Coordination chemistry of thiocarbonyl ligand

Ian S. Butler
Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec, Canada H3A 2K6

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 CO < CS < 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, Ni(CO)4 and Fe(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 Ni(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.

\[ \text{Ni} + 4\text{CO} \rightleftharpoons \text{Ni} (\text{CO})_4 \]

Unlike CO, carbon monosulfide (CS) is only stable below -160°C; above this temperature, CS polymerizes to (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-RhCl(CS)(PPh3)2 and its chlorine oxidative-addition product RhCl3(CS)(PPh3)2 (ref. 2). The Rh(1) complex was prepared by CS2 activation in the presence of the sulfur-acceptor PPh3.

\[ \text{trans-RhCl(CS)(PPh3)2} + \text{Cl}_2 \rightarrow \text{RhCl3(CS)(PPh3)2} \]

There is only one report of the co-condensation of CS vapor (produced by passing an electric discharge through CS2 vapor) and a metal vapor to afford a thiocarbonyl complex (ref. 3):

\[ \text{10K Ni(g) + 4CS(g) \rightarrow Ni(CS)_4} \]

Over the next few years, thiocarbonyl complexes were identified for several, transition metals (ref. 4). Examples of the complexes reported are [CpFe(CO)2(CS)]+ (Cp = \( \eta^6 \)-C5H5), CpMn(CO)2(CS), (\( \eta^6 \)-PhCO2Me)Cr(CO)2(CS), and Cr(CO)5(CS). The types of reagents used as in situ sources of CS encompass CS2, Cl2CS, and CSSe. Some preparative routes to metal thiocarbonyls are indicated below:

\[ \text{CpM(CO)2} + \text{CS} + \text{PPh3} \rightarrow \text{CpM(CO)}_2(\text{CS}) + \text{PPh3S} + \text{L} \]

(M = Mn, Re; L = C8H14, THF, SMe2, etc.)

\[ (\eta^6 \text{-Arene})\text{Cr(CO)}_2(\text{C8H14}) + \text{CS} + \text{PPh3} \rightarrow (\eta^6 \text{-Arene})\text{Cr(CO)}_2(\text{CS}) + \text{PPh3S} + \text{C8H14} \]

10 atm

\[ \text{(\( \eta^6 \)-PhCO2Me)Cr(CO)}_2(\text{CS}) + 3\text{CO} \rightarrow \text{Cr(CO)}_5(\text{CS}) + \text{PhCO2Me} \]

60°C

\[ \text{Na/Hg} \rightarrow \text{[M_2(CO)_{10}]^{2-}} \rightarrow \text{M(CO)}_5(\text{CS}) \]

\[ \text{Na_2[Fe(CO)_4] + Cl_2CS \rightarrow Fe(CO)_4(CS) + 2NaCl} \]
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., Cr(CO)$_2$(CSe), CpRe(CO)$_2$(CSe), and ($^6$-arene)Cr(CO)$_2$(CSe) (ref. 4). The preparative routes are analogous to those for thiocarbonyls; CSe$_2$ is used as the initial source of CSe:

$$(\eta^6$-Arene)Cr(CO)$_2$(C$_8$H$_{14}$) + CSe$_2$ + PPh$_3$ $\rightarrow$ ($\eta^6$-Arene)Cr(CO)$_2$(CSe) + PPh$_3$S$^+$ C$_8$H$_{14}$$

10 atm

$n^6$-PhCO$_2$Me)Cr(CO)$_2$(CSe) + 3CO $\rightarrow$ Cr(CO)$_5$(CSe) + PhCO$_2$Me

40°C

X-ray data have been obtained for several chalcocarbonyl derivatives and the M-C-X (X = S, Se, Te) linkages are linear (175-180°) (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 Cr(CO)$_2$(CSe)$_2$- [P(OMe)$_3$)$_3$, Cr-C(Se) = 1.785(9) and Cr-C(O)$_{av}$ = 1.893(3) Å 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 0 < S < Se (ref. 8). These data are consistent with the following order of increasing net electron withdrawal capability: CO < CS < 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 ($n^6$-o-xylene)Cr(CO)(CS)[P(OMe)$_3$] (ref. 9).

One of the few species for which some CS substitution is evident is [CpFe(CO)$_2$(CS)]$^+$ (ref. 10). It reacts with tertiary phosphines and other monodentate ligands (L) to give mixtures of [CpFe(CO)(CS)L]$^+$ and [CpFe(CO)$_2$L]$^+$; with halide ions (X$^-$), both CpFe(CO)(CS)X and CpFe(CO)$_2$X are produced. A $\nu$(CS) value of about 1350 cm$^{-1}$ is apparently a good indicator that CS substitution will take place. For instance, the manganese(I) compound, CpMn(CO)$_2$(CS), has a $\nu$(CS) mode at 1271 cm$^{-1}$ and only CO substitution has been observed. The lower $\nu$(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 $\nu$(CS) modes in the IR spectra (Table 1). Some examples of bridging CS complexes are:

![Diagram of bridging CS complexes]

The $\nu$(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 cm$^{-1}$ with the NC stretch at about 400 cm$^{-1}$. This is particularly evident in the normal coordinate calculations for ($\eta^6$-C$_8$H$_{14}$)Cr(CO)$_2$(CS) and Cr(CO)$_2$(CS) (ref. 12).

Most of our recent work on thio- and selenocarbonyl complexes has been focused on the physicochemical properties of the chromium complexes ($^6$-arene)Cr(CO)$_2$(CX) (X = S, Se). Reaction with tertiary phosphites (L) affords mixtures of the isomers Cr(CO)$_2$(CX)$_2$. 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 L = P(OMe)$_3$ for the two complexes and the corresponding fac-mer-Cr(CO)$_2$(P(OMe)$_3$)$_2$ 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°C in the presence of excess P(OPh)$_3$, there was no IR evidence for any tertiary phosphate incorporation indicating that the isomerizations take place via
TABLE 1. Approximate \( v(\text{CS}) \) ranges for various types of CS bonding

<table>
<thead>
<tr>
<th>Type of CS bonding</th>
<th>Approximate ( v(\text{CS}) ) range (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free CS</td>
<td>1273</td>
</tr>
<tr>
<td>Terminal, M-C(S)</td>
<td>1410-1160</td>
</tr>
<tr>
<td>Doubly-bridging, M-C(S)-M</td>
<td>1160-1100</td>
</tr>
<tr>
<td>Triply-bridging, M(_2)-C(S)-M</td>
<td>1080-1040</td>
</tr>
<tr>
<td>Carbon and sulfur bonded, M-C(S)-M</td>
<td>1110-1050</td>
</tr>
<tr>
<td>Triply-bridging and sulfur bonded, M(_3)-C(S)-M</td>
<td>950</td>
</tr>
</tbody>
</table>

TABLE 2. Activation parameters for the isomerization of Cr(CO)\(_2\)(CX)[P(OMe)\(_3\)]\(_3\) (X = O, S, Se) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Process</th>
<th>( \Delta H^# ) (kcal/mol)</th>
<th>( \Delta S^# ) (cal/mol/deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)(_3)[P(OMe)(_3)](_3)</td>
<td>fac ( \rightarrow ) mer</td>
<td>18.0</td>
<td>-20</td>
</tr>
<tr>
<td></td>
<td>mer ( \rightarrow ) fac</td>
<td>18.0</td>
<td>-24</td>
</tr>
<tr>
<td>Cr(CO)(_2)(CS)[P(OMe)(_3)](_3)</td>
<td>fac ( \rightarrow ) mer-I</td>
<td>16.6</td>
<td>-22</td>
</tr>
<tr>
<td></td>
<td>mer-I ( \rightarrow ) fac</td>
<td>16.6</td>
<td>-25</td>
</tr>
<tr>
<td>Cr(CO)(_2)(CSe)[P(OMe)(_3)](_3)</td>
<td>fac ( \rightarrow ) mer-I</td>
<td>15.6</td>
<td>-25</td>
</tr>
<tr>
<td></td>
<td>mer-I ( \rightarrow ) fac</td>
<td>15.5</td>
<td>-28</td>
</tr>
</tbody>
</table>

\( ^a \) Standard deviations on \( \Delta H^\# \) and \( \Delta S^\# \) are 0.3 kcal/mol and 1 cal/mol/deg, respectively. Data from ref. 13.

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Fig. 1. 2-D \(^{31}\)P NMR contour map for Cr(CO)\(_2\)(CS)[P(OMe)\(_3\)]\(_3\) at 61°C on a Varian XL-300 spectrometer. All three isomers exhibit an AB\(_2\) coupling pattern [chemical shifts (in ppm) are relative to \( H_3P0_4 \) as external standard]: \( \nabla \) mer-II \( P_3P_3(d) \) 191.4, \( P_1(t) \) 184.0 (J = 64 Hz); \( \bullet \) = mer-I \( P_2P_3(d) \) 188.6, \( P_1(t) \) 181.2 (J = 64 Hz); \( x = fac \) \( P_2P_3(d) \) 181.1, \( P_1(t) \) 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 Cr(CO)\(_2\)(CX)[P(OMe)\(_3\)]\(_3\) (X = S, Se). Top: trigonal-prismatic intermediate; bottom: bicapped-tetrahedral intermediate. For the sake of clarity, the P(OMe)\(_3\) ligands have been represented by \( P_1, P_2 \) and \( P_3 \). Reprinted from ref. 15 with permission.
non-dissociative pathways. This conclusion is supported by the formation of
\( \text{Cr(CO)}_2(\text{CS})_2(\text{CS})_2 \) by arene displacement from \( \text{(PhCO}_2\text{Me})\text{Cr(CO)}_2(\text{CS})_2 \) by \( 1 \text{CO} \). 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: \( \pi/2, \tau_1, \pi/2, \text{mix}, \pi, \tau_2 \)) was used to establish that dynamic intramolecular exchange takes
place between the \( \text{mer-I} \) and \( \text{mer-II} \) 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 \( \text{fac-to-mer-I} \) of \( \text{fac-to-mer-II} \) 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 \( \text{mer-I} \) to \( \text{mer-II} \) 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 \( \text{mer-II} \) (bottom left-hand-side of the
contour map) to the doublet and triplet of \( \text{mer-I}, \) while the triplet of \( \text{mer-II} \)
exchanges with the doublet of \( \text{mer-I} \). The \( \text{mer-I} \) to \( \text{mer-II} \) isomerizations via
the trigonal-prismatic and bicapped-tetrahedral pathways are compared in Fig.

**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 \( \text{Cr(CO)}_2(\text{CS})_2 \) 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 \( \Delta^\circ \) values observed
for the exchanges. Similar mechanisms have been proposed for a variety of
octahedral complexes, such as \( \text{cis-/trans-}{\text{Cr(CO)}_4(\text{C(OMe)Me})_2}(\text{PET}_3) \)
(ref. 16) and \( \text{M(CO)}_6-n(\text{PET}_3)_n \) \( (\text{M} = \text{Cr, Mo, W}; n = 1,2; R \end{quote}