lengths are given in Tables II and IV.

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Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms and of the fractional coordinates, including the calculated hydrogen atoms, and full listings of bond lengths and angles of compounds **1e** and **3b** (17 pages); listings of observed and calculated structure factors for **1e** and **3b** (34 pages). Ordering information is given on any current masthead page.

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(30) Herrmann, W. A.; Felixberger, J. K.; Kiprof, P. *Chem. Ber.*, in press.

Reaction of Organoisothiocyanates with [Co(η-C_5H_5)(PPh_3)$_2$]. Preparation, Structure, and Reactivity of Trinuclear Cobalt Complexes Containing a Triply Bridging, Two-Electron-Donor CNR Ligand

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The slow addition of RNCS to [Co(η-C_5H_5)(PPh_3)$_2$] in benzene at room temperature gives a good yield of green [Co_3(η-C_5H_5)$_3$(μ_3-S)(μ_3-CNR)] (**1**) where R = alkyl or aryl. A crystal structure determination (R = Et; monoclinic, space group $P2_1/c$ with a = 14.405 (4) Å, b = 9.221 (3) Å, c = 15.040 (5) Å, β = 117.9 (3)°, and Z = 4) shows that these complexes contain a planar Co_3(η-C_5H_5)$_3$ triangle (Co–Co = 2.447, 2.452, and 2.483 (1) Å) capped on one side by a μ_3-S atom and on the other by a μ_3-CNR ligand acting as a two-electron donor through C. The CNEt ligand is bent at N so that the N–Et bond lies above the center of one Co–Co bond with a C–N–Et angle of 129°. The N atoms of **1** are basic, but the basicity is a function of R. When R = Me or Et (**1**) reacts with [Ph_3C]BF_4 to give [Co_3(η-C_5H_5)$_3$(μ_3-S){μ_3-CN(H)R}]BF_4, [**2**]BF_4, although the source of the protons is unclear, and with MeI or R'SO_3CF_3 to give [Co_3(η-C_5H_5)$_3$(μ_3-S){μ_3-CN(R')R}]X, [**3**]X; both [**2**]BF_4 and [**3**]X react with excess HBF_4·OEt_2 to give [Co_3(η-C_5H_5)$_3$(μ_3-S){μ_3-CN(H)$_2$R}][BF_4]$_2$, [**4**][BF_4]$_2$, and [Co_3(η-C_5H_5)$_3$(μ_3-S){μ_3-CN(H)(R')R}][BF_4]$_2$, [**5**][BF_4]$_2$ salts, respectively. In contrast, when R = aryl, both [Ph_3C]BF_4 and excess HBF_4·OEt_2 convert **1** to [**2**][BF_4] only, and some **1** molecules are not alkylated to [**3**]I by MeI, but all are alkylated by $MeSO_3CF_3$. Infrared and NMR spectroscopic data are reported and discussed.

Introduction

CO can act as a two-electron-donor ligand that coordinates through carbon to one, two, or three metal atoms simultaneously. CS acts similarly.[4,5] Prior to the preliminary report of this work,[6] CNR ligands had been observed to coordinate only as a two-electron donor through carbon to one or two metal atoms.[4] A possible exception is [Cr(CO)$_5$CNCCo_3(CO)$_9$],[7] but this is best thought of as [Cr(CO)$_5$CNR] where R = CCo_3(CO)$_9$.

As [Co(η-C_5H_5)L_2] complexes (L = CO or PR_3) cleave carbon disulfide giving [Co_3(η-C_5H_5)$_3$(μ_3-S)(μ_3-CS)],[5,8] it seemed reasonable to anticipate that a similar reaction with organoisothiocyanates, RNCS, would lead to [Co_3(η-C_5H_5)$_3$(μ_3-S)(μ_3-CNR)] with triply bridging organoisocyanide ligands. The route has proved successful, and we describe here a series of such complexes together with their reactions with various Lewis acids that convert the μ_3-CNR ligands to [μ_3-CN(R')R]$^+$ and [μ_3-CN(R')$_2$R]$^{2+}$ ligands. The [μ_3-CNMe_2]$^+$ and [μ_3-CN(H)Me_2]$^{2+}$ ligands have been reported previously in [Co_3(CO)$_9$CNMe_2] and [Co_3(CO)$_9$CN(H)Me_2][PF_6].[9]

Experimental Section

Organoisothiocyanates were prepared by standard methods[10] or purchased and distilled prior to use. [Co(η-C_5H_5)(PPh_3)$_2$] was prepared as described[11] and used in situ. Other chemicals were purchased.

All reactions were carried out in purified solvents at room temperature under an atmosphere of nitrogen unless it is stated otherwise.

Infrared spectra were run on Perkin-Elmer 1710 FTIR or 283B spectrometers. NMR spectra were run on a JEOL JNM-GX270 spectrometer using Me_4Si as an internal standard.

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(1) University College, Belfield.

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(4) Cotton, F. A.; Wilkinson, G. *Comprehensive Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(5) Werner, H.; Leonhard, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 627.

(6) Fortune, J.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1071.

(7) Fehlhammer, W. P.; Degel, W. P.; Stolzenburg, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 214.

(8) Fortune, J.; Manning, A. R. *Organometallics* **1983**, *2*, 1719.

(9) Seyferth, D.; Hallgren, J. E.; Hung, P. K. *J. Organomet. Chem.* **1973**, *50*, 265.

(10) Crossley, F. S.; Moore, M. L. *Org. Synth.* **1941**, *21*, 81. Dyson, G. M. *Org. Synth.* **1941**, *Coll. Vol. 1*, 165.

(11) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157.

(12) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 72–78.

0276-7333/90/2309-1443$02.50/0

Table I. Melting Points, Analyses, IR Spectra {ν(CN)}, ^{1}H NMR Spectra (C_5H_5), and ^{13}C NMR Spectra of 1, [2]X, [3]X, [4]X_2, and [5]X_2 Complexes

			analyses, %												spectroscopic data			
			calcd						found						IR^b	^{1}H NMR^c	^{13}C NMR^c	
R or (R′)R	X	mp,^{a} °C	C	H	N	S	X	Co	C	H	N	S	X	Co	ν(CN)	C_5H_5	C_5H_5	μ_3-C
$[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$																		
Me		>230	45.8	4.0	3.1	7.9		39.7	45.8	4.0	2.8	7.9		39.4	1648	4.60^e	82.8	249.7^f
Et		112 (dec)	47.0	4.3	3.0	6.9		38.5	46.7	4.3	2.9	7.1		38.0	1646	4.60^e	81.3	238.5^f
C_6H_{11}		110 (dec)	51.4	5.0	2.7	6.6		34.2	51.5	4.9	2.9	6.6		34.2	1642 (br)	4.64		
Ph		117–119	52.0	3.9	2.7	6.3		34.9	51.6	3.9	2.4	6.2		35.2	1565	4.71	82.7	259.5
Ph^d		125–127	54.6	4.7	2.5	5.8		32.2	54.3	4.5	2.5	5.4		32.6	1567			
4-MeC_6H_4		142–143	53.0	4.2	2.7	5.1		33.9	52.7	4.3	2.6	5.6		33.7	1548	4.71	82.6	256.3
2-ClC_6H_4		161–163	48.7	3.5	2.5	5.9	6.5	32.6	49.1	3.7	2.4	5.9	6.2	32.4	1549	4.65^e		
3-ClC_6H_4		134–136	48.7	3.5	2.5	5.9	6.5	32.6	48.8	3.5	2.5	5.8	6.5	32.4	1553	4.71^g	83.1	254.9
4-ClC_6H_4		126–128	48.7	3.5	2.5	5.9	6.5	32.6	48.6	3.3	2.1	6.1	6.8	32.0	1543	4.68	83.2	253.6^g
4-BrC_6H_4		139 (dec)	45.0	3.2	2.3	5.4		30.2	44.7	3.1	2.2	5.6		30.6	1547	4.72	82.1	nd^g
3-$CF_3C_6H_4$		153–155	48.0	3.3	2.4	5.5	9.9	30.7	47.8	3.5	2.2	5.4	9.6	30.4	1524	4.71^g	83.0	nd^g
$[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(R')R\}]X$ Salts and Related Adducts																		
(Me)Me	I	189–190	36.8	3.6	2.4	5.5	21.6		37.0	3.7	2.1	5.6	20.0		1506	5.03	83.8	nd
(Me)Me	SO_3CF_3	159 (dec)	37.4	3.4	2.2	10.5	9.3		37.6	3.4	2.3	10.8	9.6		1501	4.95^h		
(Me)Et	I	192–195	37.9	3.8	2.3	5.3	21.1		38.3	3.9	2.2	5.0	19.2		1498	5.21^h		
(Me)Et	SO_3CF_3	211–213	38.5	3.6	2.2	10.2	9.3	28.4	38.1	3.6	2.1	10.5	9.2	27.9	1500	5.12^h		
(Et)Et	I	112–115	39.0	4.0	2.2	5.2	20.1	28.7	38.4	4.0	2.1	5.0	20.1	29.0	1478	5.10^h		
(Me)Ph	I	>230	42.5	3.5	2.1	4.6	19.5		42.8	3.7	2.1	4.8	20.9		1325	5.05		
(Me)Ph	BPh_4	>230	67.0	5.1	1.6	3.8			67.2	5.6	1.5	3.4			1316	5.11	85.6	nd
(Me)Ph	SO_3CF_3	173 (dec)	42.9	3.4	2.0	9.5	8.4		42.6	3.5	2.4	9.4	8.9		1323	5.15^h		
(Et)Ph	I	223 (dec)	43.4	3.7	2.1	4.8	19.1		43.8	3.3	2.3	5.2	19.5		1312	5.12^h		
(Me)4-MeC_6H_4	I	>230	43.4	3.7	2.1	4.8	19.1		43.4	3.8	1.8	5.2	19.8		1315	4.82^g		
(Me)4-MeC_6H_4	BPh_4	221–222	67.3	5.2	1.6	3.7			67.4	5.1	1.4	4.3			1315	4.57		
(Me)2-ClC_6H_4	BPh_4	118 (dec)	64.4	4.7	1.5	3.6			63.9	4.5	1.3	3.9			1310	4.96^g		
(Me)4-ClC_6H_4	I	243–244	40.3	3.2	2.0	4.6			40.4	3.5	1.9	4.9			1318	4.97		
(Me)4-BrC_6H_4	I	160 (dec)	37.9	3.0	1.9	4.3			37.5	3.2	2.2	4.7			1322	5.12		
(Me)4-$CF_3C_6H_4$	BPh_4	192 (dec)	63.3	4.6	1.5	3.5			63.7	4.5	1.1	3.7			1315	5.15		
(H)Me	BF_4	154 (dec)	38.2	3.5	2.6	6.0	14.2		38.6	3.8	2.5	6.2	14.5		1494^j	5.13		
(H)Ph	$BF_4{\cdot}H_2O$	228 (dec)	43.0	3.4	2.2	5.0	28.9		43.2	3.5	2.0	5.9	29.4		1309^k	5.12^h	86.1	nd^g
(H)C_6H_4Me-4	$BF_4{\cdot}2H_2O$	192–194	42.8	4.2	2.2	5.0			42.7	3.7	1.8	4.8			1327^l	5.11	87.2	nd^g
(H)C_6H_4Cl-4	BF_4	108 (dec)	41.9	3.1	2.2	5.0			42.7	3.7	1.8	4.8			1312^m	5.06		
(I)Ph	I_3	82–86	26.0	1.9	1.3	3.1	50.0		26.4	2.3	1.7	3.1	50.8		1311	5.55		
$(HgCl_2)_{1.5}$Ph		>230	28.8	2.2	1.5	3.5	11.6		28.5	2.4	1.5	3.8	10.9		1319	5.30^i		
$[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)(R')(R)\}]X_2$																		
(Me)Et	$BF_4{\cdot}1.5H_2O$	227 (dec)	32.4	4.2	1.9	4.5	21.6		31.8	3.8	1.7	4.4	22.4		1418	5.12^h		
(Me)Et	$PF_6{\cdot}0.5H_2O$	>230	29.1	3.3	1.7	4.0	29.1	22.6	28.9	3.2	1.6	4.2	27.7	22.1	1418	5.12^h		
(H)Et	$BF_4{\cdot}H_2O$	192–196	32.7	3.9	2.1	4.8			32.5	3.5	2.1	4.8			1419^n	5.08^h		
(H)Et	SO_3CF_3	169 (dec)	31.6	2.9	1.8	12.6	15.0	23.2	32.0	3.0	1.6	12.5	14.5	22.3	1419	5.10^h		

[a] Determined in sealed tubes; dec = melts with decomposition. [b] Peak positions (cm^{-1}), br = broad. Spectra run as KBr disks. [c] δ in ppm downfield from Me_4Si as an internal standard. Spectra run in $CDCl_3$ solution unless it is stated otherwise; nd = not detected. [d] MeC_5H_4 complex. δ(Me) = 2.1 ppm. [e] Spectrum run in $CD_3C_6D_5$. [f] Spectrum run in C_6D_6. [g] Spectrum run in CD_2Cl_2. [h] Spectrum run in $(CD_3)_2CO$. [i] Spectrum run in CD_3OD. [j] ν(NH) = 3314 (w). [k] ν(NH) = 3312 (w). [l] ν(NH) = 3308 (w). [m] ν(NH) = 3298 (w). [n] ν(NH) = 3290 cm^{-1} (w).

Mass spectra were obtained by using a VG 70/70M mass spectrometer.

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

Preparation of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ Complexes (1). A solution of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ (ca. 10 g) in benzene (200 mL) was prepared in situ. To it was added a solution of RNCS (1.5 mL) in benzene (50 mL). The addition was carried out dropwise and slowly over a period of at least 1 h. During this time the color of the mixture changed from red to brown. The reaction mixture was stirred for a further 5 h. It was then filtered and chromatographed on an alumina column. Benzene eluted a mixture of Ph_3P and RNCS, and then benzene–tetrahydrofuran (1:1) eluted a green band. This was collected, the solvent removed at reduced pressure, and the residue recrystallized from tetrahydrofuran–hexane mixtures to give green crystals of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ in 50–60% yields. The isolated complexes are listed in Table I. Similar compounds are also formed where R = Pr^i, Bu^t, CO_2Et, or 1-$C_{10}H_7$, but they were too unstable to be isolated.

$[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ failed to react with PhNCO, MeNCO, Pr^{i}NCNPr^i, or Bu^{t}NCNBu^t under the same conditions, and decomposition took place on heating.

Reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ with HX. $HBF_4{\cdot}OEt_2$ (0.3 mL) was added to a solution of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ (0.6 g; R = C_6H_5, C_6H_4Cl-4, and C_6H_4Me-4) in benzene (50 mL). A brown oil precipitated. The solvent was removed at reduced pressure, and the residue stirred with ethanol (10 mL) to give black crystals of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)R\}]BF_4$, which were filtered off, washed with cold ethanol and pentane, and dried (yield 40–60%).

The similar reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$ (0.5 g) with $HBF_4{\cdot}Et_2O$ (0.3 mL) in benzene (50 mL) gave a black solid which was filtered off, washed with benzene and pentane, and dried. It was identified as $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)_2Et\}][BF_4]_2{\cdot}2H_2O$ (yield 80%).

Reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ with $[Ph_3C]BF_4$. A solution of $[Ph_3C]BF_4$ (0.33 g, 1 mmol) in dichloromethane (40 mL) was added dropwise to a stirred solution of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ (1 mmol; R = Me, C_6H_5, and C_6H_4Me-4) in benzene (50 mL). Partial removal of the solvent at reduced pressure gave dark brown crystals of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)R\}]BF_4$, which were filtered off, washed, and dried (yield 70%).

Reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ with Alkylating Agents. MeI (2 mL) was added to a solution of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ (0.5 g) in benzene (30 mL). The reaction mixture was allowed to stand until the product, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)R\}]I$, precipitated from solution. It was filtered off, washed with benzene and pentane, and dried. Further purification was not necessary (yield 75%).

Table II. Crystallographic Data for $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$

compd	$[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$
formula	$C_{18}H_{20}NSCo_3$
M_r	459.03
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	14.405 (4)
b, Å	9.221 (3)
c, Å	15.040 (5)
β, deg	117.9 (3)
U, Å^3	1764.06
Z	4
D_c g cm^{-3}	1.728
cryst size, mm	0.3 × 0.2 × 0.35
radiation	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	27.89
θ_{max}, deg	24
no. of reflns	1085
no. of params	123
R	0.0556
R'	0.0689

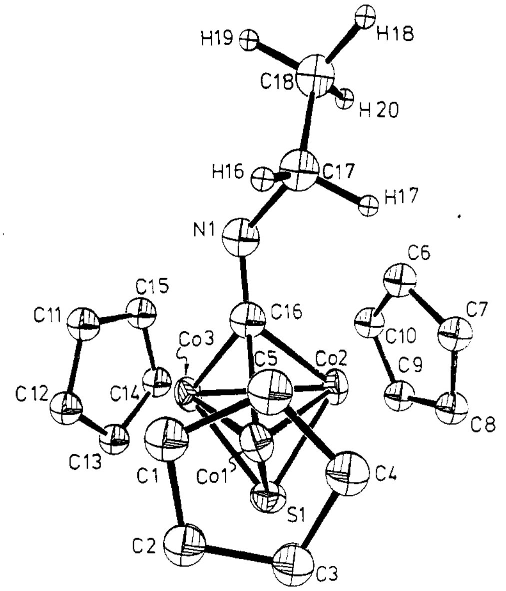

Figure 1. Perspective view of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$ with the atom-labeling scheme. Thermal ellipsoids are drawn to include 35% probability.

When R = 2-ClC_6H_4 or 3-$CF_3C_6H_4$, no reaction took place even after 1 month. When R = C_6H_{11}, the product was too unstable to isolate.

Similar reactions with EtI (5 mL) were complete within 4 days when R = Me or Et but took 7 days when R = Ph. The yields of the $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Et)R\}]I$ salts were 30–35%.

Traces of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Pr^n)R\}]I$ were obtained from $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ and Pr^nI after 1 month when R = Et but not when R = Ph. Bu^tI and PhI did not react with any $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$.

$MeOSO_2CF_3$ (0.1 mL) reacted immediately with all $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ (0.5 g) in benzene (50 mL) to give a brown tar. This was dissolved in ethanol (30 mL) containing $NaBPh_4$ (0.5 g). The brown precipitate of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)R\}]BPh_4$ was filtered off and recrystallized from chloroform (yield 50%).

Reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)Et\}]I$ with HX. $HX{\cdot}Et_2O$ (0.5 mL; X = BF_4 or PF_6) was added to a solution of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)Et\}]I$ (0.4 g) in dichloromethane (40 mL). $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)(Me)Et\}]X_2$ (X = $BF_4{\cdot}1.5H_2O$ or $PF_6{\cdot}0.5H_2O$) precipitated as black crystalline solids. They were filtered off, washed with cold dichloromethane and pentane, and dried (yield 65%).

Reaction of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$ with I_2 and $HgCl_2$. A solution of I_2 (0.25 g) and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$ (0.5 g) in benzene (40 mL) was stirred for 20 min. $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CN(I)_4Ph)]$ precipitated as an air-sensitive brown solid, which was filtered off, washed with benzene, and dried (yield 25%).

A similar reaction occurred with bromine, but the product was too unstable to be isolated.

A suspension of $HgCl_2$ (0.16 g) was stirred overnight with a solution of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$ (0.3 g) in benzene. The dark yellow precipitate of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(HgCl_2)_{1.5}Ph\}]$ was filtered off, washed, and dried (yield 40%).

The isolated products are listed in Table I together with their analyses, and IR and NMR spectra.

Structure of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)]$. Crystallographic data are listed in Table II. Data were collected on a Hilger and Watts Y290 diffractometer, and all calculations were performed on a DEC 2060 computer. Unit cell parameters were obtained by a least-squares fit of θ values for 12 reflections in the range $12 < \theta < 20°$. The angles used in the calculation were measured on the diffractometer. The structure was solved by direct methods, MULTAN,[13] and refined by full-matrix least-squares analysis using SHELX[14] with 1085 reflections that had $I > 3\sigma(I)$ and 123 variables. Data were corrected for Lorentz and polarization effects but not for absorption or extinction. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from refs 15–17, respectively. It was clear from early difference maps that the cyclopentadienyl rings were disordered, so they were refined as pairs of rigid pentagons with a site occupation of 0.5 for the atoms in the ring pairs. The cobalt and sulfur atoms were refined anisotropically. Hydrogen atoms were included in calculated positions. The final value for R was 0.0556 and for R′ was 0.0689. Heavy-atom parameters are given in Table III. Bond lengths and bond angles are listed in Table IV. The structure of the molecule is illustrated in Figure 1.[18]

Results and Discussion

Low yields of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$ may be obtained from the reaction of RNCS with $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$ in refluxing benzene when R = Me, C_6H_{11}, or Ph. However these and related compounds listed in Table I are obtained in more satisfactory yields (50–60%) by the slow addition of a dilute solution of RNCS in benzene to one of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ at room temperature. If the addition of the organoisothiocyanate is too fast, $[Co(\eta\text{-}C_5H_5)(PPh_3)(R_2N_2C_2S_2)]$ and $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNR)]$ may be formed. They will be discussed in a later publication. $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ does not react with RNCO or RNCNR in benzene at room temperature, and no products could be isolated from the reactions under reflux.

A reasonable scheme that accounts for the observed products proceeds via reactive and undetected $[Co(\eta\text{-}C_5H_5)(PPh_3)(RNCS)]$ complexes. In the presence of excess $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ these give $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)]$, but with excess RNCS they may give $[Co(\eta\text{-}C_5H_5)(PPh_3)(R_2N_2C_2S_2)]$ or $[Co(\eta\text{-}C_5H_5)(PPh_3)(S_2CNR)]$ depending on R (cf. the conversion of $[Ru(PPh_3)_2(CO)_2(\eta^2\text{-}RNCS)]$ to $[Ru(PPh_3)_2(CO)_2(S_2CNR)]$[19]).

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[13] Main, P.; Fiske, S. E.; Hull, S. L.; Germain, G.; Declerg, J. P.; Woolfson, M. M. MULTAN, *a system of computer programs for crystal structure determination from X-ray diffraction data*; Universities of York (York, England) and Louvain (Louvain, Belgium), 1980.

[14] Sheldrick, G. M. SHELX, *a computer program for crystal structure determination*; University of Cambridge, Cambridge, England, 1976.

[15] Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

[16] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[17] Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

[18] Johnson, C. K. ORTEP, Oak Ridge National Laboratory Report, ORNL (US), 1965, 3794; revised 1971.

Table III. Crystal Structure of [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)$]: Fractional Atomic Coordinates and Thermal Parameters (Å)

atom	x	y	z	U_{iso} or U_{eq}*	atom	x	y	z	U_{iso} or U_{eq}*
Co1	0.21035 (6)	0.38165 (10)	0.04398 (6)	0.0329 (6)*	C10	0.3400 (8)	−0.0653 (16)	0.1683 (9)	0.036 (3)
Co2	0.27126 (7)	0.14271 (9)	0.12731 (6)	0.0339 (6)*	C6a	0.4281 (7)	0.1139 (15)	0.2341 (11)	0.047 (4)
Co3	0.15259 (7)	0.15657 (9)	−0.05382 (6)	0.0321 (6)*	C7a	0.3661 (7)	0.1442 (15)	0.2825 (11)	0.043 (3)
S1	0.1153 (1)	0.2217 (2)	0.0616 (1)	0.043 (1)*	C8a	0.2880 (7)	0.0348 (15)	0.2544 (11)	0.054 (4)
N1	0.3678 (4)	0.2323 (6)	−0.0041 (4)	0.046 (1)	C9a	0.3018 (7)	−0.0632 (15)	0.1887 (11)	0.064 (4)
C1	0.2098 (12)	0.5700 (14)	−0.0356 (7)	0.043 (4)	C10a	0.3883 (7)	−0.0143 (15)	0.1761 (11)	0.060 (4)
C2	0.1273 (12)	0.5762 (14)	−0.0092 (7)	0.037 (4)	C11	0.1386 (11)	0.1253 (16)	−0.1971 (9)	0.049 (4)
C3	0.1730 (12)	0.5694 (14)	0.0974 (7)	0.058 (5)	C12	0.0399 (11)	0.1676 (16)	−0.2059 (9)	0.064 (5)
C4	0.2387 (12)	0.5589 (14)	0.1368 (7)	0.053 (5)	C13	0.0094 (11)	0.0622 (16)	−0.1557 (9)	0.050 (4)
C5	0.3065 (12)	0.5593 (14)	0.0546 (7)	0.057 (5)	C14	0.0892 (11)	−0.0452 (16)	−0.1160 (9)	0.039 (3)
C1a	0.1435 (10)	0.5712 (15)	−0.0341 (8)	0.062 (5)	C15	0.1691 (11)	−0.0062 (16)	−0.1416 (9)	0.051 (4)
C2a	0.1422 (10)	0.5742 (15)	0.0597 (8)	0.050 (4)	C11a	0.0995 (11)	0.1806 (10)	−0.2096 (8)	0.042 (3)
C3a	0.2477 (10)	0.5642 (15)	0.1375 (8)	0.054 (5)	C12a	0.0138 (11)	0.1444 (10)	−0.1918 (8)	0.055 (4)
C4a	0.3142 (10)	0.5550 (15)	0.0917 (8)	0.044 (4)	C13a	0.0353 (11)	0.0076 (10)	−0.1429 (8)	0.057 (4)
C5a	0.2498 (10)	0.5593 (15)	−0.0143 (8)	0.057 (5)	C14a	0.1343 (11)	−0.0408 (10)	−0.1303 (8)	0.061 (4)
C6	0.4202 (8)	0.0405 (16)	0.1945 (9)	0.039 (3)	C15a	0.1740 (11)	0.0662 (10)	−0.1715 (8)	0.051 (4)
C7	0.4127 (8)	0.1386 (16)	0.2636 (9)	0.056 (4)	C16	0.2928 (5)	0.2308 (7)	0.0139 (5)	0.037 (1)
C8	0.3278 (8)	0.0934 (16)	0.2801 (9)	0.042 (3)	C17	0.4716 (6)	0.2960 (9)	0.0523 (6)	0.058 (2)
C9	0.2828 (8)	−0.0326 (16)	0.2212 (9)	0.050 (4)	C18	0.5562 (6)	0.2025 (10)	0.0553 (7)	0.073 (2)

Anisotropic Thermal Parameters, Å

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	0.0372 (1)	0.0278 (1)	0.0338 (1)	0.0015 (1)	0.0088 (1)	−0.0018 (1)
Co2	0.0414 (1)	0.0345 (1)	0.0257 (1)	0.0039 (1)	0.0090 (1)	0.0033 (1)
Co3	0.0357 (1)	0.0339 (1)	0.0268 (1)	0.0002 (1)	0.0053 (1)	−0.0073 (1)
S1	0.0390 (1)	0.0423 (1)	0.0489 (1)	0.0047 (1)	0.0202 (1)	−0.0008 (1)

Table IV. Crystal Structure of [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)$]: Selected Bond Lengths and Bond Angles with Estimated Standard Deviations in Parentheses

Distances,[a] Å			
Co1–Co2	2.483 (1)	Co2–Co3	2.447 (1)
Co1–Co3	2.452 (1)	Co1–S1	2.112 (2)
Co2–S1	2.114 (2)	Co3–S1	2.131 (2)
Co1–C16	2.014 (6)	Co2–C16	2.040 (6)
Co3–C16	1.912 (6)	C16–N1	1.231 (8)
C17–N1	1.452 (9)	C17–C18	1.475 (10)
Co1–C1	2.106 (11)	Co1–C2	2.091 (14)
Co1–C3	2.078 (12)	Co1–C4	2.084 (12)
Co1–C5	2.101 (13)	Co2–C6	2.118 (10)
Co2–C7	2.104 (12)	Co2–C8	2.089 (11)
Co2–C9	2.094 (11)	Co2–C10	2.112 (13)
Co3–C11	2.093 (11)	Co3–C12	2.094 (13)
Co3–C13	2.095 (12)	Co3–C14	2.095 (13)
Co3–C15	2.093 (15)		
Angles, deg			
Co1–Co2–Co3	59.7 (1)	Co2–Co3–Co1	60.9 (1)
Co2–Co1–Co3	59.5 (1)	Co1–S1–Co2	71.9 (1)
Co1–S1–Co3	70.5 (1)	Co2–S1–Co3	70.3 (1)
Co1–C16–Co2	75.5 (2)	Co1–C16–Co3	77.5 (2)
Co2–C16–Co3	76.9 (2)	C16–N1–C17	130.6 (6)
N1–C17–C18	112.6 (6)		

[a] The cyclopentadienyl ligands were refined as rigid pentagons with C–C = 1.420(1) Å.

The [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNR)$] complexes (1) are green crystalline solids soluble in organic solvents but insoluble in water. They are air-sensitive in solution but less so in the solid state. Although most can be stored indefinitely under nitrogen at −25 °C, their thermal stability is a function of R. When R = 4-MeC_6H_4, the complex is very stable both in the solid state and in solution, when R = 2-ClC_6H_4, 1 is isolable but unstable in solution, and when R = Pr^i, Bu^t, 1-naphthyl, or CO_2Et, 1 cannot be isolated but may be detected in the reaction mixture. This instability is partly a consequence of steric effects with the larger R destabilizing the cluster. However this cannot be the whole story as [$Co_3(\eta\text{-}MeC_5H_4)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)$] is very much less stable than its cyclopentadienyl counterpart. Controlled thermolysis of [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)$] in refluxing Tetralin at 207 °C resulted in its decomposition, but no characterisable products were obtained. However the mass spectral data suggests that one of the thermolysis products is [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$] (see below).

Isocyanide exchange between 1 (R = Ph) and MeNC or $Co(\eta\text{-}C_5H_5)$ exchange between 1 (R = Me or Ph) and [$Ni(\eta\text{-}C_5H_5)_2$] did not take place in benzene solution at room temperature. At higher temperatures only decomposition products could be isolated from these reactions.

Structure of [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNEt)$]. This has been determined by X-ray diffraction. It is illustrated in Figure 1; bond lengths and angles are summarized in Table III. The molecules are held in the crystals by van der Waals forces, and there are no unusual intermolecular contacts. There is only one isomer in the unit cell, unlike [$Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_{11})$] where there are two, A and B, in the ratio 1:1.[6]

The molecular structures is based on a Co_3 triangle capped on one side by a μ_3-CNEt ligand and on the other by μ_3-S with a η^5-C_5H_5 group coordinated to each cobalt such that the cyclopentadienyl centroids lie virtually in the Co_3 plane and the rings lie perpendicular to it. These rings are disordered.

The complexes (I) are 48-electron systems. Bond lengths and angles (Table IV) are comparable to those in related derivatives of the general type [$Co_3(\eta\text{-}C_5R_5)_3(\mu_3\text{-}Y)(\mu_3\text{-}CX)$] where CX,Y = CO,NH;[20] CO,$NCONH_2$;[20] CO,O;[21] CO,S;[22] and CS,S.[23] In particular the Co–Co bond lengths of 2.447–2.483 Å are consistent with Dahl's suggestion that they are a function of the covalent radius of the larger μ_3-ligand, in this case S.

The μ_3-CNR ligands in 1 act as two-electron donors to the Co_3S moiety. When R = Et, the Co–C_μ (1.912–2.014

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(19) Harris, R. O.; Powell, J.; Walker, A.; Yaneff, P. V. *J. Organomet. Chem.* **1977**, *141*, 217.

(20) Bedard, R. L.; Rae, A. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 5924.

(21) Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 3763.

(22) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082.

(23) Werner, H.; Leonhard, K.; Kolb, O.; Rottinger, E.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 1654.

Å), μ_3-C–N (1.231 Å), and N–R distances (1.452 Å) are not greatly different from the Fe–C_μ (1.90–1.93 Å), μ_2-C–N (1.23–1.26 Å), and N–R (1.45–1.48 Å) distances found in various $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNR)_n]$ derivatives which contain μ_2-CNR ligands, but they are much greater than the Fe–C (1.76–1.81 Å) and C–N (1.16–1.22 Å) distances of the terminal CNR ligands in these compounds.[24,25] The values are consistent with considerable back-bonding from the Co_3S moiety into the CN π^* orbitals. The isocyanide ligand bends at N so that the R–N bond lies across the Co1–Co2 bond, as it does in $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNC_6H_{11})]$.[6] This orientation is just one of a number that are possible. Calculations on the closely related $[Co_3(\mu_3\text{-}COMe)(CO)_9]$[26] suggests that all are close in energy and that the final conformation is largely determined by steric interactions. The bending angle at N is 130.6° for **1** (R = Et). This is similar to the values of 125–131° found for the μ_2-CNR ligands, and it appears to be the value at which the π-acceptor ability of the isocyanide is at its maximum.[27] It is also similar to the C–N–R angle of 129° found for isomer B of **1** (R = C_6H_{11}) but differs from the 141° of isomer A.[6] The difference between A and B is attributed to steric effects. In both isomers the cyclohexyl ring adopts the chair conformation, but in A the cyclohexyl group is axially bonded to N and lies above the Co_3 ring while in B it is equatorially bonded and lies away from the Co_3 ring.[6] In the closely related complexes containing the $M_3(\mu_3\text{-}COMe)$ moieties, the C–O–Me angles lie between 115.6 (9)° and 122.5 (9)°.[26] In a molecule of C_{3v} symmetry, the two C–N π^* orbitals are degenerate. The bending of the C–N–R system across the Co1–Co2 bond lifts this degeneracy and implies unequal occupancy of the two π^* orbitals. This is reflected in small but probably significant variations in the dimensions of the $Co_3(S)(C)$ "trigonal bipyramid" as bond lengths to Co3 differ from those to Co1 and Co2. The Co1–Co2 bond length of 2.483 (1) Å differs from the other two, 2.452 (1) and 2.447 (1) Å, the Co3–S1 distance differs slightly from the other two, 2.130 (2) versus 2.112 (2) and 2.113 (2) Å, and Co3–C16 is much shorter than Co1–C16 and Co2–C16, 1.912 (6) versus 2.014 (6) and 2.040 (6) Å.

Reactions of 1 with Lewis Acids. The ability of the μ_2-CNR ligand to act as a Lewis base by way of the lone pair on the nitrogen atom has been well documented. It would be expected that the occupancy of the CN π^* orbitals and, therefore, the basicity of the nitrogen atom would be enhanced still further for a μ_3-CNR ligand. This expectation has been realized. Complexes **1** act as monoacidic and diacidic bases to give $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)R\}]^+$, $[\mathbf{2}]^+$, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(R')R\}]^+$, $[\mathbf{3}]^+$, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)_2R\}]^{2+}$, $[\mathbf{4}]^{2+}$, and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)(R')R\}]^{2+}$, $[\mathbf{5}]^{2+}$, salts. Some of these are listed in Table I.

Although the direct reaction of **1** with $HBF_4 \cdot Et_2O$ in benzene followed by recrystallization from ethanol gives $[\mathbf{2}][BF_4]$ when R = aryl, when R = Et the product is $[\mathbf{4}][BF_4]_2 \cdot 2H_2O$. This difference may be attributed to the electron-withdrawing ability of the aryl groups, which lowers the basicity of the N atom (cf. $PhNH_2$ and $MeNH_2$[28]). $[\mathbf{2}]BF_4$ are best prepared from **1** and $[Ph_3C]BF_4$ in either benzene or dichloromethane. Deuterated solvents give the same products, which suggests that the protons do not arise from the solvent.

The ease with which **1** react with R′X to give $[\mathbf{3}]X$ salts decreases along the series (a) $X^- = SO_3CF_3^- > I^- > Br^{-*}$; (b) R′ = Me > Et ≫ Pr^n ≫ Bu^{t*}, Ph* for X = I; (c) R = Me ~ Et > Ph for R′I = EtI; and (d) R = $4\text{-}MeC_6H_4$ > $4\text{-}BrC_6H_4$ > $4\text{-}ClC_6H_4$ > Ph ≫ $2\text{-}ClC_6H_4^*$, $3\text{-}CF_3C_6H_4^*$ for R′I = MeI. The asterick indicates no reaction. The patterns of reactivity are as would be expected. Although electronic factors influence adduct formation, steric effects are clearly important with bulky R and R′ hindering formation of $[\mathbf{3}]^+$ salts.

It is probable that steric effects also prevent the further alkylation of $[\mathbf{3}]^+$. However the less bulky H^+ converts $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)Et\}]^+$ to $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)(Me)Et\}]^{2+}$ salts, but it does not react with $[\mathbf{3}]^+$ when R or R′ is an aryl group. This also is probably a consequence of the delocalization of the N lone pair into the aryl ring.

Although solutions of **1** in nitromethane are nonconducting, those of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(R)Me\}]I$ have conductivities Λ of 68, 66, and 58 Ω^{-1} cm^2 mol^{-1}, when R = Me, Et, and Ph, respectively (concentration 10^{-3} M).

Infrared Spectra. The infrared spectra of **1** and their Lewis acid adducts show a number of absorption bands that cannot be identified or that yield no significant structural information, e.g., an intense band in all spectra at ca. 800 cm^{-1} is probably due to a cyclopentadienyl group vibration.

The absorption bands due to the ν(CN) vibrations of **1** are relatively intense and easy to identify. Their frequencies are ca. 1642–1648 cm^{-1} when R = alkyl and 1529–1548 cm^{-1} when R = aryl, in which case they are a function of the substituents on the phenyl ring. The difference between the alkyl and aryl complexes is probably a consequence of the ability of the aryl group to withdraw negative charge from the N. This correlates with the markedly lower basicity at the aryl derivatives toward Lewis acids (see above). The frequencies of the ν(CN) vibrations of **1** (R = alkyl) are very similar to those of the $\nu(CN_\mu)$ vibration of, e.g., $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)_2]$ (1640 cm^{-1}),[29] which is consistent with the C–N bond lengths (see above). On the other hand, the frequencies of the ν(CN) modes of **1** (R = aryl) are much lower than those of the $\nu(CN_\mu)$ vibration of, e.g., $[Fe_2(\eta\text{-}C_5H_5)_2(CNPh)_2(\mu\text{-}CNPh)_2]$ (1638 cm^{-1}).[30]

The alkylation and protonation of **1** results in a decrease of the ν(CN) frequency in $[\mathbf{2}]^+$ and $[\mathbf{3}]^+$ salts to 1478–1506 cm^{-1} when R = alkyl and 1308–1327 cm^{-1} when R = aryl. The absorption bands are weaker than those of **1** but can still be identified easily. The spectra of $[\mathbf{2}]^+$ contain a readily identified absorption band at ca. 3300 cm^{-1} due to their ν(NH) vibration and, when R = Ph or $4\text{-}MeC_6H_4$, another at ca. 1487 cm^{-1}. which we attribute to their δ(NH) modes. A comparison of the spectra of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Z)C_6H_4Me\text{-}4\}][BF_4]$ (Z = H or D) allows the assignment of ν(NZ) at 3305/2457 cm^{-1}, δ(NZ) at 1487/1311 cm^{-1}, and ν(CN) at 1326/1364 cm^{-1}. The increase of the ν(CN) frequency is due to coupling between the ν(CN) and δ(NZ) vibrations. When Z = H, the latter lies at higher frequencies, and as they are widely separated, coupling is limited. However, when Z = D the two vibrations have

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[24] Hunt, I. D.; Mills, O. S. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2432.

[25] Ennis, M.; Kumar, R.; Manning, A. R.; Howell, J. A. S.; Mathur, P.; Rowan, R. J.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1981**, 1251, and references therein.

[26] Aitchison, A. A.; Ferrugia, L. J. *Organometallics* **1987**, *6*, 819.

[27] Howell, J. A. S.; Saillard, J. Y.; Le Beuze, A.; Jaouen, G. *J. Chem. Soc., Dalton Trans.* **1982**, 2533.

[28] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

[29] Manning, A. R.; Murray, P. T. *J. Chem. Soc., Dalton Trans.* **1986**, 2399.

[30] McNally, G.; Murray, P. T.; Manning, A. R. *J. Organomet. Chem.* **1983**, *243*, C87.

[31] Fehlhammer, W. P.; Mayr, A.; Christian, G. *Angew. Chem., Int. Edit. Engl.* **1978**, *17*, 866.

very similar frequencies with the latter being the lower, and couple extensively. Consequently, the absorption band due mainly to the ν(CN) vibration increases in frequency while that due mainly to the δ(NZ) vibration decreases. Furthermore the ratio of the intensities of the ν(CN):δ(NH) absorption bands is 1:0.27 but that of ν(CN):δ(ND) is 1:0.58. These spectra and those of [**4**]$^{2+}$ and [**5**]$^+$ salts discussed below show readily identified absorption bands due to the counteranions where appropriate.

The absorption bands due to the ν(CN) vibrations of [**4**]$^{2+}$ and [**5**]$^{2+}$ salts have very low frequencies (1418 cm^{-1}) and are relatively weak. This is consistent with a low C–N bond order. However the mixing of this vibration with ν(C–R) is probably very extensive. We have not been able to detect absorption bands due to the ν(NH) vibrations of these compounds except for one possibility at 3290 cm^{-1} in the spectrum of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(H)_2Et\}][BF_4]_2\cdot 2H_2O$. This is probably due to hydrogen bonding between the cation and water or the anion as has been observed elsewhere.[29]

The frequencies of the absorption bands due to the Lewis acid adducts $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(E)Ph\}]$ where E = I_4 or $1.5HgCl_2$ are very close to those of [**2**]$^+$ and [**3**]$^+$. This suggests that both are monoadducts similar to the $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CSE)]$ derivatives,[8] in which electrophilic attack has occurred at the N rather than the μ_3-S ligand. Consequently we formulate them respectively as a $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(I)Ph\}]I_3$ salt and a $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(HgCl_2)_{1.5}Ph\}]_n$ polymer.

NMR Spectra. The ^{1}H NMR spectra of **1**, the [**2**]$^+$, [**3**]$^+$, [**4**]$^{2+}$, and [**5**]$^{2+}$ salts, and the $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(E)Ph\}]$ (E = I_4 or $1.5HgCl_2$) adducts are unremarkable and consistent with the molecular formulas. Only the resonances due to the C_5H_5 protons are given in Table I, but those due to R and, where appropriate, R′ groups and X$^-$ ions are readily identified. For example, the Me protons of **1** (R = Me) give rise to a singlet at 4.25 ppm (cf. 3.96 ppm for μ-CNMe in cis-$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$).[30] The spectra of all [**2**]$^+$ and some [**4**]$^{2+}$ and [**5**]$^{2+}$ salts also show a very broad resonance at 10–12.5 ppm, which disappear on the addition of a large excess of D_2O and so are attributed to the N–H protons. The spectra of **1** and [**3**]X are independent of temperature down to −50 °C. Thus, although there are at least two types of cyclopentadienyl groups in **1** with their bent μ_3-CNR ligands (see above), they are interconverted rapidly on the NMR time scale even at −50 °C. The two Me groups of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNMe_2)]I$ give rise to a singlet at 4.47 ppm and are equivalent even at −50 °C.

The ^{13}C NMR spectra of [**4**]$^{2+}$ and [**5**]$^{2+}$ salts could not be obtained due to a combination of sample stability and insolubility. It proved possible to obtain the spectra of **1** and the more stable [**2**]$^+$ and [**3**]$^+$ salts. They are unremarkable and consistent with the molecular formulas. Again, all show a single resonance due to their three cyclopentadienyl groups, indicating rapid site exchange on the NMR time scale even at −90 °C for **1** (R = 4-C_6H_4Me). A broad resonance has been detected in the spectra of **1** but not [**2**]X or [**3**]X, which are attributed to the μ_3-C atom. Its chemical shift is a function of R (238.5 ppm when R = Me and 259.5 ppm when R = Ph) and lies noticeably upfield of those of the μ_2-CNR ligands in $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CNR)_2(CNR)_2]$ (269 ppm when R = Me and 270 ppm when R = Ph[30,31]), whereas it might have been expected to lie downfield. The resonances due to the R, R′, and [X]$^-$ have been identified but are not included in Table I.

Mass Spectra. The mass spectra of **1** all show the molecular ion and ions that arise from the loss of RNC but not CS, providing more evidence that the RNCS molecule divides RNC/S and not RN/CS during its reaction. An important ion in all spectra is $[Co_3(C_5H_5)_3(S)_2]^+$, which implies that the thermolysis of **1** gives $[Co_3(\eta\text{-}C_5H_5)_3(S)_2]$, but we have not been able to isolate a characterizable product from such a reaction (see above).

Although only ions derived from **1** were found in the mass spectra of [**2**]X and [**4**]X_2 salts, the $[Co_3(C_5H_5)_3(S)\{CN(R')(R)]^+$ ions are observed in the spectra of all [**3**]X.

Registry No. **1** (R = Me), 88760-52-5; **1** (R = Et), 126111-28-2; **1** (R = C_6H_{11}), 88760-53-6; **1** (R = Ph), 88760-54-7; **1** (R = 4-MeC_6H_4), 126111-29-3; **1** (R = 2-ClC_6H_4), 126132-94-3; **1** (R = 3-ClC_6H_4), 126111-30-6; **1** (R = 4-ClC_6H_4), 126111-31-7; **1** (R = 4-BrC_6H_4), 126111-32-8; **1** (R = 3-$CF_3C_6H_4$), 126111-33-9; [**2**]BF_4 (R = Ph), 126132-95-4; [**2**]BF_4 (R = 4-ClC_6H_4), 126111-34-0; [**2**]BF_4 (R = 4-MeC_6H_4), 126111-35-1; [**2**]BF_4 (R = Me), 126111-37-3; [**2**]SO_3CF_3 (R = Et), 126111-50-0; [**2**]BF_4 (R = Et), 126111-65-7; [**3**]I (R = R′ = Me), 126111-38-4; [**3**]I (R = Et, R′ = Me), 126111-39-5; [**3**]I (R = R′ = Et), 126111-40-8; [**3**]I (R = Ph, R′ = Me), 126111-41-9; [**3**]I (R = Ph, R′ = Et), 126111-42-0; [**3**]I (R = 4-MeC_6H_4, R′ = Me), 126111-43-1; [**3**]I (R = 4-ClC_6H_4, R′ = Me), 126111-44-2; [**3**]I (R = 4-BrC_6H_4, R′ = Me), 126111-45-3; [**3**]SO_3CF_3 (R = R′ = Me), 126111-47-5; [**3**]SO_3CF_3 (R = Et, R′ = Me), 126111-49-7; [**3**]SO_3CF_3 (R = Ph, R′ = Me), 126111-67-9; [**3**]BPh_4 (R = Ph, R′ = Me), 126111-52-2; [**3**]BPh_4 (R = 4-MeC_6H_4, R′ = Me), 126111-54-4; [**3**]BPh_4 (R = 4-ClC_6H_4, R′ = Me), 126111-56-6; [**3**]BPh_4 (R = 3-$CF_3C_6H_4$, R′ = Me), 126111-58-8; [**3**]I_3 (R = Ph, R′ = I), 126111-60-2; [**4**]$[BF_4]_2$ (R = Et), 126111-36-2; [**5**]$[BF_4]_2$ (R = Et, R′ = Me), 126111-62-4; [**5**]$[PF_6]_2$ (R = Me, R′ = Et), 126111-64-6; $[Co_3(\eta\text{-}MeC_5H_4)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$, 126111-66-8; $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$, 32993-07-0; MeNCS, 556-61-6; EtNCS, 542-85-8; C_6H_{11}NCS, 1122-82-3; PhNCS, 103-72-0; 4-MeC_6H_4NCS, 622-59-3; 2-ClC_6H_4NCS, 2740-81-0; 3-ClC_6H_4NCS, 2392-68-9; 4-ClC_6H_4NCS, 2131-55-7; 4-BrC_6H_4NCS, 1985-12-2; 3-$CF_3C_6H_4$NCS, 1840-19-3; *i*-PrNCS, 628-30-8; *t*-BuNCS, 590-42-1; EtOCONCS, 16182-04-0; 1-$C_{10}H_7$NCS, 551-06-4; PhNCO, 103-71-9; MeNCO, 624-83-9; Pr^iNCNPr^i, 693-13-0; Bu^tCNBu^t, 691-24-7.

Supplementary Material Available: Tables of hydrogen atom parameters, close intramolecular contacts, and thermal parameters for the non-hydrogen atoms (6 pages); listings of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.