

## Coordination chemistry of thiocarbonyl ligand

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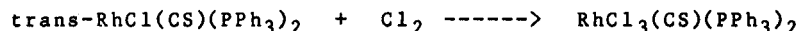
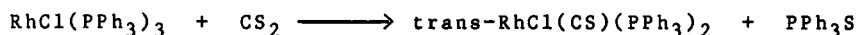
**Abstract** - The first transition-metal thiocarbonyl complexes were discovered just over 20 years ago. Since then, numerous thio-, seleno-, and even one tellurocarbonyl complex, have been reported. The physicochemical properties of these complexes have been examined and it is now generally accepted that the net electron-withdrawing capacities of the chalcocarbonyl ligands increases in the order  $\text{CO} < \text{CS} < \text{CSe}$ . The history and development of the coordination chemistry of these ligands will be briefly reviewed with particular emphasis being placed on the CS ligand and our own recent work on the chemistry of chromium thiocarbonyl compounds.

### INTRODUCTION

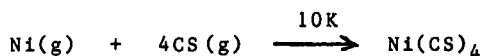
The first examples of transition-metal carbonyls,  $\text{Ni}(\text{CO})_4$  and  $\text{Fe}(\text{CO})_5$ , were discovered in the early 1890's by Mond (e.g., see ref. 1). These compounds were produced by direct reaction of CO gas with the metals. In the case of  $\text{Ni}(\text{CO})_4$ , the reaction is thermally reversible and this discovery led to the Mond process for the purification of nickel that is still employed today.



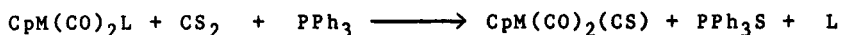
Unlike CO, carbon monosulfide (CS) is only stable below  $-160^\circ\text{C}$ ; above this temperature, CS polymerizes to  $(\text{CS})_n$  (sometimes explosively). This is presumably the reason why metal thiocarbonyls were not discovered until the late 1960's. The first examples of metal thiocarbonyls reported were *trans*- $\text{RhCl}(\text{CS})(\text{PPh}_3)_2$  and its chlorine oxidative-addition product  $\text{RhCl}_3(\text{CS})(\text{PPh}_3)_2$  (ref. 2). The  $\text{Rh}(\text{I})$  complex was prepared by  $\text{CS}_2$  activation in the presence of the sulfur-acceptor  $\text{PPh}_3$ .



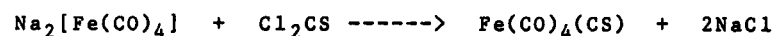
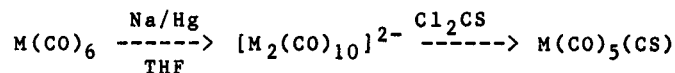
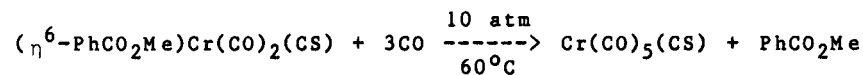
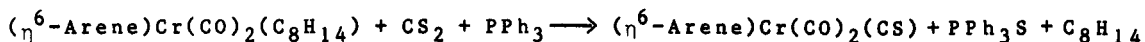
There is only one report of the co-condensation of CS vapor (produced by passing an electric discharge through  $\text{CS}_2$  vapor) and a metal vapor to afford a thiocarbonyl complex (ref. 3):



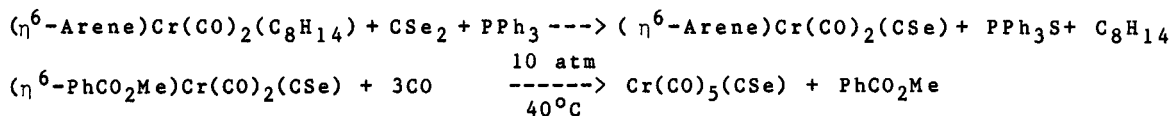
Over the next few years, thiocarbonyl complexes were identified for several, transition metals (ref. 4). Examples of the complexes reported are  $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ),  $\text{CpMn}(\text{CO})_2(\text{CS})$ ,  $(\eta^6\text{-PhCO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CS})$ , and  $\text{Cr}(\text{CO})_5(\text{CS})$ . The types of reagents used as *in situ* sources of CS encompass  $\text{CS}_2$ ,  $\text{Cl}_2\text{CS}$ , and  $\text{CSSe}$ . Some preparative routes to metal thiocarbonyls are indicated below:



(M = Mn, Re; L =  $\text{C}_8\text{H}_{14}$ , THF,  $\text{SMe}_2$ , etc.)



Carbon monoselenide is apparently more unstable than CS since it has eluded isolation, even at liquid-helium temperatures; it has been detected spectroscopically however (ref. 5). It was not until 1975 that the first metal selenocarbonyls were discovered (ref. 6) and a variety of complexes similar to the known thiocarbonyls have now been synthesized, e.g.,  $\text{Cr}(\text{CO})_5(\text{CSe})$ ,  $\text{CpRe}(\text{CO})_2(\text{CSe})$ , and  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{SCe})$  (ref. 4). The preparative routes are analogous to those for thiocarbonyls;  $\text{CSe}_2$  is used as the initial source of CSe:

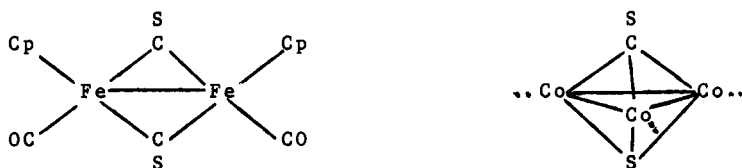


X-ray data have been obtained for several chalcocarbonyl derivatives and the M-C-X (X = S, Se, Te) linkages are linear ( $175\text{-}180^\circ$ ) (ref. 4). Therefore, similar bonding to that in M-C-O groups is anticipated. The M-C(X) distances are significantly shorter than M-C(O) distances, e.g., in  $\text{Cr}(\text{CO})_2(\text{CSe})\text{-}[\text{P}(\text{OMe})_3]_3$ ,  $\text{Cr-C}(\text{Se}) = 1.785(9)$  and  $\text{Cr-C}(\text{O})_{\text{av}} = 1.893(3)$ . A suggesting extensive  $\pi$ -backbonding (ref. 7). Kinetic studies for arene replacement in the same series of complexes indicate that the reaction rates increase with changes in X as  $\text{O} < \text{S} < \text{Se}$  (ref. 8). These data are consistent with the following order of increasing net electron withdrawal capability:  $\text{CO} < \text{CS} < \text{CSe}$ . Final confirmation of this order has come from a wide range of spectroscopic investigations (PE, NMR, IR/Raman, UV/visible, etc.) and ab initio MO and normal coordinate calculations (ref. 4).

The substitution reactions of mixed carbonyl-thiocarbonyl and -selenocarbonyl complexes are particularly interesting in that CO is almost always replaced in preference to CS or CSe. By making use of this property, it has been possible to synthesize optically-active chromium complexes such as  $(\eta^6\text{-o-xylene})\text{Cr}(\text{CO})(\text{CS})[\text{P}(\text{OMe})_3]$  (ref. 9).

One of the few species for which some CS substitution is evident is  $[\text{CpFe}(\text{CO})_2(\text{CS})]^+$  (ref. 10). It reacts with tertiary phosphines and other monodentate ligands (L) to give mixtures of  $[\text{CpFe}(\text{CO})(\text{CS})\text{L}]^+$  and  $[\text{CpFe}(\text{CO})_2\text{L}]^+$ ; with halide ions ( $\text{X}^-$ ), both  $\text{CpFe}(\text{CO})(\text{CS})\text{X}$  and  $\text{CpFe}(\text{CO})_2\text{X}$  are produced. A  $\nu(\text{CS})$  value of about  $1350\text{ cm}^{-1}$  is apparently a good indicator that CS substitution will take place. For instance, the manganese(I) compound,  $\text{CpMn}(\text{CO})_2(\text{CS})$ , has a  $\nu(\text{CS})$  mode at  $1271\text{ cm}^{-1}$  and only CO substitution has been observed. The lower  $\nu(\text{CS})$  values reflect more extensive  $\pi$ -backbonding and, therefore, stronger M-C bonding in the case of the thiocarbonyl complexes.

In addition to terminal M-CS linkages, there is now a variety of bridged CS complexes that can usually be distinguished by the position of the  $\nu(\text{CS})$  modes in the IR spectra (Table 1). Some examples of bridging CS complexes are:



The  $\nu(\text{CS})$  values for terminal M-CS linkages appear both above and below the value for free CS itself since CS stretching motions are not "pure" because of substantial mixing of the CS stretch at about  $1300\text{ cm}^{-1}$  with the MC stretch at about  $400\text{ cm}^{-1}$ . This is particularly evident in the normal coordinate calculations for  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_2(\text{CS})$  and  $\text{Cr}(\text{CO})_5(\text{CS})$  (ref. 12).

Most of our recent work on thio- and selenocarbonyl complexes has been focussed on the physicochemical properties of the chromium complexes  $(\eta^6\text{-arene})\text{Cr}(\text{CO})_2(\text{CX})$  (X = S, Se). Reaction with tertiary phosphites (L) affords mixtures of the isomers  $\text{Cr}(\text{CO})_2(\text{CX})\text{L}_3$ . The rates of isomerization of these isomers have been monitored by FT-IR spectroscopy (ref. 13). The activation parameters obtained from the IR studies in the CO stretching region for the isomerizations when  $\text{L} = \text{P}(\text{OMe})_3$  for the two complexes and the corresponding fac-mer- $\text{Cr}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$  complexes are given in Table 2. The reactions are clearly simple isomerizations from the observed isobestic point behavior.

When the mer-I to fac isomerizations were allowed to proceed at  $60^\circ\text{C}$  in the presence of excess  $\text{P}(\text{O}^i\text{Pr})_3$ , there was no IR evidence for any tertiary phosphite incorporation indicating that the isomerizations take place via

TABLE 1. Approximate  $\nu(\text{CS})$  ranges for various types of CS bonding<sup>a</sup>

Type of CS bonding	Approximate $\nu(\text{CS})$ range ( $\text{cm}^{-1}$ )
Free CS	1273
Terminal, M-CS	1410-1160
Doubly-bridging, M-C(S)-M	1160-1100
Triply-bridging, $\text{M}_2\text{-C(S)-M}$	1080-1040
Carbon and sulfur bonded, M-CS-M	1110-1050
Triply-bridging and sulfur bonded, $\text{M}_3\text{-CS-M}$	ca. 950

<sup>a</sup>Adapted from ref. 11

TABLE 2. Activation parameters for the isomerization of  $\text{Cr}(\text{CO})_2(\text{CX})[\text{P}(\text{OMe})_3]_3$  (X = O, S, Se) complexes<sup>a</sup>

Complex	Process	$\Delta H^\ddagger$ ( $\text{kcal mol}^{-1}$ )	$\Delta S^\ddagger$ ( $\text{cal mol}^{-1} \text{deg}^{-1}$ )
$\text{Cr}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	<u>fac</u> $\rightarrow$ <u>mer</u>	18.0	-20
	<u>mer</u> $\rightarrow$ <u>fac</u>	18.0	-24
$\text{Cr}(\text{CO})_2(\text{CS})[\text{P}(\text{OMe})_3]_3$	<u>fac</u> $\rightarrow$ <u>mer-I</u>	16.6	-22
	<u>mer-I</u> $\rightarrow$ <u>fac</u>	16.6	-25
$\text{Cr}(\text{CO})_2(\text{CSe})[\text{P}(\text{OMe})_3]_3$	<u>fac</u> $\rightarrow$ <u>mer-I</u>	15.6	-25
	<u>mer-I</u> $\rightarrow$ <u>fac</u>	15.5	-28

<sup>a</sup>Standard deviations on  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are 0.3 kcal/mol and 1 cal/mol/deg, respectively. Data from ref. 13.

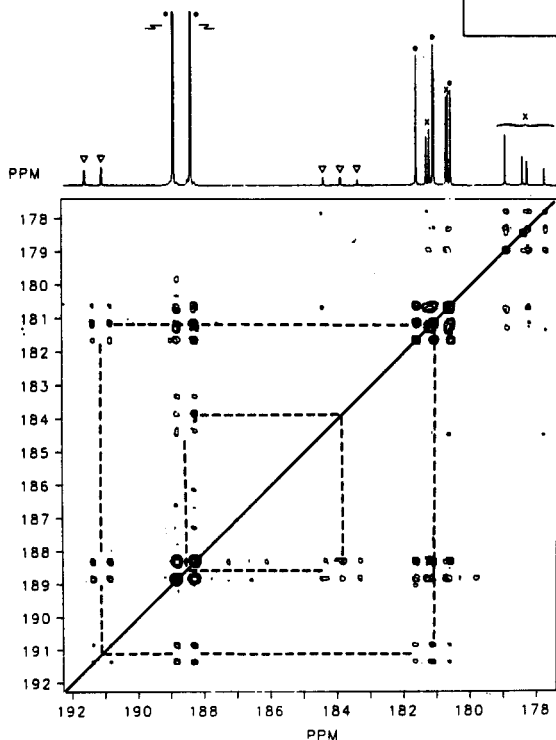
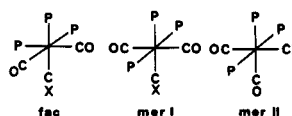


Fig. 1.

Fig. 2. →

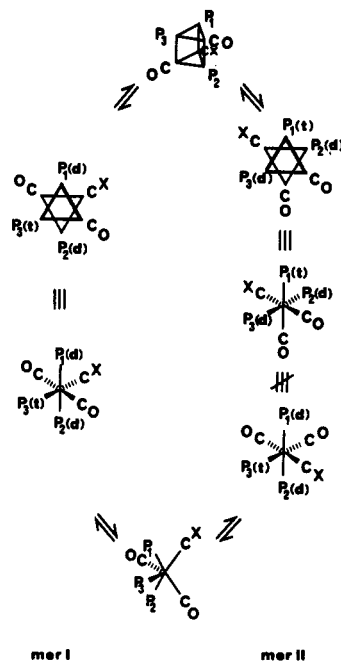


Fig. 1. 2-D  $^{31}\text{P}$  NMR contour map for  $\text{Cr}(\text{CO})_2(\text{CS})[\text{P}(\text{OMe})_3]_3$  at  $61^\circ\text{C}$  on a Varian XL-300 spectrometer. All three isomers exhibit an  $\text{AB}_2$  coupling pattern [chemical shifts (in ppm) are relative to  $\text{H}_3\text{PO}_4$  as external standard]:  $\nabla$  mer-II  $\text{P}_2, \text{P}_3(\text{d})$  191.4,  $\text{P}_1(\text{t})$  184.0 ( $J = 64$  Hz);  $\bullet$  = mer-I  $\text{P}_2, \text{P}_3(\text{d})$  188.6,  $\text{P}_1(\text{t})$  181.2 ( $J = 64$  Hz);  $\times$  = fac  $\text{P}_2, \text{P}_3(\text{d})$  181.1,  $\text{P}_1(\text{t})$  178.5 ( $J = 72$  Hz). Reprinted from ref. 15 with permission.

Fig. 2. Schematic comparison of the possible pathways for the interconversion of the mer-I and mer-II isomers of  $\text{Cr}(\text{CO})_2(\text{CX})[\text{P}(\text{OMe})_3]_3$  (X = S, Se). Top: trigonal-prismatic intermediate; bottom: bicapped-tetrahedral intermediate. For the sake of clarity, the  $\text{P}(\text{OMe})_3$  ligands have been represented by  $\text{P}_1, \text{P}_2$  and  $\text{P}_3$ . Reprinted from ref. 15 with permission.

non-dissociative pathways. This conclusion is supported by the formation of  $\text{Cr}(\text{CO})_2(^{13}\text{CO})_3(\text{CS})$  by arene displacement from  $(\eta^6\text{-PhCO}_2\text{Me})\text{Cr}(\text{CO})_2(\text{CS})$  by  $^{13}\text{CO}$ . A fourth CO ligand would have been incorporated if isomerization occurred by a dissociative mechanism (ref. 14.)

Two-dimensional  $^{31}\text{P}$  NMR spectroscopy (accordian pulse sequence:  $\pi/2, t_1, \pi/2, \text{mix}, \pi, t_2$ ) was used to establish that dynamic intramolecular exchange takes place between the mer-I and mer-II isomers (Fig. 1) (refs. 14, 15). The intramolecular nature of the processes was demonstrated by the lack of correlation between resonances of the complexes and those of excess ligand present in solution. No fac to mer-I or fac to mer-II interconversions were observed at temperatures up to  $80^\circ\text{C}$ .

The 2-D NMR studies also provide convincing evidence of the nature of the intermediates involved in the mer-I to mer-II isomerizations. The distinct symmetrical, off-diagonal contours on the 2-D NMR exchange maps illustrate possible chemical exchange between P nuclei of the same molecule. Moreover, only the trigonal prismatic route would afford the observed correlation of the off-diagonal peak of the doublet of mer-II (bottom left-hand-side of the contour map) to the doublet and triplet of mer-I, while the triplet of mer-II exchanges with the doublet of mer-I. The mer-I to mer-II isomerizations via the trigonal-prismatic and bicapped-tetrahedral pathways are compared in Fig. 2.

## CONCLUSIONS

The chemistry of transition-metal thio- and selenocarbonyls is now well developed. It is clear that CS and CSe are usually more strongly bound to a metal than is CO. This non-lability makes the CS and CSe ligands especially attractive in mechanistic studies of the isomerizations of stereochemically, non-rigid complexes such as the octahedral  $\text{Cr}(\text{CO})_2(\text{CS})\text{L}_3$  complexes described above. It is probable that these intramolecular isomerizations involve some bond lengthening in the activated states due to the presence of the trans-labilizing CS and CSe ligands. Through the use of 2-D  $^{31}\text{P}$  NMR spectroscopy it has been possible to demonstrate definitively for the first time that these isomerizations take place exclusively via a trigonal-prismatic pathway. This mechanistic route is supported by the large negative  $\Delta S^\ddagger$  values observed for the exchanges. Similar mechanisms have been proposed for a variety of other octahedral complexes, such as cis-/trans- $\{\text{Cr}(\text{CO})_4[\text{C}(\text{OMe})\text{Me}](\text{PEt}_3)\}$  (ref. 16) and  $\text{M}(\text{CO})_{6-n}(\text{PR}_3)_n$  ( $\text{M} = \text{Cr, Mo, W}$ ;  $n = 1, 2$ ;  $\text{R} = \text{Me, Et, etc.}$ ) (ref. 17), but conclusive evidence has not been presented before.

## Acknowledgements

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