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SYNTHESIS AND REACTIONS OF XANTHATE AND THIOXANTHATE CARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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Summary

A series of complexes $CpM(CO)_nS_2CX$ (M = Mo, W; n = 2, 3; X = OR, SR; R = Me, Et) has been prepared by the reaction of xanthates and thioxanthates with $CpM(CO)_3Cl$. The dicarbonyl compounds are the exclusive products after sufficiently long reaction times and are produced at least partially through the tricarbonyl species as intermediates. The conversion of $CpM(CO)_3S_2CX$ to $CpM(CO)_2S_2CX$ is not a simple first-order process but is catalyzed by Cl^- and/or S_2CX^-. The tricarbonyl species can be alkylated at the uncoordinated sulfur atom to give ionic di- or tri-thiocarbonate complexes.

Introduction

Recently we have been interested in the behavior of metal complexes of sulfur-containing ligands, and particularly in reactions where sulfur atoms are gained or lost by such complexes, with the idea in mind that such systems might serve as sulfur-atom carriers in catalytic desulfurization processes. One such reaction, observed by us and by other workers [1], occurs between $CpMo(CO)_3^-$ and carbon disulfide, giving a mixture which on methylation yields $CpMo(CO)_2S_2CSMe$ (eq. 1). Here the product contains one more sulfur atom than the

$$CpMo(CO)_3^- + CS_2 \xrightarrow{CH_3I} CpMo(CO)_2S_2CSMe \qquad (1)$$

reactants.

In order to understand this and other such reactions more completely, we have undertaken the preparation and study of a series of metal carbonyl complexes containing xanthate (S_2COR^-) and thioxanthate (S_2CSR^-) ligands. Their properties and reactions are reported here.

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Experimental

Starting materials ($CpM(CO)_3Cl$, M = Mo, W) were prepared from the hydrides $CpM(CO)_3H$ [2] by treatment with carbon tetrachloride [3]. $[CpM(CO)_4]PF_6$ (M = Mo, W) was prepared according to the literature method [4].

Tetramethylammonium methylxanthate was prepared by dissolving 3.1 g of sodium (0.132 mol) in 50 ml of methanol, and adding 17 ml (0.264 mol, 100% excess) of carbon disulfide. A solution of NMe_4Cl (14.5 g, 0.132 mol) in 50 ml of methanol was added, and the precipitated sodium chloride was removed by filtration. Diethyl ether (100 ml) was then added in 5 ml portions and the solution was chilled to —20°C overnight, yielding the yellow crystalline product $NMe_4[S_2COCH_3]$.

Tetramethylammonium methylthioxanthate was prepared in a similar manner, except that 6.34 g of methanethiol (0.132 mmol) was added to the sodium/methanol solution prior to adding CS_2. $NMe_4[S_2CSMe]$ was obtained as a bright yellow crystalline solid. The ethyl analogs of both compounds ($NEt_4[S_2COEt]$ and $NEt_4[S_2CSEt]$) were prepared in the same way, substituting ethanol, ethanethiol, and NEt_4Br where appropriate.

Methanol and ethanol were dried by distillation from magnesium metal; tetrahydrofuran and benzene were distilled from calcium hydride. Other solvents were used as obtained.

All reactions were carried out under a nitrogen atmosphere. The solid products were stable for periods of several weeks in air, but decompose more rapidly in solution unless oxygen is rigorously excluded. Samples were prepared for long-term NMR analysis by evacuating the sample tube through a rubber septum and filling the tube with nitrogen after degassing the solution. Samples prepared in this way were stable for several weeks.

Infrared spectra were obtained in solution on a Perkin—Elmer 467 spectrophotometer calibrated with gaseous CO and DBr. Proton NMR spectra were taken on Varian EM-360 and Jeol JNM-MH-100 spectrometers. Analyses were performed by Atlantic Microlab. Inc., Atlanta, GA. Molecular weights were determined in benzene solution using a Mechrolab vapor pressure osmometer.

Synthesis of xanthate and thioxanthate complexes:

Complexes of the types $CpM(CO)_nS_2CX$ (M = Mo, W; X = OR, SR; R = Me, Et; $n = 2, 3$) were synthesized by one of two procedures described below:

Procedure A. Xanthate complexes: Sodium metal was dissolved in methanol or ethanol and a twofold excess of CS_2 was added, giving a solution of sodium methyl- or ethyl-xanthate. After stirring for 10 min, an equimolar quantity of $CpM(CO)_3Cl$ was added and the mixture was stirred at room temperature while the progress of the reaction was monitored by infrared spectroscopy. In order to obtain the tricarbonyl products, the reactions were stopped short of completion (M = Mo, 1—3 days; W, 8—10 days). Longer reaction times led to exclusive formation of dicarbonyl products.

Thioxanthate complexes were prepared by the same method, except that an equimolar quantity of methanethiol or ethanethiol was added to the sodium alkoxide solution prior to adding the carbon disulfide.

Procedure B. The xanthate and thioxanthate complexes could also be

TABLE 1

MELTING POINTS, YIELDS, INFRARED AND NMR DATA [a] OF THE COMPLEXES OBTAINED

	M.p. (°C)	Yield (%) (procedure)	ν(CO) (cm^{-1})		$\tau(C_5\underline{H}_5)$ (ppm)	$\tau(C\underline{H}_3)$ ($\tau(C\underline{H}_2CH_3)$) (ppm)		$\tau(CH_2\text{-}CH_3)$ (ppm)
A. Xanthate complexes								
$CpW(CO)_3S_2COEt$	115–116	72 (A)	2067, 1969, 1919		4.32	(5.43)		8.35
$CpMo(CO)_2S_2COMe$	92–94	76 (B)	1986, 1941		4.58	5.98		
$CpMo(CO)_2S_2COEt$	84–85	61 (A)	1982, 1940		4.58	(5.50)		8.60
$CpW(CO)_2S_2COMe$	112–114	29 (B)	1964, 1884		4.43	6.02		8.55
$CpW(CO)_2S_2COEt$	105–106	9 (A)	1963, 1885		4.40	(5.48)		8.55
B. Thioxanthate complexes								
$CpMo(CO)_3S_2CSMe$	92–94	trace (A)	2046, 1976, 1952		4.32	6.28		
$CpMo(CO)_3S_2CSEt$	83–86	trace (A)	2051, 1976, 1951		4.32	(6.68)		8.70
$CpW(CO)_3S_2CSMe$	122–123	14 (A)	2044, 1973, 1948		4.28	7.27		
$CpW(CO)_3S_2CSEt$	48–50	18 (A)	2048, 1974, 1947		4.28	(6.80)		8.69
$CpMo(CO)_2S_2CSMe$	120–122	69 (B)	1972, 1907		4.53	7.41		
$CpMo(CO)_2S_2CSEt$	50–52	36 (A)	1974, 1898		4.60	(5.55)		8.60
$CpW(CO)_2S_2CSMe$	140–141	40 (A)	1975, 1891		4.42	7.45		
$CpW(CO)_2S_2CSEt$	103–104	48 (A)	1968, 1892		4.40	(6.80)		8.56
				$\tau(C_5\underline{H}_5)$ (ppm)	$\tau(SC\underline{H}_3)$ ($\tau(SC\underline{H}_2CH_3)$) (ppm)	$\tau(SCH_2C\underline{H}_3)$ (ppm)	$\tau(OC\underline{H}_3)$ ($\tau(OC\underline{H}_2CH_3)$) (ppm)	$\tau(OCH_2\text{-}CH_3)$ (ppm)
C. Di- and tri-thiocarbonate complexes								
$[CpW(CO)_3SC(SMe)OEt]BF_4$	135–136	64	2058, 1968(br)	3.78	7.01		(4.98)	8.31
$[CpW(CO)_3SC(SEt)OEt]BF_4$	91–92	66	2048, 1973sh, 1951	3.73	(6.43)	8.50	(4.96)	8.30
$[CpW(CO)_3SC(SMe)_2]BF_4$	151–154	26	2056, 1983sh, 1966	3.65	6.81			
$[CpW(CO)_3SC(SMe)SEt]BF_4$	114–115	29	2057, 1983sh, 1966	3.66	6.81, (6.22)	8.43		
$[CpW(CO)_3SC(SEt)_2]BF_4$	104–106	28	2057, 1983sh, 1963	3.66	(6.22)	8.46		

[a] Infrared spectra were taken in solution in heptane (neutral complexes) or chloroform (ionic complexes). NMR spectra were taken in chloroform-*d*.

prepared by stirring equimolar amounts of $CpM(CO)_3Cl$ and tetraalkylammoniu alkyl-xanthate or -thioxanthate in methanol. The reaction required about the same time as by procedure A (Mo, ca. 5 days; W, ca. 15 days) but yields were generally higher.

All products were purified by column chromatography over alumina. When present, the compounds eluted in this order: $CpM(CO)_2S_2CX$ (red-orange band, hexane); $CpM(CO)_3S_2CX$ (orange band, 20% $CHCl_3$/hexane); $CpM(CO)_3Cl$ (orange band, 35—40% $CHCl_3$/hexane). The products were recrystallized from dichloromethane/heptane; the dicarbonyl products were dark red crystalline solids, while the tricarbonyl products were light orange.

In general it seems that the tricarbonyl products are more difficult to obtain in the case of molybdenum than in the case of tungsten, and in the case of xanthates than thioxanthates. Thus, $CpMo(CO)_3S_2COMe$, $CpMo(CO)_3S_2COEt$, and $CpW(CO)_3S_2COMe$ were not obtained, while $CpW(CO)_3S_2COEt$, $CpMo(CO)_3S_2CSMe$, and $CpMo(CO)_3S_2CSEt$ were produced only in very low yield. In an effort to improve the yields of these complexes, attempts were made to prepare them by the reaction of $[CpM(CO)_4]PF_6$ with $NMe_4[S_2CSMe]$ or $NMe_4[S_2COMe]$. The reactants were stirred in methanol for several days, but only trace yields of the dicarbonyl complexes were isolated.

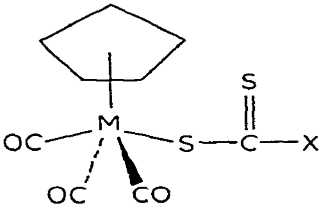
Alkylation of the tricarbonyl complexes

The tricarbonyl complexes ($CpW(CO)_3S_2CX$ (X = OEt, SMe, SEt) were alkylated by stirring for ca. 30 min with an excess of trimethyl- or triethyloxonium tetrafluoroborate in chloroform. The reactions were monitored by infrared spectrocopy and when complete the solutions were filtered and the solvent was removed. The orange products ($[CpW(CO)_3SC(SR)X]BF_4$, R = Me, Et) were crystallized from acetone/ether or chlorform/ether. Analogous molybdenum complexes were not prepared due to the lack of starting materials.

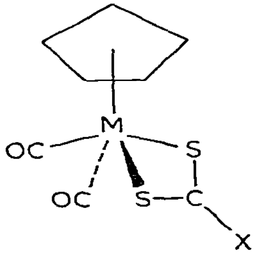
Satisfactory analyses (for C, H, and S) were obtained for all compounds, and satisfactory molecular weights were obtained for all nonionic compounds. Melting points, yields, infrared and NMR spectroscopic data for all compounds are presented in Table 1.

Results and discussion

The reaction of alkyl-xanthates or -thioxanthates with $CpM(CO)_3Cl$ yields in many cases both tricarbonyl complexes $CpM(CO)_3S_2CX$ (I) and dicarbonyl complexes $CpM(CO)_2S_2CX$ (II) as products, with the latter species being the sole products after sufficiently long reaction times. The infrared spectra of



(I)



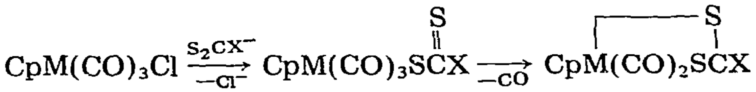
(II)

these complexes in the C—O stretching region are consistent with their formulation as containing monodentate and bidentate ligands, respectively.

The tricarbonyl species appear to be the first reported complexes of this type containing monodentate substituted dithioformate ligands. In other instances only the dicarbonyl complexes ($CpM(CO)_2S_2CX$, X = Ph [5], NR_2 [6,7], CN [8]) have been isolated, though in one case [8] a tricarbonyl intermediate was proposed.

A series of NMR spectra showing the progress of a typical reaction ($CpW(CO)_3Cl + S_2CSEt^-$) is presented in Fig. 1. (The C_5H_5 resonances are shown; reaction conditions approximate those of the synthetic reactions.) Along with the peaks due to $CpW(CO)_3Cl$ and $CpW(CO)_2S_2CSEt$, a signal due to $CpW(CO)_3S_2CSEt$ (identified by comparison with the spectrum of pure material) is seen. This rises to a fairly constant level which is maintained during most of the reaction, and disappears at the end as complete conversion to the dicarbonyl product takes place. Similar spectra are obtained for the analogous $CpMo(CO)_3Cl + S_2CSEt^-$ reaction; this reaction is complete after about three days under similar conditions.

It is clear from these spectra that the tricarbonyl complexes I are intermediates in this reaction. The simplest interpretation of the spectra would be a mechanism involving initial displacement of chloride ion by xanthate or thioxanthate to give the tricarbonyl complex, followed by first-order chelate ring closure with loss of CO (eq. 2).



$$CpM(CO)_3Cl \xrightarrow[-Cl^-]{S_2CX^-} CpM(CO)_3S\overset{\overset{S}{\|}}{C}X \xrightarrow[-CO]{} CpM(CO)_2S\overset{\overset{S}{|}}{C}X \quad (2)$$

(I) (II)

However, when we attempted to study the kinetics of this reaction, it became apparent at once that the mechanism could not be this simple. In particular, we found that solutions of pure $CpMo(CO)_3S_2CSEt$, $CpW(CO)_3S_2CSEt$, and $CpW(CO)_3S_2COEt$ in methanol were stable, with no conversion to the corresponding dicarbonyl complexes being observed in either infrared or NMR spectra over periods of several weeks, a longer time than that required to obtain the dicarbonyl products from the chlorides. Thus the conversion of I to II cannot be a simple first-order process; a catalyst appears to be required.

Of the species present in the synthetic reaction mixtures, the most likely catalysts are unreacted or excess xanthate or thioxanthate ion, and chloride ion (produced in the first step). We found that the addition of either $[NMe_4]Cl$ or $[NEt_4]S_2CSEt$ to methanol solutions of $CpW(CO)_3S_2CSEt$ did result in a slow but complete conversion to $CpW(CO)_2S_2CSEt$ over a period of about four weeks at room temperature under conditions approximating those of the synthetic reactions. (NMR spectra showing the progress of the S_2CSEt^--catalyzed reaction are presented in Fig. 2.)

We propose that the conversion of I to II proceeds via displacement of a carbonyl group in the tricarbonyl complex by a chloride, xanthate, or thioxanthate ion, followed by rapid ring closure with loss of an ionic ligand (eq. 3).

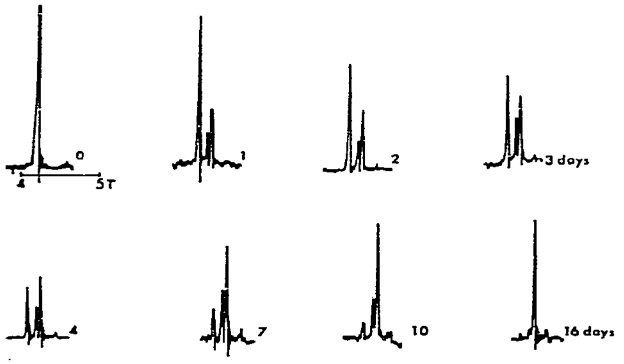
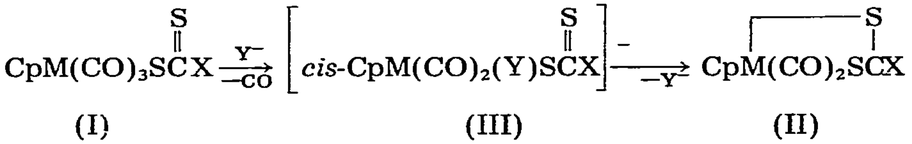


Fig. 1. NMR spectra showing the reaction of $CpW(CO)_3Cl$ (0.067 mmol) with $NEt_4(S_2CSEt)$ (0.070 mmol) in CH_3OD (1 ml). C_5H_5 resonances are shown.

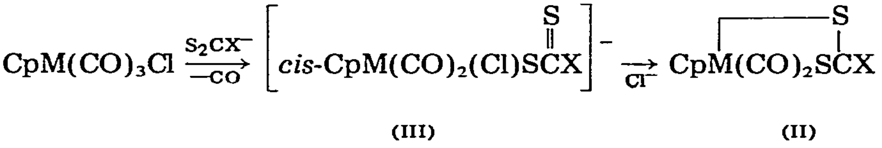


$$\underset{\text{(I)}}{\mathrm{CpM(CO)_3S\overset{\overset{S}{\|}}{C}X}} \xrightarrow[-\mathrm{CO}]{\mathrm{Y^-}} \underset{\text{(III)}}{\left[cis\text{-}\mathrm{CpM(CO)_2(Y)S\overset{\overset{S}{\|}}{C}X}\right]^-} \xrightarrow[-\mathrm{Y^-}]{} \underset{\text{(II)}}{\mathrm{CpM(CO)_2SCX}} \qquad (3)$$

($Y = Cl^-$ or monodentate S_2CX^-; $X = OR, SR$)

It seems unlikely, however, that all of the dicarbonyl product is formed via reaction 3. Indirect evidence suggests that there must be another pathway leading directly from $CpM(CO)_3Cl$ to $CpM(CO)_2S_2CX$. Such a pathway is needed to explain the appearance of a substantial amount of dicarbonyl product at an early stage in the reaction (see Fig. 1). Also, as shown in Fig. 1 and 2, complete conversion to $CpW(CO)_2S_2CSEt$ is obtained more rapidly from $CpW(CO)_3Cl$ (16 days) than via catalyzed conversion of $CpW(CO)_3S_2CSEt$ (>29 days under similar conditions). This would not be possible if all of the dicarbonyl product were formed through the tricarbonyl intermediate as in reaction 3.

As an alternative pathway (eq. 4), we propose that xanthate or thioxanthate ion may displace a carbonyl group in $CpM(CO)_3Cl$ (rather than Cl^- as in reaction 2) to give an ionic species which then undergoes rapid chelate ring closure as in reaction 3. (The intermediate species is, of course, the same as the intermediate



$$\mathrm{CpM(CO)_3Cl} \xrightarrow[-\mathrm{CO}]{\mathrm{S_2CX^-}} \underset{\text{(III)}}{\left[cis\text{-}\mathrm{CpM(CO)_2(Cl)S\overset{\overset{S}{\|}}{C}X}\right]^-} \xrightarrow[\mathrm{Cl^-}]{} \underset{\text{(II)}}{\mathrm{CpM(CO)_2SCX}} \qquad (4)$$

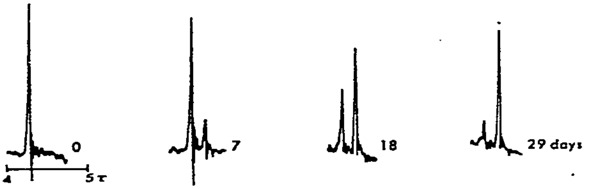
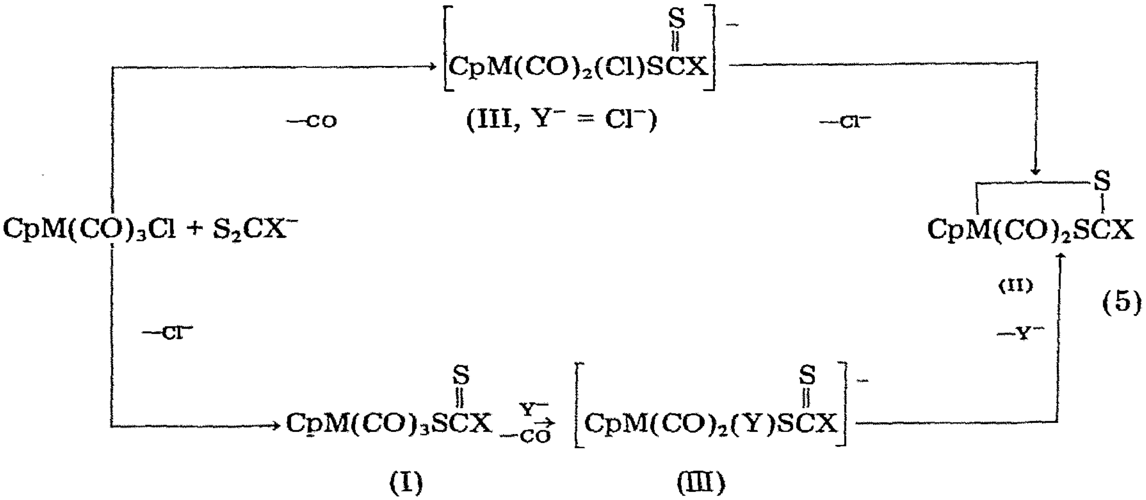


Fig. 2. NMR spectra showing the reaction of $CpW(CO)_3S_2CSEt$ (0.069 mmol) and $NEt_4(S_2CSEt)$ (0.071 mmol) in CH_3OD (1 ml). C_5H_5 resonances are shown.

in the chloride-catalyzed conversion of I to II.)

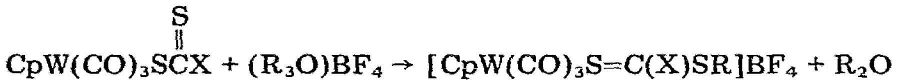
The first step of reaction 4 is consistent with the known reactions of nucleophiles with $CpM(CO)_3Cl$ and similar species. Phosphines, for example, may displace either CO or (in the presence of $AlCl_3$) chloride ion to give $CpM(CO)_2(phos)Cl$ or $[CpM(CO)_3(phos)]Cl$, respectively [9], while with $CpFe(CO)_2Br$, both $CpFe(CO)(phos)Br$ and $[CpFe(CO)_2(phos)]Br$ are obtained from the same reaction [10].

Reactions 3 and 4 may be combined to give an overall scheme for the reactions between $CpM(CO)_3Cl$ and S_2CX^- (eq. 5).



(M = Mo, W; $Y^- = Cl^-, S_2CX^-$; X = OR, SR)

On treatment with trialkyloxonium salts, the tricarbonyltungsten complexes undergo alkylation at the uncoordinated sulfur atom to give ionic species characterized (on the basis of their infrared and NMR spectra) as dialkyl trithiocarbonate or *O,S*-dithiocarbonate complexes:



$$CpW(CO)_3S\overset{\overset{S}{\|}}{C}X + (R_3O)BF_4 \rightarrow [CpW(CO)_3S{=}C(X)SR]BF_4 + R_2O \qquad (6)$$

(X = OEt, SMe, SEt; R = Me, Et)

The corresponding dicarbonyl species were not obtained; the chelated xanthate and thioxanthate complexes II displayed no reactivity toward trialkyloxonium salts. This is in contrast to the behavior of chelating thiocarboxamido complexes, where the coordinated sulfur atom displays sufficient basicity to be alkylated under these conditions, without becoming detached from the metal atom [11,12].

Acknowledgment

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