Journal of Organometallic Chemistry, 253 (1983) 81–91
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DITHIOCARBAMATE COMPLEXES OF CYCLOPENTADIENYLCOBALT(III), $[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]$ (L = ligand)

JOHN DOHERTY and A.R. MANNING*

Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)

(Received March 31st, 1983)

Summary

The reactions of $[Co(\eta\text{-}C_5H_5)(L)I_2]$ with $Na[S_2CNR_2]$ (R = alkyl or phenyl) give $[Co(\eta\text{-}C_5H_5)(I)(S_2CNR_2)]$ (I) when L = CO and $[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]I$ (II) when L is a tertiary phosphine, phosphite or stibine, or organo-isocyanide ligand. In similar reactions $[Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)I]$ gives $[Co(\eta\text{-}C_5H_5)(C_3F_7)(S_2CNMe_2)]$ and $[Mn(\eta\text{-}MeC_5H_4)(CO)_2(NO)]PF_6$ forms $[Mn(\eta\text{-}MeC_5H_4)(NO)(S_2CNR_2)]$. The iodide ligands in I may be displaced by L, to give II, or by other ligands such as $[CN]^-$, $[NCS]^-$, H_2O or pyridine whilst $SnCl_2$ converts it to $SnCl_2I$. The iodide counter-anion in II may be replaced by others to give $[BPh_4]^-$, $[Co(CO)_4]^-$ or $[NO_3]^-$ salts. However $[CN]^-$ acts differently and displaces $(PhO)_3P$ from $[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe)]I$ to give $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$ which may be alkylated reversibly by MeI and irreversibly by $MeSO_3F$ to $[Co(\eta\text{-}C_5H_5)(CNMe)(S_2CNMe_2)]^+$ salts. Conductivity measurements suggest that solutions of I in donor solvents are partially ionized with the formation of $[Co(\eta\text{-}C_5H_5)(solvent)(S_2CNR_2)]^+\ I^-$ species. The IR and ^1H NMR spectra of the various complexes are reported. They are consistent with pseudo-octahedral "pianostool" molecular structures in which the bidentate dithiocarbamate ligands are coordinated to the metal atoms through both sulphur atoms.

Introduction

We have reported recently on the previously unknown $[Co(\eta\text{-}C_5H_5)(L)(S_2CS)]$ [1] and $[Co(\eta\text{-}C_5H_5)(L)(S_2CO)]$ [2] derivatives (L is a ligand). Both thiocarbonate ions are 1,1′-dithiolate ligands, and it is clear from reviews [3,4] that their dithiocarbamate counterparts have not been obtained. Here we describe the preparation, reactions and spectra of $[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]^+$ complexes (R = alkyl or phenyl, L = I^-, CN^-, NCS^-, $SnCl_2I^-$, $C_3F_7^-$, H_2O, pyridine, phosphorus(III) ligands, Ph_3Sb, or organo-isocyanides). Related $[Mn(\eta\text{-}MeC_5H_4)(NO)(S_2CNR_2)]$ derivatives were also prepared so that their spectra could be compared with those of the cobalt complexes. Some of them have been reported previously by McCleverty et al. [5].

0022-328X/83/$03.00

Experimental

Previously published methods were used to prepare [Co(η-C_5H_5)(CO)I_2] [6], [Co(η-C_5H_5)(L)I_2] (L = phosphorus(III) ligand, Ph_3Sb or organoisocyanide) [7], [Co(η-C_5H_5)(CO)(C_3F_7)I] [8], [Mn(η-MeC_5H_4)$(CO)_2$(NO)]PF_6 [9], tertiary phosphines [10], organoisocyanides [11], and most Na[S_2CNR_2] salts (R = alkyl or phenyl) [3]. Other chemicals were purchased and generally used as received.

Unless stated otherwise, reactions were carried out under nitrogen at room temperature. The solvents used were of reagent grade which were not purified further, except for tetrahydrofuran which was dried over calcium hydride and distilled from sodium and benzophenone prior to use.

IR spectra were measured on a Perkin–Elmer 283B spectrometer and calibrated with polystyrene [12]. ^1H NMR spectra were measured on a Perkin–Elmer R12B spectrometer in $CDCl_3$ solution using tetramethylsilane as an internal standard.

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

The melting points, analyses, IR spectra and ^1H NMR spectra of the various compounds prepared in this study are summarised in Tables 1–3.

Preparation of [Co(η-C_5H_5)(I)(S_2CNR_2)]

An ethanol solution of Na[S_2CNR_2] (2 mmol) was added dropwise over a period of 20 min to a solution of [Co(η-C_5H_5)(CO)I_2] (2 mmol) in dichloromethane (40 ml). After a further 20 min, the solvent was removed at reduced pressure from the reaction mixture, the residue redissolved in dichloromethane, and column chromatographed on alumina. With dichloromethane as the eluant, green [Co$(S_2CNR_2)_3$] was eluted; dichloromethane/ethanol mixtures (8/2) eluted dark green [Co(η-C_5H_5)(I)(S_2CNR_2)] which were crystallized from the dichloromethane/ethanol mixtures. The yields of these last increase with increasing mass of R from 50% when R_2N = Me_2N to 85% when R_2N is a morpholino radical.

An alternative route used to prepare [Co(η-C_5H_5)(I)(S_2CNMe_2)] was from [Co(η-C_5H_5)(I)(dimethylglyoxime)]I · $2H_2O$ [13] (2 mmol) and Na[S_2CNMe_2] (2 mmol) in dichloromethane (25 ml)/ethanol (25 ml) mixtures. After 30 min the solution was filtered, the solvent removed at reduced pressure and the residue crystallized from dichloromethane. The yield of [Co(η-C_5H_5)(I)(S_2CNMe_2)] was 60%.

Preparation of [Co(η-C_5H_5)(L)(S_2CNR_2)]I

A solution of Na[S_2CNR_2] (2 mmol) in ethanol (20 ml) was added over a period of 20 min to one of [Co(η-C_5H_5)(L)I_2] (2 mmol; L = phosphorus(III) ligand or organo-isocyanide) in dichloromethane (40 ml). After a further 20 min the solvent was removed from the reaction mixture at reduced pressure. The residue was dissolved in a dichloromethane/ethanol mixture (4/1) and chromatographed on alumina using this as eluant. The deep red crystals of the [Co(η-C_5H_5)(L)(S_2CNR_2)]I salts thus obtained were recrystallized from dichloromethane in yields of between 60%, e.g. for [Co(η-C_5H_5)(PPh_3)(S_2CNMe_2)]I, and 90% e.g. for [Co(η-C_5H_5)($PMePh_2$){$S_2CN(C_2H_4)_2O$}]I.

An alternative route to complexes of this type was from the reaction of [Co(η-C_5H_5)(I)(S_2CNR_2)] (2 mmol) with L (2 mmol; L = phosphorus(III) ligand, Ph_3Sb, or organo-isocyanide) in dichloromethane (25 ml)/ethanol (25 ml) solution. The red

(Continued on p. 87)

TABLE I

MELTING POINTS, ANALYSES, IR SPECTRA AND ^{1}H NMR SPECTRA OF [Co(η-C_5H_5)(I)(S_2CNR_2)] (I) AND RELATED [Co(η-C_5H_5)(X)(S_2CNMe_2)] COMPLEXES

	M.p.(°C)	Analyses (Found(calcd.)(%))			IR spectra [a]				^{1}H NMR spectra [b]	
		C	H	N	ν(Co–S)	ν(C–S)		ν(C–N)	R_2N protons	C_5H_5
R_2N [c] in [Co(η-C_5H_5)(I)(S_2CNR_2)]										
Me_2N [d]	> 230	25.5 (25.9)	3.0 (3.0)	3.9 (3.8)	343m	1009m	1056m	1530s	3.08	5.11
Et_2N	178–180	30.5 (30.1)	3.6 (3.8)	3.5 (3.5)	340m	1010m		1510s	1.4(t. *J* 6.6), 3.50(q. *J* 6.6)	5.22
$C_5H_{10}N$ [e]	185–186	32.7 (32.1)	3.9 (3.7)	3.6 (3.4)	333m	1014m		1515s	1.66(m), 3.78(m)	5.27
$O(C_2H_4)_2N$ [f]	216–217	29.1 (29.1)	2.8 (3.2)	3.5 (3.4)	385m	1060m		1498s	3.78(m)	5.30
Ph(Me)N	194–195	36.9 (36.1)	3.2 (3.0)	3.2 (3.2)	360m	1002m	1018m	1482s 1495s	3.67,7.43(m)	5.33
X [c] in [Co(η-C_5H_5)(X)(S_2CNMe_2)]										
C_3F_7	150–152	31.4 (32.0)	3.2 (2.7)	3.6 (3.4)	350m	1022s		1540s	3.10	5.09
CN·1/4CH_2Cl_2	> 320	38.5 (38.1)	4.0 (4.0)	9.4 (9.6)	342m	1002m	1011m	1542s	3.14, (CH_2Cl_2 at 5.3)	5.23
NCS·1/4CH_2Cl_2	146–148	34.8 (34.3)	3.4 (3.6)	8.7 (8.7)	345m	1001m		1549s		
$SnCl_2I\cdot C_4H_8O$		22.6 (22.7)	3.5 (3.0)	1.7 (2.2)	339m	995m	1008m	1532s		

[a] Run in CsBr discs. Peak positions in cm^{-1}. w = weak, m = medium, and s = strong. [b] Chemical shifts δ in ppm downfield from Me_4S; measured in $CDCl_3$ solution. Resonances are singlets unless stated otherwise t = triplet, q = quartet, and m = multiplet. *J* quoted in Hz. [c] Including solvent of crystallization. C_4H_8O = tetrahydrofuran. [d] S, 17.5(17.3)% and I, 34.9(34.2)%. [e] S, 15.4(15.6)%. [f] S, 15.1(15.5)%.

TABLE 2

MELTING POINTS, ANALYSES, IR SPECTRA AND ^{1}H NMR SPECTRA OF [Co(η-C_5H_5)(L)(S_2CNMe_2)]I (II) AND RELATED COMPLEXES

	M.p.(°C)	Analyses (Found(calcd.)(%))			IR spectra [a]			^{1}H NMR spectra [b]	
		C	H	N	ν(Co–S)	ν(C–S)	ν(C–N)	R_2N	C_5H_5
L [c] in [Co(η-C_5H_5)(L)(S_2CNMe_2)]I									
Ph_3P	190–191	49.4 (49.3)	4.3 (4.1)	2.0 (2.2)	350m	1012m	1546s	2.85	5.41
Ph_2MeP	204–206	44.1 (43.8)	4.8 (4.2)	2.5 (2.4)	349m	1002m	1548s	2.84	5.54
$Ph_2(C_6H_{11})P$	180–181	48.9 (48.8)	5.5 (5.0)	2.0 (2.2)	343m	1022m	1547s	2.99	5.15
$PhMe_2P$	190–192	49.0 (49.2)	4.1 (4.3)	2.2 (2.1)	318m	1002m	1542s	3.13	5.50
n-Bu_3P	161–163	41.0 (41.9)	6.7 (6.6)	2.4 (2.4)	339m	1014m	1545s	2.23	5.52
Ph(i-PrO)$_2$P	150–152	40.4 (40.2)	5.4 (5.0)	2.1 (2.3)	350m	1011m	1549s	3.07	5.39
$(PhO)_3P \cdot H_2O$	158–160	44.3 (44.6)	3.8 (4.0)	2.0 (2.0)	349m	1021m	1541s	3.18	5.12

$(i\text{-}PrO)_3P$	127–128	35.4 (35.2)	6.3 (5.2)	2.5 (2.4)	350m	1002m	1548s	3.55	5.73
$Ph_3Sb \cdot H_2O$	280–281	41.8 (42.0)	3.6 (3.8)	1.8 (1.9)	345m	1018m	1545s	3.25	5.25
$MeNC \cdot H_2O$ [d]	158–160	27.9 (27.9)	3.6 (3.7)	6.5 (6.5)	350m	1053s	1545s [d]	3.35	5.78
$C_6H_{11}NC \cdot 1/3C_6H_6$ [e]	137–139	39.9 (40.3)	4.8 (4.7)	5.9 (5.5)	348m	1051m	1547s [e]	3.38	5.75
C_5H_5N	–	34.0 (34.6)	3.7 (3.6)	6.2 (6.2)	346m	1002m	1540s		
H_2O [f]	198–200	26.9 (26.5)	3.7 (3.6)	4.2 (3.9)	342m	1012s	1538s [g]		
R_2N [c] in [Co(η-C_5H_5)($PMePh_2$)(S_2CNR_2)]I									
Et_2N	208–210	45.6 (46.1)	4.2 (4.7)	2.3 (2.3)	348w	1025m	1528s	0.92(t, *J* 7.2) 3.27(q, *J* 7.2)	5.44
$O(C_2H_4)_2N$	214–216	45.4 (45.0)	4.2 (4.2)	2.3 (2.3)	329w	1025s	1500s	3.64(m)	5.74

---

[a] Run in KBr discs. Peak positions in cm^{-1}. w = weak, m = medium, and s = strong. [b] Chemical shifts δ in ppm downfield from Me_4Si measured in $CDCl_3$ solution. Resonances are singlets unless stated otherwise; t = triplet, q = quartet and m = multiplet. *J* quoted in Hz. [c] Including solvent of crystallization. [d] $\nu(C{\equiv}NMe)$ 2220 cm^{-1}. [e] $\nu(C{\equiv}NC_6H_{11})$ 2222 cm^{-1}. [f] SO_3F^- is the counteranion in place of I^-. [g] ν(S–O) 1254 and 1305 cm^{-1}.

TABLE 3

MELTING POINTS, ANALYSES, AND IR SPECTRA OF $[Mn(\eta\text{-}MeC_5H_4)(NO)(S_2CNR_2)]$ (III) COMPLEXES

R_2N [a]	M.p.(°C)	Analyses (Found(calcd.)(%))				IR spectra [b]			
		C	H	N	S	ν(Mn–S)	ν(C–S)	ν(C–N)	ν(NO)
$Me_2N \cdot H_2O$	118–120	36.6 (36.9)	4.3 (4.8)	9.8 (9.8)	22.1 (21.8)	361m	1020m	1526s	1694s
Et_2N	58– 60	41.8 (42.3)	5.2 (5.4)	8.3 (9.0)	21.5 (21.5)	360w	1020m	1492s	1703s
n-Pr_2N		46.2 (45.9)	6.0 (6.2)	8.0 (8.2)	19.8 (18.9)	n.o.	1028m	1495s	1708s
n-Bu_2N		48.5 (48.4)	6.9 (6.8)	7.5 (7.6)		n.o.	1029m	1489s	1707s
$C_5H_{10}N$	99–100	43.8 (44.4)	5.2 (5.3)	8.5 (8.6)		348m	1027m	1502s	1700s
$O(C_2H_4)_2N$	104–106	39.7 (40.5)	4.7 (4.6)	8.6 (8.6)		349m	1028m	1498s	1710s
Ph(Me)N	105–107	48.1 (48.6)	4.7 (4.3)	8.0 (8.1)		367m	1001m	1494s	1695s

[a] $C_5H_{10}N$ = piperidyl; $O(C_2H_4)_2N$ = morpholinyl. [b] Run in CsBr discs. Peak positions in cm^{-1}. w = weak, m = medium, s = strong. n.o. = not observed.

$[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]I$ complexes were separated and purified as described above, and isolated in yields of 80–90% e.g. 85% for $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)]I$.

Preparation of $[Mn(\eta\text{-}MeC_5H_4)(NO)(S_2CNR_2)]$

Equimolar amounts of $Na[S_2CNR_2]$ (2 mmol) and $[Mn(\eta\text{-}MeC_5H_4)(CO)_2(NO)]PF_6$ (2 mmol) in acetone (20 ml) were stirred for 30 min. Carbon monoxide gas was evolved. The brown solution was chromatographed on an alumina column using acetone as eluant. The product was isolated by removal of the solvent and recrystallization of the residue from acetone/ethanol mixtures. The yields decreased with increasing mass of R from 70% when R = Me to 30% when R = n-Bu.

Reaction of $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ with NaX ($X^- = [CN]^-$, $[SCN]^-$ or OH^-).

When $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ (2 mmol) and Na[CN] (2 mmol) in dichloromethane (25 ml)/ethanol (25 ml) were stirred for 60 min the colour of the solution changed from green to red. Removal of the solvent and recrystallization of the residue from dichloromethane gave red $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]\cdot 1/4CH_2Cl_2$ in 85% yield.

The use of Na[SCN] instead of Na[CN] allowed the isolation of $[Co(\eta\text{-}C_5H_5)(NCS)(S_2CNMe_2)]\cdot 1/4CH_2Cl_2$ in 80% yield. Replacement of Na[CN] by Na[OH] gave only $[Co(S_2CNMe_2)_3]$ and a solid insoluble in dichloromethane.

Reaction of $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ with $SnCl_2$

$[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ (2 mmol) and $SnCl_2$ (2 mmol) were dissolved in tetrahydrofuran (20 ml). After 20 min part of the solvent was removed at reduced pressure, and crystals of $[Co(\eta\text{-}C_5H_5)(SnCl_2I)(S_2CNMe_2)]\cdot C_4H_8O$ obtained in near quantitative yield.

Reaction of $[Co(\eta\text{-}C_5H_5)(I)(S_2CNR_2)]$ with pyridine and other neutral ligands

$[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ (2 mmol) and pyridine (20 mmol) in dichloromethane (10 ml) were allowed to stand for one day. The solution was filtered and concentrated at reduced pressure. A trace of purple $[Co(\eta\text{-}C_5H_5)(NC_5H_5)(S_2CNMe_2)]I$ crystallized (yield ca 1%). The corresponding reactions of $[Co(\eta\text{-}C_5H_5)(I)(S_2CNR)_2]$ with phosphorus(III) ligands, Ph_3Sb or organoisocyanides have been described above.

Preparation of $[Co(\eta\text{-}C_5H_5)(H_2O)(S_2CNMe_2)]SO_3F$

$MeSO_3F$ (2 mmol) was added to a stirred benzene solution (50 ml) of $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ (2 mmol). A purple solid precipitated. It was washed with much benzene and then dried. The analytically pure $[Co(\eta\text{-}C_5H_5)(H_2O)(S_2CNMe_2)]SO_3F$ was obtained in a yield of 90%.

Reactions of $[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]I$ with $Na[BPh_4]$, $Na[NO_3]$ and $Na[Co(CO)_4]$

A mixture of $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)]I$ (2 mmol) and $Na[BPh_4]$ (2 mmol) in a dichloromethane (25 ml)/ethanol (25 ml) mixture was stirred for 30 min. The solution was filtered, the solvent removed at reduced pressure, and the residue recrystallized from a dichloromethane/ethanol mixture to give $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)][BPh_4]\cdot CH_2Cl_2$ in 95% yield.

$[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe_2)]I \cdot H_2O$ and $Na[NO_3]$ reacted similarly to give $[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe_2)]NO_3$ in 95% yield. The reaction of $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)]I$ and $Na[Co(CO)_4]$ prepared in situ gave $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)][Co(CO)_4] \cdot 1/2CH_2Cl_2$ in 40% yield after recrystallization from dichloromethane.

Reaction of $[Co(\eta\text{-}C_5H_5)\{P(OPh)_3\}(S_2CNMe_2)]I \cdot H_2O$ *with* $Na[CN]$

This was carried out as above using $[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe_2)]I \cdot H_2O$ and $Na[CN]$. The product, $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$, was recrystallized from dichloromethane (yield 60%).

Reactions of $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$ *with MeI and* $MeSO_3F$

A solution of $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$ (2 mmol) and MeI(20 mmol) in dichloromethane (20 ml) was shown by IR spectroscopy to contain a mixture of the reactants together with $[Co(\eta\text{-}C_5H_5)(CNMe)(S_2CNMe_2)]^+$ salts (presumably as the iodide) but the latter reverted to the reactant on attempts to isolate it.

If $MeSO_3F$ (2 mmol) replaced the MeI, it brought about complete conversion of the reactant to $[Co(\eta\text{-}C_5H_5)(CNMe)(S_2CNMe_2)][SO_3F]$ but this could not be purified.

Results and discussion

The reaction of $[Co(\eta\text{-}C_5H_5)(CO)I_2]$ with $Na[S_2CNR_2]$ (R = alkyl or phenyl) in dichloromethane/ethanol solution gives a mixture of green $[Co(\eta\text{-}C_5H_5)(I)(S_2CNR_2)]$ (I) and light green $[Co(S_2CNR_2)_3]$. The side-products arise from cleavage of the ring–metal bond as has been reported previously in related reactions [14]. They are obtained in significant quantities when R = Me or Et, but they decrease in importance as the mass of R increases and are insignificant when R_2N is the morpholino or piperidino radical. The yields of the desired products correspondingly increase from 50% for $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ to 85% for $[Co(\eta\text{-}C_5H_5)(I)(S_2CNC_5H_{10})]$. An alternative route to these compounds is from $Na[S_2CNR_2]$ and $[Co(\eta\text{-}C_5H_5)(I)(\text{dimethylglyoxime})]I \cdot 2H_2O$. A similar reaction is that of $[Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)I]$ with $Na[S_2CNMe_2]$ which gives $[Co(\eta\text{-}C_5H_5)(C_3H_7)(S_2CNR_2)]$.

Other $[Co(\eta\text{-}C_5H_5)(L)I_2]$ complexes where L is a phosphorus(III) ligand or an organo-isocyanide react with $Na[S_2CNR_2]$ to give the red salts, $[Co(\eta\text{-}C_5H_5)(L)(S_2CNR_2)]I$ (II) in yields which were always > 60% and often as high as 90%, e.g. for $[Co(\eta\text{-}C_5H_5)(PPh_3)\{S_2CN(C_2H_4)_2O\}]I$. Alternatively, II may be obtained from $[Co(\eta\text{-}C_5H_5)(I)(S_2CNR_2)]$ and L (see below).

The deep brown $[Mn(\eta\text{-}MeC_5H_4)(NO)(S_2CNR_2)]$ (III) complexes were obtained from the salts $[Mn(\eta\text{-}MeC_5H_4)(CO)_2NO]PF_6$ and $Na[S_2CNR_2]$ in acetone. The same method was used by McCleverty et al. [5]. The yield and stability of III decrease with increasing mass of R from 70% when R = Me to 30% when R = n-Bu.

The above complexes, and the other $[Co(\eta\text{-}C_5H_5)(X)(S_2CNR_2)]$ derivatives discussed below, are listed in Tables 1–3 together with their analyses, IR spectra, and ^1H NMR spectra. Some $\eta\text{-}MeC_5H_4$ counterparts have been obtained but are not included. They are air-stable solids soluble in organic solvents, but complexes II are only soluble in polar ones. Not surprisingly, such solutions of II conduct electricity, e.g. for $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)]I$ Λ_0 61.0 ohm^{-1} cm^2 mol^{-1} in CH_2Cl_2, 87.0 in $MeNO_2$ and 134 in MeCN, whilst those of III do not. Intermediate behaviour is shown by I, e.g. for $[Co(\eta\text{-}C_5H_5)(I)(S_2CNEt_2)]$ Λ_0 0.9 ohm^{-1} cm^2 mol^{-1} in CH_2Cl_2, 25.0 in $MeNO_2$ and 87.7 in MeCN. We attribute this to the reversible, partial displacement of I^- from I by the polar solvent molecule to give $[Co(\eta\text{-}C_5H_5)(solvent)(S_2CNR_2)]^+$ in $MeNO_2$ or MeCN solution.

Ligand exchange and related reactions

$[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ undergoes many reactions which involve replacement of I^- by other ligands. Thus Na[CN] gives $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$ ν(CN) 2013 cm^{-1}; Na[SCN] gives the N-bonded $[Co(\eta\text{-}C_5H_5)(NCS)(S_2CNMe_2)]$ with ν(N–CS) 2116 cm^{-1} and ν(NC–S) 809 cm^{-1} but with no IR absorption band at ca. 700 cm^{-1} attributable to a S-bonded SCN ligand (cf. ref. 15); and $SnCl_2$ gives $[Co(\eta\text{-}C_5H_5)(SnCl_2I)(S_2CNMe_2)]\cdot C_4H_8O$ which, though soluble in polar organic solvents and insoluble in hexane, is soluble in benzene and hence is unlikely to be ionic. It shows a strong absorption band in its IR spectrum with a frequency of 295 cm^{-1} which is due to ν(Sn–Cl) vibrations. Pyridine displaces I^- to give a very low yield of the purple $[Co(\eta\text{-}C_5H_5)(NC_5H_5)(S_2CNMe_2)]I$. Phosphorus(III) ligands, Ph_3Sb and organoisocyanides, L, react similarly to give good yields (up to 90%) of $[Co(\eta\text{-}C_5H_5)(L)(S_2CNMe_2)]I$. The isocyanide complexes are also formed by the reaction of $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$ with alkylating agents. Spectroscopic studies show that with a ten-fold excess of MeI, methylation is only partial, and reverses on the attempted isolation of the product. $MeSO_3F$ brings about complete methylation and the formation of a $[Co(\eta\text{-}C_5H_5)(CNMe)(S_2CNMe_2)]^+$ salt but analytically pure samples of it could not be isolated by this pathway. $MeSO_3F$ also reacts with $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ in benzene to give the purple salt $[Co(\eta\text{-}C_5H_5)(H_2O)(S_2CNMe_2)]SO_3F$ with a broad IR absorption band at ca. 3400 cm^{-1} due to the ν(OH) vibration of the coordinated water molecule which compares with ca. 3300 cm^{-1} in non-coordinated water. It seems probable that the $MeSO_3F$ methylates the iodo ligand and that the resultant MeI molecule is only weakly bound to the cobalt. Consequently it is readily displaced by the water present in the reagent-grade benzene which was used as reaction solvent. Attempts to prepare $[Co(\eta\text{-}C_5H_5)(OH)(S_2CNMe_2)]$ from $[Co(\eta\text{-}C_5H_5)(I)(S_2CNMe_2)]$ and Na[OH] failed. The products were $[Co(S_2CNMe_2)_3]$ and what appeared to be a cobalt hydroxide.

$[Co(\eta\text{-}C_5H_5)(L)(S_2CNMe_2)]I$ salts react with $Na[BPh_4]$, $Na[NO_3]$ and $Na[Co(CO)_4]$ by way of anion exchange to give e.g. $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNMe_2)][BPh_4]\cdot CH_2Cl_2$ (m.p. 212–214°C) and $[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe_2)][NO_3]$ (m.p. 143–144°C) in 90–95% yields, and $[Co(\eta\text{-}C_5H_5)(PMePh_2)(S_2CNMe_2)][Co(CO)_4]\cdot 1/2CH_2Cl_2$ (m.p. 96–98°C) in 50% yield. This last shows an IR absorption band due to the ν(CO) mode of the $[Co(CO)_4]^-$ ion at 1886 cm^{-1} in tetrahydrofuran solution, and its conductance in CH_2Cl_2 solution is Λ_0 82.5 ohm^{-1} cm^2 $mole^{-1}$. In contrast Na[CN] displaces the phosphite ligand from $[Co(\eta\text{-}C_5H_5)(P(OPh)_3)(S_2CNMe_2)]I$ to give $[Co(\eta\text{-}C_5H_5)(CN)(S_2CNMe_2)]$.

Spectra and structure

Both the IR and ^1H NMR spectra of the various complexes (Tables 1–3) are consistent with molecular structures similar to those illustrated in Fig. 1. These are based on the structure found for the 1,1′-dithiolate complex [Co(η-C_5H_5)(P(n-

Bu)$_3$)(S$_2$CS)] on the one hand [1] and those of various complexes with bidentate dithiocarbamate ligands on the other [3,4].

The IR spectra show absorption bands due to cyclopentadienyl and other ligands which, with the exception of the ν(NO) frequencies of III, are not included in the Tables, and those due to the vibrations of the Co(S$_2$CN) moieties which are. As is usual for dithiocarbamate complexes these last are found in three regions of the spectrum [15], strong, broad absorption bands between 1480 and 1550 cm^{-1}; sharp bands of medium intensity between 1000 and 1060 cm^{-1}; and medium to weak, sharp bands between 310 and 385 cm^{-1} (with most in the 340–350 cm^{-1} region) which have not always been detected. These are respectively assigned to vibrations of predominantly ν(C–N), ν(C–S) and ν(M–S) character, but it must be remembered that in complexes of this type there is often extensive mixing between vibrations of different types but the same symmetry (cf. ref. 16). For example the ν(C–N) frequencies decrease as the mass of the group R increases and especially in going from R = Me to Et or Ph. This has been observed elsewhere and attributed to ν(C–N)/ν(N–R) mixing [15]. The frequencies of these ν(C–N) vibrations are indicative of C–N bond orders greater than one, and suggest that resonance forms (a) in Fig. 2 contribute towards an overall description of the bonding in these compounds. However, the ν(C–S) frequencies are very high when compared with those of the thiocarbonate complexes [Co(η-C$_5$H$_5$)(L)(S$_2$CO)] (830–865 cm^{-1}) [2] and [Co(η-C$_5$H$_5$)(L)(S$_2$CS)] (855–875 cm^{-1}) [1]. This suggests that the resonance forms b and c in Fig. 2 are relatively important. The frequencies of the ν(M–S) vibrations are comparable to those found for the dithiocarbonate [2] (ca. 350 cm^{-1}) and trithiocarbonate [1] complexes (290–325 cm^{-1}).

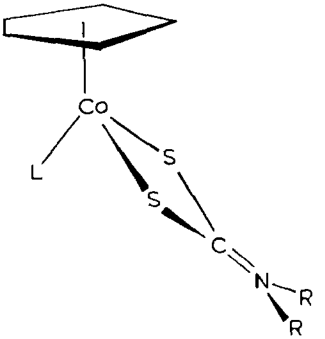

Fig. 1. Proposed structure of [Co(η-C$_5$H$_5$)(X)(S$_2$CNR$_2$)] complexes.

The ^{1}H NMR spectra of the dithiocarbamate complexes show resonances due to

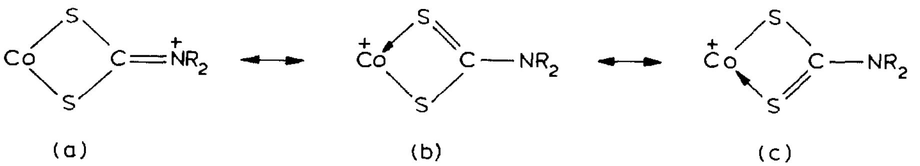

Fig. 2. Resonance forms of the Co(S$_2$CNR$_2$) moieties.

cyclopentadienyl and dithiocarbamate ligands (which are included in Tables 1–3) and other ligands (which are not included) which show the anticipated integrated intensities. All resonances are sharp. Although there may be restricted rotation about the $S_2C{-}NR_2$ bonds of the dithiocarbamate ligands [2,3] this cannot be detected because of the plane of symmetry which bisects the $Co(S_2CNR_2)$ plane. It is assumed that the C_5H_5, L and X ligands rotate freely about the metal–ligand axes.

The relevant chemical shifts are comparable to those observed in the ^1H NMR spectra of other dithiocarbamate complexes and of other 1,1′-dithiolate complexes of $(\eta\text{-}C_5H_5)Co(III)$ [1–4].

References

1 J. Fortune and A.R. Manning, submitted.
2 J. Doherty and A.R. Manning, submitted.
3 D. Coucouvanis, Progr. Inorg. Chem., 11 (1970) 233, and ref. therein.
4 R.P. Burns, F.P. McCullogh and C.A. McAuliffe, Adv. Inorg. Radiochem., 23 (1980) 211, and ref. therein.
5 J.A. McCleverty, T.A. Jones and E.J. Wharton, Inorg. Chem., 8 (1969) 1340.
6 R.B. King, Inorg. Chem., 5 (1966) 82.
7 R.F. Heck, Inorg. Chem., 4 (1965) 855.
8 R.B. King, P.M. Treichel, and F.G.A. Stone, J. Amer. Chem. Soc., 83 (1961) 3593.
9 R.B. King, Organometallic Syntheses, 1 (1965) 163.
10 L. Maier, Progr. Inorg. Chem., 5 (1963) 27, and ref. therein.
11 G.W. Gokel, R.P. Widera, and W.P. Weber, Org. Synth., 55 (1975) 96.
12 Tables for the Calibration of Infrared Spectrometers, Butterworths, London, 1961.
13 J. Doherty, and A.R. Manning, unpublished work.
14 T.A. James and J.A. McCleverty, J. Chem. Soc. A, (1970) 3318.
15 T.E. Sloan and A. Wojcicki, Inorg. Chem., 7 (1968) 1269.
16 D.A. Brown, W.K. Glass, and M.A. Burke, Spectrochim. Acta A, 32 (1976) 137.