

# The Preparation and Structure of $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNC}_6\text{H}_{11})(\mu_3\text{-S})]$ ; the First Example of an Organoisocyanide as a Triply Bridging, Two-electron Donor Ligand

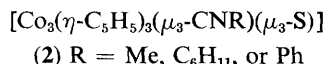
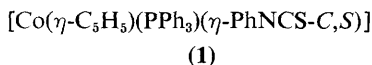
John Fortune,<sup>a</sup> A. R. Manning,<sup>\*a</sup> and F. S. Stephens<sup>b</sup>

<sup>a</sup> Department of Chemistry, University College, Belfield, Dublin 4, Ireland

<sup>b</sup> School of Chemistry, Macquarie University, North Ryde, New South Wales, Australia 2113

The reaction of  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]$  with RNCS in refluxing benzene gives  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^2\text{-PhNCS-C,S})]$  and  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNR})(\mu_3\text{-S})]$  (**2**) ( $\text{R} = \text{Me}$ ,  $\text{C}_6\text{H}_{11}$ , or  $\text{Ph}$ ); the structure of (**2**;  $\text{R} = \text{C}_6\text{H}_{11}$ ) has been determined by an X-ray diffraction study.

At elevated temperatures  $\text{CS}_2$  is cleaved by  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PR}'_3)]$  ( $\text{R}' = \text{alkyl}$  or  $\text{aryl}$ ) to give  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CS})(\mu_3\text{-S})]$  and other products.<sup>1,2</sup> We felt that if  $\text{CS}_2$  were replaced by RNCS it might be possible to use this reaction to prepare for the first time a complex containing a  $\mu_3\text{-CNR}$  ligand acting as a two-electron donor bonded solely through C. As we have previously reported,<sup>3</sup>  $\text{PhNCS}$  and  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]$  react in refluxing benzene to give  $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)(\eta^2\text{-PhNCS-C,S})]$  (**1**) and  $[\text{Co}_n(\eta\text{-C}_5\text{H}_5)_n(\text{PhNCS})]$  where  $n = 3$  or 4. It has been shown that  $n = 3$  by the preparation of other  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\text{RNCS})]$  derivatives (**2**) where  $\text{R} = \text{Me}$  or  $\text{C}_6\text{H}_{11}$  as well as  $\text{Ph}$ , and the spectroscopic data described below.



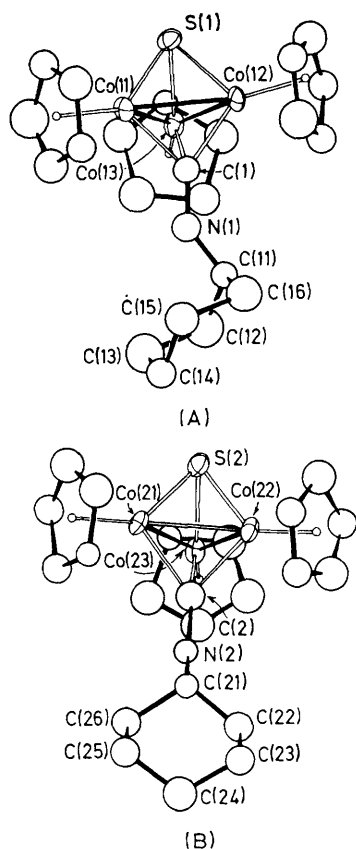
The complexes (**2**) are black, air-stable, crystalline solids. The  $^1\text{H}$  n.m.r. spectra of all three confirm their  $\text{Co}_3(\text{C}_5\text{H}_5)_3$  formulation ( $n = 3$ ), *e.g.* when  $\text{R} = \text{Me}$  the cyclopentadienyl and methyl proton resonances are singlets at  $\delta$  4.77 and 4.52 respectively in  $\text{CDCl}_3$  solution. Their i.r. spectra each show an intense absorption band at  $1550\text{--}1555\text{ cm}^{-1}$  which may be due to a  $\nu(\text{CN})$  vibration, but they do not show one between  $1000$  and  $1100\text{ cm}^{-1}$  attributable to the  $\nu(\text{CS})$  mode of a  $\mu_3\text{-CS}$  ligand [*cf.*  $1075\text{ cm}^{-1}$  for  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CS})(\mu_3\text{-S})]^{1,2}$ ]. 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  $[\text{Co}_3\text{-}$

$(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNR})(\mu_3\text{-S})]$  complexes. This was confirmed by an X-ray diffraction study of a single crystal of the cyclohexyl derivative. *Crystal data:*  $\text{C}_{22}\text{H}_{26}\text{Co}_3\text{NS}$ ,  $M = 513.32$ , monoclinic with  $a = 15.673(8)$ ,  $b = 9.587(7)$ ,  $c = 27.834(19)\text{ \AA}$ ,  $\beta = 94.4(1)^\circ$ ,  $U = 4169.93\text{ \AA}^3$ ,  $D_m = 1.65\text{ g cm}^{-3}$ ,  $Z = 8$ ,  $D_c = 1.635\text{ g cm}^{-3}$ ,  $F(000) = 2096$ . 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  $0kl\text{--}4kl$  and  $hk0\text{--}hk6$ ). Final  $R = 0.092$  and  $R' [= (\sum \omega \Delta^2 / \sum \omega |F_o|^2)^{1/2}] = 0.120$ .

Its structure (Figure 1) is based on a trigonal bipyramidal  $\text{Co}_3(\text{C})(\text{S})$  core with C and S atoms at axial positions and with  $\eta^5\text{-C}_5\text{H}_5$  ligands completing the co-ordination shell about each Co atom so that each lies approximately perpendicular to the  $\text{Co}_3$  plane. In broad outline the structure is similar to that of  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CS})(\mu_3\text{-S})]^\dagger$  but with the  $\mu_3\text{-CS}$  ligand replaced by  $\mu_3\text{-CNC}_6\text{H}_{11}$ . This is the first time that an organoisocyanide ligand has been observed to bridge symmetrically a metal-metal bonded  $\text{M}_3$  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  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNC}_6\text{H}_{11})(\mu_3\text{-S})]$  in the unit cell which are illustrated in Figure 1. In both, the C-N-C( $\text{C}_6\text{H}_{11}$ ) system is bent at N. However in isomer (A)  $\angle \text{C-N-C}$  is  $141^\circ$  and the cyclohexyl group lies above the  $\text{Co}_3$  ring. In isomer (B)

<sup>†</sup> 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.



**Figure 1.** Structures of the two isomers of  $[\text{Co}_3(\eta\text{-C}_5\text{H}_5)_3(\mu_3\text{-CNC}_6\text{H}_{11})(\mu_3\text{-S})]$ . Some dimensions: isomer (A):  $\text{Co}(11)\text{--Co}(12)$  2.487(4),  $\text{Co}(11)\text{--Co}(13)$  2.454(5),  $\text{Co}(12)\text{--Co}(13)$  2.409(4),  $\text{Co}(11)\text{--C}(1)$  1.95(2),  $\text{Co}(12)\text{--C}(1)$  1.88(2),  $\text{Co}(13)\text{--C}(1)$  2.06(3),  $\text{Co--S}$  2.116(6)–2.129(7),  $\text{C}(1)\text{--N}(1)$  1.29(3) Å, and  $\angle \text{C}(1)\text{--N}(1)\text{--C}(\text{C}_6\text{H}_{11})$   $141^\circ$ ; isomer (B):  $\text{Co}(21)\text{--Co}(22)$  2.458(4),  $\text{Co}(21)\text{--Co}(23)$  2.460(4),  $\text{Co}(22)\text{--Co}(23)$  2.448(4),  $\text{Co}(21)\text{--C}(2)$  1.99(3),  $\text{Co}(22)\text{--C}(2)$  1.97(3),  $\text{Co}(23)\text{--C}(2)$  1.90(2),  $\text{Co--S}$  2.105(7)–2.117(7),  $\text{C}(2)\text{--N}(2)$  1.26(3) Å, and  $\angle \text{C}(2)\text{--N}(2)\text{--C}(\text{C}_6\text{H}_{11})$   $129^\circ$ .

$\angle \text{C--N--C}$  is  $129^\circ$  and the cyclohexyl group lies away from the  $\text{Co}_3$  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  $\text{S} \cdots \text{C}$  axes which lie almost perpendicular to the  $\text{Co}_3$  planes.

In (2) the  $\mu_3\text{-CNR}$  ligand may be considered as acting (a) as a two-electron donor to the  $\text{Co}_3$  triangle through its C lone pair of electrons, and (b) as a  $\pi$ -acceptor ligand utilizing its two vacant  $\pi^*$  C–N orbitals. The relatively low  $\nu(\text{CN})$  frequencies of (2) are consistent with extensive back-bonding {cf.  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe})_2]^4$  where  $\nu(\text{CN}\mu) = 1640 \text{ cm}^{-1}$ }. When the  $\mu_3\text{-CNR}$  ligand is axially symmetric the two  $\pi^*$  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  $\mu_3\text{-CNR}$  ligand bending is determined to a large extent by non-bonding interactions rather than electronic factors. This contrasts sharply with the situation in a  $\text{M}_2(\mu_2\text{-CNR})$  system where the two  $\pi^*$  orbitals are not equivalent and would be expected to interact differently with the  $\text{M}_2$  moiety (cf. ref. 5).

Received, 9th May 1983; Com. 581

## 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.