# Carbon-13 Nuclear Magnetic Resonance Studies of Isonitrile Derivatives of Tetracarbonylbis-(η-cyclopentadienyl)di-iron

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*Summary* Variable temperature $^{13}C$ n.m.r. studies on $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3(CNR)]$ (II; R = $Bu^t$) and (III; R = Ph) show that (II), which contains a terminally bonded CNR ligand, exhibits fluxional properties while (III), which contains a bridging CNR ligand, does not; it is also shown that $^{13}C$ resonances of isonitrile ligands are diagnostic of the presence of bridging or terminal CNR groups.

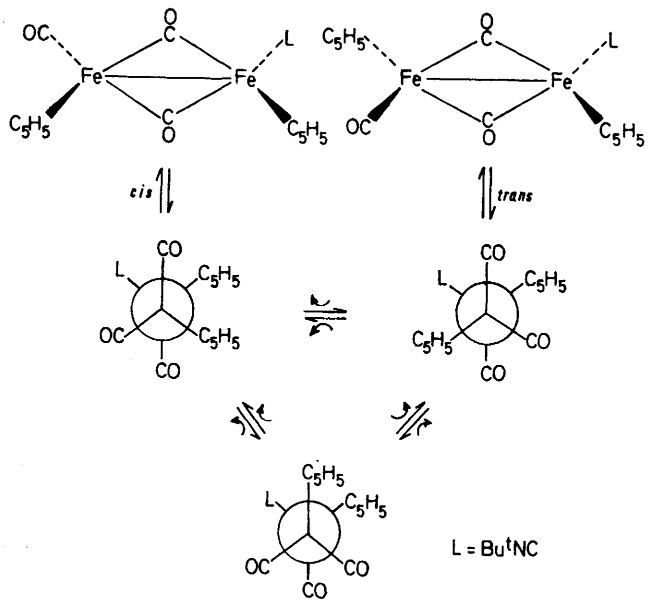
Cotton and Adams have recently presented evidence in support of a simple bridge opening–bridge closing mechanism for bridge–terminal carbonyl exchange and *cis–trans* isomerisation in simple binuclear complexes such as $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ (I).[1] We report here spectroscopic studies of two isonitrile substitution products of (I), $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3CNR]$ (II; R = $Bu^t$), and (III; R = Ph) which support this mechanism and show that isonitrile $^{13}C$ resonances provide a useful tool for studying the structure and fluxional properties of complexes containing this ligand. I.r. (cyclohexane) and $^1H$ decoupled low-temperature limiting $^{13}C$ n.m.r. $(CH_2Cl_2)$ data are reported in the Table.

Table. I.r. and $^{13}C$ n.m.r. data for (II) and (III)

| | I.r./cm$^{-1}$ | Low temperature limiting $^{13}C$ n.m.r. spectra (p.p.m. from $Me_4Si$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Bridging CO | Bridging CNR | Terminal CO | Terminal CNR | $C_5H_5$ | $T$/°C |
| (II) | 2114, 2077, 1954, and 1773 | 281·8 | — | 214·0 | 158·7 | 86·5 and 85·7 | −30 |
| (III) | 1997, 1954, 1807, and 1702 | 275·9[a] | 257·9[a] | 215·1[a] | — | 89·5[a] | +20 |

[a] Absorptions attributed to small amounts of *trans* isomer (also apparent in the i.r. spectrum) are observed.

Complex (II), with a terminal isonitrile ligand, exhibits fluxional behaviour. We observed only one set of signals in the low-temperature limiting $^{13}$C n.m.r. spectrum, even though room-temperature i.r. studies[2,3] show the presence of an isomeric *cis–trans* mixture. Similar behaviour has been observed in variable temperature (−30 to −120 °C) $^{1}$H n.m.r. studies[3,4] of complex (II), and has been interpreted in terms of a rapid *cis–trans*-isomerization even at −120 °C. However, this explanation is not tenable in the light of our results, which show that bridge-terminal carbonyl exchange does not occur below −30 °C. A consideration of the processes allowed by the Adams–Cotton mechanism (Scheme) shows that, unlike complex (I), bridge–terminal carbonyl exchange must be accompanied by *cis–trans*-isomerization and *vice versa*. This has been verified for $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_3P(OEt)_3]$.[5] We believe that only one set of signals is observed in the n.m.r. spectra because one of the isomers is present in undetectable amounts. In accord with this, a variable-temperature i.r. study shows a great decrease in intensity of the 2077 cm$^{-1}$ $\nu_{NC}$ absorption relative to the 2114 cm$^{-1}$ absorption on cooling to −40 °C (hexane). In addition, a similar large reduction in relative intensity is observed on changing from hexane to dichloromethane as solvent. Following the reasoning of Manning,[6] we assign the predominant isomer in solution to be the *cis*-form.



SCHEME

On warming to 0 °C, the bridge and terminal CO and the $C_5H_5$ n.m.r. signals broaden and coalesce, indicating that bridge–terminal CO exchange is occurring, as well as exchange of the isonitrile ligand between the two metal atoms. The isonitrile resonance remains sharp up to *ca.* 50 °C, when it begins to broaden, most probably owing to $^{14}$N quadrupolar relaxation. A high-temperature limiting spectrum could not be obtained owing to decomposition.

The $^{13}$C n.m.r. spectrum of (III), in which the isonitrile ligand occupies a bridging position, shows that it is non-fluxional up to +40 °C, above which extensive decomposition occurs (Table). It is consistent with the *cis*-structure found in the solid state.[7]

This represents the first report of a $^{13}$C resonance of a bridging isonitrile carbon atom. It shows a large downfield shift of *ca.* 100 p.p.m. relative to the terminal isonitrile resonance in (II). This may be compared to typical chemical shift differences between bridging and terminal carbonyl groups of *ca.* 65 p.p.m.

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