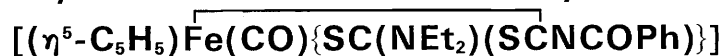


Reactivity of the Unco-ordinated Sulphur Atom in Monodentate Dithiocarbamates: Formation of the Heterometallobicycles FeS_2C_2 by Reaction of KCN with $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\{\eta^1\text{-SC}(\text{S})\text{NR}_2\}]$ and X-Ray Crystal Structure of the Benzoylation Product



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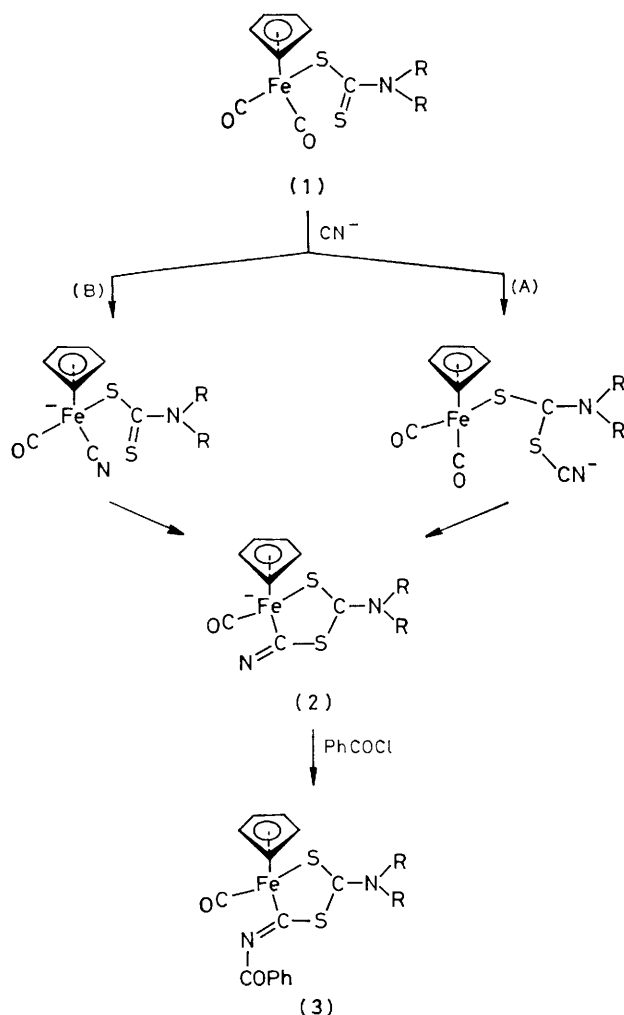
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The complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\{\eta^1\text{-SC}(\text{S})\text{NR}_2\}]$ ($\text{R} = \text{Me}$ or Et) react with KCN in methanol to give the five-membered-metallobicycles $\text{K}[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\{\text{SC}(\text{NR}_2)(\text{SCN})\}]$ (**2**) which can be acylated by PhCOCl giving $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})\{\text{SC}(\text{NR}_2)(\text{SCNCOPh})\}]$ (**3**) which has been characterized by X-ray diffraction for the complex with $\text{R} = \text{Et}$.

There are only a few complexes in which the dithiocarbamate (dtc) ligand¹ is monodentate^{1,2} and their reactivity has not been investigated.³ We report the reaction of KCN followed by PhCOCl with the readily available complexes $[(\text{cp})\text{Fe}$

$\{\eta^1\text{-SC}(\text{S})\text{NR}_2\}]$ (**1**) ($\text{cp} = \eta^5\text{-cyclopentadienyl}$).^{2,3} A methanol solution of (**1**) and KCN was heated under reflux for 3 h; removal of the solvent *in vacuo*, washing with dry ether, extraction with CH_2Cl_2 and precipitation with ether then



Scheme 1. a; R = Me
b; R = Et

gave an 85% yield of the very air-sensitive purple potassium salt (2), characterized spectroscopically† (*vide infra*).

Reaction of the complexes (2) with PhCOCl in CH₂Cl₂ (reflux; 3 h) gave the air-stable red-brown neutral complexes (3) in 80% yield after purification by t.l.c. on silica gel (1 mm; hexane-ether, 1:1 as eluant) and recrystallization from ether. ¹H and ¹³C N.m.r. data are consistent with the formulation [(cp)Fe(CO)(CNCOPh)(SCSNR₂)]‡ but the isonitrile i.r. stretching frequency is very low (1760 cm⁻¹) compared with the values found in [(η⁶-arene)Cr(CO)₂(CNCOPh)] complexes (2020 cm⁻¹). Therefore, an X-ray crystal structure determination was undertaken for complex (3b).

Crystal data: C₁₉H₂₀FeN₂O₂S₂, *M* = 428.4, triclinic, space group $\bar{P}1$, *a* = 10.703(4), *b* = 11.677(4), *c* = 9.588(3) Å,

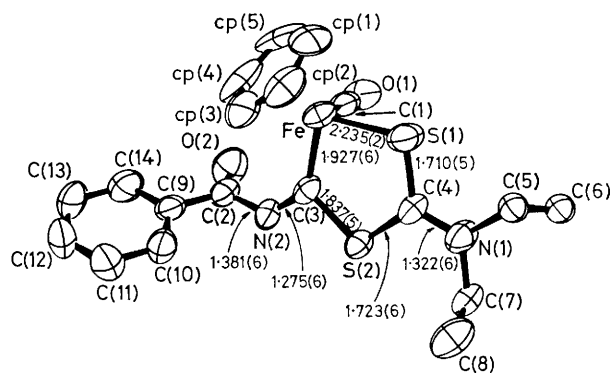


Figure 1. Molecular structure of complex (3b); selected angles: Fe-C(3)-S(2), 120.4(3); Fe-C(3)-N(2), 134.6(4); S(2)-C(3)-N(2), 105.0(4); C(3)-N(2)-C(2), 128.1(5); S(1)-Fe-C(3), 91.0(2); Fe-S(1)-C(4), 106.7(2); S(1)-C(4)-S(2), 119.6(3); C(4)-S(2)-C(3), 102.4(3)°. Selected bond lengths are shown in Å.

$\alpha = 97.41(9)$, $\beta = 109.95(9)$, $\gamma = 63.51(8)^\circ$, $U = 1008.2 \text{ \AA}^3$, $Z = 2$, $D_c = 1.59 \text{ g cm}^{-3}$. Intensity data were collected on a Nonius-CAD4 diffractometer; 2702 symmetry-independent reflexions [$I > 2\sigma(I)$] were used in the structure solution by the heavy-atom method and anisotropic refinement for non-hydrogen atoms by full-matrix least-squares techniques ($R_1 = 0.063$ and $R_2 = 0.048$). The ethyl carbon atoms C(5) and C(6) were not refined anisotropically; these atoms have large isotropic thermal parameters of 10.8(3) and 18.3(5) Å² owing to disorder. The positions of the 20 hydrogen atoms were calculated and included as fixed contributions in the final refinement.§

The perspective view (Figure 1) clearly shows the formation of a strictly planar metallocycle FeS₂C₂. Although the dtc ligand is chelated to both Fe and C(CN), the C-S distances are equal (1.72 Å). The S-C(CN) bond (1.84 Å) is slightly longer than normal and the exocyclic C(3)-N distance (1.27 Å) corresponds exactly to a double bond. In contrast with the report of a quasi-linear *N*-acylisocyanide of Cr,⁴ this ligand is bent in the present case ($\angle \text{FeCN}: 133^\circ$; $\angle \text{CNC}: 129^\circ$). It is noteworthy that the arrangement found here has been postulated as an intermediate in the mechanism of disproportionation of isothiocyanates.⁵

The cyclic structure of the anion (2) was deduced from a comparison of its spectroscopic data with data for (3). In particular, the cyclopentadienyl ¹H and ¹³C n.m.r. resonances and the Mössbauer parameters of (2) and (3) are very similar†‡ and very different from those for (1) (I.S. = -0.15 mm s⁻¹; Q.S. = 1.69 mm s⁻¹).

Complex (2) may be formed by direct attack of the free sulphur by CN⁻ followed by displacement of CO (A) or the alternative mechanism (B), *e.g.* replacement of CO by CN⁻ followed by cyclization (Scheme 1). Since (1) decomposes in refluxing methanol at the same rate ($t_{1/2}$ ca. 1 h) in the presence or absence of KCN, we favour route (B) over (A). The free sulphur in (1) is also nucleophilic rather than electrophilic as indicated by alkylation by Me₃O⁺BF₄⁻.⁶

† (2a): satisfactory elemental analyses were obtained; ν_{max} (Nujol) 2080, 2030 (CO); 1500 (CN); 995, 940 cm⁻¹ (CS); n.m.r. (CD₂Cl₂; Me₄Si reference), ¹H: δ 4.63 (s, 5H, cp) and 3.53 (s, 6H, Me); ¹³C: δ 83.4 (cp), 46 (Me), 210.9 (CO), and 195.3 p.p.m. (CS); Mössbauer: (mm s⁻¹), I.S. = -0.01; Q.S. = 1.94.

‡ (3b): ν_{max} (Nujol) 1975 (CO), 1575 (CN), 1075 (CS₂), 1660 cm⁻¹ (COPh); n.m.r. (CDCl₃; Me₄Si reference), ¹H: δ 4.79 (s, 5H, cp); ¹³C: δ 82.8 (cp), 54.4 and 48.9 (CH₂), 12.2, 11.9 (Me); ¹H-¹³C: δ 83.4 (cp), 54.4 and 48.9 (CH₂), 12.2, 11.9 (Me); 204.3 (CS); 219.8 and 217.8 (CO and FeCN); 174.7 (COPh); 134.1, 132.3, 129.8, and 128.2 p.p.m. (Ph); Mössbauer: (mm s⁻¹), I.S. = -0.016; Q.S. = 1.855.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23238 (11 pp.) from the British Library, Lending Division. For details, see Notice to Authors No. 7, *J. Chem. Soc., Dalton or Perkin Trans.*, Index issues.

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