striking feature is the non linearity of the C–S–Cr bond with a bond angle of 110° which is close to that for a sp^3 hybridization at the sulfur atom. A very short Cr–C (174.7 pm), a long C–S (160.4 pm) and very long S–Cr distance (248.6 pm) indicate, that the compound can best be described as bearing a transition metal substituted carbyne ligand with main contribution of the canonical form **a** as depicted in Chart 25. The long S–Cr distance is also indicative for only a weak bond [59].

The reaction of the anionic complex $[HB(pz)_3W(CO)_2(CS)]^-$ either with $ClAuPPh_3$ [45] or with $IndMo(CO)_2(NCMe)_2$ [46] affords the semibridging type **C** compound **166** or the μ-η^1-η^2 side-on bridging type **D** complex **167**, respectively. Both types of compounds clearly distinguish in the distances of the sulfur atom to the adjacent metal atom. Whereas a normal bonding distance of 251 pm is found to Mo, the distance of about 300 pm to Au does not agree with a bond. Also a nearly linear W–C–S angle in the side-on coordination contrasts with the more bent angle in the semibridging species (Chart 26).

From the compounds $Cr(CO)_2(CE)(P(OMe)_3)_3$ both species with E = S (**3a**) [55] and Se (**178**) [163] have been studied by X-ray analyses adopting a *mer*-geometry. The C–P distance *trans* to the CE ligand is about 2 pm longer in the selenocarbonyl complex indicating the better electron withdrawing capacity of CSe versus CS.

The structure of $(PhCCPh)Os(CS)(PPh_3)_2$ (**78**) is that of a distorted tetrahedron [97] and not planar as reported earlier [14].

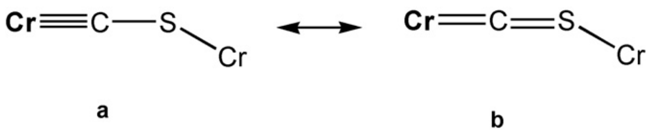


Chart 25.

Table 5
Structural parameters of compounds with terminal CE groups (E = S, Se, Te) of type **A**

Compound	C–E	M–CE	M–CO	Ref.
CS				
mer,trans-Cr(CO)$_3$(CS)[P(OPh)$_3$]$_2$ (**3**)	136(1)	187(1)	188(1)[a]	[53]
Cr(CO)$_2$(CS)(P(OMe)$_3$)$_3$ (**3a**)	158.5	178.2(9)	183.9(9)[a]	[55]
trans-Cr(CO)$_4$(CS)(PPh$_3$) (**6b**)	153.7(13)	178.6(13)	190.6(14)[a]	[54]
[(η^6-C$_6$Et$_6$)Cr(CO)(CS)(NO)]$^+$ (**8**)	151.5(10)	184.6(10)	180.2(11)	[56]
Cp′(CO)$_3$WCH$_2$C(O)SWCp′(CO)$_2$(CS) (**16b**)	149(2)	200(2)	203(2), 197(2)	[61]
[Re$_2$(μ-S)(μ-Br)Br$_2$(CS)(μ-dpam)$_2$(NCEt)]$^+$ (**21n**)	140(4)	202(3)	–	[35,34]
Re$_2$(μ-SO$_2$)(μ-Cl)Cl$_3$(CS)(μ-dppm)$_2$ (**22d**)	147.6(9)	194.7(8)	–	[35,65]
Re(CS)(PMe$_2$Ph)$_3$(Et$_2$dtc) (**23**)	160(2)	184(2)	–	[39]
Re(CS)(Et$_2$dtc)$_3$ (**24**)	159.8(7)	181.1(7)	–	[39]
(CO)$_2$(CS)Fe(PPh$_3$)$_2$ (**26e**)	155.0(7)	176.8(8)	175.1(8)[a]	[26]
(OEP)(CS)Fe(Py) (**35a**)	156.5(2)	170.7(2)		[74]
(OEP)(CS)Fe(1-MeIm)) (**35b**)	156.3(4)	170.3(4)		[74]
(OEP)(CS)Fe(CH$_3$OH) (**35f**)	157.6(12)	180.0(12)		[74]
RuCl$_2$(CS)(Pcy$_3$)$_2$ (**39**)	157.6(2)	173.8(2)		[37]
Ru(CS)Cl(PPh$_3$)(HB(pz)$_3$) (**51b**)	156.9(11)	176.8(11)	–	[164]
RuCl(CS)(η^2*C,N-o*-C$_6$H$_4$N = NC$_6$H$_5$)(PPh$_3$)$_2$ (**53a**)	157.2(6)	178.8(6)	–	[84]
RuI(CS)(η^2*C,N-o*-C$_6$H$_4$N = NC$_6$H$_5$)(PPh$_3$)$_2$ (**53c**)	152.0(11)	180.6(11)	–	[84]
Ru(CS)Cl(PPh$_3$)$_2$(η^2-SCPh) (**62**)	–	–	–	[30]
[(C$_5$Me$_5$)Ru(P∼O)$_2$(CS)]BPh$_4$ (**63**)	155.4(4)	183.2(4)	–	[89]
Ru$_3$(CO)$_5$(CS)(μ-H)(μ-P^{t}Bu$_2$)(μ-PCy$_2$)$_2$(μ$_3$-S)] (**74**)	155.2(5)	181.9(5)		[36]
(PhCCPh)Os(CS)(PPh$_3$)$_2$ (**78**)	159(2)	179(2)	–	[97]
OsH(CO)(CS)(C$_2$Me)(PPh$_3$)$_2$ (**81**)	156.3(5)	189.4(5)	191.7(5)	[99]
Os[C$_7$H$_2$O(OMe-7)(CO$_2$Me-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**84**)	158.8(3)	184.6(3)	–	[102]
Os[C$_7$H$_2$O(OMe-7)(CO$_2$Et-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**85**)	159.9(4)	186.6(4)	–	[102]
Os[C$_7$HO(OMe-7)(Br-6)(CO$_2$Me-4)(Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$ (**86**)	157.1(4)	185.3(4)	–	[102]
[Os[C$_5$H (CH$_2$CO$_2$Me-5)(CO$_2$Me-4) (Ph-1)(Ph-2)](CS)(PPh$_3$)$_2$]I$_3$ (**87b**)	156.6(6)	190.1(6)	–	[102]
OsCl$_2$(CO)(CS)(PPh$_3$)$_2$ (**90**)	148(1)	188(1)	198(2)	[8]
OsCl$_2$(CS)(PCy$_3$)$_3$ (**93**)		175.8(2)	–	[104]
IrI(CS)(PPh$_3$)$_2$(O$_2$) (**124**)		183.3(9)	–	[118]
dpmbPt(μ-Se)Pt(CS)PPh$_3$ (**132c**)	152(5)	183(4)	–	[120,31]
CSe				
(η^6-C$_6$H$_5$COOMe)Cr(CO)$_2$(CSe) (**176**)	172.8(10)	178.6(11)	186.2(12)	[165,166]
Cr(CO)$_2$(CSe)(P(OMe)$_3$)$_3$ (**178**)	175.0(3)	178.5(3)	189.3(3)	[163]
RuCl$_2$(CO)(CSe)(PPh$_3$)$_2$ (**188a**)	167(2)	183(2)	189(2)	[3]
OsCl$_2$(CO)(CSe)(PPh$_3$)$_2$ (**192**)	160.9(15)	191.3(15)	192.0(20)	[8]
CTe				
OsCl$_2$(CO)(CTe)(PPh$_3$)$_2$ (**198a**)	192.3(12)	181.3(12)	185.6(11)	[8]
Os(CO)$_2$(CTe)(PPh$_3$)$_2$ (**199**)	194.7(20)	185.7(19)	188.5(18)	[101]

[a] Average values.

Table 6
Structural parameters of compounds with μ-bridging CS groups of type **B**

Compound	C–S	C–M^1	C–M^2	M^1–M^2	Ref.
Cp(CO)Fe^2(μ-CS)(μ-CSMe)Fe^1(CO)(η^4-C$_5$H$_5$th) (**144**)	160.5(2)	187.4(2)	193.8(2)	250.77(7)	[125]
Cp$_2$Fe$_2$(μ-CS)(μ-CSMe)(μ-S$_2$CNMe$_2$) (**147**)	161.6(3)	188.1(3)	186.5(3)	245.3(1)	[126]
[Co$_2$(μ-CS)(μ-S$_2$C$_2$R$_2$)(CO)$_3$(μ-dppm)] R = CO$_2$Me (**149a**)	160.9(5)	191.2(5)	188.3(5)	244.98(11)	[50]
Cp(CO)Fe(μ-CO)(μ-CS)Mn(CO)$_4$ (**151**)	159.6(3)	199.8(3)Mn	192.0(3)Fe	263.1(1), 263.3(1)[a]	[44]
	158.5(3)	198.2(3)	192.7(3)		

[a] Two molecules in the assymmetric unit.

Table 7
Structural parameters of compounds with a semibridging CS groups of type **C**

Compound	C–S	C–M^1	C–M^2	M^1–M^2	Ref.
HB(pz)$_3$(CO)$_2$(CS)WAuPMe$_3$ (**166a**)	163.1(25)	190.5(24)W	215.1(24)Au	282.4(1)	[45]
HB(pz)$_3$(CO)$_2$(CS)WAuPPh$_3$ (**166b**)	163.0(8)	191.1(7)W	216.2(7)Au	282.5(1)	[45]

Table 8
Structural parameters of compounds with a bridging four-electron donor CS groups of type **D**

Compound	C–S	C–M^1	C–M^2	M^1–M^2	Ref.
HB(pz)$_3$](CO)$_2$W(μ-CS)Mo(CO)$_2$Ind (**167**)	164.0(6)	189.5(5)W	222.9(4)Mo	331.02(2)	[46]

Table 9
Structural parameters of compounds with end to end-bridging CS groups of type **E**

Compound	C–S	C–M	S–M	Ref.
(*η^6-PhMe)(CO)$_2$CrCSCr(CO)$_5$ (**168a**)	160.4(5)	174.7(5)	248.6(2)	[59]
(Ar[R]N)$_3$MoCSMo(N[R]Ar)$_3$ (R = C(CD$_3$)$_2$Me; Ar = 3,5-C$_6$H$_3$Me$_2$) (**173**)		175.2(12)	228.9(3)	[131]

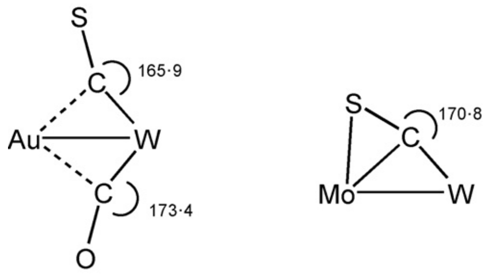
Table 10
Structural parameters of compounds with μ$_3$-bridging CS groups of type **F**

Compound	C–S	C–M^1	C–M^2	C–M^3	Ref.
(C$_5$Me$_5$)$_2$Co$_3$(μ$_3$-CS)(μ$_3$-S) (**160**)	163.4(5)	195.8(5)	193.6(5)	194.9(5)	[128]
Ni$_3$Cp$_3$(μ$_3$-CS)(μ$_3$-CO) (**161a**)	155	192			[49]
Ni$_3$Cp$_3$(μ$_3$-CS)$_2$ (**161b**)	153.9(11)	192.2(7)			[49]
Ni$_3$Cp$'_3$(μ$_3$-CS)(μ-CO) (**161c**)	159.8(2)	191.8			[49]
Ni$_3$Cp$'_3$(μ$_3$-CS)$_2$ (**161d**)	161	190			[49]
(CpCo)$_2$Fe(PPh$_3$)(CO)$_2$(S)(μ$_3$-CS) (**163a**)	164.6(3)	208.5(3)Fe	191.0(3)Co	192.2(3)Co	[47,48]

Table 11
Structural parameters of compounds with μ-bridging CS groups of type **G**

Compound	C–S	M^1–C	M^2–C	S–M	Ref.
Cp(PMe$_3$)Co(μ-CO)(μ-CSMn(CO)Cp)Mn(CO)Cp (**156a**)	164.8(8)	190.4(8)Co	183.8(8)Mn	229.7(3)Mn	[43]
[{Cp$_2$Fe$_2$(CO)$_3$(CS)}$_3$Ag]BF$_4$ (**157**)	161(2)	190(1)Fe	186(1)Fe	251.7(3)Ag[a]	[16]

[a] Only for one Cp$_2$Fe$_2$(CO)$_3$(CS) unit.



166 **167**

Chart 26.

The structure of Cl$_2$Os(CS)(PCy$_3$)$_2$ (**93**) is close to that of a square pyramid with the CS ligand in the apical position [104] (Tables 5–11).

9. Electrochemistry

Some electrochemical studies mainly on various porphyrin complexes were performed and the cyclic voltagramms were reported.

The oxidative electrochemistry of (TTP)Fe(CS) was studied in 1,2-dichlorethane solution. It can be oxidized in two chemically reversible one-electron transfers. In the first step a thiocarbonyl Fe(III) porphyrin is formed whereas the second oxidation step occurs at the porphyrin ring producing a radical. A similar first step oxidation is found with (TTP)Fe(CS)(L) (L = nitrogen base) compounds, however, the second step is connected with a nucleophilic attack of excess uncomplexed ligand [136]. The same behavior was reported for the selenocarbonyl analogue (TTP)Fe(CSe) (**186**) [137,167]. Similar quasi-reversible two-electron transfer steps by the electrochemical oxidation of (TPP)Ru(CS)L (**76a** to **p**) were found. In the first step the π-cation (TTP$^{\bullet+}$)Ru(CS)L is formed with Ru(II) whereas the second irreversible step leads to Ru(III) derivatives [94].

Cyclic voltammograms of the 49-electron trinuclear Ni-cluster compounds Cp$_3$Ni$_3$(μ$_3$-CS)$_2$ and Cp$_3$Ni$_3$(μ$_3$-CO)(μ$_3$-CS) exhibit an one-electron oxidation to the 48-electron cation and a one-electron reduction to the 50-electron anion in reversible redox processes. Increasing number of bridging CS ligands makes oxidation more difficult but reduction easier [49].

The electrochemical reduction of Re$_2$(μ-S)(μ-Cl)Cl$_2$(CS)(dppm)$_2$(L)]PF$_6$ (**21**) was studied, leading to one- and two-electron reduction products which are the same as reduction with Cp$_2$Co [34,64].

10. Theoretical considerations

Various theoretical studies have been performed, mainly by Ziegler and Frenking involving bonding aspects and reactivity of the metal bonded CS group.

From earlier calculations it was concluded, that a terminal CS ligand is both a better π-acceptor and a better σ-donor than CO and is more strongly bonded to the metal. Using the Hartree–Fock–Slater method calculating the bond energies of CE complexed to $Ru(CO)_4$ an increase of D(Ru–CE) in going from E=O to S to Se to Te was found; the donor and acceptor abilities for CE increase along this series which was explained in terms of the drop in electronegativity from O to Te; thus, the orbital energies (eV) for σ_{CE} increase while those of π^*_{CE} decrease through this series [168].

The enthalpy of migration of H or R to CS in $RMn(CO)_4(CS)$ was calculated and compared with the migration to CO in $RMn(CO)_4CO$ as shown in Eq. (30).

$$RMn(CO)_4(CS) \rightarrow Mn(CO)_4C(S)R \qquad (30)$$

Thus, thioformyl formation is less endothermic than the formylation reaction and also methyl migration in the thioacylation process is more favorable than the methyl migration in the acylation process. This is due to the enhanced strength of the C–R bond in the thioacyl case. The subsequent dihapto stabilization from the coordinatively unsaturated $Mn(CO)_4C(S)R$ fragments to $Mn(CO)_4(\eta^2\text{-}CSR)$ is larger than that for the formyl and acyl complexes [169].

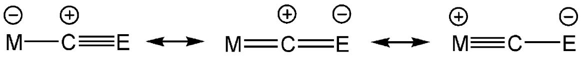
Although the CS carbon atom bears more negative charge than the CO carbon atom according to MO calculations, the reactivity towards nucleophiles is increased. A frontier orbital controlled reaction was suggested with the LUMO being the antibonding CS π^*-orbital [170].

Bond dissociation energies D_0 for the $(CO)_3M$–CS bond have been calculated at the MP2 and CCSD(T) level for the nickel triad as well as for the group 6 $(CO)_5M$–CS series. For the non-existing group10 thiocarbonyls values of 35.7 (Ni), 18.0 (Pd), and 26.9 (Pt) kcal/mol were estimated while those of the group 6 thiocarbonyls are 63.6 (Cr), 59.2 (Mo), and 68.8 (W) kcal/mol; the latter agree well with the experimental values [171].

Using the CCSD(T)/II//B3LYP/II combination of theoretical methods a ligand preference in $(CO)_4FeL$ complexes was studied. In the case of L = CS, it was found that the axial (C_{3v} symmetry) and the equatorial (C_{2v} symmetry) isomers are nearly degenerate and for both the same $(CO)_4Fe$–CS dissociation energy of 64.2 kcal/mol was calculated. The Fe–CS bond lengths were calculated to be 178.7 (C_{3v}) and 177.9 (C_{2v}) pm and the C–S bond lengths to be 155.1 and 155.9 pm, respectively. The donation/back donation ratio for the CS ligand was estimated as 1.17 which is significantly smaller than for CO (1.62) indicating that CS is a better π-accepting ligand [172].

Calculations of the chemical bond in the series M(CS) (M = Sc, Ti, V, Cr, Cu) showed that the M–CS bonding is much stronger and the electron sharing between M and CS is much larger than in the corresponding MCO series. The bond strength between M and CS decrease consistently going from Sc(CS) to Cu(CS). The stronger M(CS) bonds may also be explained with the lower activation energy of $CS \rightarrow CS^-$ when compared to of $CO \rightarrow CO^-$ [173]. A special study concerning the Sc(CS) bond is presented in [174].

The compounds can be described using the following canonical formulas starting from a 16-electron fragment M on the left side. On the right side, a heteroacetylene like formulation is required. It is the same transition as found from a Fischer type carbene ligand (the carbon atom of which is electrophilic) bound to a low valent transition metal to a Schrock carbene ligand with a nucleophilic carbon atom and coordinated to a highly oxidized transition metal.



$$\overset{\ominus}{M}-\overset{\oplus}{C}\equiv E \longleftrightarrow M=\overset{\oplus}{C}=\overset{\ominus}{E} \longleftrightarrow \overset{\oplus}{M}\equiv C-\overset{\ominus}{E}$$

The decreasing rate of electronegativity in the series O > S > Se > Te is opposite to the ability of forming multiple bond to the carbon atom. This leads to an increase of electron density at the chalcogene element in this series.

The difference between the two bridging modes **C** and **D** is demonstrated by MO calculations [175]. In both cases linear M–C–S arrangements to the basic metals M are formed. In **C**, the secondary metal fragment contains a late transition metal which as d^8 or d^{10} species are content with less than 18 electrons. In this case the semibridging CS ligand functions predominantly as a π acceptor. However, if the secondary metal center is an electron deficient earlier transition metal fragment the CS ligand functions as a four-electron donor and electron density flows from the π CS orbital to fill in holes in the d shell of the secondary metal [175]. Linear semibridging CS ligand acts as a π-acceptor of electron density, when the secondary metal center is a late transition metal, even if it has less than 18 electrons. In this case holes in d shells are less prominent than holes in earlier transition metals because the higher nuclear charge pulls the d-electron closer to the nucleus [175].

However, to early transition metals a four-electron π-donor function of the linear semibridging CS group is operative. This was confirmed by contour plots of the corresponding valence orbitals of $\{HB(pz)_3\}(CO)_2W(\mu\text{-}CS)Mo(CO)_2Cp$. It was also predicted that on replacing the CS ligand by CO the molecule would be less stable due to the reduced interaction between the semibridging ligand and Mo [175].

From MO calculations on $Cp_3Ni_3(\mu_3\text{-}CS)_2$ it was also concluded, that the capping μ_3-CS ligand is a much better π^*-acceptor than a capping CO but is an equal σ-donor; in contrast to CO it is also a weak π-donor. More negative charge is found on a CS carbon atom than on a CO carbon atom; this is a composite effect of the greater π^*-acceptor ability of the capping CS ligand and the sulfur atom being less electronegative than the oxygen. The dominant effect is a stronger Ni_3–CS bond and a weaker C–S bond also observed in terminal CS containing compounds [49].

The nonparameterized Fenske–Hall MO approach establishes that the large downfield shift of the CS carbon atom ($\eta^6\text{-}C_6H_6Cr(CO)_2CS$ was chosen for example) correlates with the magnitude of the "paramagnetic" term of the nuclear shielding [176].

11. Conclusion

This overview covers all publications which have been appeared after the first summary given by P.V. Broadhurst in 1985 [14]. During this time the number of compounds has increased to about 200 including CSe and CTe analogues but the number of compounds with unusual complex bonding modes such as the modes **I**–**M** remained constant or has not increased markedly. Although CSe and CTe compounds have been synthesized close to the beginning of this area of chemistry the bonding mode has restricted to type **A** complexes. However, this restriction is not understandable; their excellent acceptor properties should favor any of the bridging modes and the preparation of such compounds will be a challenge to synthetic chemists in the future.

If we compare the carbonyl chemistry with that of thiocarbonyl, selenocarbonyl and tellurocarbonyl derivatives, some interesting features become apparent.

Thus, the extended chemistry of carbonylate anions does not find parallels in its higher homologues. If anions are available, they arise from anionic co-ligands and not from replacement of a ligand pair of electrons by a two-fold negative charge. Our own attempts of reducing $Fe(CO)_4(CS)$ by the usual methods known from carbonyl chemistry with the aim of $[Fe(CO)_3(CS)]^{2-}$ or similar di- or trinuclear species have failed. It seems that reduction exclusively occurs at the CS ligand; besides brownish insoluble materials no definite products could be obtained [177]. This lack of creating reactive anionic species hinders the introduction of a second CS ligand, thus the number of compounds with more than one CS ligand is limited.

The proof for the existence of the earlier reported complex $Ni(CS)_4$ [9] is not convincing.

There are also no parallels to the new field of "non classical carbonyl compound" in which the CO ligand behaves mainly as a σ donor to metals in high oxidation states [178].

No stable CS complex could be obtained from reaction of free CS (via matrix isolation) [179] with metal fragments. The chemistry of this unstable compound was reviewed earlier [180,181].

As already mentioned in the first review by Broadhurst, no theoretical studies have been made during the last time with others than terminal CS ligands; however, extension were made to the higher homologues as shown in Section 10.

Although our knowledge on this area has considerably increased during the last 20 years, particularly with help of new X-ray structure determinations and high level calculations, many remarks made earlier, such as the catalytic potential of these compounds, remained unexplored.

After a period of relatively high numbers of contributions concerning this area of chemistry between 1985 and 1998 a strong decrease was observed later on. May this summary initiate new activities in the chemistry of these fascinating 10-electron systems.

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