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# THIOCARBONYL COMPLEXES OF IRON

## IV *. CONCERNING THE REACTION OF $(CO)_4FeCS$ WITH MERCURY CHLORIDE IN VARIOUS SOLVENTS

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## Summary

Mercury chloride, suspended in n-pentane, reacts with the iron carbonyl complexes $(CO)_4FeCS$ and $Fe(CO)_5$ at room temperature to yield adducts of the composition $(CO)_4FeCS \cdot 3HgCl_2$ (**1a**) and $(CO)_5Fe \cdot 3HgCl_2$ (**1b**), respectively. The IR spectra reveal that both carbonyl compounds contain an iron–mercury donor bond. In ethanol as the solvent, the thiocarbonyl complex incorporates a solvent molecule, to yield the bright yellow thioalkoxycarbonyl complex *cis*-$(CO)_4Fe(HgCl)(C(S)OC_2H_5)$ (**2**), whereas $Fe(CO)_5$ undergoes an oxidative addition to form the well known *cis*-$(CO)_4Fe(HgCl)_2$ (**4**) under the same reaction conditions. The mass spectrum of **2** exhibits the molecular ion as well as that of a dimer with the composition $Fe_2(CO)_5[C(S)OC_2H_5]_2$ (**6**), which is probably formed during the process by the thermal decomposition of **2**. Attempts to isolate **6** by pyrolysis of **2** gave a red-brown oil which could not be purified. From Mössbauer spectroscopic studies a carbenoid formula for **2** can be excluded. In aqueous solution the reaction of $(CO)_4FeCS$ with mercury chloride results in the formation of the yellow insoluble $HgFe(CO)_3CS$ (**3**). A polymer structure similar to that of $HgFe(CO)_4$ is proposed for **3**.

## Introduction

Complexes with an iron–mercury bond were first described by Hock and Stuhlmann, who showed that the reaction of $HgCl_2$ with $Fe(CO)_5$ in aqueous or ethanolic

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[*] For Part III see ref. 19.

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solution results in the formation of $(CO)_4Fe(HgCl)_2$ [1]. The *cis*-configuration of the HgCl groups was later established by an X-ray analysis [2], and this has been found to be the favored configuration in the majority of $(CO)_4FeXY$ complexes. For a summary of this field of chemistry up to 1978, see ref. 3.

Some time ago we published the synthesis of the first thiocarbonyl derivative of pentacarbonyliron, the volatile and fairly stable complex $(CO)_4FeCS$, which has similar physical properties to $Fe(CO)_5$ [4]. Besides the iron atom, which is usually involved in the bond to mercury compounds, the sulfur atom in the outer sphere of this complex represents a second "mercurophilic" center capable of bond formation. Such a sulfur–metal bond for instance has been found in an isolable adduct of $(CO)(dpe)_2WCS$ ($dpe = (C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$) and $HgCl_2$, where a linear W–C–S–Hg arrangement was indicated by IR analysis [5].

In order to study the site preference in $(CO)_4FeCS$ we extended our investigations to reactions of this compound with mercury halides under various conditions. To our knowledge no similar studies have previously been undertaken with iron thiocarbonyl complexes and in this paper we describe the first results from our investigations concerning the reaction of $(CO)_4FeCS$ with mercury salts in various solvents such as water, ethanol and pentane.

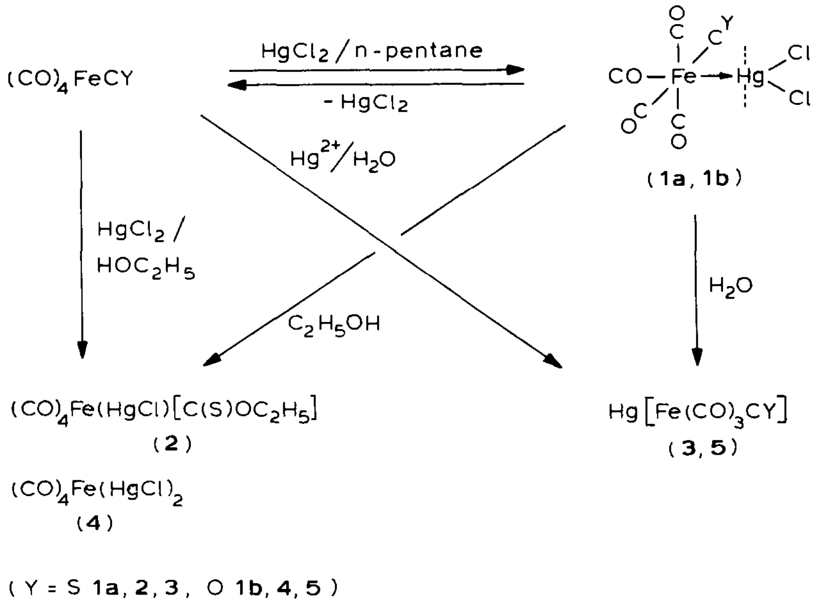
## Results and discussion

If a suspension of finely ground $HgCl_2$ in n-pentane is vigorously stirred at room temperature with an excess of $(CO)_4FeCS$ or $Fe(CO)_5$ the yellow adducts **1a** and **1b** may be isolated. The samples have Fe/Hg ratios of about 1/3, which are somewhat lower than in the previously described adducts $(CO)_5Fe \cdot HgCl_2$ and $(CO)_5Fe \cdot 2HgCl_2$, obtained from other non-hydroxylic solvents like acetone by Hock and Stuhlmann [1]. In vacuo, the volatile carbonyl compounds can be removed quantitatively from **1a** and **1b**.

Similarly, on standing at room temperature, even under $N_2$, the reverse reaction is complete within several days. In contrast to the chemistry of $Fe(CO)_5$, no reaction is observed for $(CO)_4FeCS$ with $HgBr_2$ or $HgI_2$ under comparable conditions.

With n-pentane as the reaction medium, both starting carbonyl complexes form mercury-bonded species without cleavage of the mercury–chloride bond, comparable with the previously prepared adducts of $Fe(CO)_5$, but with more "lattice" mercury chloride which probably arises from the low solubility of $HgCl_2$ in this solvent. The thermal lability of the adducts is due to the relatively weak donor properties of the iron atom in both starting compounds. Adducts with mercury compounds, involving phosphine-substituted iron carbonyl complexes, have been found to be considerably more stable because of the enhanced electron density at the iron nucleus resulting from the more donating ligands [6].

If $(CO)_4FeCS$ is allowed to react with $HgCl_2$ in ethanol as the solvent, a bright yellow solid precipitates out immediately; it is soluble in $CH_2Cl_2$ or THF, but forms very unstable solutions. The solid, found to be **2**, decomposes at room temperature within several h, even under an atmosphere of dry $N_2$, to give a dirty green-brown solid. At $-20\,^\circ C$, **2** can be stored for a period of time without decomposition. The formation of **2** proceeds without gas evolution, but the solvent becomes acidic, thus indicating the formation of HCl. The mercuric halide has effectively split into $Cl^-$ and the HgCl group and the resulting product contains a metal–mercury–halogen bond as shown by the spectroscopic data. This reaction differs markedly from that with $Fe(CO)_5$ which gives $(CO)_4Fe(HgCl)_2$ (**4**) under the same reaction conditions [1] (Scheme 1).



SCHEME 1

In contrast, gas evolution is observed from the reaction of $(CO)_4FeCS$ with $Hg^{2+}$ in water to give the bright yellow complex **3**, which is found to be insoluble in all common organic solvents. Compound **3** is infinitly stable at room temperature under an atmosphere of $N_2$, and seems to be stable for a period of time on exposure to air. We suggest that **3** has a polymeric or tetrameric structure similar to $HgFe(CO)_4$ (**5**), whose structure was derived from similarities of the IR spectrum with that of $CdFe(CO)_4$ [7]. Compound **3** is probably formed in a manner similar to **5** by oxidative elimination of $CO_2$, and is also obtained when the adduct **1a** is stirred in water.

The IR spectrum of the adducts **1a** and **1b** exhibit sharp bands in the $\nu(CO)$ region, which are shifted to higher frequencies relative to the starting carbonyl complexes, as shown in Fig. 1. The $\nu(CS)$ vibration of **1a** appears as a single sharp absorption shifted in the same direction, thus indicating the presence of only one type of ligand arrangement. In contrast, the starting complex $(CO)_4FeCS$ shows two $\nu(CS)$ bands of nearly equal intensities, indicating two isomers with the CS ligand in either the axial or an equatorial position in the trigonal bipyramid [4].

The shifts of the $\nu(CO)$ and $\nu(CS)$ frequencies are consistent with both a change in stereochemistry and a decrease in electron density, which is in agreement with the formation of an Fe → Hg donor bond. The four intense CO stretching vibrations of **1a** point to a local $C_s$ symmetry of the iron carbonyl moiety, with a *cis*-arrangement of the CS ligand and the mercury group. A *trans*-arrangement of both ligands would give rise to three different intense $\nu(CO)$ absorption bands ($A_1$, $B_1$ and E), as shown for complexes of the type $(CO)_4ML^1L^2$ with $L^1 \neq L^2$ [8]. Weak peaks at lower frequencies indicate also the presence of small amounts of the uncomplexed starting materials due to the equilibrium reaction, and these bands increase in intensity on further runs of the same IR sample. The carbonyl stretching frequencies of **1b** show an average shift of ca. 90 $cm^{-1}$ to higher energies relative to $(CO)_4Fe(HgCl)_2$ and $(CO)_4Fe(HgCl \cdot HgCl_2)_2$, thus indicating more powerful electron withdrawal from the iron atom in the $(CO)_5Fe \rightarrow$ acceptor bond. The number and intensities of the CO bands are consistent with a local $C_{4v}$ symmetry for the iron carbonyl moiety. The IR data for the (CO) and (CS) region of the compounds are collected in Table 1.

The IR spectrum of **2** exhibits no band near to 1300 $cm^{-1}$ due to the vibration of a terminal CS group, but an intense band appears at 1200 $cm^{-1}$, which can probably be attributed to the C=S stretching absorption of the thioalkoxycarbonyl group. Similar bands were observed in the IR spectrum of $CpFe(CO)_2C(S)OCH_3$ [9] and $[P(C_6H_5)_3]_2ClPtC(S)OCH_3$ [10]. Bridging thiocarbonyl groups between two metal atoms absorb at slightly lower frequencies [11]. The number and relative intensities of the $\nu$(CO) frequencies for **2** give good information about the positions of the groups HgCl and $C(S)OC_2H_5$ in the octahedral arrangement around the iron atom. Similar to the adduct **1a**, the complex **2** exhibits four CO bands of nearly equal intensity making a *cis*-arrangement valid.

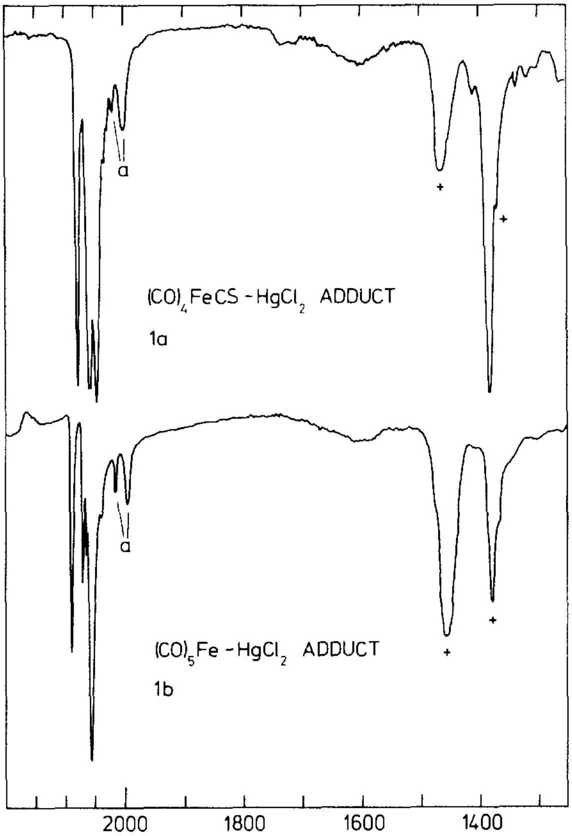


Fig. 1. Relevant parts of the IR spectra of **1a** and **1b** (in $cm^{-1}$). (a) Traces of the starting materials, $(CO)_4FeCS$ or $Fe(CO)_5$. Nujol peaks are indicated by +

TABLE 1

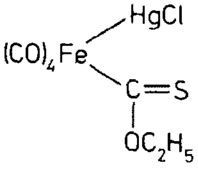
SELECTED IR DATA OF THE COMPLEXES **1a**, **1b**, **2** and **3** IN COMPARISON WITH OTHER COMPOUNDS CONTAINING Fe–Hg BONDS OR THE C(S)OR LIGAND[a]

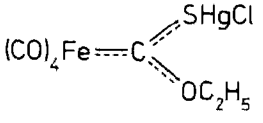
| Compound | $\nu$(CO) | $\nu$(CS) | $\nu$(C=S) | Reference |
|---|---|---|---|---|
| $(CO)_4FeCS\cdot 3HgCl_2$ (**1a**) | 2155vs, 2119vs, 2112vs<br>2092vs, 2065sh | 1380vs | – | this work |
| $(CO)_5Fe\cdot 3HgCl_2$ (**1b**) | 2180s, 2141m, 2110vs<br>2130sh, 2085w | – | – | this work |
| $(CO)_4Fe(HgCl)_2$ | 2095sh, 2087m, 2032sh<br>2008s, 1980sh | – | – | 18 |
| $(CO)_4Fe(HgCl\cdot HgCl_2)_2$ | 2109m, 2077m, 2050s,<br>2040s, 2015sh, 2090m,<br>2076sh, 2020s, 2000sh | – | – | 18 |
| $Hg[Fe(CO)_3CS]$ (**3**) | 2030s, | 1280s | – | this work |
| $HgFe(CO)_4$ (**5**) | 2045, 1980, 1970, 1946 | – | – | 3 |
| $(CO)_4Fe(HgCl)C(S)OC_2H_5$ (**2**) | 2108vs, 2055vs, 2045vs<br>2037vs | – | 1200s | this work |
| $CpFe(CO)_2C(S)OCH_3$ | 2031s, 1990s | | 1193s | 9 |
| $[P(C_6H_5)_3]_2ClPtC(S)OCH_3$ | – | – | 1200 | 10 |

[a] In cm$^{-1}$, Nujol mull.

On going from **1a** to **2**, the $\nu$(CO) absorptions are shifted by about 50 cm$^{-1}$ to lower frequencies, which indicates an increase in back bonding from the central metal atom to the CO ligands in **2**. This arises from the better $\sigma$-donor properties of the C(S)OR ligands relative to the CS group. The average $\nu$(CO) absorption for **2** is somewhat higher in energy than that of complex **4**.

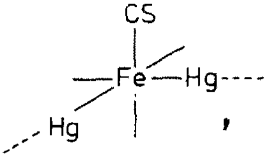
The constitution of **2** includes a carbenoid formula as outlined in structure **2b**, as well as the formula **2a** with an iron–mercury bond.


(2a)

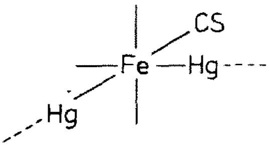

(2b)

The IR spectrum, however, is not consistent with the formation of a carbenoid ligand and with the mercury atom bonded to the sulfur atom. Such a complex would give a typical $C_{3v}$-Fe(CO)$_4$ pattern in the $\nu$(CO) region at lower frequencies, because carbene ligands stabilized by the two heteroatoms sulfur and oxygen are good $\sigma$-donors similar to phosphine ligands. This type of ligands would usually occupy an axial position in the trigonal bipyramidal arrangement around the iron atom.

The IR spectrum of **3** exhibits three relatively broad absorption bands in the CO region, along with a band at lower frequency which is assigned to a terminal CS group. Assuming a *cis*-arrangement, the CS ligand may be *trans* to either CO or Hg in the polymeric or tetrameric Fe–Hg–Fe chain. Isomeric (CO)$_3$FeCS units in the chain and the insolubility of the complex in organic media are probably responsible for the unresolved broad IR absorptions and a shoulder at the $\nu$(CS) band. Both $\nu$(CO) and $\nu$(CS) vibrations have shifted to lower frequencies relative to the starting complex $(CO)_4FeCS$. A structure as outlined in **3a** or **3b** is assumed.



(3a)



(3b)

The $^1H$ NMR spectrum of **2** shows only the signals of the $C_2H_5$ group ($CH_3$, t, $\delta$ 1.11 ppm; $CH_2$, q, $\delta$ 4.25 ppm; $J$ 6.7 Hz), and the shift does not differ significantly from the shift of similar thioalkoxycarbonyl ligands. Solutions of **2** were not stable enough to obtain $^{13}C$ NMR signals and the complexes **3**, **1a** and **1b** were too insoluble for any NMR investigations.

The $^{57}$Fe-Mössbauer spectrum of **2** has been studied to obtain more information on the chemical environment of the central iron atom and the Mössbauer parameters, along with those of similar complexes, are summarized in Table 2. Only a few data are known concerning iron carbonyl complexes of the $(CO)_4FeXY$ type with a coordination number six at the iron atom and two $\sigma$-bonded ligand in a *cis*-position. Furthermore, no data on complexes containing an iron–mercury bond are available, and the parameters for **2** represent the first in this area.

As with the results of the IR spectrum, the Mössbauer spectrum also excludes the carbenoid formulation **2b**. In this case the central iron atom would be surrounded by five ligands, whereas in **2a** a coordination number of six with a formal $Fe^{2+}$ is operative, and both types differ markly in isomer shift $\delta$ and quadrupole splitting $\Delta E^Q$. The estimated parameters clearly favor structure **2a** because complexes of the type $(CO)_4FeL$ (L represents a carbene ligand) exhibit higher $\Delta E^Q$ values, which range between 1.75 and 2.00 mm $s^{-1}$ [12]. The mercury atom in the outer coordination sphere of the Mössbauer nucleus should not affect the chemical environment so dramatically as is found in **2**, assuming the carbenoid arrangement **2b**. Sixfold coordinated complexes of this type $(CO)_4FeXY$ generally exhibit lower $\Delta E^Q$ values, thus indicating a minor deviation from cubic symmetry, and the parameters of **2** are found to be close to those of other complexes, as summarized in Table 2. The $\delta$-value of this compound is the lowest one in this series and indicates an enhanced *s*-electron density at the iron nucleus. This probably arises from the good $\sigma$-donor property of the $C(S)OC_2H_5$ ligand.

TABLE 2

MOSSBAUER PARAMETERS OF SOME *cis*-$(CO)_4FeXY$ COMPLEXES[a]

| X | Y | Isomer shift | $\Delta E^Q$ | References |
|---|---|---|---|---|
| $C(S)OC_2H_5$ | HgCl | 0.201 | 0.37 | this work |
| $SnBr_3$ | Br | 0.270 | 0.47 | 13 |
| $SnCl_3$ | Cl | 0.290 | 0.45 | 13 |
| Br | Br | 0.32 | 0.27 | 14,15 |
| $SnI_3$ | I | 0.29 | 0.38 | 13 |

[a] In mm $sec^{-1}$, relative to $Na[Fe(CN)_5NO]$ at room temperature

TABLE 3

MASS SPECTROSCOPIC FRAGMENTATION OF $(CO)_4Fe(HgCl)C(S)OC_2H_5$ (**2**)[a]; $(M)^+$ and $(M')^+$ ARE THE MOLECULAR IONS OF **2** AND **6**, RESPECTIVELY (see text)

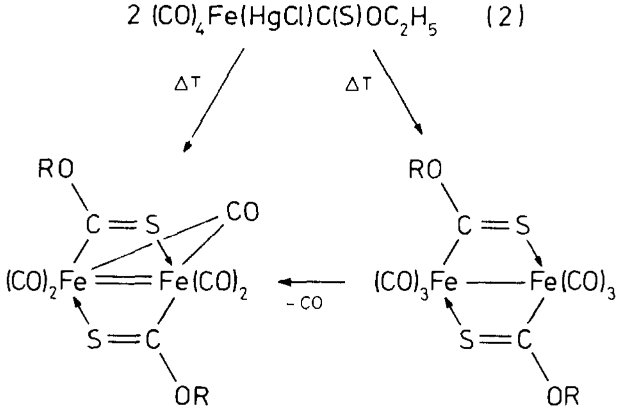
| *m/e* | Relative intensity (%) | Composition/Assignment |
|---|---|---|
| 494 | 1.2 | $C_7H_5ClFeHgO_5S/(M)^+$ |
| 466 | 1.7 | $C_6H_5ClFeHgO_4S/(M-CO)^+$ |
| 438 | 2.4 | $C_5H_5ClFeHgO_3S/(M-2CO)^+$ |
| 430 | 14.8 | $C_{11}H_{10}Fe_2O_7S_2/(M')^+$ |
| 402 | 20.5 | $C_{10}H_{10}Fe_2O_6S_2/(M'-CO)^+$ |
| 374 | 17.2 | $C_9H_{10}Fe_2O_5S_2/(M'-2CO)^+$ |
| 346 | 34 | $C_8H_{10}Fe_2O_4S_2/(M'-3CO)^+$ |
| 318 | 31.6 | $C_7H_{10}Fe_2O_3S_2/(M'-4CO)^+$ |
| 290 | 43.4 | $C_6H_{10}Fe_2O_2S_2/(M'-5CO)^+$ |
| 257 | 40.8 | $C_7H_5FeO_5S/(M-HgCl)^+$ |
| 233 | 25.5 | $C_2HFe_2O_2S_2$ |
| 232 | 21.7 | $C_2Fe_2O_2S_2$ |
| 229 | 43 | $C_6H_5FeO_4S/(M-HgCl-CO)^+$ |
| 202[b] | | Hg |
| 177 | 33 | $HFe_2S_2$ |
| 176 | 80 | $Fe_2S_2$ |
| 173 | 100 | $C_4H_5FeO_2S/(M-HgCl-3CO)^+$ |
| 157 | 27.4 | $Fe_2CS$ |
| 145 | 67 | $C_3H_5FeOS/(M-HgCl-4CO)^+$ |
| 144 | 41 | $Fe_2S$ |

[a] For Hg = 202, Cl = 35; fragments below *m/e* = 120 are omitted. [b] The fragment at *m/e* = 201, $(M-HgCl-2CO)^+$ is obscured by $Hg^+$.

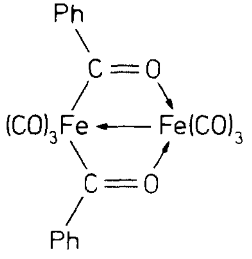
The electron impact mass spectrum of **2** shows the molecular ion at the mass number 494, followed by the fragments $[M-CO]^+$ and $[M-2CO]^+$ (mass numbers 466 and 438 relative to $^{202}Hg$ and $^{35}Cl$). Besides these fragments no others with a mercury atom could be detected. The most striking feature is the appearance of further fragments with much higher intensities, starting from the mass number 430, without chlorine and mercury atoms. If it is considered to be that of a molecular ion, this mass corresponds to a compound of the composition $(CO)_5Fe_2(C(S)OC_2H_5)_2$ (**6**) which has apparantly been generated by the thermal decomposition of **2** under electron impact conditions. For electron bookkeeping purposes the ion must have a structure involving bridging thioalkoxycarbonyl ligands and a formal iron–iron double bond.

The appearance of the molecular ion of **6** in the mass spectrum of **2**, and its fragmentation, can be explained by the thermal instability of **2** which decomposes at room temperature even under inert gas within several h, as indicated by a change of color from bright yellow to dirty grey-green. Further fragmentation of **6** proceeds via the successive loss of five CO groups, leading to the $Fe_2L_2^+$ ion ($L = C(S)OC_2H_5$). The relative stability of the Fe–L bond is a result of the better $\sigma$-donor property of L relative to CO.

It should also be taken into account, that the peak at the mass number 430 probably does not indicate the molecular ion which really is at 458, equivalent to structure **7** and not observed in the spectrum. In this case a relationship exists to the structure of compound **8**, which was obtained by Fischer et al. [16] by the reaction of $Fe(CO)_5$ with $LiPh/Me_3OBF_4$. This compound contains an iron–iron single bond, as confirmed by an X-ray study [16,17]. Preliminary efforts to isolate **6** or **7** from the pyrolysis of **2** resulted in the isolation of small amounts of an unidentified orange-brown oil containing only terminal CO groups, as shown by IR spectroscopy (see experimental section).

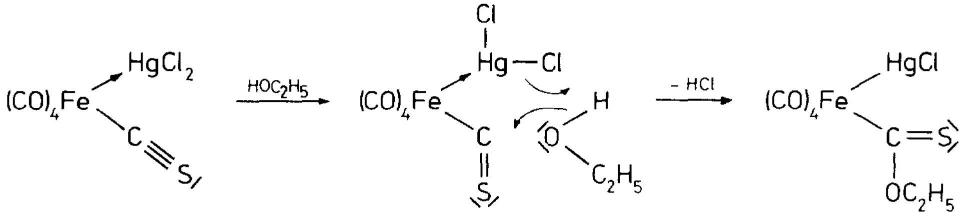


(6) (7)



(8)

The incorporation of a solvent molecule during the reaction of $HgCl_2$ with $(CO)_4FeCS$ in ethanol to give **2** is surprising and without parallel in the chemistry of similar thiocarbonyl complexes. A plausible explanation for the mechanism of the process is obtained if we consider the adduct **1a**, formed by the reaction of the components in n-pentane. The shift of the $\nu$(CS) absorption to higher frequencies relative to the starting material suggests that the most electrophilic site in $(CO)_4FeCS$, the thiocarbonyl carbon atom, has become more electrophilic on adduct formation. And if we assume, that **1a** has formed in the first step even in ethanol, this carbon atom is now more susceptible to attack by less nucleophilic reagents, such as alcohols, to yield a thioalkoxycarbonyl ligand. Apparently the electron-withdrawal is essential, because no reaction of $(CO)_4FeCS$ with ethanol is observed in the absence of $HgCl_2$. A possible meachanism is shown in Scheme 2.



(1a) (2)

SCHEME 2

The attack of the solvent molecule at the thiocarbonyl carbon atom causes the proton to become acidified and HCl is formed. This process is in contrast to the "internal" oxidation of CO during the reaction of $Fe(CO)_5$ to give complex **4** and phosgene. For this process, an intermediate like the **1b** adduct possibly plays an important role in the activation of one CO molecule towards the reaction with the nucleophilic halide ion. The adduct **1b** probably resembles the complex described by Pardue and Dobson, who proposed a dimer structure for the adduct $(CO)_5Fe \cdot 2HgCl_2$ [18].

The behavior of $(CO)_4FeCS$ towards mercury compounds, as described in this paper, demonstrates further that the iron atom is the preferred site of reaction, in spite of the presence of a sulfur atom. This is in agreement with the results of Dombek and Angelici [5], who showed that only the introduction of electron-donating ligands enhances the nucleophilicity of the terminal CS group so that adduct formation is realized.

Further studies on this field of chemistry are currently in progress.

## Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. IR spectra were recorded on a Perkin-Elmer PE 457 spectrometer and calibrated against the absorption band of polystyrene at 1601 $cm^{-1}$. Proton NMR spectra were obtained on a Varian T 60 instrument with tetramethylsilane as internal reference. Mass spectra were recorded on a CH 7 instrument from MAT (Bremen). The Mössbauer data were collected, using methods described earlier [12], at 77 K vs. a $^{57}Co(Pd)$ source at 298 K. Microanalyses were performed by the analytical service of the Fachbereich Chemie der Universitaet Marburg (Germany). For the preparation of $(CO)_4FeCS$, a modified literature procedure [4] was applied, and $Fe(CO)_5$ was used without further purification.

### *Adduct of $(CO)_4FeCS$ with $HgCl_2$ (**1a**)*

To a suspension of 1.12 g (4.1 mmol) $HgCl_2$ in 100 ml pentane was added 0.85 g (4.0 mmol) $(CO)_4FeCS$ and the mixture was vigorously stirred over a period of 6 h at 0 °C. During the reaction time the solid changed color from white to bright yellow. This was collected on a fritted-glass funnel, washed with small portions of cold pentane, and dried in a stream of purified $N_2$, yielding a yellow crystalline powder, **1a**, 1.3 g (92%). The adduct decomposes on heating. Found: C, 5.45; Cl, 21.40; S, 3.55. $C_5Cl_6FeHg_3O_4S$ calcd.: C, 5.85; Cl, 20.72; S, 3.12%. IR ($\nu$, $cm^{-1}$, Nujol mull): further bands at 615s, 599s, 512w, 445w.

### *Adduct of $Fe(CO)_5$ with $HgCl_2$ (**1b**)*

$HgCl_2$ (3 g, (11.1 mmol) was similarly treated with 4 ml $Fe(CO)_5$ in pentane to give a yellow crystalline powder, **1b**, 3.60 g (97%). The adduct decomposes on heating. Found: C, 5.64; Cl, 21.63; Fe, 5.06. $C_5Cl_6FeHg_3O_5$ calcd.: C, 5.94; Cl, 21.05; Fe, 5.53%. IR ($\nu$, $cm^{-1}$, Nujol mull): further bands at 628s, 618s, 454w.

### *Preparation of $(CO)_4Fe(CSOC_2H_5)(HgCl)$ (**2**)*

To a solution of 1.5 g (5.6 mmol) $HgCl_2$ in about 100 ml absolute EtOH was added at room temperature, over a period of 10 min, dropwise with stirring, an ethanolic solution of 1.0 g (4.7 mmol) $(CO)_4FeCS$. Immediately on addition, a bright yellow solid precipitated out without gas evolution. The mixture was stirred for an additional 10 min and the solid separated off by filtration. Washing this solid with a few portions of ethanol and pentane, and drying in vacuo, gave bright yellow microcrystals, **2**, 2.10 g (90%). The solution was acidic, thus indicating the presence of HCl. The crystals can be handled in air for a short time but must be stored at temperatures below −30 °C. Solutions of the complex are very unstable. Found: C, 16.83; H, 0.95; Cl, 7.99; S, 6.36. $C_7H_5ClFeHgO_5S$ calcd.: C, 17.05; H, 1.02; Cl, 7.19; S, 6.56%. IR spectrum ($\nu$, $cm^{-1}$, Nujol mull): further bands at 1220m, 1145w, 1108m, 1020m, 1000m, 975sh, 968s, 821w,sh, 812w, 647w, 615s, 603s, 560m, 520w, 498m.

### *Preparation of* $Hg[Fe(CO)_3CS]$ *(3)*

To a solution of an excess $Hg(CH_3COO)_2$ in degassed water was added, dropwise at room temperature, a pentane solution of 0.8 g (3.7 mmol) $(CO)_4FeCS$. On gas evolution a yellow solid precipitated, which was separated by filtration. Washing with water and ether, and drying in vacuo, gave a yellow material which was insoluble in the common organic solvents, **3**, 2.8 g (72%). The compound is not sensitive to air. Found: C, 12.72; Fe, 14.56; S, 8.77. $C_4HgFeO_3S$ calcd.: C, 12.49; Fe, 14.52; S, 8.34%. IR spectrum ($\nu$, $cm^{-1}$, Nujol mull): further band at 590br.

### *Pyrolysis of* **2**

In a flask, equipped with a cold finger, a sample of freshly prepared **2** was heated in vacuo to about 100 °C. During 1 h at this temperature the yellow color of the solid changed to grey and finally to black, and small amounts of a red-brown oil were collected at the cooler which was kept at 0 °C. No other volatile material could be trapped at liquid nitrogen temperature. The IR spectrum of the oil showed only absorptions of terminal CO groups at 2080m, 2075sh, 2042s, 2033sh and 1996s $cm^{-1}$. Attempts to purify the crude material by chromatography caused decomposition.

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