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Reactions of Carbon Disulfide with (η-Cyclopentadienyl)cobalt(I) Complexes

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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 at elevated temperatures give a mixture of orange $[Co(\eta\text{-}C_5H_5)(L)(CS)]$ (I), red $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ (II), green $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ (III), and dark red $[Co(\eta\text{-}C_5H_5)(L)(CS_3)]$ (IV) when L is a tertiary phosphine or organoisocyanide but not when it is a tertiary phosphite or arsine. The product ratio depends to some extent on L but mainly on the reaction temperature. II appears to be the source of I and IV and decomposes slowly to approximately equal amounts of them at 40 °C. II is also the source of III and may be converted to it by photolysis at room temperature or thermolysis at temperatures >80 °C or by reaction with $[Co(\eta\text{-}C_5H_5)(CO)_2]$. The IR and ^1H NMR spectra of I, II, and III are reported and discussed. II undergoes ligand replacement reactions. Thus $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ reacts slowly with $n\text{-}Bu_3P$ to give $[Co(\eta\text{-}C_5H_5)\{P(n\text{-}Bu)_3\}(\eta^2\text{-}CS_2)]$ and with PhNCS to give $[Co(\eta\text{-}C_5H_5)(PPh_3)\{\eta^2\text{-}(CS)\text{-}PhNCS\}]$. I, II, and III are organometallic bases. With I electrophilic attack may occur at the CS ligand to give, e.g., $[Co(\eta\text{-}C_5H_5)(PPh_3)(CSMe)][SO_3F]$ or at the metal atom to give, e.g., $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)(HgCl_2)]$. Metal attack does not take place with II or III as these form $[Co(\eta\text{-}C_5H_5)(L)\{\eta^2\text{-}C(S)S{\rightarrow}E\}]$ and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS{\rightarrow}E)(\mu_3\text{-}S)]$ adducts, respectively, with many electrophiles (E) such as Me^+, $HgCl_2$, Ag^+, etc. The reactions of II and III with halogens differ as the former lose their CS_2 ligands to give $[Co(\eta\text{-}C_5H_5)(L)X_2]$ (X = Cl, Br, or I) but the latter gives the adduct $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CSI)(\mu_3\text{-}S)]I$.

Introduction

As a continuation of investigations into the preparations, structure, and reactions of carbon disulfide complexes of iron(0) by ourselves[1] and others,[2] we have carried out similar studies of the reactions of carbon disulfide with $\eta\text{-}C_5H_5$ derivatives of cobalt(I) and of the properties of the compounds thus obtained. A preliminary report has been published.[3]

Prior to our work it was found that $[M(\eta\text{-}C_5H_5)(PPh_3)_2]$ and CS_2 gave $[M(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$. The reaction was fast when M = Co[4] but slower than M = Rh, and some $[Rh(\eta\text{-}C_5H_5)(PPh_3)(CS_3]$ was also formed.[5] During the course of our work, Werner et al. showed that $[Co(\eta\text{-}C_5H_5)(PMe_3)_2]$ and CS_2 gave $[Co(\eta\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}CS_2)]$.[6] This they converted to $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ either by reaction with $[CoMn(\eta\text{-}C_5H_5)(\eta\text{-}MeC_5H_4)(CO)_3(PMe_3)]$ or by its thermal decomposition.[7] However, they could only prepare $[Co(\eta\text{-}C_5H_5)(PMe_3)(CS)]$ from $[Co(\eta\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}CSSe)]$ and Ph_3P.[8] They determined the structures of the three products by X-ray diffraction techniques.

Related rhodium complexes were prepared from $[Rh(\eta\text{-}C_5H_5)(L)(C_2H_4)]$ (L = Me_3P or $PhMe_2P$) which with CS_2 gave $[Rh(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ and some $[Rh(\eta\text{-}C_5H_5)(PMe_3)(C_2S_4)]$.[9] The thiocarbonyl derivatives $[M(\eta\text{-}C_5H_5)(L)(CS)]$ were obtained from $[Rh(\eta\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}CSSe)]$ and Ph_3P [M(L) = $Rh(PMe_3)$][8] or from $Na[C_5H_5]$ and $[M(PPh_3)_2(CS)Cl]$ (M = Rh or Ir; L = Ph_3P).[10]

Experimental Section

Previously published methods were used to prepare tertiary phosphines,[11] t-BuNC,[12] $SnBr_2$,[13] $[Co(\eta\text{-}C_5H_5)(CO)_2]$,[14] $[Co(\eta\text{-}C_5H_5)(CO)(L)]$ and their methylcyclopentadienyl counterparts (L = Et_3P, $n\text{-}Pr_3P$, $n\text{-}Bu_3P$, $PhMe_2P$, Ph_2MeP, Ph_3P, and t-Bu NC),[15] and $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}I_2]$.[16] Other chemicals were purchased and used as received.

Unless it is stated otherwise, all reactions were carried out at room temperature under a atmosphere of nitrogen. Solvents were dried by refluxing over calcium hydride and distilled prior to use. Tetrahydrofuran was further purified by distilling from sodium and benzophenone.

IR spectra (Tables I and II) was measured on Perkin-Elmer 337 or 283B spectrometers. They were calibrated with polystyrene. ^1H NMR spectra (Tables I and II) were obtained on a Perkin-Elmer R12B spectrometer in $CDCl_3$ or $(CD_3)_2CO$ solutions using Me_4Si as an internal standard. Mass spectra were measured on a VG 70/70M mass spectrometer.

Analyses (Tables I and II) were carried out in the Analytical Laboratory of University College, Dublin.

Reactions of CS_2 with $[Co(\eta\text{-}C_5H_5)(CO)_2]$ and L or $[Co(\eta\text{-}C_5H_5)(CO)(L)]$. Equimolar amounts of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (2 mL) and L (Et_3P, $n\text{-}Pr_3P$, $n\text{-}Bu_3P$, $PhMe_2P$, Ph_2MeP, Ph_3P, and t-BuNC) in benzene (100 mL) and carbon disulfide (30 mL) were refluxed. The reactions were monitored by IR spectroscopy and were deemed to be complete when no carbonyl-containing species were present. This required 10 h when L = Ph_3P.

An alternative approach was to prepare $[Co(\eta\text{-}C_5H_5)(CO)(L)]$ in situ from $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (2 mL) and L (mole ratio 1:1) in refluxing benzene solution (100 mL) for 24 h. The solution was cooled, carbon disulfide (30 mL) added, and the reflux continued until the reactions were complete.

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Table I. Melting Points, Analyses, IR Spectra and ^1H NMR Spectra of Some CS Complexes and Their Derivatives Described in the Text

compound	decomp pt[a]	analyses[b] % C	% H	% S	IR,[h] $\nu(CS_u)$	^1H NMR[i] (η-C_5H_5)
$[Co(\eta\text{-}C_5H_5)\{P(n\text{-}Bu)_3\}(CS)]$	58	58.1 (58.3)	8.8 (8.6)	8.2 (8.6)	1260*	4.72
$[Co(\eta\text{-}C_5H_5)(PMePh_2)(CS)]$	116	61.6 (61.9)	4.6 (4.9)	7.8 (8.7)	1267*	4.55
$[Co(\eta\text{-}C_5H_5)(PPh_3(CS)]\cdot Ph_3P$	98	73.3 (72.8)	4.8 (5.1)	4.9 (4.6)	1275*	4.57
$[Co(\eta\text{-}C_5H_5)(PPh_3)(CSMe)]BPh_4$	166	73.9 (73.8)	5.7 (5.4)		1130	4.71[j]
$[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)(HgCl_2)]$[c]	134	41.3 (41.1)	3.0 (2.8)	4.6 (4.5)	1310	
$[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)(HgBr_2)]$[d]	137	38.0 (36.5)	3.3 (2.8)	5.4 (4.0)	1310	
$[Co_3(\eta\text{-}C_5H_5)_3(CS)(S)]$	289	43.0 (42.8)	3.5 (3.3)	13.9 (14.2)	1039, 1075	4.65
$[Co_3(\eta\text{-}MeC_5H_4)_3(CS)(S)]$	274	46.8 (46.5)	4.1 (4.2)	12.8 (13.0)	1059, 1069	4.15 (m), 4.32 (m)[k]
$[Co_3(\eta\text{-}MeC_5H_4)_3(CSMe)(S)]I$[e]	190	37.8 (37.9)	4.0 (3.8)	10.5 (10.1)	953	4.60 (m), 4.65 (m)[j]
$[Co_3(\eta\text{-}MeC_5H_4)_3(CSMe)(S)]BPh_4$	171	64.5 (64.1)	5.6 (5.3)	8.0 (7.7)	953	4.60 (m), 4.65 (m)[i]
$[Co_3(\eta\text{-}MeC_5H_4)_3(CSAg)(S)]BF_4$	>340	29.0 (29.8)	1.7 (2.3)	8.0 (9.9)	953	
$[Co_3(\eta\text{-}C_5H_5)_3(CSZnCl_2\cdot 2H_2O)(S)]$	>340	31.3 (30.9)	3.3 (3.0)	9.7 (10.3)	964	
$[Co_3(\eta\text{-}C_5H_5)_3(CSCdI_2\cdot 2H_2O)(S)]$	>340	22.5 (22.5)	2.2 (2.2)	6.7 (7.5)	940 (br)	
$[Co_3(\eta\text{-}C_5H_5)_3(CSHgCl_2)(S)\}$	>340	26.3 (26.7)	2.4 (2.1)	8.3 (8.9)	951 (br)	
$[Co_3(\eta\text{-}C_5H_5)_3(CSHgBr_2)(S)]$	>340	23.9 (23.7)	1.8 (1.8)	8.0 (7.9)	934	
$[Co_3(\eta\text{-}C_5H_5)_3(CSHgI_2)(S)]$	>340	20.5 (21.3)	1.6 (1.6)	5.2 (7.0)	936	
$[Co_3(\eta\text{-}C_5H_5)_3(CSSbCl_3)(S)]$[f]	140	28.3 (28.4)	2.4 (2.2)	9.7 (9.4)	937 (br)	
$[Co_3(\eta\text{-}C_5H_5)_3(CSI)(S)]I$[g]	>340	26.9 (27.3)	2.2 (2.1)	8.6 (9.1)	945 (br)	

[a] Decomposition point. [b] Calculated values in parentheses. [c] % Cl = 10.3 (10.1). [d] % Br = 21.6 (20.3). [e] % I = 20.1 (20.1). [f] % Cl = 16.0 (15.7). [g] % I = 37.1 (36.1). [h] Peak positions (cm^{-1}). Measured in KBr disks except those with an asterisk for which carbon disulfide was used; br = broad. [i] Measured in $CDCl_3$ solution unless otherwise stated. Resonance positions ppm downfield from Me_4Si; m = multiplet. [j] Measured in $(CD_3)_2CO$ solution. Me resonances obscured.

Table II. Analyses, Decomposition Points, IR Spectra, and ^1H NMR Spectra of Some η^2-CS_2 Complexes and Their Derivatives Described in the Text

complex	decomp pt,[a] °C	analyses[b] % C	% H	% S	% X	IR, $\nu(CS_u)$	^1H NMR (C_5H_5)
$[Co(C_5H_5)(PEt_3)(CS_2)]$	87	45.2 (45.3)	6.5 (6.3)	20.0 (20.1)		1160*	4.80 (s)
$[Co(C_5H_5)\{P(n\text{-}Pr)_3\}(CS_2)]$	65	49.7 (50.0)	7.3 (7.2)	17.4 (17.7)		1160	4.76 (s)
$[Co(C_5H_5)\{P(n\text{-}Bu)_3\}(CS_2)]$	53	54.0 (53.7)	7.8 (7.9)	15.8 (15.9)		1160	4.78 (s)
$[Co(C_5H_5)(PMe_2Ph)(CS_2)]$	131	49.6 (49.7)	5.1 (4.7)			1163*	4.70 (s)
$[Co(C_5H_5)(PMePh_2)(CS_2)]$	101	57.0 (57.0)	4.3 (4.5)	15.5 (16.0)		1165*	4.66 (s)
$[Co(C_5H_5)(PPh_3)(CS_2)]$	137	62.1 (62.3)	4.3 (4.3)	13.5 (13.8)		1170*	4.62 (s)
$[Co(C_5H_5)\{P(OPh)_3\})CS_2)]$	128	55.9 (56.4)	4.0 (3.9)	12.9 (12.5)		1172*	4.54 (s)
$[Co(C_5H_5)\{CN(t\text{-}Bu)\}(CS_2)]$	78	46.0 (46.6)	4.9 (4.9)		N = 4.1 (4.9)	1167[f]	
$[Co(C_5H_5)(PPh_3)(PhNCS)]$	81	68.9 (69.0)	5.0 (4.7)	6.3 (6.1)	N = 2.6 (2.7)		4.94 (s)
$[Co(C_5H_5)(PPh_3)(CS_2Me)][BPh_4]$	142	74.2 (73.9)	5.0 (5.4)	8.3 (8.0)		1145	4.33 (s)[e]
$[Co(C_5H_5)(PPh_3)(CS_2HgCl_2)]$	160	39.6 (39.3)	3.0 (2.7)	8.3 (8.7)	Cl = 10.0 (9.6)	1127	
$[Co(C_5H_5)(PPh_3)(CS_2\cdot HgBr_2)]$	125	35.8 (35.0)	2.5 (2.4)	8.1 (7.8)		1125	
$[Co(C_5H_5)(PPh_3)(CS_2\cdot HgI_2)]$	121	31.8 (31.4)	2.4 (2.2)		I = 27.2 (27.7)	1125	
$[Co(C_5H_5)(PPh_3)(CS_2\cdot 2SnCl_2)]$	152	33.8 (34.8)	2.6 (2.4)	7.4 (7.6)		1121	
$[Co(C_5H_5)(PPh_3)(CS_2\cdot SnBr_2)]$	134	39.3 (38.9)	3.0 (2.7)	7.5 (8.6)	Br = 21.1 (21.6)	1123	
$[Co(C_5H_5)(PPh_3)(CS_2\cdot 2SnBr_2)]$	148	29.0 (28.3)	2.5 (1.9)	6.2 (6.2)	Br = 29.5 (31.4)	1120	
$[Co(C_5H_5)\{P(n\text{-}Bu_3)_3\}Cl_2]$	104	51.3 (50.3)	8.3 (8.8)		Cl = 17.8 (17.1)		5.34 (s)
$[Co(C_5H_5)(PMePh_2)Cl_2]$	138	54.4 (54.7)	4.5 (4.5)		Cl = 17.9 (17.9)		5.21 (s)
$[Co(C_5H_5)(PPh_3)Br_2]$	141	49.3 (50.5)	4.0 (3.6)				
$[Co(C_5H_5)(PPh_3)I_2]$	169	43.7 (43.4)	2.8 (2.4)		I = 39.3 (40.0)		

[a] All complexes decomposed before melting. [b] Calculated values in parentheses. [c] Measured in KBr disks except those with an asterisk for which carbon disulfide was used. [d] Measured in $CDCl_3$ solution. Resonance positions ppm downfield from Me_4Si. [e] $(CD_3)_2CO$ solution. Me resonance obscured. [f] $\nu(CN)$ = 2197 cm^{-1}.

At the completion of the reactions the solvents were removed from the filtered reactions mixtures at reduced pressures and the residues chromatographed on alumina using benzene and then dichloromethane as eluents. Four products were usually obtained. They eluted in the order $[Co(\eta\text{-}C_5H_5)(L)(CS)]$, $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$, and $[Co(\eta\text{-}C_5H_5)(L)(CS_3)]$. They were isolated by removing the solvents at reduced pressure and crystallizing the residues from hexane or dichloromethane–hexane mixtures. The yields of the above four products are variable but generally ca. 10, 25, 5, and 15% respectively.

A third and very inefficient method involved the photolysis of a solution of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (1 g), Ph_3P (1.45 g), and CS_2 (20 mL) in toluene 50 (mL) using a Philips HPR 125-W lamp. It gave the above products in <1% yield.

Preparation of $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(\eta^2\text{-}CS_2)]$. A solution of $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}_2]$ was prepared from a slurry of $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}I_2]$ (14 g), *i*-PrMgBr (0.08 mol), and $(PhO)_3P$ (10 mL) in benzene (150 mL) and ether (150 mL). After being left standing the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution (200 mL). The red organic layer was washed repeatedly with water and dried over anhydrous magnesium sulfate and its volume reduced to ca. 50 mL by removal of the solvent at reduced pressure. The addition of CS_2 (100 mL) was followed by gentle heating. The procedures described above were then used to isolate and purify $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(\eta^2\text{-}CS_2)]$ as dark red crystals (yield 7%).

Pyrolysis and Photolysis of $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ (L = Ph_2MeP and Ph_3P). A solution of $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ (1 g) (L = Ph_2MeP or Ph_3P) in toluene (30 mL) was refluxing for 8 h. The mixture was cooled. The products were separated and purified as described above. They were $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$, $[Co(\eta\text{-}C_5H_5)(L)(CS)]$, and $[Co(\eta\text{-}C_5H_5)(L)(CS_3)]$ in yields of 60, 4, and 4%, respectively. $[Co(\eta\text{-}MeC_5H_4)(PPh_3)(\eta^2\text{-}CS_2)]$ underwent a similar reaction.

The breakdown of $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ in refluxing dichloromethane (30 mL) was slow and was not allowed to go to completion. Only $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)]$ and $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ were formed.

Photolysis of a solution of Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$) in toluene using a Philips HPR 125-W lamp gave [Co$_3$(η-C$_5$H$_5$)(μ$_3$-CS)(μ$_3$-S)] in 35% yield after 4 days.

Other Methods of Preparing [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] and Related Compounds. (i) The reaction between [Co(η-C$_5$H$_5$)(CO)$_2$] (1 mL) and carbon disulfide (30 mL) in refluxing toluene (50 mL) was monitored by IR spectroscopy. After 24 h all carbonyl-containing species had disappeared. Product separation by chromatography (tetrahydrofuran/alumina) and purification by recrystallization from tetrahydrofuran gave [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] as the only isolable product in 60% yield.

(ii) A solution of [Co(η-C$_5$H$_5$)(PMePh$_2$)(η^2-CS$_2$)] (1 g) and [Co(η-C$_5$H$_5$)(CO)$_2$] (mole ratio 1:2) in benzene (50 mL) was refluxed for 48 h. All of the [Co(η-C$_5$H$_5$)(CO)$_2$] was consumed. Product separation and purification as described in (i) gave [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] (yield 55%) together with trace amounts of [Co(η-C$_5$H$_5$)(PMePh$_2$)(CS)] and [Co(η-C$_5$H$_5$)(PMePh$_2$)(CS$_3$)].

A similar procedure using (a) [Co(η-C$_5$H$_5$)(PMePh$_2$)(η^2-CS$_2$)] and [Co(η-MeC$_5$H$_4$)(CO)$_2$] (mole ratio 1:2) or (b) [Co(η-MeC$_5$H$_5$)(PMePh$_2$)(η^2-CS$_2$)] and [Co(η-C$_5$H$_5$)(CO)$_2$] (mole ratio 1:2) in refluxing toluene each gave a single band on chromatography. Products could be isolated from these which respectively analyzed as (a) [Co$_3$(η-C$_5$H$_5$)(η-MeC$_5$H$_4$)$_2$(μ$_3$-CS)(μ$_3$-S)] and (b) [Co$_3$(η-C$_5$H$_5$)$_2$(η-MeC$_5$H$_4$)(μ$_3$-CS)(μ$_3$-S)]. [Co$_3$(η-C$_5$H$_5$)(η-MeC$_5$H$_4$)$_2$(μ$_3$-CS)(μ$_3$-S)]: ^{1}H NMR (CHCl$_3$ solution) methyl protons at δ 1.65 (s, 6 H) and cyclopentadienyl protons at δ 4.50 (s) and 4.55 (s) with minor multiplets between δ 4.30 and 4.50 (total 12.8 H). Anal. Calcd: C, 45.4; H. 3.9; S, 13.4. Found: C, 45.4; H, 4.1; S, 13.8. [Co$_3$(η-C$_5$H$_5$)$_2$(η-MeC$_5$H$_4$)(μ$_3$-CS)(μ$_3$-S)]: ^{1}H NMR (CHCl$_3$ solution) methyl protons at δ 1.86 (3 H) and cyclopentadienyl protons at δ 4.43 (s) and 4.48 (s) superimposed on minor multiplets (total 14.2 H). Anal. Calcd: C, 44.1; H, 3.7; S, 13.8. Found: C, 44.2; H, 3.9; S, 13.6.

If [Co(η-MeC$_5$H$_4$)(CO)$_2$] in (a) was replaced by [Ni(η-C$_5$H$_5$)$_2$], [Fe$_2$(CO)$_9$], or [Fe(benzylideneacetone)(CO)$_3$], only [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] was obtained.

Substitution Reactions of [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)]. (i) With R$_3$P. A solution of [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] (1 g) and *n*-Bu$_3$P (1 mL) in dichloromethane (50 mL) was stirred for 24 h. The mixture was worked up as described above to give [Co(η-C$_5$H$_5$){P(*n*-Bu)$_3$}(η^2-CS$_2$)] in 58% yield. Similar reactions took place with Et$_3$P and *n*-Pr$_3$P but not with *t*-BuNC or CO.

(ii) With PhNCS. A solution of [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] (1 g) and PhNCS (1 mL) in dichloromethane (30 mL) was stirred in sunlight for 6 days. The mixture was worked up as above to give purple [Co(η-C$_5$H$_5$)(PPh$_3$)(PhNCS)] in 50% yield.

(iii) With SO$_2$. When [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] (0.5 g) was dissolved in liquid SO$_2$ (10 mL) or a saturated solution of SO$_2$ in benzene (50 mL), a light red unidentified powder was obtained.

Reactions with Alkylating Agents. (i) With Alkyl Halides. MeI (2 mL) was added to a solution of [Co$_3$(η-MeC$_5$H$_4$)$_3$(μ$_3$-CS)(μ$_3$-S)] (0.5 g) in benzene (30 mL). On standing analytically pure [Co$_3$(η-MeC$_5$H$_4$)$_3$(μ$_3$-CSMe)(μ$_3$-S)]I precipitated as a brown powder (85% yield). Some of this was recrystallized from methanol containing NaBPh$_4$ to give [Co$_3$(η-MeC$_5$H$_4$)$_3$(μ$_3$-CSMe)(μ$_3$-S)][BPh$_4$].

Color changes indicated that [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] reacted with RI (R = Me, Et, or allyl) but no products could be isolated. [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)]·Ph$_3$P did not react with MeI.

(ii) With MeSO$_3$F. MeSO$_3$F (0.2 mL) was added to a stirred solution of [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)]·Ph$_3$P (1 g) in benzene (50 mL). The red oil that separated was dissolved in methanol containing NaBPh$_4$. The red precipitate was recrystallized from acetone/hexane to give [Co(η-C$_5$H$_5$)(PPh$_3$)(CSMe)][BPh$_4$] (yield 55%).

A similar procedure was used to convert [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] to [Co(η-C$_5$H$_5$)(PPh$_3$){η^2-C(S)SMe}][BPh$_4$] (yield 50%).

Reactions with Metal Salts. (i) A solution of HgCl$_2$ (0.19 g) in acetone (3 mL) was added to one of [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)]·Ph$_3$P (0.39 g) in acetone (20 mL). The pale red [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)(HgCl$_2$)] that precipitated required no further purification. It was filtered off, washed with benzene, and dried (yield 95%). [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)(HgBr$_2$)] was obtained similarly.

(ii) To a stirred solution of [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] (0.3 g) in dichloromethane (30 mL) was added a solution of HgCl$_2$ (0.175 g, mole ratio 1:1) in acetone (5 mL). Slow removal of the solvent at reduced pressure gave a fine red powder, [Co(η-C$_5$H$_5$)(PPh$_3$){η^2-C(S)S·HgCl$_2$}, which was filtered off and dried (yield 68%). HgBr$_2$ and HgI$_2$ reacted similarly; SnCl$_2$ gave [Co(η-C$_5$H$_5$)(PPh$_3$){η^2-C(S)S·2SnCl$_2$}] (30% yield), and SnBr$_2$ gave 1:1 and 1:2 adducts [Co(η-C$_5$H$_5$)(PPh$_3$){η^2-C(S)S·*n*SnBr$_2$}] (*n* = 1 or 2) (yields ca. 35%).

When HgCl$_2$ was replaced by SnCl$_4$, a reaction took place, but only [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] could be isolated from the reaction mixture.

Under similar conditions SbCl$_3$ (0.17 g) and [Co(η-C$_5$H$_5$){P(*n*-Bu)$_3$}(η^2-CS$_2$)] (0.3 g) gave an unstable brown precipitate in benzene/acetone solution. It decomposed on standing, and [Co(η-C$_5$H$_5$){P(*n*-Bu)$_3$}Cl$_2$] was isolated in 17% yield.

(iii) To a solution of [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] (0.3 g) in benzene (20 mL) was added HgX$_2$ (X = Cl, Br, or I; mole ratio 1:1) in acetone (5 mL). [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CSHgX$_2$)(μ$_3$-S)] precipitated as deep red solids that were filtered off, washed with benzene, and dried (yields ca. 70%).

If HgX$_2$ in acetone was replaced by tetrahydrofuran solutions of E = SbCl$_3$, ZnCl$_2$·2H$_2$O, CdI$_2$·2H$_2$O, or AgBF$_4$, black solids were obtained that analyzed as [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] without further purification (yields 50–70%).

Reactions with Halogens. (i) Cl$_2$ was bubbled through a solution of [Co(η-C$_5$H$_5$)(PMePh$_2$)(η^2-CS$_2$)] (1 g) in benzene (30 mL) until the color changed to purple. Removal of the solvent and recrystallization of the residue from dichloromethane/hexane mixtures gave [Co(η-C$_5$H$_5$)(PMePh$_2$)Cl$_2$] in 85% yield.

Similar reactions between [Co(η-C$_5$H$_5$)(PPh$_3$)(η^2-CS$_2$)] (0.5 g) and Br$_2$ or I$_2$ (mole ratio 1:1) in tetrahydrofuran (30 mL) gave purple [Co(η-C$_5$H$_5$)(PPh$_3$)X$_2$] (X = Br or I) in 75% yields.

(iii) A solution of [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] (0.5 g) and I$_2$ (0.28 g; mole ratio 1:1) in benzene (30 mL) was stirred for 30 min. A fine black solid precipitation that resulted was filtered off, washed with benzene, and dried. It analyzed as [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CSI)(μ$_3$-S)]I, and if recrystallized from ethanol containing NaBPh$_4$, it gave impure [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CSI)(μ$_3$-S)][BPh$_4$].

A similar reaction with Br$_2$ gave an unstable green precipitate, which could not be isolated.

The melting points, analyses, and spectra of the various products are given in Tables I and II.

Results and Discussion

The reactions of carbon disulfide with [Co(η-C$_5$H$_5$)(L)(CO)] or [Co(η-C$_5$H$_5$)(CO)$_2$] and L (L = tertiary phosphine or organoisocyanide) in refluxing benzene give mixtures containing, in general, four principal products: orange [Co(η-C$_5$H$_5$)(L)(CS)] (I), red [Co(η-C$_5$H$_5$)(L)(η^2-CS$_2$)] (II), green [Co$_3$(η-C$_5$H$_5$)$_3$(μ$_3$-CS)(μ$_3$-S)] (III), and dark red [Co(η-C$_5$H$_5$)(L)(CS$_3$)] (IV). These are crystalline solids soluble in organic solvents. Solid II and III are stable at room temperature in air. I is air-sensitive, except for [Co(η-C$_5$H$_5$)(PPh$_3$)(CS)]·Ph$_3$P, and their thermal stability decreases with decreasing ligand size from L = Ph$_3$P to (*n*-Bu)$_3$P. The trithiocarbonate complexes IV are best prepared by another route. They will be described elsewhere together with their dithiocarbonate counterparts.

Typical yields of purified I–IV, e.g., when L = Ph$_3$P, are 10, 25, 5, and 17%, respectively, but they depend on both L and the reaction conditions. Thus when L = *t*-BuNC, III is not formed and [Co(η-C$_5$H$_5$){CN(*t*-Bu)}(CS)] decomposes during chromatography. There are no reactions when L is a tertiary phosphite or arsine, but [Co(η-C$_5$H$_5$){P(OPh)$_3$}$_2$] and CS$_2$ give [Co(η-C$_5$H$_5$){P(OPh)$_3$}(η^2-CS$_2$)] (cf. res 4 and 6). In general, however, the importance of II declines with increasing reaction times or temperature while that of III increases; e.g., in refluxing carbon disulfide very little III is formed, but in toluene it is the principal product. The ^{1}H NMR spectra of the crude reaction mixture show that in general approximately equal amounts of I and IV are formed. However in an irreproducible and inexplicable experiment, the last of an old sample of $(n\text{-Bu})_3P$ gave $[Co(\eta\text{-}C_5H_5)\{P(n\text{-Bu})_3\}(CS_3)]$ in 60% yield.

II appears to be the principal source of I, III, and IV. The slow thermal decomposition of $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ in dichloromethane at 40 °C gives only $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)]$ and $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS_3)]$ in approximately equal amounts (^1H NMR spectroscopy). This reaction is thus one of the class summarized by $2M(CX_2) \rightarrow M(CX) + M(CX_3)$ where M is a transition metal and ligands and X = O, NR, or S. These may proceed via intermediates of the type $[\{Co(\eta\text{-}C_5H_5)(L)\}_nC_2S_4]$ that contain C_2X_4 ligand[17,18] (cf. $[Rh(\eta\text{-}C_5H_5)(PMe_3)(C_2S_4)]$[19]). The presence of free Ph_3P did not increase the yield of $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)]$, and no Ph_3PS was formed.

The conversion of II to III may be brought about photolytically or thermally. In refluxing toluene it is quite fast and proceeds in high yields with the formation of only traces of I and IV. III is also formed in high yields from the thermal reactions of $[Co(\eta\text{-}C_5H_5)(CO)_2]$ with CS_2 (refluxing toluene) or of $[Co(\eta\text{-}C_5H_5)(PMePh_2)(\eta^2\text{-}CS_2)]$ with $[Co(\eta\text{-}C_5H_5)(CO)_2]$ (mole ratio 1:2 in refluxing benzene). Variations of this last reaction are those of (a) ($[Co(\eta\text{-}C_5H_5)(PMePh_2)(\eta^2\text{-}CS_2)]$ with $[Co(\eta\text{-}MeC_5H_4)(CO)_2]$ and (b) $[Co(\eta\text{-}MeC_5H_4)(PMePh_2)(\eta^2\text{-}CS_2)]$ with $[Co(\eta\text{-}C_5H_5)(CO)_2]$. Both gave single green bands on chromatography. From these could be isolated products that analyzed well for the mixed species (a) $[Co_3(\eta\text{-}C_5H_5)(\eta\text{-}MeC_5H_4)_2(CS)(S)]$ and (b) $[Co_3(\eta\text{-}C_5H_5)_2(\eta\text{-}MeC_5H_4)(CS)(S)]$ and whose ^1H NMR spectra showed methyl:cyclopentadienyl proton ratios of (a) 6:12.8 (formula 6:13) and (b) 3:14.2 (formula 3:14). Unfortunately the mass spectra of these samples show the molecular ions $[Co_3(\eta\text{-}C_5H_5)_n(\eta\text{-}MeC_5H_4)_{3-n}(CS)(S)]^+$ where (a) n = 0–3 and (b) n = 0–4. It is possible that the temperature employed in our mass spectrometer (>200 °C) may have caused cluster redistribution. Consequently we are not sure if the products from (a) or (b) are pure compounds or mixtures. III was also the only product if $[Co(\eta\text{-}MeC_5H_4)(CO)_2]$ in (a) was replaced by $[Ni(\eta\text{-}C_5H_5)_2]$, $[Fe_2(CO)_9]$, or $[Fe(\text{benzylideneacetone})(CO)_3]$. No mixed-metal derivatives were formed.

Spectra and Structure. The IR and ^1H NMR spectra of I, II, and III are consistent with the structures (Figure 1) similar to those determined by X-ray crystallography for $[Co(\eta\text{-}C_5H_5)(PMe_3)(CS)]$,[8] $[Co(\eta\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}CS_2)]$, $Co(\eta\text{-}C_5H_5)(PMe_3)(\eta^2\text{-}CS_2)]$,[6] and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$,[7] respectively. They show absorption bands and resonances appropriate to L and $\eta^5\text{-}C_5H_5$ ligands (only the chemical shift of the C_5H_5 protons are included in Tables I and II) and to the vibrations of CS or CS_2 ligands (Tables I and II). The ν(CS) vibrations of I give rise to absorption bands at ca. 1260 cm^{-1} which, as anticipated, increase for L = $(n\text{-Bu})_3P < Ph_2MeP < Ph_3P$ (cf. ref 20 and 21). The ν(CS) modes of II give rise to strong absorption bands between 1160 and 1170 cm^{-1} (Table I and II) (cf. ref 20 and 21), but those due to vibrations of the CoCS ring have not been found. For both III and $[Co_3(\eta\text{-}MeC_5H_4)(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ (III′) there are two intense IR absorption bands that could be attributed to the ν(CS) mode of the μ_3-CS ligand.[7] In going from III to III′ there are changes in the frequencies of these absorption bands and their mean that are only consistent with the bands at higher frequencies being due to the ν(CS) vibrations (cf. $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and $[Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_4]$ in ref 22). The others are probably due to artifacts.

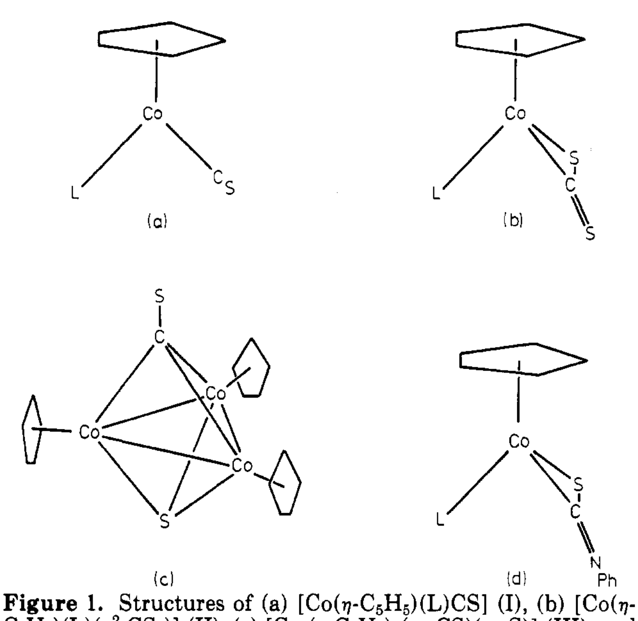

Figure 1. Structures of (a) $[Co(\eta\text{-}C_5H_5)(L)CS]$ (I), (b) $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ (II), (c) $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ (III), and (d) $[Co(\eta\text{-}C_5H_5)(L)\{\eta^2\text{-}(CS)\text{-}PhNCS\}]$.

Ligand Exchange Reactions. The $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}CS_2)]$ and $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ complexes are closely related, but whereas the Ph_3P ligands in the former are labile,[1,2] that in the latter is not. It is displaced only slowly by R_3P (R = Et, n-Pr, or n-Bu) to give $[Co(\eta\text{-}C_5H_5)(PR_3)(\eta^2\text{-}CS_2)]$ and not at all by CO or CNR. However SO_2 replaces the CS_2 ligands in both complexes (cf. ref 1 and 23), but the cyclopentadienylcobalt product has not been identified. On the other hand, whereas PhNCS does not react with $[Fe(PPh_3)_2(CO)_2(\eta^2\text{-}CS_2)]$, it does react with $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ to give $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}PhNCS)]$.[3] This purple complex is rather unstable. Its IR spectrum shows a strong absorption band at 1535 cm^{-1} with shoulders at 1515 and 1545 cm^{-1} that is due to the ν(CN) mode of a η^2-(CS)PhNCS ligand (Figure 1). There is no absorption band between 900 and 1200 cm^{-1} attributable to the ν(CS) vibration of an uncoordinated C=S group. An alternative route to this compound is from $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ and PhNCS (cf. $[Fe(PPh_3)_2(CO)_2\{\eta^2\text{-}(CS)PhNCS\}$ from $[Fe(PPh_3)_3(CO)_2]$[24].

Reactions with Electrophiles. All three series of complexes (I–III) are potential organometallic bases. Electrophilic attack may occur at the uncoordinated S_u atoms of their CS or CS_2 ligands, their metal atoms, or, for III, the μ_3-S ligand. As a consequence of the first the frequencies of the $\nu(CS_u)$ vibrations would be expected to decline; otherwise they would probably increase or remain constant.

IR spectroscopic data show that for II and III, or III′, only attack at S_u is observed and $\nu(CS_u)$ frequencies decrease on adduct formation. The μ_3-CS ligands in III and III′ are, as might be expected, extremely basic, and a wide variety of $[Co_3(\eta\text{-dienyl})_3(\mu_3\text{-}CS{\rightarrow}E)(\mu_3\text{-}S)]$ adducts are obtainable with electrophiles E (dienyl = C_5H_5 or MeC_5H_5). Werner et al. have reported the structure of an adduct where E = $Cr(CO)_5$,[7] and we have obtained others where E = Me^+ (from MeI) isolable as I^- and BPh_4^- salts, the halides of Zn(II), Cd(II), or Hg(II), Ag^+ from $AgBF_4$, and I^+ (from I_2) isolated as its I^- or impure $[BPh_4]^-$ salts. Br_2

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also gave an unstable adduct, but it reverted to III on attempted purification. Neither $AgBF_4$ nor the halogens effected cluster oxidation to give $[Co_3(\eta\text{-dienyl})_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]^+$ salts.

The S_u atoms in II are much less nucleophilic than those in III or III′. The latter are irreversibly alkylated by MeI, but the reaction of RI (R = Me, Et, or allyl) with $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}CS_2)]$ is reversible and $MeSO_3F$ is required to bring about irreversible alkylation to $[Co(\eta\text{-}C_5H_5)(PPh_3)\{\eta^2\text{-}C(S)S{\rightarrow}Me\}]^+$ isolated as its BPh_4^- salt. Stable $[Co(\eta\text{-}C_5H_5)(L)\{\eta^2\text{-}C(S)S{\rightarrow}E\}]$ adducts where L = Me_3P and E = $Cr(CO)_5$ or $Mn(\eta\text{-}C_5H_5)(CO)_2$ have been reported and structurally characterized, by Werner et al.[6] We have obtained others with metal halides that are nonconducting in $MeNO_2$ solution, e.g., E = $HgCl_2$, $HgBr_2$ HgI_2, $2SnCl_2$, $SnBr_2$, or $2SnBr_2$, but that where E = $SbCl_3$ decomposes readily and only $[Co(\eta\text{-}C_5H_5)(PPh_3)Cl_2]$ could be isolated. Furthermore II, unlike III, do not give detectable adducts with halogens and only $[Co(\eta\text{-}C_5H_5)(L)X_2]$ was formed (X = Cl, Br, or I).

The sulfur atoms in I are even less nucleophilic than those in II. $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)]{\cdot}Ph_3P$ does not react with MeI, but with $MeSO_3F$ it gives $[Co(\eta\text{-}C_5H_5)(PPh_3)(CSMe)]^+$ (isolable as its $[BPh_4]^-$ salt). The very low $\nu(CS_u)$ frequency of this cation is consistent with a $S_u{\rightarrow}Me$ bond, and a considerable contribution of carbyne resonance forms such as $[Co({\equiv}CSMe)(\eta\text{-}C_5H_5)(PPh_3)]^+$ toward an overall description of the structure. The analogous Ir complex $[Ir(\eta\text{-}C_5H_5)(PPh_3)(CS)]$ does react with MeI, but because of the greater basicity of Ir over Co, the initial attack occurs at the metal atom and the final product is $[Ir(\eta\text{-}C_5H_5)(PPh_3)(I)\{CMe(SMe)\}]^+$.[10] However, $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)]$ resembles its Rh and Ir counterparts in that its 1:1 adducts with HgX_2 (X = Cl or Br) contain $Co{\rightarrow}HgX_2$ bonds (cf. $[Co(\eta\text{-}C_5H_5)(CO)_2(HgCl_2)]$[25]). As a consequence of electrophilic attack at the metal atom, the $\nu(CS_u)$ frequency increases (Table I).

It is interesting to compare the reactivities of complexes I–IV toward electrophiles and hence the Lewis basicities of their uncoordinated sulfur atoms S_u. These may then be correlated with the frequencies of their $\nu(CS_u)$ vibrations: I, $[Co(\eta\text{-}C_5H_5)(L)(CS)]$ (νCS_u) ≈ 1265 cm^{-1}); II, $[Co(\eta\text{-}C_5H_5)(L)(\eta^2\text{-}CS_2)]$ (~1165 cm^{-1}); III, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ (1039 and 1075 cm^{-1}); IV, $[Co(\eta\text{-}C_5H_5)(L)(CS_3)]$ (~1030 cm^{-1}). (The information for IV is taken from ref 16.) I–IV may all be methylated at S_u, but $MeSO_3F$ is necessary to accomplish this with I and II whereas MeI suffices for the others. Mercury(II) halides form adducts with all four types of complex, but those of I contain $Co{\rightarrow}HgX_2$ bonds and those of the others $S_u{\rightarrow}HgX_2$ bonds. Finally iodine displaces CS_2 from II, but with III and IV it forms adducts containing $S_u{\rightarrow}I$ bonds. Thus it can be seen that the basicity of S_u increases I < II < III, IV while $\nu(CS_u)$ declines. This suggests that along the series, resonance forms containing the $C\text{–}S_u^-$ fragment contribute increasing toward the overall bonding within the cobalt–CS_n moiety.

Registry No. I (L = $P(n\text{–}Bu)_3$), 87137-23-3; I (L = $PMePh_2$), 87137-24-4; I (L = PPh_3), 75170-71-7; II (L = PEt_3), 87137-39-1; II (L = $P(n\text{-}Pr)_3$), 87137-40-4; II (L = $P(n\text{-}Bu)_3$), 87137-41-5; II (L = PMe_2Ph), 87137-42-6; II (L = $PMePh_2$), 87145-09-3; II (L = PPh_3), 33677-54-2; II (L = $P(OPh)_3$), 87145-10-6; II (L = CN(*t*-Bu)), 87145-11-7; III, 71118-12-2; IV, 75170-72-8; $[Co(\eta\text{-}C_5H_5)(PPh_3)(CSMe)(CSMe)]BPh_4$, 87137-26-6; $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)(HgCl_2)]$, 87137-27-7; $[Co(\eta\text{-}C_5H_5)(PPh_3)(CS)(HgBr_2)]$, 87137-28-8; $[Co_3(\eta\text{-}MeC_5H_4)_3(CS)(S)]$, 87137-29-9; $[Co_3(\eta\text{-}MeC_5H_4)_3(CSMe)(S)]I$, 87137-30-2; $[Co_3(\eta\text{-}MeC_5H_4)_3(CSMe)(S)]BPh_4$, 87137-32-4; $[Co_3(\eta\text{-}MeC_5H_4)_3(CSAg)(S)]BF_4$, 87145-07-1; $[Co_3(\eta\text{-}C_5H_5)_3(CSZnCl_2{\cdot}2H_2O)(S)]$, 87137-33-5; $[Co_3(\eta\text{-}C_5H_5)_3(CSCdI_2{\cdot}2H_2O)(S)]$, 87137-34-6; $[Co_3(\eta\text{-}C_5H_5)_3(CSHgCl_2)(S)]$, 87137-35-7; $[Co_3(\eta\text{-}C_5H_5)_3(CSHgBr_2)(S)]$, 87145-08-2; $[Co_3(\eta\text{-}C_5H_5)_3(CSHgI_2)(S)]$, 87137-36-8; $[Co_3(\eta\text{-}C_5H_5)_3(CSSbCl_3)(S)]$, 87137-37-9; $[Co_3(\eta\text{-}C_5H_5)_3(CSI)(S)]I$, 87137-38-0; $[Co(C_5H_5)(PPh_3)(PhNCS)]$, 87145-12-8; $[Co(C_5H_5)PPh_3)(CS_2Me)[BPh_4]$, 87145-14-0; $[Co(C_5H_5)(PPh_3)(CS_2{\cdot}HgCl_2)]$, 87145-15-1; $[Co(C_5H_5)(PPh_3)(CS_2{\cdot}HgBr_2)]$, 87145-16-2; $[Co(C_5H_5)(PPh_3)(CS_2{\cdot}HgI_2)]$, 87145-17-3; $[Co(C_5H_5)(PPh_3)(CS_2{\cdot}SnBr_2)]$, 87145-18-4; $[Co(C_5H_5)\{P(n\text{-}Bu)_3\}Cl_2]$, 87145-19-5; $[Co(C_5H_5)(PMePh_2)Cl_2]$, 87145-20-8; $[Co(C_5H_5)(PPh_3)Br_2]$, 87145-21-9; $[Co(C_5H_5)(PPh_3)I_2)$, 12194-27-3; $[Co(\eta\text{-}C_5H_5)(CO)(Et_3P)]$, 66652-85-5; $[Co(\eta\text{-}C_5H_5)(CO)(n\text{-}Pr_3P)]$, 87145-22-0; $[Co(\eta\text{-}C_5H_5)(CO)(n\text{-}Bu_3P)]$, 87145-23-1; $[Co(\eta\text{-}C_5H_5)(CO)(PhMe_2P)]$, 32800-45-6; $[Co(\eta\text{-}C_5H_5)(CO)(Ph_2MeP)]$, 32824-34-3; $[Co(\eta\text{-}C_5H_5)(CO)Ph_3P)]$, 12203-85-9; $[Co(\eta\text{-}C_5H_5)(CO)(t\text{-}BuNC)]$, 31760-69-7; $[Co(\eta\text{-}C_5H_5)(CO)_2]$, 12078-25-0; $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}_2]$, 32611-34-0; $[Co_3(\eta\text{-}C_5H_5)(\eta\text{-}MeC_5H_4)_2(\mu_3\text{-}CS)(\mu_3\text{-}S)]$, 87145-24-2; $[Co_3(\eta\text{-}C_5H_5)_2(\eta\text{-}MeC_5H_4)(\mu_3\text{-}CS)(\mu_3\text{-}S)]$, 87145-25-3; CS_2, 75-15-0.

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