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ORGANOMETALLIC DERIVATIVES OF TRITHIONES

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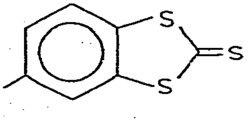
Summary

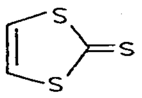
Complexes of the type $LM(CO)_5$ (M = Cr, Mo) were prepared from (diolefin)$M(CO)_4$ and the 1,3-dithiolene-2-thione ligands, L = $C_3H_2S_3$, $C_3H_4S_3$ and $C_8H_6S_3$. Infrared, ^1H and ^{13}C NMR data indicated C_{4v} symmetry about the metal centre. The reaction of 3-methylbenzo-1,3-dithiolene-2-thione with $(C_5H_5)Co(C_8H_{12})$ produced a cobalt(III) methylbenzothiete derivative $(C_7H_6S_2)$-$Co(C_5H_5)$.

Introduction

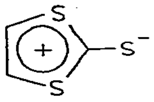
The cyclic trithiones I, II and III are potentially polyfunctional ligands which can bond to transition metals through either the exo- or endocyclic sulfur atoms. In II, the carbon—carbon double bond can also participate in bonding interactions either by direct utilization of 2 *p* orbitals or by stabilization of the dipolar structure IIa. Synthesis and characterization of organometallic trithione complexes might help elucidate the coordination chemistry of these ligands [1]. Furthermore, a review of the coordination complexes of thioketones discloses numerous transition metal complexes of apparently unusual stoichiometry [2] for which materials organometallic trithione complexes should provide tractable model compounds.



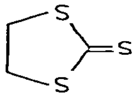
(I)



(II)



(IIa)

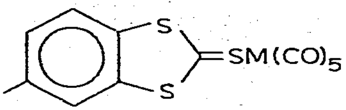


(III)

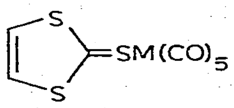
Results and discussion

Synthesis of the metal carbonyl complexes of I, II and III proceeded by displacement of the chelating olefin from (bicyclo[2.2.1]heptadiene)$M(CO)_4$ (M =

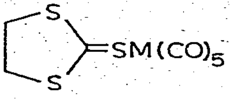
Cr, Mo) in the expectation of the obtaining compounds of the type (ligand)$_2$M(CO)$_4$. Instead, however, the products were of the (ligand)M(CO)$_5$ class. Preparation of tungsten analogs of VII and VIII by photochemical methods has been reported [3]. Compounds IV—VIII were characterized by elemental analyses (Table 1), and by their infrared spectra (Table 2), which exhibited the characteristic three band pattern of carbonyl absorptions ($E_1 + A_1$) indicative of C_{4v} symmetry about the octahedral metal center. In fact, the spectra of IV, VI and VIII strongly resembled that of (CH$_3$CN)Mo(CO)$_5$ [4], (ν(CO) 1931s, 1948vs, 2085w cm^{-1}), suggesting that the trithiones behave as very weak π acceptors toward zero valent Group VIb metals. The thiocarbonyl stretching frequencies decrease by 5—10 cm^{-1} on complexation, confirming this idea. This small shift may reflect an increased contribution from the dipolar C$^+$—S$^-$ thiocarbonyl resonance forms.



(IV), M = Mo



(V), M = Cr
(VI), M = Mo



(VII), M = Cr
(VIII), M = Mo

Additional information about structure and bonding in these complexes was obtained from NMR spectral data (Table 3). The ligand protons in III are shifted upfield by δ 0.5 ppm on complexation to the M(CO)$_5$ moiety and those of V and VI are shielded by δ 0.1 ppm relative to the free thiones. The small magnitude of the shifts suggests that the dipolar from IIa does not contribute significantly to the bonding in the compounds studied. The ^{13}C NMR spectra of V and VII indicate the presence of equivalent sets of *cis* carbonyls and ligand

TABLE 1

ANALYTICAL AND MELTING POINT DATA FOR TRITHIONE METAL COMPLEXES

Compound	M.p. (°C)	Analysis found (calcd.) (%)				
		C	H	S	Metal	Mol. wt. [a]
IV	117 (dec)	36.16	1.51			
		(35.94)	(1.38)			
V	96—98	29.24	0.59	29.68	Cr, 16.21	314
		(29.45)	(0.61)	(29.45)	(15.95)	(326)
VI	92 (dec)	25.59	0.35		Mo, 25.88	
		(25.95)	(0.54)		(25.95)	
VII	116—118	29.40	0.90	29.20	Cr, 16.36	
		(29.27)	(1.22)	(29.27)	(15.85)	
VIII	96—98 (dec)	25.98	1.12	25.99	Mo, 26.02	353
		(25.81)	(1.08)	(25.81)	(25.81)	(372)
IX [c]	136—137	42.70	4.13	22.01	Rh, 23.40	426 [b]
		(43.34)	(4.05)	(21.62)	(23.20)	(444)
X	193—194	52.08	4.10	22.86	Co, 21.48	263
		(51.80)	(3.96)	(23.02)	(21.22)	(278)

[a] Osmometric in benzene. [b] Osmometric in CHCl$_3$. [c] Cl, 8.12 (7.88).

TABLE 2

INFRARED AND ELECTRONIC SPECTRAL DATA

Compound	ν(CO) (cm^{-1})[a]	ν(CS) (cm^{-1})[b]	λ_{max} (log ϵ)[c] (nm)
I		1065	290(3.51), 363(4.37), 4.22(2.10)
II		1060, 1095	360(4.22), 420(sh, 2.06)
III		1072	325(4.17), 450(1.92)
IV	2070, 1955, 1935	1045, 1060	338(3.95), (365(3.92), 482(4.08)
V	2060, 1950, 1933	1032, 1048	327(3.85), 363(3.74), 4.08(3.51), 495(3.90)
VI	2070, 1955, 1935	1030, 1048	323(3.83), 362(3.87), 470(3.98)
VII	2065, 1950, 1938	1063, 1060w(sh)	273(4.15), 395(3.57), 490(3.95)
VIII	2075, 1960, 1937	1060	294(4.00), 3.76(3.57), 465(3.95)
IX		1020	373(4.21), 400(3.96)[d]
X			289(4.46), 586(4.18)

[a] Cyclohexane solution. [b] KBr disc. [c] Benzene solution. [d] 1,2-$C_2H_4Cl_2$ solution.

ring carbons [5] *. Thus, the infrared and NMR data both imply that V—VIII all have C_{4v} symmetry in solution. No evidence of direct bonding interaction between the metal and the C=C unit was obtained.

The molybdenum compounds IV, VI and VIII were of relatively low stability. Decomposition in cyclohexane was complete after several hours, resulting in the formation of insoluble black solids and molybdenum hexacarbonyl (ν(CO) 1988 cm^{-1}). The mass spectra were not reproducible, indicative of decomposition on heating, and peaks at *m/e* 266 due to $Mo(CO)_6$ were observed. The mass spectra of the more stable chromium complexes displayed, as expected, peaks due to ligand$^+$ and (ligand)$M(CO)_n{}^+$ (n = 0—5) as well as peaks at *m/e* 84 and

TABLE 3

^{1}H AND ^{13}C NMR DATA [a]

Compound	δ ^{1}H (ppm)	δ ^{13}C (ppm)			
		ring carbon	C=S	*cis*-CO	*trans*-CO
I	1.85, 6.43(m)				
II	5.67	129.6	213.3		
III	2.87	43.4	228.5		
IV	1.78, 6.33(m)				
V	5.53	[d]	223.0	215.3	216.8
VI	5.53				
VII	2.33	43.4	231.0	214.8	227.5
VIII	2.37 [b]				
IX [c]	7.8(m, 3H) 5.57(s, 5H), 3.92(s, 3H)				

[a] In benzene-d_6 unless otherwise noted; positive shifts are arbitrarily defined as being downfield of the reference. [b] $CDCl_3$. [c] Acetone-d_6. [d] Obscured by benzene-d_6 signal.

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* Assignment of *cis* and *trans* carbonyl resonances was made on the basis of the observation that, in $LW(CO)_5$ derivatives, their difference in chemical shift is only about 2 ppm unless L is a strong π acceptor, such as a carbene.

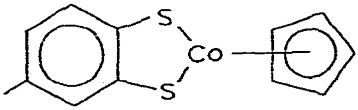
52, attributed to CrS^+ and Cr^+. The observation of a CrS fragment is surely suggestive of strong metal—sulfur bonding.

The mechanism(s) by which substituted pentacarbonyls are formed is not known. It is suggested that an intermediate such as (ligand)—$M(CO)_4$ is initially formed which disproportionates or abstracts a carbonyl group from the (diolefin)$M(CO)_4$ starting materials at a rate faster than which it reacts with additional ligand. Indeed, IV was the only soluble metal carbonyl derivative isolated from the reaction of I with (cycloheptatriene)$Mo(CO)_3$. The presence of such a reactive intermediate is also suggested by the observation that when the reaction of II with $(C_7H_8)Cr(CO)_4$ was carried out under an atmosphere of carbon monoxide, the yield of VII increased from 13 to 51%. Other examples of carbonyl transfer reactions have also been reported [6,7].

The structures of IV—VIII are of interest. The presence of C_{4v} symmetry implies a linear carbon—sulfur—metal bond but in fact, a C—S—M angle less than 180° might be anticipated. For example ∠C—S—Cu in tris(ethylenethiourea)-copper hemisulfate is 104.5° [8] and ∠P—S—Cr in $(CH_3)PSCr(CO)_5$ [9] is 112.5° [10]. However, a linear P—O—Cu bond has been observed in $CuOCl_6[OP(C_2H_5)_3]_4$ [11]. The data may indicate that rehybridization about the exocyclic sulfur has occurred leading to greater *s* character in the metal—sulfur bond and a larger C—S—M bond angle. A less startling explanation is that deviation from C_{4v} does in fact occur but that additional, infrared bands or degeneracies are not detected and that rotation about the Cr—S bond averages the *cis*-carbonyl environments [12]. A similar situation has been encountered with the chromium pentacarbonyl complex of 4,5-tetramethyl-1,3-dioxolan-2-thione which, by infrared and ^{13}C NMR criteria, also has C_{4v} symmetry [13].

The reaction of trithione I with the dimer of (cyclooctadiene)rhodium(I) chloride resulted in the cleavage of the halogen bridge, but not olefin displacement, and the isolation of a 1 : 1 adduct $(C_8H_6S_3)Rh(Cl)(C_8H_{12})$, IX. This material exhibited ν(Rh—Cl) at 280 cm^{-1} [14] and was monomeric in chloroform solution. Consistent with the proposed structure, the ^1H NMR spectrum was a composite of resonances due to the trithione and cyclooctadiene ligands.

Displacement of the chelating diolefin from cyclopentadienyl cobalt cyclooctadiene by I was attempted. However, a more extensive reaction took place, with formal elimination of the thiocarbonyl group to form deep blue X. The ^1H NMR spectrum of this material in acetone-d_6 revealed singlets at δ 5.57 (5H) and 2.25 (3H) ppm and a multiplet at δ 7.9 ppm (3H). These resonances may be assigned to the cyclopentadienyl, methyl, and aromatic protons respectively. The mass spectrum contained a strong parent ion peak as well as a



(X)

peak at *m/e* 244, possibly formed by loss of hydrogen sulfide. The elemental composition of X is further substantiated by the observation of ^{34}S and ^{13}C peaks whose intensities were in good agreement with those calculated from natural isotopic abundances *. Cyclic voltammetry revealed that X underwent a reversible one electron reduction in acetonitrile at E_p −0.61 vs. SCE($E_p - E_{1/2}$ = 0.57 mV). The electrochemical oxidation was characterized by irreversible processes and a stable cobalt(IV) derivative was not isolated. No reaction occurred between benzene solutions of the cobalt heterocycle and oxygen or methyl iodide.

Formation of X may involve methylbenzo-1,2-dithiete or the isomeric *o*-dithioquinone, and Kusters and deMayo [15] have shown that ultraviolet irradiation of diphenylvinylene dithiocarbonate in the presence of $Mo(CO)_6$ or $Ni(CO)_4$ led to the formation, presumably by trapping of a highly reactive dithiete, of metal dithiolene complexes.

Experimental **

Unless otherwise indicated, all reactions were carried out under a nitrogen atmosphere. Reagent grade thiophene-free benzene was used as received. Metal carbonyls were commercial materials. ^1H and ^{13}C NMR spectra were obtained at 60 and 22.6 MHz and are referenced to internal tetramethylsilane. Infrared spectra were recorded on a Perkin—Elmer 457 grating spectrometer which was calibrated with polystyrene. Melting points were obtained in evacuated, sealed capillaries. Elemental analyses were carried out by Schwarzkopf Laboratories, Woodside, N.Y. Vinylene trithiocarbonate [16] and commercial ethylene trithiocarbonate were purified by sublimation. 5-Methylbenzo-1,3-dithiol-2-thione was prepared from 3,4-toluene dithiol by the method of Klingsberg [17] and recrystallized from hexane, m.p. 84.5—86°C.

Reaction of ethylene trithiocarbonate (III) with bicyclo[2.2.1]heptadienechromium tetracarbonyl

A solution of 0.4 gm of II (3 mmol). 0.76 gm of the diene complex (3 mmol) and 15 ml benzene was stirred for 3 h at room temperature, then evaporated to dryness under reduced pressure. The residue was extracted with six 30 ml portions of hot hexane. The filtered extracts were concentrated to ca. 10 ml on a rotary evaporator. Cooling to −78°C and filtration afforded a crude product which was heated at 45°C/10^{-3} mmHg in a sublimer fitted with a −78°C cold finger to remove any remaining, volatile III. An additional recrystallization from hexane gave 0.13 gm (13% based on Cr) of VII as scarlet flakes. Mass spectrum (*m/e*, assignment, relative abundance): 328 (M^+, 30), 300 ($M^+ - CO$, 2), 272 ($M^+ - 2CO$, 6), 244 ($M^+ - 3CO$, 55), 216 ($M^+ - 4CO$, 40), 188 ($M^+ - 5CO$, 100), 160(34), 136($C_3H_4S_3^+$, 57), 84(CrS^+, 43), 76(CS_2^+, 21), 52(Cr^+, 47). A similar reaction, run under an atmosphere of carbon monoxide, gave a 51% yield of VII.

The chromium complex V was similarly prepared under CO in 48% yield starting with vinylene trithiocarbonate, II. Mass spectrum: 326(M^+, 35), 298

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* The presence of ^{33}S 0.75% abundance, has been ignored.

** Certain commercial equipment, instruments, materials or services are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is neccessarily the best available for the purpose.

($M^+ - CO$, 6), 260 ($M^+ - 2CO$, 10), 242 ($M^+ - 3CO$, 13), 214 ($M^+ - 4CO$, 29), 186 ($M^+ - 5CO$, 69), 158(6), 134 ($C_3H_2S_3^+$, 100), 110 (21), 118(17), 84 (CrS^+, 25), 76 (CS_2^+, 31), 58 ($C_2H_2S^+$, 77), 52 (Cr^+ 94). The molybdenum complexes IV, VI and VII were prepared and purified in an analogous manner except that the sublimation step was omitted in the case of VII.

Reaction of cyclooctadienerhodium chloride dimer with I

A mixture of 0.24 gm of the rhodium complex (0.5 mmol), 0.4 gm (2 mmol) I and 25 ml benzene was stirred at room temperature for 16 h, then filtered. The solid phase was washed with dichloromethane. The filtrate and washings were evaporated to dryness in vacuo. The residue was washed with acetone, then ethanol and crystallized by slow evaporation of an acetone/dichloromethane solution. The yield of small orange plates was 0.05 gm (11%). ^1H NMR ($CDCl_3$): δ 7.45 (m, 3H), 4.36 (br, s, 4H), 2.45(s), 1.82(d) ppm. The methyl singlet overlapped a broad resonance at $\sim\delta$ 2.5 ppm. The ^1H spectrum of cyclooctadienerhodium chloride dimer (C_6D_6) shows resonances at δ 4.25 (unresolved singlet) and $\sim\delta$ 2.2 ppm (br, q) [18].

Reaction of I with cyclopentadienylcobalt cyclooctadiene

A solution of 0.39 gm I (2 mmol) and 0.48 gm cyclopentadienylcobalt cyclooctadiene in 20 ml toluene was refluxed for 36 h. The reaction mixture was filtered and chromatographed on a 9" × 1" column of neutral alumina. Benzene/cyclohexane 1 : 1, eluted a small amount of I. The blue product was eluted with 2 : 1 benzene/cyclohexane. Slow removal of the benzene caused the separation of 0.27 gm (50%) of X as deep blue microcrystals. Mass spectrum: 280($^{12}C_{12}{}^1H_{11}{}^{59}Co^{34}S^{32}S$, 9 calcd.: 8.4), 279($^{13}C^{12}C_{11}{}^1H_{11}{}^{59}Co^{32}S_2^+$, 14, calcd.: 13.2), 278(M^+, 100), 246 ($^{12}C_{12}{}^1H_{11}{}^{59}Co^{34}S^+$, 4, calcd.: 4.2), 245 ($^{13}C^{12}C_{11}{}^1H_{11}{}^{59}Co^{32}S$, 16, calcd.: 13.2), 244($M - H_2S^+$, 37), 185.

References

1 A.R. Siedle, Inorg. Nucl. Chem. Lett., 11 (1975) 345.
2 E. Campaigne, Chem. Rev., 39 (1946) 1.
3 J.A. Gladysz and R.W. Avakian, Syn. React. Inorg. Metal-Org. Chem., 5 (1975) 247.
4 G.R. Dobson, M.F. ElSayed, I.W. Staltz and R.K. Sheline, Inorg. Chem., 1 (1962) 526.
5 B.E. Mann, Adv. Organomet. Chem., 1[illegible] (1974) 135.
6 B.L. Booth, M.J. Else, R. Fields, and R.N. Hazeldine, J. Organometal. Chem., 14 (1968) 417.
7 J.J. Alexander and A. Wojcicki, Inorg. Chem., 12 (1973) 74.
8 M.S. Weiniger, B.W. Hunt and E.L. Amma, J. Chem. Soc. Chem. Commun., (1972) 1140.
9 E.W. Ainschough, A.M. Brodie and A.R. Furness, J. Chem. Soc. Chem. Commun., (1971) 1357.
10 E.N. Baker and B.R. Reay, J. Chem. Soc. Dalton Trans., (1973) 2205.
11 M.R. Churchill, B.G. DeBoer and S.J. Mendak, Inorg. Chem., 14 (1975) 2496.
12 F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
13 J. Daub and J. Kappler, J. Organometal. Chem., 80 (1974) C5.
14 M.A. Bennett, R.J.H. Clark and D.L. Milner, Inorg. Chem., 6 (1967) 1647.
15 W. Kusters and P. de Mayo, J. Amer. Chem. Soc., 96 (1974) 4502.
16 L.R. Melby, H.D. Hartzler and W.A. Sheppard, J. Org. Chem., 39 (1974) 2456.
17 E. Klingsberg, Synthesis, (1972) 29.
18 R.B. King, Organometallic Syntheses, Academic Press, New York, 1965, p. 132.