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Formation of Metal Carbonyl Derivatives of Monothiocarbamates and Dithiocarbamates from CS_2 and COS

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The reaction of $(C_5H_5)Fe(CO)_2CONHCH_3$ *with CSX* (X = O, S) *gives* $(C_5H_5)Fe(CO)_2SC(X)NHCH_3$, *where the mono or dithio-carbamate act as monodentate ligands. In the case of carbon disulfide small variable quantities of* $(C_5H_5)Fe(CO)S_2CNHCH_3$ *are obtained depending on reaction conditions. The carbamoyl derivatives* $(C_5H_5)Re(CO)(NO)CONHCH_3$, cis-$(CO)_4M(NH_2CH_3)CONHCH_3$ (M = Mn, Re) *react with* CS_2 *to give* $(C_5H_5)Re(CO)(NO)S_2CNHCH_3$ *and* $(CO)_4MS_2CNHCH_3$ *respectively. The mechanism of thiocarbamate formation is discussed on the basis of chemical evidence which indicates nucleophilic attack of the N-carbamoylic atom on the carbon of the CSX reagents.*

Introduction

Carbamoyl complexes of transition metals, easily prepared from cationic carbonyl derivatives and primary or secondary amines, have been extensively studied. In particular their reactivity toward electrophilic or nucleophilic reagents has received great attention since carbamoyl derivatives are postulated to be intermediates in a large number of metal promoted reactions of CO and amines [1]. For example, both $Hg(CON(CH_3)_2)_2$ [2] and $Ni(CO)_3CON(CH_3)_2^-$ [3] react with organic acid chlorides to give amides, $RCON(CH_3)_2$ resulting from migration of the $N(CH_3)_2$ group to the electrophilic carbon center of the organic substrates.

With the aim to extend these studies to weak electrophilic agents, we have found that CS_2 and COS react with a variety of carbamoyl derivatives of transition metals, LnMCONHR, to give *di-* or *mono*-thiocarbamates, LnMSC(X)NHR (X = S, O), as products of an insertion-like reaction.

Since metal carbonyl thiocarbamate complexes have been synthesized from thiocarbamate anions, thiuram disulfide, trimethyltinthiocarbamates $(CH_3)_3SnS(X)CN(CH_3)_2$ [4–9] or, more recently, by CS_2–CO_2 exchange on the carbamate derivatives [10], the present work also provides a new synthetic route to obtain such type of complexes in very mild conditions.

Experimental

The carbamoyl complexes $(C_5H_5)Fe(CO)_2CONHR$ [11], $(C_5H_5)Re(CO)(NO)CONHCH_3$ [12], $(CO)_4M(NH_2CH_3)CONHCH_3$ (M = Mn [13], Re [14]) were prepared as described previously. Methylammonium salts of N-methylmonothiocarbamate $(CH_3NH_3)(SCONHCH_3)$ [15] and dithiocarbamate $(CH_3NH_3)(S_2CNHCH_3)$ [16], were obtained by literature methods. Bromopentacarbonylmanganese [17] or rhenium [18], $(CO)_5MBr$, and $(C_5H_5)Fe(CO)_2Cl$ [19] were prepared in the usual manner. All manipulations were carried out under dry nitrogen. Infrared spectra were recorded with 0.1 mm KBr cells on a Perkin-Elmer 180 spectrophotometer, and nmr on a JEOL C-60 ML and on a Varian XL-100 spectrometer, using TMS as internal reference. Mass spectra were recorded on a JEOL JMS-D100 working at 75 eV.

N-methyldithiocarbamato(π-cyclopentadienyl)dicarbonyl Iron

a) 0.470 g (2.0 mmol) of $(C_5H_5)Fe(CO)_2CONHCH_3$ were shaken with freshly distilled carbon disulfide (25 ml). After 1 hr the colour of the starting carbamoyl derivative had disappeared, but the terminal carbonyl region of the i.r. spectrum continued to change for a further 12 hr, when only two bands at 2040 and 1997 cm^{-1} were present. Removal of the solvent left a brown residue which was washed with carbon tetrachloride, taken up in few milliliters of dichloromethane and the crystallization by adding hexane gave pure red-brown $(C_5H_5)Fe(CO)_2S_2CNHCH_3$ (0.250 g, 44%). The title compound may be purified also dissolving the residue in benzene and, after filtration, by chromatography on

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an alumina column using benzene–dichloromethane (1:1) as eluent. The first eluted yellow brown band gives, on crystallization from benzene–hexane, the red $(C_5H_5)Fe(CO)S_2CNHCH_3$ (less than 5%), whereas the second red band afforded $(C_5H_5)Fe(CO)_2S_2CNHCH_3$.

b) 0.212 g (1 mmol) of $(C_5H_5)Fe(CO)_2Cl$ and 0.150 g (1.1 mmol) of $(CH_3NH_3)(S_2CNHCH_3)$ were refluxed in 50 ml of acetone for 3 hr. The filtered solution was evaporated, dissolved in benzene and chromatographed on alumina using CH_2Cl_2–C_6H_6 (1:1) as eluent; 0.013 g (5%) of $(C_5H_5)Fe(CO)S_2CNHCH_3$ and 0.100 g (35%) of $(C_5H_5)Fe(CO)_2S_2CNHCH_3$ were recovered after crystallization as described above.

N-alkylmonothiocarbamato(π-cyclopentadienyl)dicarbonyliron (Alkyl = CH_3, C_2H_5)

Carbonyl sulfide was slowly bubbled into a stirred solution of $(C_5H_5)Fe(CO)_2CONHR$ (1 mmol). After three days an i.r. spectrum of the reaction mixture showed that the reaction had gone almost to completion. Removal of the solvent left a brown residue which was taken up with hexane. The filtered solution was evaporated, dissolved in benzene and transferred to an alumina column. Elution with benzene–dichloromethane (1:1) gave first a small quantity of unstable substances and then the major product as a red-orange band. Recovery by evaporation and precipitation from benzene–hexane afforded the red orange complex $(C_5H_5)Fe(CO)_2SCONHCH_3$ (~30%). These derivatives have been also prepared in about 60% yield from $(C_5H_5)Fe(CO)_2Cl$ and the desired thiocarbamate salt $(RNH_3)(SCONHR)$ in acetone.

N-methyldithiocarbamato(π-cyclopentadienyl)carbonylnitrosylrhenium

0.367 g (1 mmol) of $(C_5H_5)Re(CO)(NO)CONHCH_3$ were refluxed in CS_2. After 40 hr the red-orange solution was cooled, the solvent evaporated to dryness under reduced pressure and the residue chromatographed on alumina using dichloromethane–hexane (1:1) as eluent. The first fraction showed no νCO absorptions in the 2000 cm^{-1} region, whereas the red zone was collected and after evaporation of the solvent the complex $(C_5H_5)Re(CO)(NO)S_2CNHCH_3$ was obtained by crystallization from benzene–hexane (0.040 g, 10%).

N-methyldithiocarbamato(tetracarbonyl)manganese(I)

0.256 g (1 mmol) of $(CO)_4Mn(NH_2CH_3)CONHCH_3$ were stirred with 50 ml of CS_2 for 24 hr and the solvent evaporated to dryness under reduced pressure. The residue was then sublimed (55 °C, 10^{-1} mm Hg) to give 0.100 g (36% yield) of the yellow $(CO)_4MnS_2CNHCH_3$.

N-methyldithiocarbamato(tetracarbonyl)rhenium(I)

a) The title compound was prepared from $(CO)_4Re(NH_2CH_3)CONHCH_3$ following the same procedure described above for the analogous manganese derivative. The white $(CO)_4ReS_2CNHCH_3$ was obtained in about 35% yield after sublimation (70 °C, 0.5 mmHg).

b) 0.203 g (0.5 mmol) of $(CO)_5ReBr$ and 0.095 g (0.7 mmol) of $(CH_3NH_3)(S_2CNHCH_3)$ were refluxed for 3 hr in 50 ml of acetone. The solution was evaporated to dryness leaving a red oil which was taken up with 5 ml of ether and evaporated again to dryness to give the desired product, which was sublimed (50% yield).

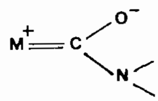
c) 0.150 g (0.30 mmol) of $[(CO)_5Re(NH_2CH_3)]PF_6$ were stirred for 3 hr with 0.048 g (0.35 mmol) of $(CH_3NH_3)(S_2CNHCH_3)$ in 50 ml of acetone. The resulting solution was then evaporated to dryness, dissolved in ether and filtered; the residue, after evaporation of the solvent, was sublimed to give $(CO)_4ReS_2CNHCH_3$ (35%).

N-isopropyldithiocarbamato(tetracarbonyl)rhenium(I)

0.150 g (0.36 mmol) of $(CO)_4Re(NH_2CH_3)CONHCH(CH_3)_2$ [14] were stirred for 24 hr in 50 ml of carbon disulfide and then filtered. The solution was evaporated to dryness and the residual product sublimed at 50 °C, 0.5 mm Hg (35% yield).

Results and Discussion

Infrared evidence, X-ray and nmr studies on Ln-MCONHR complexes have pointed out a decrease both in the νC=O bond strength and in the double bond character of the C–N group with respect of the organic counterparts [1]. These spectroscopic results are indicative of the importance of the resonance form in which metal donates electron charge through



π-bond to the carbamoyl group. On this basis it would be anticipated that the reactivity of the carbamoyl ligand will resemble that of the organic amines rather than that of organic amides.

Like primary and secondary amines the carbamoyl derivative $(C_5H_5)Fe(CO)_2CNHCH_3$ reacts with CS_2 or COS at room temperature to give the corresponding thiocarbamate complexes according to equation (1):

$$(C_5H_5)Fe(CO)_2CONHR + CSX \rightarrow (C_5H_5)Fe(CO)_2SCXNHR + CO \qquad (1)$$

$$(X = S, R = CH_3; X = O, R = CH_3, C_2H_5)$$

TABLE I. Analytical Data.

Complex	Colour	M.p. (°C)[a]	Analysis (%)[b]		
			C	H	N
$(C_5H_5)Fe(CO)_2S_2CNHCH_3$	red-brown	104–105	38.1	3.2	5.0
			(38.18)	(3.20)	(4.95)
$(C_5H_5)Fe(CO)S_2CNHCH_3$	red	108–109	37.4	3.5	5.3
			(37.66)	(3.56)	(5.49)
$(C_5H_5)Fe(CO)_2SCONHC_2H_5$	red-brown	88–89	42.9	3.8	5.0
			(42.73)	(3.94)	(4.98)
$(CO)_4MnS_2CNHCH_3$	yellow	81–82	26.2	1.5	5.1
			(26.38)	(1.48)	(5.13)
$(CO)_4ReS_2CNHCH_3$	white	78–79	17.6	1.0	3.4
			(17.82)	(1.00)	(3.46)
$(CO)_4ReS_2CNHCH(CH_3)_2$	white	77–78	22.1	1.8	3.2
			(22.22)	(1.86)	(3.24)
$(CO)_4ReS_2CN(CH_3)_2$	white	79–80	20.0	1.4	3.3
			(20.09)	(1.45)	(3.35)

[a] Melting Points are uncorrected. [b] Calculated values are given in parentheses.

The reaction proceeds to completion in CS_2 as solvent during 24 hr and, in these conditions, only small amount of the disubstituted $(C_5H_5)Fe(CO)S_2CNHCH_3$ is formed. Longer reaction time or higher temperature (boiling CS_2) slightly increase the yield in the bidentate species according with the observation that the formation of unidentate dithiocarbamate or dithiocarboxylate complexes occur only if the reactions conditions are sufficiently mild for a ligand not to be displaced [6, 20], which would result in the formation of the chelate complex.

If carbonyl sulfide is bubbled in a toluene solution of the iron carbamoyl derivatives the monothiocarbamate complexes are slowly formed. I.r. spectra of the reaction mixture showed after three days the presence, in small quantity, of the starting derivatives, which could be separated by column chromatography; no presence of bidentate complexes was detected even at higher temperature or for longer reaction time.

The nature of mono and dithiocarbamate complexes have been established from elemental analyses (Table I) and their spectral data (Table II) which are identical to those of the same complexes prepared from $(C_5H_5)Fe(CO)_2Cl$ and $S_2CNHCH_3^-$ or $SCONHR^-$ anions, as described in the experimental section.

The mass spectra show the parent ions along with fragments corresponding to the loss of CO groups; in all cases the completely decarbonylated fragment $(C_5H_5)FeSCXNHR$ was the base peak. The i.r. spectra of the monothiocarbamate complexes exhibit, together with the two terminal νCO absorptions, a medium intensity band at *ca.* 1600 cm^{-1} attributable to the $\nu(C {\cdots} N, C {\cdots} O)$ frequency. Since the position of this absorption has been used to predict the bonding mode of monothiocarbamate ligands [9], the high values here observed suggest that the –SCONHR group is bonded to iron through the sulfur with the oxygen atom unbound to the metal. A comparison between the $\nu C{=}N$ and the νCO of N-methyldithiocarbamate derivatives and the N,N-dimethyl analogs (in Table II these values are reported in parentheses) shows that these absorptions are respectively higher and lower with respect to the same bands of the monomethyl complexes. This trend is attributable to the electron releasing effect of the $-NR_2$ group, with respect to that of the NHR, forcing the S atoms to accept more electrons from it and thus to a less extent from the metal.

In order to further probe the general applicability of the CS_2 route to dithiocarbamate complexes, the reaction with carbon disulfide was extended to other carbamoyl derivatives of transition metals. Thus $(C_5H_5)Re(NO)(CO)CONHCH_3$ and $(CO)_4M(NH_2CH_3)CONHCH_3$ (M = Mn, Re) react with CS_2 at room temperature to give $(C_5H_5)Re(CO)(NO)S_2CNHCH_3$ and $(CO)_4MS_2CNHCH_3$ respectively:

$$(CO)_4M(NH_2CH_3)CONHCH_3 + CS_2 \rightarrow$$

$$(CO)_4MS_2CNHCH_3 + CO + NH_2CH_3 \qquad (2)$$

the latter compounds were also prepared from $M(CO)_5Br$ or $(CO)_5M(NH_2CH_3)^+$ and $(CH_3NH_3)(S_2CNHCH_3)$.

TABLE II. Spectral Data for Dithiocarbamate Complexes.

Complex	Infrared frequencies (cm^{-1})^{a}			^{1}H n.m.r. (δ values)^{e}			Mass fragments (m/e)^{g}				
	νC≡O	νC=O, νC=N^{c}	νNH^{b}	NH	CH$_3$ (J$_{NH-CH_3}$, Hz)	C$_5$H$_5$	M$^+$	(M−CO)$^+$	(M−2CO)$^+$	(C$_5$H$_5$Me)$^+$ (M−3CO)$^+$	Me$^+$ (M−4CO)$^+$
$(C_5H_5)Fe(CO)_2S_2CNHCH_3$	2040s, 1997s^{a}	1465m	3400w	7.86	^{2}3.16(4.5)	^{1}5.16	283	255	227	121	56
	(2030), (1990)* [3]	(1480)* [3]					(<1)	(29)	(100)	(66)	(38)
$(C_5H_5)Fe(CO)S_2CNHCH_3$	1960s^{a}	1520m	3395w	6.66	^{2}2.82(5.0)	^{1}4.62	255	227	–	121	56
	(1940)* [4]	(1530)* [4]					(21)	(100)		(40)	(31)
$(C_5H_5)Fe(CO)_2SCONHCH_3$	2035s, 1995s^{a}	1605m	3400w	–	–	–	267	239	211	121	56
							(15)	(13)	(100)	(55)	(23)
$(C_5H_5)Fe(CO)_2SCONHC_2H_5$	2020s, 1998s^{a}	1600m	3410w	5.65	^{3}1.22(6.5)^{f}, ^{m}3.80(CH$_2$)	^{1}4.95	281	253	225	121	56
							(10)	(11)	(100)	(85)	(27)
$(C_5H_5)Re(CO)(NO)S_2CNHCH_3$	1978s^{a}	1735s(νNO)	3400w	–	–	–	416	388	358^{h}	252	187
							(<1)	(21)	(100)	(79)	(22)
$(CO)_4MnS_2CNHCH_3$	2087m, 2012vs, 1998s, 1958s^{b}	1528m	3405w	6.70	^{2}2.85(4.5)	–	273	245	217	189	161
	(2087), (2008), (1994), (1956)* [6]^{d}	(1542)* [6]					(43)	(<1)	(29)	(100)	(90)
$(CO)_4ReS_2CNHCH_3$	2103m, 2005vs, 1988s, 1948s^{b}	1526m	3400w	6.65	^{2}2.95(5.0)	–	405	377	349	321	293
							(77)	(100)	(19)	(81)	(93)
$(CO)_4ReS_2CNHCH(CH_3)_2$	2102m, 2002vs, 1986s, 1950s^{b}	1520m	3390w	6.40	^{2}1.20(6.0)^{f}, ^{m}4.05(CH)	–	433	405	377	349	321
							(61)	(100)	(57)	(67)	(51)
$(CO)_4ReS_2CN(CH_3)_2$	2100m, 1999vs, 1984s, 1945s^{b}	1550m	–	–	^{1}3.24	–	419	391	363	335	307
							(42)	(70)	(15)	(46)	(100)

Measured in ^{a}CHCl$_3$. ^{b}CCl$_4$. ^{c}Nujol mull. ^{d}Cyclohexane. ^{e}Run in chloroform-d solutions with TMS as internal standard. ^{f}J$_{CH-CH}$, Hz. ^{g}Referred to ^{56}Fe and ^{187}Re, relative intensities are given in parentheses. ^{h}(M–CO–NO)$^+$ fragment. *Values from references as quoted and referred to N,N-dimethyldithiocarbamate complexes.

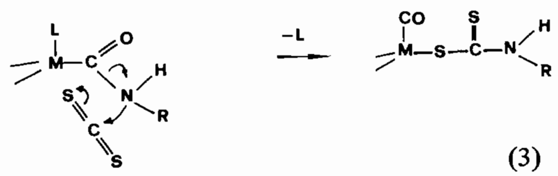
TABLE III. Calculated Carbonyl Force Constants (mdyn/A).

Complex	K_1[a]	K_2[b]	K_i[c]
$(CO)_4MnS_2CNHCH_3$	15.79	16.90	0.28
$(CO)_4MnS_2CN(CH_3)_2$[d]	15.75	16.89	0.32
$(CO)_4ReS_2CNHCH_3$	15.66	16.92	0.34
$(CO)_4ReS_2CN(CH_3)_2$	15.63	16.84	0.35
$(CO)_4ReS_2CNHCH(CH_3)_2$	15.70	16.88	0.35

[a] *trans* to L. [b] *cis* to L. [c] CO–CO interaction constants. [d] Data from ref. 6.

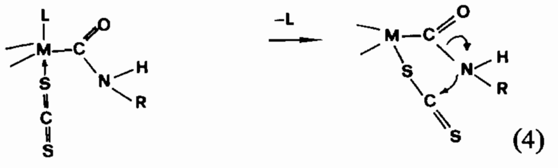
The i.r. spectra of $(CO)_4MS_2CNHCH_3$ compounds contain four terminal ν(CO) stretching frequencies which are required by the C_{2v} local symmetry of these complexes and, as proposed for $(CO)_4MnS_2PR_2$ [21] and $(CO)_4MnS_2CN(CH_3)_2$ [7] the highest frequency band can unequivocally be assigned to the A_1 mode, whereas bands in the range 2012–1999 cm^{-1} and 1998–1984 cm^{-1} may be attributed to B_1 and A_1 modes, respectively. In the present assignment ($A_1 > B_1 > A_1 > B_2$) k_1 is smaller than k_2 for all the compounds in Table III, as is expected from the Cotton–Kraihanzel theory [22]. In addition, both k_1 and k_2 of the N,N-dimethyldithiocarbamatotetracarbonyl complexes are smaller than those of the N-methyl analog. This trend again indicates a reduced π-bonding ability of the $S_2CN(CH_3)_2$ group with respect to the compounds in which the CH_3 is substituted by a hydrogen atom.

Two main alternatives offer themselves for the mechanism of the reaction of carbamoyl derivatives with carbonyl sulfide or carbon disulfide: in one, attack of CSX (X = S, O) is followed by ligand displacement (CO, NH_2R) and migration of –NHR group at the electrophilic carbon center of the activated CSX molecule, and in the other attack at the carbamoyl nitrogen is followed by ligand displacement. These are outlined respectively as reaction (3) and (4) below:



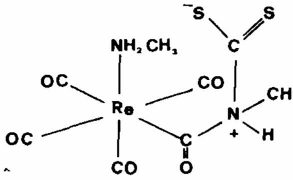
(3)

L = CO, NH_2CH_3



(4)

A mechanism similar to (3) has been proposed for the CS_2 insertion into Pt–H [23] or M–R [24] (M = Mn, Re) bonds, whereas mechanism (4) has been suggested to explain the CS_2 insertion reactions into Sn–N [25], P–N [26] and into early transition metal nitrogen bonds [27]. An indication that the carbon disulfide reaction involves the nitrogen of the carbamoyl group rather than displacement of the coordinated ligand may come from the reaction of the $(CO)_4Re(NH_2CH_3)CONHCH(CH_3)_2$ and CS_2, which leads only to N-isopropyldithiocarbamate derivative, $(CO)_4ReS_2CNHCH(CH_3)_2$, presumably *via* the labile adduct*:



Moreover, owing to its insolubility in the carbon disulfide reaction medium a light precipitate is formed during the course of the reaction (2) (M = Re). An i.r. analysis of the solid showed, together with the ν(CO) of the $(CO)_4ReS_2CNHCH_3$, bands at 2050 and 2021 cm^{-1}, which have been associated to the E and A_1 stretching modes of the cationic $(CO)_5Re(NH_2CH_3)^+$ [14]. Although this latter evidence is not conclusive because we were unable to obtain $[(CO)_5Re(NH_2CH_3)][S_2CNHCH_3]$ in pure form, we tend to favour reaction (4), in absence of possible evidence for (3). It is worth pointing out that the yields in dithiocarbamate derivatives are lower with respect to that obtained from other already improved methods. This must be related: a) to the great tendency of the metal carbonyl complexes used here to add amines unfavouring the CS_2 addition product intermediate**; b) to the formation, in the case of Mn and Re carbamoyl derivatives, of dimeric species due to decomposition of dithiocarbamates as previously reported for the analogous $(CO)_4MnS_2CN(CH_3)_2$ [6, 7]

$$(CO)_4MnS_2CNHCH_3 \xrightarrow{-2\,CO} [(CO)_3MnS_2CNHCH_3]_2 \qquad (5)$$

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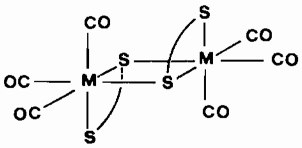
*Presumably the strong nucleophilic sulfur atom replaces more easily the NH_2CH_3 with respect to the CO group, according to the reaction of $(CO)_5Re(NH_2CH_3)^+$ and I^- which leads to $(CO)_5ReI$ [14]. However no evidence has been obtained either for $(CO)_5ReS_2CNHR$ or for $(CO)_4Re(NH_2CH_3)S_2CNHR$ in which the dithiocarbamate acts as monodentate ligand.

**It has been shown [1] that the reaction: $LnMCONHR + H^+ \rightleftarrows LnMCO^+ + NH_2R$ depends on the tendency of cationic carbonyl complexes to add amines, which has been related to the positive carbonyl carbon charge. Presumably the same factors influence the reactions with the weak electrophiles CSX.



In fact if reaction (2) is carried out in refluxing carbon disulfide or for longer time at room temperature, three new ν(CO) stretching frequencies at 2038, 2020 and 1930 cm^{-1} appear in the i.r. spectra of the reaction mixture. The number and the position of these bands are similar to those already attributed to dimeric structures in which the S_2CNHCH_3 are bridging *trans* to the M_2S_2 plane. Similar i.r. spectra have been found on a sample obtained from thermal decomposition of pure $(CO)_4MnS_2CNHCH_3$.

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