Trithiocarbonate and Dithiocarbonate Complexes of η-Cyclopentadienylcobalt(III): *X*-Ray Crystal Structure of $[Co(\eta\text{-}C_5H_5)(CNBu^t)(CS_3)]$ †

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Complexes $[Co(\eta\text{-}C_5H_5)L(CS_3)]$ have been prepared (*a*) by the thermal reaction of CS_2 with $[Co(\eta\text{-}C_5H_5)(CO)L]$, or $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and L (L = tertiary phosphine or organoisocyanide only), or (*b*) from $[Co(\eta\text{-}C_5H_5)(L)I_2]$ and $Na_2[CS_3]$ in dichloromethane solution (L = tertiary phosphine, phosphite, arsine, or organoisocyanide). A variant of (*b*), the reaction of $Na[S_2COR]$ (R = Me or Et) with $[Co(\eta\text{-}C_5H_5)(L)I_2]$, has been used to prepare the dithiocarbonate complexes $[Co(\eta\text{-}C_5H_5)(L)(CS_2O)]$. The i.r. and ^1H n.m.r. spectra of the complexes have been measured and are assigned. They are consistent with molecular structures in which the CS_2Y^{2-} ions (Y = O or S) chelate to cobalt *via* the two S atoms; this has been confirmed unambiguously for $[Co(\eta\text{-}C_5H_5)(CNBu^t)(CS_3)]$ by an *X*-ray diffraction study which shows that the co-ordination about Co is of the well known pseudo-octahedral, 'piano-stool' type. The structure was solved by the heavy-atom method and refined by least squares to $R = 0.074$ for 1 593 non-zero unique reflections. Crystals of the compound are monoclinic, space group $P2_1/c$, with $a = 9.085(4)$, $b = 12.386(5)$, $c = 12.997(5)$ Å, and $\beta = 107.7(1)°$ for $Z = 4$. The unco-ordinated S_u atoms of the CS_3 ligands are very basic and with electrophiles, E, form adducts containing $S_u \rightarrow E$ bonds; MeI gives $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(S_2CS_uMe)]I$ and $[Co(\eta\text{-}C_5H_5)I(S_2CS_uMe)]$, mercury(II) halides form $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(S_2CS_u{\cdot}nHgX_2)]$ (X = Cl, n = 2; X = Br or I, n = 1), and I_2 gives $[Co(\eta\text{-}C_5H_5)(PPr^n_3)(S_2CS_uI)]I$. The $\nu(C-S_u)$ vibrations of these adducts have lower frequencies, and their $\nu(C-S_c)$ vibrations (S_c is the co-ordinated S atom) have higher frequencies, than do their trithiocarbonate precursors. The dithiocarbonate complexes also form adducts with electrophiles but the unco-ordinated O atom, O_u, is only weakly basic. Consequently MeI fails but $MeSO_3F$ is successful in forming the xanthate cation $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(S_2CO_uMe)]^+$, and although $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(S_2CO_u{\cdot}2HgX_2)]$ are obtained, their i.r. spectra give no clear guide as to their structure. With iodine, $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)I_2]$ is formed. The bonding between the cobalt atoms and the CS_2Y^{2-} ligands is discussed on the basis of the i.r. spectra of the complexes where Y = S, O, SMe^+, or OMe^+.

Previously we have reported that the thermal reaction of carbon disulphide with $[Co(\eta\text{-}C_5H_5)(CO)L]$, or $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and L (L = tertiary phosphine or organoisocyanide), gives four major series of products.[1,2] Three of them have been described in detail elsewhere:[2] $[Co(\eta\text{-}C_5H_5)L(\eta^2\text{-}CS_2)]$, $[Co(\eta\text{-}C_5H_5)L(CS)]$, and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$. Here we describe the fourth series of compounds $[Co(\eta\text{-}C_5H_5)L(CS_3)]$, a more convenient and generally applicable way to prepare them, some of their properties, and the structure of one member as determined by an *X*-ray diffraction study. We also describe some related dithiocarbonate complexes of the general type $[Co(\eta\text{-}C_5H_5)L(CS_2O)]$ which we compare and contrast with their trithiocarbonate counterparts.

Both the CS_3^{2-} and CS_2O^{2-} ions act as 1,1′-dithiolate ligands. Their complexes have been reviewed recently.[3,4] Relatively few dithiocarbonate derivatives have been prepared since they were first isolated by Fackler and Seidel.[5] However, with respect to the trithiocarbonate compounds and their preparation from η^2-CS_2 derivatives, results have been published which are directly relevant to ours. It has been shown that although the major product of the reaction of CS_2 with $[Rh(\eta\text{-}C_5H_5)(PPh_3)_2]$ is $[Rh(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$, the complex $[Rh(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ is obtained as a side-product. On the basis of its i.r. spectrum, it has been suggested that it contains the $S^1\text{-}S^2\text{-}C{=}S$ ligand bonded to Rh through C and S^1.[6] Our results suggest that this is probably incorrect.

Experimental

Previously published methods were used to prepare $[Co(\eta\text{-}C_5H_5)(CO)_2]$,[7] $[Co(\eta\text{-}C_5H_5)(CO)L]$ (L = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, $PMePh_2$, PPh_3, $CNBu^t$, or CNC_6H_{11}),[8,9] $[Co(\eta\text{-}C_5H_5)(CO)I_2]$,[8] $[Co(\eta\text{-}C_5H_5)(L')I_2]$ [L′ = L, $P(OPh)_3$, $PPh(OPr^i)_2$, $AsMe_2Ph$, or $CNCH_2Ph$],[8] tertiary phosphines,[10] tertiary arsines,[11] organoisocyanides,[12] $Na[S_2COR]$ and $K[S_2COR]$ (R = Me or Et),[13] and $Na_2[CS_3]$.[14] Other chemicals were purchased.

Unless stated otherwise, all reactions were carried out at room temperature under an atmosphere of nitrogen. Benzene, toluene, hexane, dichloromethane, and tetrahydrofuran were dried by refluxing over calcium hydride under nitrogen and distilled prior to use. Tetrahydrofuran was further purified by distilling from sodium and benzophenone.

Infrared spectra were measured on a Perkin-Elmer 283B spectrometer in the range 250—4 000 cm⁻¹ and calibrated with polystyrene. ^1H N.m.r. spectra were obtained on a Perkin-Elmer R12B spectrometer using $CDCl_3$ or $(CD_3)_2CO$ solutions with $SiMe_4$ as internal standard. Mass spectra were measured on a VG 70/70 M mass spectrometer. They generally showed only fragment ions due to L so they will not be mentioned again.

Analyses were carried out in the Analytical Laboratory of University College, Dublin.

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† (η^5-Cyclopentadienyl)(t-butyl isocyanide)(trithiocarbonato-*SS′*)-cobalt(III).

Supplementary data available (No. SUP 23875, 12 pp.): structure factors, anisotropic thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Melting points, analyses, and spectra of some $[Co(\eta\text{-}C_5H_5)L(CS_3)]$ complexes and their derivatives

Compound	M.p.[a]/°C	Analysis [b] (%) C	H	S	I.r. spectra [c] (cm^{-1}) ν(Co–S)	ν(C–S)	ν(C=S)	^1H N.m.r. spectra [d] ($\eta\text{-}C_5H_5$)
$[Co(\eta\text{-}C_5H_5)(PEt_3)(CS_3)]\cdot CH_2Cl_2$	192	33.4(33.1)	4.8(5.0)	22.2(22.1)	324w	858m	1 030s	5.25
$[Co(\eta\text{-}C_5H_5)(PPr^n_3)(CS_3)]\cdot 0.5C_7H_8$	176	51.2(50.7)	7.4(7.0)	21.2(21.9)	318w	858m	1 038s	5.20
$[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3)]$	150	49.7(49.7)	7.5(7.5)	21.7(22.1)	320w	860m	1 035s	5.18
$[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(CS_3)]$	175	45.1(45.4)	4.3(4.3)	25.6(25.9)	n.d.	864m	1 033s	4.96
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_3)]$	186	52.7(52.7)	4.0(4.1)	21.9(22.2)	293w	866m	1 037s	5.10
$[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$	179	57.9(58.3)	4.2(4.0)	19.0(19.4)	n.d.	867m	1 038s	5.00
$[Co(\eta\text{-}C_5H_5)\{PPh(OPh)_2\}(CS_3)]$	181	54.6(54.7)	3.5(3.8)	18.7(18.3)	n.d.	855m	1 044s	4.91
$[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(CS_3)]$	161	53.7(53.1)	3.5(3.7)	17.5(17.7)	323w	n.d.	1 048s	4.77
$[Co(\eta\text{-}C_5H_5)(AsMe_2Ph)(CS_3)]$	135	40.7(40.6)	3.5(3.8)	23.0(23.2)	n.d.	n.d.	1 015s	5.00
$[Co(\eta\text{-}C_5H_5)(CNBu^t)(CS_3)]$ [e]	164	41.8(41.9)	4.4(4.4)	28.0(30.5)	n.d.	869m	1 035s	5.27
$[Co(\eta\text{-}C_5H_5)(CNC_6H_{11})(CS_3)]$ [f]	140	45.7(45.7)	5.2(4.7)		320w	873m	1 038s	5.38
$[Co(\eta\text{-}C_5H_5)(CNCH_2Ph)(CS_3)]$ [g]	156	48.6(48.1)	3.4(3.4)	27.0(27.5)	n.d.	874m	1 028s	4.95
$[Co(\eta\text{-}C_5H_5)(PBu^n_3)(S_2CSMe)]I$ [h]	111	39.2(39.5)	5.8(6.0)	16.5(16.6)	n.d.	926m	988s	5.10
$[Co(\eta\text{-}C_5H_5)I(S_2CSMe)]$ [i]	125	22.3(22.4)	2.1(2.1)	25.8(25.6)	n.d.	n.d.	988s	5.36
$[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3\cdot 2HgCl_2)]$ [j]	65	22.1(22.1)	3.3(3.2)	9.4(9.8)	n.d.	940m	992s	5.13
$[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3\cdot HgBr_2)]$ [k]	135	26.8(27.2)	4.1(4.0)	11.6(12.0)	n.d.	934m	992s	5.02
$[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3\cdot HgI_2)]$ [l]	140	24.0(24.3)	3.7(3.6)	10.7(10.8)	n.d.	n.d.	990s	5.01
$[Co(\eta\text{-}C_5H_5)(PPr^n_3)(S_2CSI)]I$ [m]	121	27.5(27.8)	3.9(4.0)	15.0(14.8)	n.d.	931m	981s	5.35

[a] With decomposition. [b] Calculated values in parentheses. [c] Measured in CsBr pressed discs; n.d. = not detected; for assignment see text. [d] δ/p.p.m. downfield from $SiMe_4$ in $CDCl_3$ solution. Only C_5H_5 resonances given (see text). [e] %N = 4.3(4.4). [f] %N = 4.1(4.7). [g] %N = 3.7(4.0). [h] %I = 22.6(22.0). [i] %I = 32.9(33.9). [j] %Cl = 14.9(14.5). [k] %Br = 19.8(20.4). [l] %I = 27.9(28.6). [m] %I = 37.6(39.3).

Preparation of Complexes $[Co(\eta\text{-}C_5H_5)L(CS_3)]$.—*Method* (*a*). A mixture of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (2 cm^3) and PPh_3 (4 g) in boiling benzene (80 cm^3) was heated for 24 h to give $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$. Carbon disulphide (30 cm^3) was added to the mixture and heating continued for a further 36 h. The solvent was then removed at reduced pressure. The residue was redissolved in benzene and chromatographed on an alumina column using benzene as eluant. The $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ remained at the top of the column and was eluted with dichloromethane. Partial removal of the solvent, the addition of an equal volume of hexane (3 cm^3), and cooling to −30 °C gave red crystals of $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ in *ca.* 17% yield. This method was used to prepare other complexes where L = PEt_3, PPr^n_3, PBu^n_3, PMe_2Ph, $PMePh_2$, PPh_3, $CNBu^t$, or CNC_6H_{11}.

Method (*b*). To a solution of $[Co(\eta\text{-}C_5H_5)(PPh_3)I_2]$ (1 g) in dichloromethane (30 cm^3) was added slightly more than an equimolar amount of $Na_2[CS_3]$. NaI precipitated and was filtered off. The fitrate was concentrated to *ca.* 10 cm^3 at reduced pressure, an equal volume of hexane added if necessary, and the whole cooled to −30 °C. Red crystals of $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ precipitated and were filtered off (yield >80%).

The same method was used to prepare all the $[Co(\eta\text{-}C_5H_5)L(CS_3)]$ complexes listed in Table 1.

Preparation of Complexes $[Co(\eta\text{-}C_5H_5)L(CS_2O)]$.—*Method* (*b*). A solution of the complex $[Co(\eta\text{-}C_5H_5)(L)I_2]$ [2 mmol; L = PPh_3, $PMePh_2$, PMe_2Ph, $PPh_2(C_6H_{11})$, PBu^n_3, $P(OPh)_3$, or $PPh(OPr^i)_2$] in dichloromethane (25 cm^3) was added to one of $Na[S_2COR]$ or $K[S_2COR]$ (2 mmol) in ROH (25 cm^3; R = Me or Et) prepared *in situ*. The mixtures were stirred for 30 min during which time their colour changed from green to red. They were then filtered and the solvents removed at reduced pressure. The residues were chromatographed (alumina column, CH_2Cl_2–EtOH). The solvents were removed from the red bands and the residues recrystallized from dichloromethane–ethanol (60 : 40) mixtures to give red crystals of the $[Co(\eta\text{-}C_5H_5)L(CS_2O)]$ derivatives listed in Table 2. Reaction yields varied from 70% when L = PBu^n_3 to 95% when L = $PMePh_2$.

Reaction of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3)]$ *with* MeI.—Methyl iodide (0.1 cm^3) was added to a solution of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3)]$ (0.5 g) in tetrahydrofuran (30 cm^3). After 24 h the solvent was removed at reduced pressure. The residue was extracted with toluene to give a green solution to which was added an equal volume of hexane. On cooling this, green crystals of $[Co(\eta\text{-}C_5H_5)I(S_2CSMe)]$ were obtained (yield 15%). The toluene-insoluble fraction was recrystallized from dichloromethane–hexane mixtures to give red crystals of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(S_2CSMe)]I$ (yield 50%).

Reaction of $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(CS_2O)]$ *with* $MeSO_3F$ *and Alkyl Halides.*—A solution of $[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(CS_2O)]$ (2 mmol) and $MeSO_3F$ (*ca.* 2 mmol) in dichloromethane (50 cm^3) was stirred for 20 min. The solvent was removed at reduced pressure and the residue recrystallized from dichloromethane to give $[Co(\eta\text{-}C_5H_5)(PMePh_2)(S_2COMe)]SO_3F\cdot 2.5H_2O$ in 80% yield.

If $MeSO_3F$ is replaced by MeI, $PhCH_2Br$, or $BrCH_2CH_2Br$, no reaction takes place even after three days.

Reactions of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3)]$ *and* $[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O)]$ *with* HgX_2 (X = Cl, Br, *or* I).—To a solution of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3)]$ (0.42 g) in benzene (50 cm^3) was added $HgCl_2$ (0.26 g) dissolved in acetone (30 cm^3). A dark red precipitate of $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3\cdot 2HgCl_2)]$ was obtained and isolated without further purification (yield 30%). $[Co(\eta\text{-}C_5H_5)(PBu^n_3)(CS_3\cdot HgX_2)]$ (X = Br or I) were obtained similarly.

Similar reactions between HgX_2 (4 mmol; X = Cl or Br) in diethyl ether (10 cm^3) and $[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O)]$ gave $[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O\cdot 2HgX_2)]\cdot 0.5Et_2O$ (yields 90%).

Reactions of $[Co(\eta\text{-}C_5H_5)(PPr^n_3)(CS_3)]$ *and* $[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O)]$ *with* I_2.—A benzene solution of I_2 (0.13 g in 25 cm^3) was added rapidly to one of $[Co(\eta\text{-}C_5H_5)(PPr^n_3)(CS_3)]$ (0.2 g in 30 cm^3). $[Co(\eta\text{-}C_5H_5)(PPr^n_3)(S_2CSI)]I$ precipitated as a fine red powder which was filtered off and washed with benzene but not purified further (yield 54%).

When a solution of I_2 (2 mmol) in dichloromethane (20

Table 2. Melting points, analyses, and spectra of $[Co(\eta\text{-}C_5H_5)L(CS_2O)]$ complexes and their adducts

Compound	M.p./°C	Analysis [a] (%)		I.r. spectra [b]/cm^{-1}				^1H N.m.r. spectra [c] $(\eta\text{-}C_5H_5)$
		C	H	ν(Co–S)	ν(C–S)	ν(C=O)		
$[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_2O)]\cdot 0.5CH_2Cl_2$	121—122	56.4(56.5)	4.1(4.3)	361w	830m	1 600vs	1 682s	5.07
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O)]$	138—140	54.5(54.8)	4.4(4.3)	340w	841m	1 597vs	1 690s	5.04
$[Co(\eta\text{-}C_5H_5)\{PPh_2(C_6H_{11})\}(CS_2O)]\cdot 0.25CH_2Cl_2$	142—144	57.7(57.6)	5.3(5.2)	352w	839m	1 589vs	1 693s	4.62
$[Co(\eta\text{-}C_5H_5)(PMe_2Ph)(CS_2O)]\cdot CH_2Cl_2$	141—143	45.1(45.0)	4.1(4.4)	314w	853m	1 590vs	1 700s	5.03
$[Co(\eta\text{-}C_5H_5)(PBu^n{}_3)(CS_2O)]$	120—121	51.4(51.7)	7.5(7.7)	362w	840m	1 580vs	1 709s	5.15
$[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(CS_2O)]$	142—143	54.7(54.8)	3.5(3.8)	353w	835m	1 601vs	1 690s	4.85
$[Co(\eta\text{-}C_5H_5)\{PPh(OPr^i)_2\}(CS_2O)]$	139—140	48.5(48.9)	5.6(5.4)	350w	845m	1 602vs	1 690s	5.05
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(S_2COMe)]SO_3F\cdot 2.5H_2O$	>150	41.9(41.7)	4.1(4.5)	n.d.	845m	1 585s	1 645s	
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O\cdot 2HgCl_2)]\cdot 0.5Et_2O$	>150	25.0(25.3)	2.6(2.3)	332w	840m	1 615s		
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O\cdot 2HgBr_2)]\cdot 0.5Et_2O$	>150	21.0(21.5)	2.1(2.0)	349w	838m	1 613s		

[a] Calculated values in parentheses. [b] Determined as CsBr pressed discs; n.d. = not detected; for assignments see text. [c] δ/p.p.m. downfield from $SiMe_4$ in $CDCl_3$ solution. Only C_5H_5 resonances are given (see text).

cm^3) was added dropwise over a period of 10 min to one of $[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS_2O)]$ (2 mmol) in dichloromethane (20 cm^3), the colour changed from red to green. Removal of the solvent gave a virtually quantitative yield of $[Co(\eta\text{-}C_5H_5)(PMePh_2)I_2]$ which was identified by analysis and spectroscopy.

The melting/decomposition points, analyses, and ^1H n.m.r. and i.r. spectra of the complexes are summarised in Tables 1 and 2.

X-Ray Crystal Structure Determination of $[Co(\eta\text{-}C_5H_5)(CNBu^t)(CS_3)]$.—*Crystal data*. $C_{11}H_{14}CoNS_3$, $M = 315.4$, monoclinic, $a = 9.085(4)$, $b = 12.386(5)$, $c = 12.997(5)$ Å, $\beta = 107.7(1)°$, $U = 1\,393.3$ Å^3, $Z = 4$, $D_c = 1.503$ g cm^{-3}, $F(000) = 648$, $\mu(\text{Mo-}K_\alpha) = 16.8$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å. Systematic absences $0k0$ if $k \neq 2n$ and $h0l$ if $l \neq 2n$, space group $P2_1/c$ (no. 14).

Cell parameters were determined from precession photographs using Mo-K_α radiation. Intensities were estimated visually from precession photographs for the layers 0—3kl and h 0–4 l. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation and 1 593 non-zero unique reflections were obtained. Neutral-atom scattering factors were taken from ref. 15, and were not corrected for anomalous dispersion. All calculations were carried out on a UNIVAC 1106 computer with programs written by F. S. S.

Structure determination. The structure was solved by the heavy-atom method. Refinement was by full-matrix least-squares procedures in which $\Sigma w\Delta^2$ was minimised. The weight w for each reflection was initially unity and in the final cycles given by $w = (3.0 + 0.5|F_o| - 0.001|F_o|^2)^{-1}$, a scheme chosen such that the average values for $w\Delta^2$ for ranges of increasing $|F_o|$ were almost constant. At the completion of the isotropic refinement a difference map was calculated which yielded the approximate positions of all hydrogen atoms. These positions were optimised and C–H assumed to be 1 Å. The contributions of these hydrogen atoms were included in subsequent calculations, but their parameters were not refined. The anisotropic refinement was terminated when the maximum shift in any parameter was $<0.05\ \sigma$. The final value for R was 0.074 and $R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$ was 0.098. A final difference map showed no features $>|0.7|$e Å^{-3}. The molecular structure and atom labelling are shown in Figure 1. Final atomic co-ordinates are given in Table 3, bond distances and angles in Table 4, and least-squares planes in Table 5.

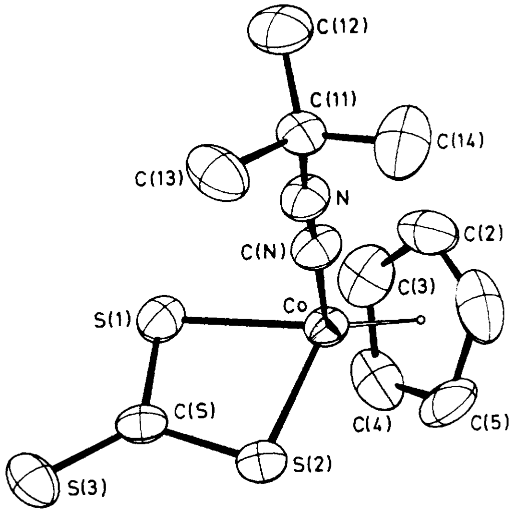

Figure 1. Perspective drawing of the $[Co(\eta\text{-}C_5H_5)(CNBu^t)(CS_3)]$ molecule showing the atom-labelling scheme. Thermal ellipsoids are drawn to include 35% probability

Results and Discussion

The reactions of CS_2 with $[Co(\eta\text{-}C_5H_5)(CO)L]$, or $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and L (L = tertiary phosphine or organoisocyanide), on heating in solution usually gives four series of products, $[Co(\eta\text{-}C_5H_5)L(\eta^2\text{-}CS_2)]$, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$, $[Co(\eta\text{-}C_5H_5)L(CS)]$, and $[Co(\eta\text{-}C_5H_5)L(CS_3)]$. The last two are obtained from $[Co(\eta\text{-}C_5H_5)L(\eta^2\text{-}CS_2)]$ by its reaction with free or complexed CS_2.[2] The reaction times required for the consumption of $[Co(\eta\text{-}C_5H_5)(CO)L]$ in refluxing benzene vary from 5—6 h when L is a trialkylphosphine to 26 h when it is PMe_2Ph or $PMePh_2$, and 36 h when it is PPh_3, whilst 10 h suffice when L = CNC_6H_{11} or $CNBu^t$.

Apart from these long reaction times, this method of preparing $[Co(\eta\text{-}C_5H_5)L(CS_3)]$ complexes [Method (*a*)] has many other disadvantages. Product purification is tedious, yields are low (10—17%), and the reaction does not take place when

Table 3. Final atomic co-ordinates (fractional × 10^4) with estimated standard deviations given in parentheses

Atom	*x*	*y*	*z*
Co	3 303(1)	1 418(1)	1 983(1)
C(N)	4 978(10)	1 501(9)	3 190(6)
N	6 038(8)	1 600(7)	3 956(6)
C(11)	7 390(9)	1 620(9)	4 908(7)
C(12)	8 743(13)	1 812(13)	4 527(10)
C(13)	7 165(15)	2 528(12)	5 631(10)
C(14)	7 455(17)	541(12)	5 458(10)
S(1)	3 324(3)	3 181(2)	1 619(2)
S(2)	1 724(3)	2 152(3)	2 834(2)
S(3)	1 486(4)	4 590(3)	2 671(2)
C(S)	2 140(9)	3 412(9)	2 396(6)
C(1)	3 434(20)	−225(11)	1 769(11)
C(2)	4 281(13)	298(13)	1 200(10)
C(3)	3 353(17)	972(11)	450(8)
C(4)	1 871(14)	889(11)	537(9)
C(5)	1 860(15)	1 363(13)	1 346(12)

Table 4. Bond distances (Å) and angles (°) with estimated standard deviations given in parentheses *

Co–S(1)	2.235(3)	Co–C(N)	1.827(8)
Co–S(2)	2.252(3)	C(N)–N	1.161(10)
Co–cp	1.690	N–C(11)	1.455(9)
Co–C(1)	2.063(13)	C(11)–C(12)	1.477(15)
Co–C(2)	2.074(12)	C(11)–C(13)	1.518(16)
Co–C(3)	2.082(10)	C(11)–C(14)	1.508(16)
Co–C(4)	2.041(9)	C(1)–C(2)	1.379(20)
Co–C(5)	2.065(12)	C(2)–C(3)	1.363(18)
C(S)–S(1)	1.709(9)	C(3)–C(4)	1.389(18)
C(S)–S(2)	1.742(10)	C(4)–C(5)	1.407(20)
C(S)–S(3)	1.654(10)	C(5)–C(1)	1.439(20)
S(1)–Co–S(2)	76.0(1)	cp–Co–C(N)	125.2
S(1)–Co–C(N)	93.9(4)	cp–Co–S(1)	125.5
S(2)–Co–C(N)	92.5(3)	cp–Co–S(2)	129.7
Co–S(1)–C(S)	89.5(4)	Co–C(N)–N	177.2(10)
Co–S(2)–C(S)	88.1(3)	C(N)–N–C(11)	174.8(11)
S(1)–C(S)–S(2)	106.3(6)	N–C(11)–C(12)	106.9(8)
S(1)–C(S)–S(3)	127.4(6)	N–C(11)–C(13)	107.5(8)
S(2)–C(S)–S(3)	126.3(5)	N–C(11)–C(14)	106.9(8)
C(5)–C(1)–C(2)	107.5(12)	C(12)–C(11)–C(13)	111.8(11)
C(1)–C(2)–C(3)	110.3(11)	C(12)–C(11)–C(14)	112.7(11)
C(2)–C(3)–C(4)	107.5(12)	C(13)–C(11)–C(14)	110.9(11)
C(3)–C(4)–C(5)	109.7(11)	C(4)–C(5)–C(1)	105.1(12)

* cp is the centroid of the cyclopentadienyl ring.

L is a triorgano-phosphite, -arsine, or -stibine. Consequently we have also prepared the complexes listed in Table 1 (and many others) by the reactions of $[Co(\eta-C_5H_5)(L)I_2]$ with freshly prepared $Na_2[CS_3]$ in dichloromethane at room temperature [Method (*b*)]. Here the yields are high (80—90%), the reaction is fast and product purification is straightforward. The nature of any complex is independent of its mode of preparation.

A modification of Method (*b*) is used to prepare the $[Co(\eta-C_5H_5)L(CS_2O)]$ derivatives listed in Table 2 from $[Co(\eta-C_5H_5)(L)I_2]$ and the xanthate salts $Na[S_2COR]$ or $K[S_2COR]$ (R = Me or Et) which had previously been prepared *in situ* (for example from NaOR and CS_2). It is probable that the initial products are the xanthate derivatives $[Co(\eta-C_5H_5)L(S_2COR)]I$ which are very susceptible to nucleophilic attack by I^- at R which results in loss of RI (see below). A similar reaction pathway has been proposed by Cole-Hamilton and Stephenson [16] for related reactions of *mer*-$[Rh(PMe_2Ph)_3Cl_3]$.

Table 5. Least-squares planes and their equations given by $lX' + mY' + nZ' - p = 0$ where X', Y', Z' are orthogonal co-ordinates related to the atomic co-ordinates X, Y, and Z by $X' = X\sin\beta$, $Y' = Y$, $Z' = Z + X\cos\beta$. Deviations (Å) of the most relevant atoms from the planes are given in square brackets and cp is the centroid of the cyclopentadienyl ring

	l	*m*	*n*	*p*
Plane 1: C(S), S(1)—S(3)	0.7970	0.0833	0.5982	3.3319
[C(S) 0.006; S(1), S(2), S(3) −0.002; Co 0.09]				
Plane 2: C(1)—C(5)	0.1960	0.7393	0.6443	1.2425
[C(1) 0.004; C(2) <|0.001|; C(3) −0.004; C(4) 0.006; C(5) −0.006; Co 1.69]				
Plane 3: Co, S(1), S(2)	0.7788	0.1283	0.6141	3.4739
[C(S) 0.06; S(3) 0.14]				
Plane 4: cp, Co, C(N)	0.5005	0.5051	−0.7031	1.1471
[N 0.03; C(11) 0.02]				

Dihedral angles (°) between planes: 1—3 2.9; 2—3 50.0; 4—2 88.9; 4—3 88.7.

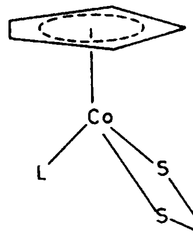

Figure 2. Schematic representation of the structures of $[Co(\eta-C_5H_5)L(CS_2Y)]$ molecules

The $[Co(\eta-C_5H_5)L(CS_3)]$ complexes and their dithiocarbonate counterparts are dark red, air-stable crystalline solids which are soluble in organic solvents. Their solutions in nitromethane do not conduct electricity.

Spectra, Structure, and Bonding.—The i.r. spectra of the $[Co(\eta-C_5H_5)L(CS_2Y)]$ complexes (Y = O or S) are independent of their mode of preparation when Y = S and are consistent with the structures illustrated in Figure 2. These are based on structures found by *X*-ray diffraction studies for $[Co(\eta-C_5H_5)(CNBu^t)(CS_3)]$ (see below) and $[Co(\eta-C_5H_4Me)(PBu^n_3)(CS_3)]$,[17] and various dithiocarbonate complexes such as $K[Rh(PMe_2Ph)_2(CS_2O)_2]\cdot3H_2O$.[18] The bidentate CS_2Y^{2-} ligands chelate through their S atoms to the metal whilst Y are not co-ordinated.

It is useful to compare the i.r. spectra of $[Co(\eta-C_5H_5)L(CS_2Y)]$ with those of their $[Co(\eta-C_5H_5)(L)I_2]$ counterparts. Unfortunately not all absorption bands due to the vibrations of the $Co(CS_2Y)$ moieties could be identified unambiguously as some are apparently weak and obscured by bands due to C_5H_5 and L. However when Y = S we were able to identify (*i*) in all spectra a strong and often broad absorption band at 1 015—1 048 cm^{-1}, (*ii*) in most spectra a medium intensity band at 855—874 cm^{-1}, and (*iii*) tentatively and in only a few spectra, a very weak band at 293—324 cm^{-1}. These are listed in Table 1. When Y = O we were able to identify (*iv*) two intense absorption bands at *ca.* 1 600 cm^{-1}, (*v*) a medium intensity band at 830—853 cm^{-1}, and (*vi*) a weak absorption band at 314—362 cm^{-1}. These are listed in Table 2. It is clear that (*i*) are due to $\nu(C{-}S_u)$ and (*iv*) to $\nu(C{-}O_u)$ vibrations. There are always two of the latter although only

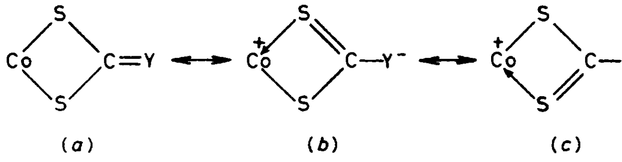

Figure 3. Resonance structures of the $Co(CS_2Y)$ moieties

one would be expected. The same phenomenon has been observed in the spectra of other dithiocarbonate complexes.[19,20] It has been suggested [20] that the weaker and higher frequency member of the pair is due primarily to the first overtone of a $\nu(C-S_c)$ vibration of the CS_2O ligand which gains intensity by Fermi resonance with the fundamental $\nu(C-O_u)$ mode of the same symmetry. This last mode is primarily responsible for the stronger and lower frequency absorption band which thus has a lower frequency than it would if there were no Fermi resonance. By reference to the work of others [20,21] we assign (*ii*) and (*v*) to vibrations which are largely of asymmetric $\nu(C-S_c)$ character, and (*iii*) and (*vi*) to modes of largely symmetric $\nu(Co-S_c)$ character. Subscripts c and u indicate co-ordinated and unco-ordinated S/O atoms. As has been shown for related systems,[21] there is probably considerable mixing between vibrations of different types which have the same symmetry.

The bonding in the $Co(CS_2Y)$ moieties may be represented as a hybrid of the three resonance forms shown in Figure 3. The frequencies of the asymmetric $\nu(C-S_c)$ vibrations decrease for $Y = S > O$, *e.g.* for $[Co(\eta-C_5H_5)(PMePh_2)(CS_2Y)]$ $\nu(C-S_c) = 866$ cm^{-1} when Y = S and 841 cm^{-1} when Y = O. This implies that along the same series the $C-S_c$ bond orders decrease as do the contributions that resonance forms (*b*) and (*c*) in Figure 3 make towards the overall structure. This is consistent with the behaviour of $[Co(\eta-C_5H_5)L(CS_2Y)]$ towards Lewis acids and the i.r. spectra of the adducts thus obtained (see below).

The ^1H n.m.r. spectra of the $[Co(\eta-C_5H_5)L(CS_2Y)]$ complexes (Y = O or S) are consistent with the proposed structures. They show resonances due to the ligands C_5H_5 and L, and solvents of crystallization. Only those for C_5H_5 are included in Tables 1 and 2. They appear as singlets at *ca.* δ 5 with no evidence for ^{31}P coupling to the cyclopentadienyl protons. The other resonances have integrated intensities which are consistent with the formulae given in the Tables and show the anticipated chemical shifts, proton–proton couplings, and phosphorus–proton couplings.

Reactions with Electrophiles.—In view of the rich chemistry of dithiocarbonate complexes of Pt^{II} with organohalogens,[5] the failure of $[Co(\eta-C_5H_5)L(CS_2O)]$ to react with MeI, $PhCH_2Br$, or $BrCH_2CH_2Br$ was disappointing. However alkylation of the CS_2O^{2-} ligand has been achieved using $MeSO_3F$. This affords $[Co(\eta-C_5H_5)(PMePh_2)(S_2COMe)]SO_3F$ with its only weakly nucleophilic counter anion. In the presence of more strongly nucleophilic anions such as I^- these methyl xanthate complexes are unstable towards loss of MeI (see above). In contrast the trithiocarbonate complexes are strong nucleophiles (*cf.* ref. 22) which react rapidly with excess MeI to give two methyl thioxanthate derivatives, the ionic $[Co(\eta-C_5H_5)(PBu^n_3)(S_2CSMe)]I$ which may be converted to $[Co(\eta-C_5H_5)(PBu^n_3)(S_2CSMe)]BPh_4$, and the covalent $[Co(\eta-C_5H_5)I(S_2CSMe)]$. It is probable that the salt is formed first and that nucleophilic attack by I^- is at the metal atom rather than the methyl group as in the xanthate complexes. This results in displacement of PBu^n_3 which may react with excess MeI and thus prevent the reverse reaction.

The i.r. spectra of the thioxanthate complexes (Table 1) are consistent with the formation of $S-Me^+$ bonds. The $\nu(C-S_u)$ frequencies decrease markedly on methylation, whereas attack elsewhere in the molecule would be expected to leave them unchanged or cause them to increase. At the same time the frequencies of the asymmetric $\nu(C-S_u)$ vibrations increase; for $[Co(\eta-C_5H_5)(PBu^n_3)(CS_2Y)]$ $\nu(C-S_u)$ and $\nu(C-S_c) = 1\,035$ and 860 cm^{-1} respectively when Y = S, and 988 and 926 cm^{-1} when $Y = SMe^+$. These observations suggest that in the methyl thioxanthate complexes the resonance forms (*b*) and (*c*) (Figure 3; $Y = SMe^+$) are more important and (*a*) is less important than for the trithiocarbonate complexes where Y = S.

A similar but much less important effect is observed on methylation of $[Co(\eta-C_5H_5)(PMePh_2)(CS_2O)]$, with the $\nu(C-O_u)$ and asymmetric $\nu(C-S_c)$ vibrations having frequencies of 1 597 and 841 cm^{-1} respectively when Y = O, and 1 585 and 845 cm^{-1} when $Y = OMe^+$. Although a similar explanation may be evoked, it is clear that adduct formation does not have such a dramatic effect on $C-S_c$ bond orders in the dithiocarbonate complexes where Y = O as it does in the trithiocarbonate complexes where Y = S. Similar conclusions have been reached for xanthate and thiocarbonate complexes of Pd^{II} and Pt^{II} on the basis of their i.r. spectra.[20]

The complex $[Co(\eta-C_5H_5)(PBu^n_3)(CS_3)]$ forms 1 : 2 adducts with $HgCl_2$ and 1 : 1 adducts with $HgBr_2$ and HgI_2. These again show low frequencies for their $\nu(C-S_u)$ vibrations (Table 1). This indicates $S_u \rightarrow HgX_2$ bond formation in all three cases, but the difference between 1 : 1 and 1 : 2 adducts is not obvious.

The complex $[Co(\eta-C_5H_5)(PMePh_2)(CS_2O)]$ also forms adducts of the general type $[Co(\eta-C_5H_5)(PMePh_2)(CS_2O\cdot 2HgX_2)]\cdot 0.5Et_2O$ (X = Cl or Br) which are virtually insoluble in organic solvents. However it is not clear from the i.r. spectroscopic data (Table 2) if these contain $O_u \rightarrow HgX_2$ bonding, $S_c \rightarrow HgX_2$ bonding related to that in $[Cl(Et_3P)Pt(S_2CNMe_2)Pt(PEt_3)Cl_2]$,[23] or some previously unencountered alternative.

The dithiocarbonate and trithiocarbonate complexes differ markedly in their reactions with iodine; $[Co(\eta-C_5H_5)(PMePh_2)(CS_2O)]$ gives $[Co(\eta-C_5H_5)(PMePh_2)I_2]$ in quantitative yields. On the other hand, $[Co(\eta-C_5H_5)(PPr^n_3)(CS_3)]$ forms an interesting adduct which is air-stable and sparingly soluble in dichloromethane. The frequency of its $\nu(C-S_u)$ vibration is lower, and that of its asymmetric $\nu(C-S_c)$ vibration is higher, than that of the corresponding vibration of its precursor. This indicates S_u-I bond formation. We suggest that we have either the salt $[Co(\eta-C_5H_5)(PPr^n_3)(S_2CSI)]I$ or a related species with an I–I bond.

Description of the Structure of $[Co(\eta-C_5H_5)(CNBu^t)(CS_3)]$.—The molecular geometry and the atom labelling scheme are shown in Figure 1.[24] The closest intermolecular contact is $S(3) \cdots C(3)$ at $x, \frac{1}{2} - y, \frac{1}{2} + z$ of 3.56(1) Å whilst all other contacts are >3.6 Å. The bond lengths and bond angles are given in Table 4 and relevant mean-plane data in Table 5. The cobalt atom lies in a ' pseudo-octahedral ' environment with a planar cyclopentadienyl ring occupying three co-ordination positions and hence one triangular face of the octahedron, whilst the two sulphur atoms and isocyanide carbon atom occupy the other three vertices of the octahedron. The $CNBu^t$ ligand is linearly co-ordinated to the metal atom and has normal bond lengths and bond angles. The planar trithiocarbonate ligand bonds through two of its sulphur atoms to the cobalt to give a four-membered CoS_2C ring system in which the metal atom lies only *ca.* 0.1 Å out of the CS_3 plane. This arrangement is similar to that found in the $[Ni(S_2CS)_2]^{2-}$ ion.[25] Bond lengths and bond angles in the present structure are in good agreement with those in the nickel complex. Like other 1,1′-dithiolate ligands,[3,4] CS_3^{2-} has a relatively small ' bite ' with S_c–C–S_c ~ 76°. The relatively short C–S distances [C–S_u — 1.65(1), C–S_c = 1.71(1), 1.74(1) Å] indicate that all have some multiple-bond character, but that the C–S_u bond order is higher than the C–S_c. This is consistent with the bonding arguments which were discussed above.

The [Co(η-C_5H_5)(CNBu^t)(CS_3)] used in this structure determination was prepared by Method (*a*). We have also used *X*-ray diffraction techniques to determine the structure of [Co(η-C_5H_4Me)(PBu$^n_3$)(CS_3)] which was prepared by Method (*b*).[17] Unfortunately the quality of the structure determination is not as high as that reported here, but it is sufficiently good to show that the two structures are very similar.

Structure of [Rh(η-C_5H_5)(PPh_3)(CS_3)].—This complex was prepared from [Rh(η-C_5H_5)(PPh_3)$_2$] and CS_2.[6] Its reported i.r. spectrum is very similar to that of our [Co(η-C_5H_5)(PPh_3)(CS_3)] with its ν(C–S) vibrations giving rise to absorption bands at 870 and 1 045 cm^{-1}.[6] Consequently we suggest that it is a bidentate trithiocarbonate-*S*$^-$,*S*$^-$ complex, [Rh(η-C_5H_5)(PPh_3)(S_2CS)], and not [Rh(η-C_5H_5)(PPh_3)(S–S–C=S)] as was proposed.[6]

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Received 13*th June* 1983; *Paper* 3/995