Preparation and Characterization of two Isocyanide Derivatives of Monosubstituted $[Fe_3(CO)_9S_2]$; Crystal Structure of $[Fe_3(CO)_8(CNPh)(\mu_2\text{-}S)_2]$ *

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Irradiation of $[Fe(CO)_5]$ in the presence of PhNCS produced $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ and two isomeric phenyl isocyanide derivatives, $[Fe_3(CO)_8(CNPh)(\mu_3\text{-}S)_2]$, substituted on either a central or a terminal iron atom. The crystal structure of the centrally substituted isomer was determined by X-ray diffraction.

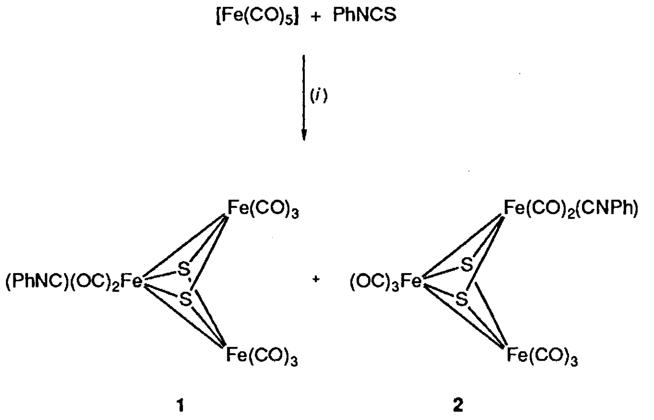
Substitution of carbonyl ligands in $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ normally occurs at a terminal iron atom of the open Fe_3 triangle. X-Ray crystallography was previously used to determine the structures of $[Fe_3(CO)_8L(\mu_3\text{-}S)_2]$ complexes with L = $NHMe_2$,[1] 2,3-diphenylcyclopropenylidene[2] and 1,3-dithiolene.[3] Similar structures were assigned to $[Fe_3(CO)_8L(\mu_3\text{-}Se)_2]$ [L = PBu_3 or $P(OPh)_3$] on the basis of their ^{13}C NMR spectra.[4] A stable monomeric PhNCS derivative of $[Fe(CO)_5]$ was prepared by substitution of phosphine ligands in $[Fe(CO)_2(PPh_3)_3]$ to produce $[Fe(CO)_2(\eta^2\text{-}SCNPh)(PPh_3)]$.[5]

We have shown previously that irradiation of $[Fe(CO)_5]$ in the presence of thiones yields mainly di- and tri-nuclear iron compounds.[6] To find out whether a monomeric sulphur-donor complex would form or whether desulphurization accompanied by metal–metal bonding would occur, $[Fe(CO)_5]$ was irradiated in the presence of an isothiocyanate, PhN=C=S, which, like the thiones, also contains a carbon–sulphur double bond.

Results and Discussion

Reaction of equimolar quantities of $[Fe(CO)_5]$ and PhNCS under UV irradiation produced a red solution from which low yields of $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ and two products of composition $Fe_3(CO)_8(CNPh)S_2$ were separated by column chromatography. No other isocyanides of the $Fe_3(CO)_8LS_2$ family are known. We established by X-ray crystal structure determination and ^{13}C NMR spectroscopy that in compound **1** the isocyanide ligand is bonded to the central iron atom and we propose on the basis of spectroscopic data that in the other product the ligand is bonded to a terminal iron (**2** in Scheme 1).

Crystal Structure.—The crystal structure of compound **1** was determined by X-ray diffraction. It reveals (Fig. 1) a unique co-ordination of the isocyanide ligand to the central iron atom. The open Fe_3S_2 framework is well established in carbonyl chemistry.[1–3,7,8] The two iron–iron bonds in **1** are identical [2.587(1) Å] and the average Fe–S distance is 2.235(6) Å. The Fe–Fe and Fe–S separations fall within the ranges reported for other similar complexes (2.535–2.645 and 2.214–2.297 Å).[1–3,8] When the substitution has occurred terminally (in contrast to the regular configuration observed here), the internal differences in Fe–Fe and Fe–S distances emphasize the asymmetry of the molecules. The Fe–Fe–Fe bond angle of 81.46(3)° found here is normal. The Fe–C(isocyanide) bond [1.848(6) Å] in **1** is longer than the Fe–C(carbonyl) bond distances [average 1.791(15) Å], in accordance with the variation in metal–carbon bond distances observed in the complex $[Cr(CO)_4\{C(NH_2)Ph\}(CNBu^t)]$.[9]



Scheme 1 (*i*) *hν*, tetrahydrofuran

Infrared Spectroscopy.—Five to eight carbonyl vibrations have been reported for terminally substituted $Fe_3(CO)_8S_2$ complexes.[1,2,10,11] We found (see Experimental section) eight vibration bands for **1** and nine for **2**. The two strongest absorption bands of **1** occur at 2075 and 2036 cm^{-1} and both were completely absent in the spectrum of compound **2**, ruling out the possibility that traces of **1** could have been responsible for the molecular ion and other mass peaks obtained for **2**. Complex **2** has its strongest ν(CO) band in hexane at 2025 cm^{-1} whereas terminally substituted $[Fe_3(CO)_8(NHMe_2)S_2]$ has such a band at 2042 cm^{-1} in the same solvent.[10] The spectra of other terminally substituted complexes were measured in various solvents and show very little mutual correspondence in position and intensity. Infrared spectroscopy is, therefore, not an effective tool for discriminating between the two types of substitution. The spectrum of crystalline **1** in the far-infrared region was obtained.

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* Octacarbonyl-1κ^3*C*,2κ^2*C*,3κ^3*C*-phenyl isocyanide-2κ*C*-di-μ_3-sulphidotriiron (2*Fe–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 ^{13}C NMR data[a] for $Fe_3(CO)_8L(\mu_3\text{-}S)_2$ complexes

	L				
Assignment	CNPh (**1**)	CNPh (**2**)	CO[b]	C(Ph)=CPh[c]	CSCH=CHS[d]
CO	211.4	206.7	204.8	198.8	205.6[e]
		212.6	210.3	206.1	211.4
		213.6		211.3	214.3
CN	126.2	126.0			
Ph	126.6	128.9–129.4			

[a] Measured in $CDCl_3$; δ relative to $SiMe_4$. [b] Ref. 4. [c] Ref. 2. [d] Prepared according to ref. 3. [e] Measured in CD_2Cl_2 at 273 K.

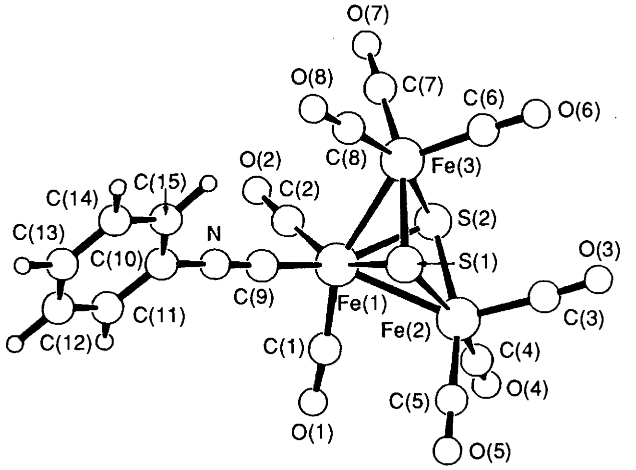

Fig. 1 Structure of $[Fe_3(CO)_8(CNPh)(\mu_3\text{-}S)_2]$ **1** showing the atomic numbering scheme. Bond lengths (Å) are: Fe–Fe 2.587(1)(both), Fe(1)–C(9) 1.848(6), C(9)–N 1.154(7) and N–C(10) 1.395(7). Bond angles (°) are: Fe(2)–Fe(1)–Fe(3) 81.46(3), S(1)–Fe(1)–S(2) 80.21(5), S(1)–Fe(2)–S(2) 80.59(5), S(1)–Fe(3)–S(2) 80.14(5), Fe(1)–C(9)–N 178.0(4) and C(9)–N–C(10) 175.6(4)

NMR Spectroscopy.—Carbon-13 NMR data for compounds **1** and **2** and three other comparable complexes are given in Table 1. It is clear that **1** has only one CO resonance whereas all the others (including **2**) exhibit two or three. Benoit *et al.*[3] reported only two signals at δ 210 and 205 for $[Fe_3(CO)_8(CSCH{=}CHS)(\mu_3\text{-}S)_2]$, but we established by variable-temperature 500 MHz spectrometry that the room-temperature spectrum consists of a strong singlet at δ 211.4 and a weaker broad multiplet at 205.6 and that at 273 K another peak appears at δ 214.3. It appears that the CNPh substituent on Fe(1) lowers the energy barrier sufficiently for carbonyl exchange to occur amongst all the carbonyl ligands at room temperature. Apart from X-ray crystallography, ^{13}C NMR spectroscopy seems the only physical method suitable for determining the position of isocyanide addition in an $Fe_3(CO)_8LS_2$ type of complex.

It is difficult to assign any signal to the C≡N carbon atom since no reference to the chemical shift of a terminal PhNC ligand was found in the literature. The ^{13}C NMR spectrum of the free ligand was no help either. We, therefore, tentatively assign the signals at δ 126.2 and 126.0 in the spectra of compounds **1** and **2** respectively to the isocyanide carbon, based on the fact that the signal for the *ipso* carbon of the phenyl ring is usually to low field of the multiplet representing the remaining carbons of the phenyl ring. The signals at δ 126.6 and 128.9–129.4 are assigned to the phenyl carbon atoms of **1** and **2** respectively.

Table 2 Fractional coordinates for non-hydrogen atoms of complex **1**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe(1)	0.722 64(7)	0.373 45(6)	0.215 73(6)
Fe(2)	0.776 81(7)	0.321 92(7)	0.439 82(6)
Fe(3)	0.469 92(7)	0.282 75(7)	0.370 19(6)
S(1)	0.688 5(1)	0.169 5(1)	0.395 0(1)
S(2)	0.585 0(1)	0.452 6(1)	0.367 2(1)
O(1)	1.021 5(4)	0.464 2(6)	0.132 4(4)
O(2)	0.603 8(5)	0.612 5(4)	0.013 2(3)
O(3)	0.625 7(4)	0.222 5(3)	0.721 3(3)
O(4)	0.899 3(4)	0.576 6(3)	0.408 0(3)
O(5)	1.058 9(3)	0.156 1(4)	0.454 5(4)
O(6)	0.309 8(4)	0.158 8(4)	0.648 4(3)
O(7)	0.248 3(4)	0.495 9(4)	0.257 0(4)
O(8)	0.408 2(4)	0.086 4(4)	0.275 1(3)
N	0.780 5(4)	0.205 9(4)	0.050 3(3)
C(1)	0.904 5(6)	0.427 4(6)	0.170 3(5)
C(2)	0.653 5(6)	0.520 6(5)	0.090 8(4)
C(3)	0.688 3(5)	0.260 7(5)	0.612 4(4)
C(4)	0.853 8(5)	0.477 2(5)	0.422 4(4)
C(5)	0.949 3(5)	0.219 7(5)	0.449 5(4)
C(6)	0.369 1(5)	0.208 0(5)	0.538 6(4)
C(7)	0.332 5(5)	0.412 0(5)	0.300 9(4)
C(8)	0.430 6(5)	0.162 4(5)	0.313 7(4)
C(9)	0.761 0(4)	0.269 9(5)	0.113 9(4)
C(10)	0.805 4(5)	0.119 1(4)	−0.018 0(4)
C(11)	0.924 5(5)	0.137 4(5)	−0.124 3(4)
C(12)	0.949 2(5)	0.045 8(6)	−0.185 1(5)
C(13)	0.855 3(6)	−0.061 1(6)	−0.140 9(6)
C(14)	0.736 6(6)	−0.071 8(6)	−0.039 8(6)
C(15)	0.710 0(5)	0.014 9(5)	0.024 8(5)

Experimental

General.—All operations were carried out under nitrogen using Schlenk techniques. For column chromatography, Merck Kieselgel 60 was partly dried under vacuum and saturated with nitrogen. Infrared spectra were recorded on a Perkin-Elmer 297 and a Bruker IFS 114C spectrometer, ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra on a Varian VXR 200 and mass spectra on a Finnigen Mat 8200 apparatus. A Philips 93136 E mercury-vapour lamp without filters was used for photochemical reactions in a water-cooled quartz reactor. Elemental analyses were carried out at the Council for Scientific and Industrial Research, Pretoria. The compounds $[Fe(CO)_5]$ (Strem) and PhNCS (Merck) were used as supplied.

Preparation of Complexes **1** *and* **2**.—A mixture of $[Fe(CO)_5]$ and PhNCS (5 mmol each) in tetrahydrofuran (200 cm^3) was irradiated with UV light for 7 h at room temperature. The resulting dark red mixture was stripped of solvent under vacuum and the residue chromatographed on a silica gel column at −10 °C. Elution with hexane–dichloromethane (4:1) gave successively $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$, **1** and **2**. Crystallization from CH_2Cl_2–hexane mixtures afforded red crystals of the first product in *ca.* 7% yield and dark red crystals of **1** in *ca.* 14% yield. Compound **2** was obtained as a dark red oil in *ca.* 10% yield. It decomposed slowly at room temperature and was not analysed. Spectroscopic data for $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ were consistent with those in the literature.[12]

$[Fe_3(CO)_8(CNPh)S_2]$ **1**. IR: ν(CO) at 2075vs, 2050m, 2036vs, 2023s, 2014s, 2002m, 1992w and 1965vw cm^{-1}. FIR (polyethylene disc): 605vs, 590(sh), 577vs, 548vs, 535(sh), 513m, 502m, 483m, 472m, 442m, 414m, 372m, 363m, 346m, 253m, 187m, 118w, 94w and 73w cm^{-1}. M.p. 182 °C (decomp.), M^+ at m/z 559 (Found: C, 32.30; H, 0.85. Calc. for $C_{15}H_5Fe_3NO_8S_2$: C, 32.25; H, 0.90%).

$[Fe_3(CO)_8(CNPh)S_2]$ **2**. IR: 2124m, 2063s, 2052m, 2046m, 2025vs, 2013s, 1989m, 1980m and 1959vw cm^{-1}. M^+ at m/z 559.

Crystal Structure Determination.—Single crystals of compound **1** were grown from a CH_2Cl_2–hexane (1:6) solution.

Crystal data. $C_{15}H_5Fe_3NO_8S_2$, $M = 558.90$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.509(1)$, $b = 10.536(1)$, $c = 11.521(1)$ Å, $\alpha = 64.44(2)$, $\beta = 73.05(2)$, $\gamma = 80.00(2)°$, $U = 994.5$ Å^3 [by least-squares fit to 25 reflections, $\theta(Mo) < 18°$], $Z = 2$, $D_c = 1.87$ g cm^{-3}. Fluorescent green-purple crystals, 0.01 × 0.06 × 0.02 mm, $\mu(Mo\text{-}K\alpha) = 23.0$ cm^{-1}, $F(000) = 540$.

Data collection. CAD4 diffractometer, ω–2θ mode with ω scan width = 0.47 + 0.34 tan θ, variable scan speed with maximum 5.5° θ min^{-1}, graphite-monochromated Mo-Kα radiation, 4332 reflections measured ($3 < \theta < 27°$, $+h$, $\pm k$, $\pm l$), 3621 observed with $F > \sigma(F)$. No crystal decay was observed. No absorption corrections were applied.

Structure solution and refinement. Direct methods (Fe atoms) were applied and followed by normal heavy-atom procedures. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with U_{iso} constant (0.063 Å^2). The weights were $w = \sigma^{-2}(F)$ with $\sigma(F)$ calculated from counting statistics. Final R and R' values are 0.050 and 0.032. Programs and scattering factor data used are given in ref. 13.

Final coordinates are listed in Table 2 and selected bond lengths and angles in the caption to Fig. 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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