The Preparation and Structure of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNC_6H_{11})(\mu_3\text{-}S)]$; the First Example of an Organoisocyanide as a Triply Bridging, Two-electron Donor Ligand

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The reaction of $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$ with RNCS in refluxing benzene gives $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}PhNCS\text{-}C,S)]$ and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNR)(\mu_3\text{-}S)]$ (**2**) (R = Me, C_6H_{11}, or Ph); the structure of (**2**; R = C_6H_{11}) has been determined by an *X*-ray diffraction study.

At elevated temperatures CS_2 is cleaved by $[Co(\eta\text{-}C_5H_5)(CO)(PR'_3)]$ (R′ = alkyl or aryl) to give $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$ and other products.[1,2] We felt that if CS_2 were replaced by RNCS it might be possible to use this reaction to prepare for the first time a complex containing a μ_3-CNR ligand acting as a two-electron donor bonded solely through C. As we have previously reported,[3] PhNCS and $[Co(\eta\text{-}C_5H_5)(CO)(PPh_3)]$ react in refluxing benzene to give $[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta^2\text{-}PhNCS\text{-}C,S)]$ (**1**) and $[Co_n(\eta\text{-}C_5H_5)_n(PhNCS)]$ where $n = 3$ or 4. It has been shown that $n = 3$ by the preparation of other $[Co_3(\eta\text{-}C_5H_5)_3(RNCS)]$ derivatives (**2**) where R = Me or C_6H_{11} as well as Ph, and the spectroscopic data described below.

$[Co(\eta\text{-}C_5H_5)(PPh_3)(\eta\text{-}PhNCS\text{-}C,S)]$
(**1**)

$[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNR)(\mu_3\text{-}S)]$
(**2**) R = Me, C_6H_{11}, or Ph

The complexes (**2**) are black, air-stable, crystalline solids. The ^1H n.m.r. spectra of all three confirm their $Co_3(C_5H_5)_3$, formulation ($n = 3$), *e.g.* when R = Me the cyclopentadienyl and methyl proton resonances are singlets at δ 4.77 and 4.52 respectively in $CDCl_3$ solution. Their i.r. spectra each show an intense absorption band at 1550—1555 cm^{-1} which may be due to a $\nu(CN)$ vibration, but they do not show one between 1000 and 1100 cm^{-1} attributable to the $\nu(CS)$ mode of a μ_3-CS ligand {*cf.* 1075 cm^{-1} for $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$[1,2]}. The mass spectra of the three complexes (**2**) show peaks due to the molecular ions and to ions which have lost an RNC moiety but not to ions which have lost CS.

These data suggest that complexes (**2**) are indeed $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNR)(\mu_3\text{-}S)]$ complexes. This was confirmed by an *X*-ray diffraction study of a single crystal of the cyclohexyl derivative. *Crystal data*: $C_{22}H_{26}Co_3NS$, $M = 513.32$, monoclinic with $a = 15.673$ (8), $b = 9.587(7)$, $c = 27.834(19)$ Å, $\beta = 94.4(1)°$, $U = 4169.93$ Å^3, $D_m = 1.65$ g cm^{-3}, $Z = 8$, $D_c = 1.635$ g cm^{-3}, $F(000) = 2096$. Systematic absences: $h0l$ if $h+l \neq 2n$ and $0k0$ if $k = 2n$. Space group $P2_1/n$ (non standard No. 14). 2113 non-zero unique reflexions (photographic, precession $0kl$—$4kl$ and $hk0$—$hk6$). Final $R = 0.092$ and R' $[= (\Sigma\omega\Delta^2/\Sigma\omega|F_o|^2)^{\frac{1}{2}}] = 0.120$.†

Its structure (Figure 1) is based on a trigonal bipyramidal $Co_3(C)(S)$ core with C and S atoms at axial positions and with $\eta^5\text{-}C_5H_5$ ligands completing the co-ordination shell about each Co atom so that each lies approximately perpendicular to the Co_3 plane. In broad outline the structure is similar to that of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CS)(\mu_3\text{-}S)]$[1] but with the μ_3-CS ligand replaced by $\mu_3\text{-}CNC_6H_{11}$. This is the first time that an organoisocyanide ligand has been observed to bridge symmetrically a metal–metal bonded M_3 triangle with three more or less equivalent M–C bonds. Unfortunately the crystal and the data obtained from it were not of the highest quality and so we were not able to obtain anisotropic thermal parameters for C and N atoms. However it is clear that there are two isomeric forms of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNC_6H_{11})(\mu_3\text{-}S)]$ in the unit cell which are illustrated in Figure 1. In both, the $C\text{–}N\text{–}C(C_6H_{11})$ system is bent at N. However in isomer (A) ∠ C–N–C is 141° and the cyclohexyl group lies above the Co_3 ring. In isomer (B)

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

∠ C–N–C is 129° and the cyclohexyl group lies away from the Co_3 ring. In both (A) and (B) the bend in the isocyanide ligand is approximately away from one Co atom towards the opposite Co–Co bond when the molecules are viewed along the S · · · · C axes which lie almost perpendicular to the Co_3 planes.

In (**2**) the μ_3-CNR ligand may be considered as acting (a) as a two-electron donor to the Co_3 triangle through its C lone pair of electrons, and (b) as a π-acceptor ligand utilizing its two vacant π^* C–N orbitals. The relatively low ν(CN) frequencies of (**2**) are consistent with extensive back-bonding {*cf.* $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe)_2]$[4] where $\nu(CN\mu) = 1640$ cm^{-1}}. When the μ_3-CNR ligand is axially symmetric the two π^* orbitals are degenerate and are equally capable of accepting electron density from the three metal atoms. Consequently, although the C–N bond would be expected to lengthen, it is not necessary that the ligand should bend. This leads us to suggest that the direction and extent of the μ_3-CNR ligand bending is determined to a large extent by non-bonding interactions rather than electronic factors. This contrasts sharply with the situation in a $M_2(\mu_2\text{-CNR})$ system where the two π^* orbitals are not equivalent and would be expected to interact differently with the M_2 moiety (*cf.* ref. 5).

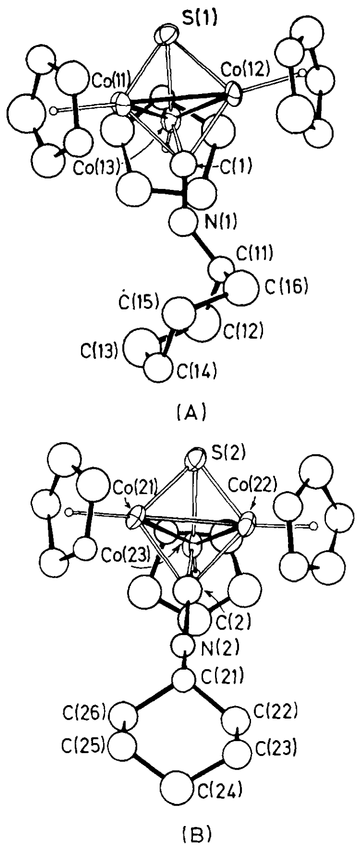

Figure 1. Structures of the two isomers of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}CNC_6H_{11})(\mu_3\text{-}S)]$. Some dimensions: isomer (A): Co(11)–Co(12) 2.487(4), Co(11)–Co(13) 2.454(5), Co(12)–Co(13) 2.409(4), Co(11)–C(1) 1.95(2), Co(12)–C(1) 1.88(2), Co(13)–C(1) 2.06(3), Co–S 2.116(6)—2.129(7), C(1)–N(1) 1.29(3) Å, and ∠C(1)–N(1)–C(C_6H_{11}) 141°; isomer (B): Co(21)–Co(22) 2.458(4), Co(21)–Co(23) 2.460(4), Co(22)–Co(23) 2.448(4), Co(21)–C(2) 1.99(3), Co(22)–C(2) 1.97(3), Co(23)–C(2) 1.90(2), Co–S 2.105(7)—2.117(7), C(2)–N(2) 1.26(3) Å, and ∠C(2)–N(2)–C(C_6H_{11}) 129°.

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References

1 H. Werner and K. Leonhard, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 627; H. Werner, K. Leonhard, O. Kolb, E. Rottinger, and H. Vahrenkamp, *Chem. Ber.*, 1980, **113**, 1654.

2 J. Fortune and A. R. Manning, manuscript in preparation.

3 J. Fortune and A. R. Manning, *J. Organomet. Chem.*, 1980, **190**, C95.

4 G. McNally, P. T. Murray, and A. R. Manning, *J. Organomet. Chem.*, 1983, **243**, C87.

5 J. A. S. Howell, J.-Y. Saillard, A. LeBeuze, and G. Jaouen, *J. Chem. Soc., Dalton Trans.*, 1982, 2533.