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Preliminary communication

THE PREPARATION AND STRUCTURAL CHARACTERIZATION OF *trans-anti*-$(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_2(PhNC)_2$

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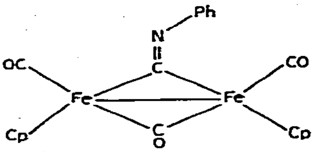
Summary

Reaction of phenylisonitrile with $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ yields mono- and di-substituted derivatives. The latter has a doubly-bridged isonitrile structure both in solution and in the solid, where it has the *trans-anti* configuration.

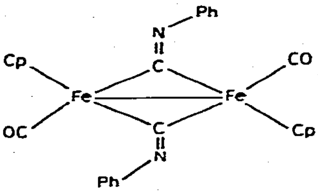
The preparation of low valent, polymetallic transition-metal complexes which contain isonitriles as ligands has recently become a subject of interest [1], in part due to the similarity in behaviour of the isonitrile group as a ligand with carbon monoxide, but more especially because of its ability to participate in the general fluxional processes which intense research over the last few years has shown to be a general feature of transition metal carbonyl clusters [2]. During our ^{13}C NMR studies on monosubstituted phenyl- and t-butyl-isonitrile derivatives of $Cp_2Fe_2(CO)_4$ ($Cp = \eta^5\text{-}C_5H_5$) [3], we have also isolated in small yield a complex of the stoichiometry $Cp_2Fe_2(CO)_2(PhNC)_2$, and report here its synthesis and structural characterization.

$Cp_2Fe_2(CO)_4$ and an excess of PhNC were refluxed in benzene under nitrogen. After removal of solvent from the deep red solution, the mixture of mono- and di-substituted complexes was separated by preparative thin-layer chromatography on silica gel. The complexes were crystallised from dichloromethane/petroleum ether.

	$Cp_2Fe_2(CO)_3(PhNC)$(A)	$Cp_2Fe_2(CO)_2(PhNC)_2$(B)
yield:	10%	0.7%
analysis (found):	C, 56.7; H, 3.78; N, 2.99%	C, 62.3; H, 4.19; N, 6.10%
(calcd.):	C, 55.9; H, 3.49; N, 3.26%	C, 61.8; H, 3.97; N, 5.56%
IR (CS_2)	ν(CO) 1997, 1954, 1807 cm^{-1}	ν(CO) 1985, 1945 cm^{-1}
	ν(NC) 1702 cm^{-1}	ν(NC) 1683 cm^{-1}
[illegible]	M^+ [illegible]	M^+ 504

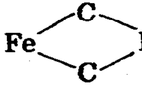


(A)



(B)

Complex A has previously been synthesized by the reduction of CpFe(CO)(PhNC)I with sodium borohydride, and has been shown to have the *cis*-configuration in the solid state [4]. We are currently examining crystals of our product to see if the configuration is identical. In any case, infrared and ^{13}C NMR studies show that the product obtained here exists in solution solely as the isonitrile-bridged isomer. Disubstituted derivatives of the stoichiometry $Cp_2Fe_2(CO)_2(RNC)_2$ (R = Me, cyclohexyl) have previously been isolated [1a, 5], and infrared and NMR studies have shown that they exist in solution as mixtures of isomers in which both bridging and terminally bonded isonitrile is present. Complex B shows no bridging carbonyl absorption in its infrared spectrum, and therefore exists in solution exclusively as the doubly-bridged isonitrile isomer.

The complex also exists as the same isomer in the solid. In contrast with previously reported structures which contain one [4] or two [5] isonitrile groups (PhNC and MeNC respectively) bridging two iron atoms, the cyclopentadienyl and carbonyl groups in the present complex are positioned *trans*. The presence of a crystallographic centre of symmetry also means that the two phenylisonitrile groups are *anti* (∠ C—N—Ph 129°), and that the central  ring is strictly planar (∠ Fe—μ-C—Fe 81.7°, ∠ μ-C—Fe—μ-C 98.2°). It is, however, not an exact rhombus. Finally, the Fe—Fe (2.53 Å) and Fe—μ-C (1.93 Å) average bond distances are in close agreement with those found previously for $Cp_2Fe_2(CO)_3(PhNC)$ [4].

References

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