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An Iron Complex with a Bridging Isonitrile Group

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MANY isonitrile complexes of transition metals are analogous to the corresponding metal carbonyls¹ in composition and structure. Examples have recently been described²⁻⁴ showing that this similarity of isonitriles and carbon monoxide extends to their cyclopentadienylmetal derivatives. However, no compounds have been reported in which isonitriles can act as bridging groups. In a preliminary communication² we tentatively assigned an unbridged structure to bis[cyclopentadienyl(phenyl isocyanide)nickel]. This assignment was based on the appearance of a maximum at 2174 cm^{-1} in infrared spectra taken in carbon tetrachloride or dichloroethane. It is now known that the compound decomposes in these solvents. A potassium chloride disc of a freshly prepared sample showed only a peak at 1785 cm^{-1} . This is more compatible with a bridged structure analogous to that of bis(carbonylcyclopentadienylnickel).

The ability of isonitriles to act as bridging groups has now been demonstrated by the preparation of the iron complex (I). Indeed, this example suggests that phenyl isocyanide has a greater tendency to be bridging than carbon monoxide.

When iodocarbonyl(phenyl isocyanide)cyclopentadienyliron³ (II) was reduced with an excess of sodium borohydride in refluxing tetrahydrofuran, the product, on chromatography, gave ferrocene (16%), bis(dicarbonylcyclopentadienyliron) (8.4%), and the bridged isonitrile (I) (5.3%). A further fraction had an infrared spectrum consistent with the presence of bis[carbonylcyclopentadienyl(phenyl isocyanide)iron] but was obtained in insufficient quantity for complete purification. The structure of the isonitrile complex (I) was suggested by its infrared spectrum which showed strong bands at 2004, 1949, 1795, and 1704 cm^{-1} (KI disc). All terminal isonitrile ligands examined to date have frequencies higher than 2100 cm^{-1} . We therefore assign the peak at 1704 cm^{-1} to a bridging phenyl isocyanide group. That at 1795 cm^{-1} may be assigned to the bridging carbonyl and the other two peaks to the terminal carbonyl groups.

The structure (I) has been fully confirmed by X-ray-crystallographic examination. The analysis, based on 1300 reflexions ($R = 11\%$), shows that the metal atoms are 2.53 Å apart and bridged by one carbonyl and one isocyanide group. There is

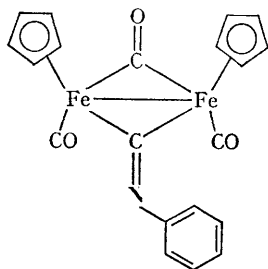
¹ J. Chatt, P. L. Pauson, and L. Venanzi in 'Organometallic Chemistry,' ed. H. Zeiss, Reinhold, New York, 1960; L. Malatesta in 'Progress in Inorganic Chemistry,' Vol. I, ed. F. A. Cotton, Interscience, New York, 1959.

² P. L. Pauson and W. H. Stubbs, *Angew. Chem.*, 1962, **74**, 466, (*Internat. Ed.* 1962, **1**, 333).

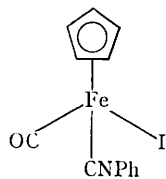
³ K. K. Joshi, P. L. Pauson, and W. H. Stubbs, *J. Organometallic Chem.*, 1963, **1**, 51.

⁴ C. E. Coffey, *J. Inorg. Nuclear Chem.*, 1963, **25**, 179.

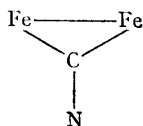
no significant difference between the bridging Fe-C distances (1.91 Å to carbonyl, 1.90 Å to isocyanide). The angle subtended at the bridging carbon atoms is 84° in both cases. In the compound the isocyanide group is no longer linear but



(I)



(II)



(III)

bent, through an angle of 131°, at the nitrogen atom. At the same time the phenyl group is rotated out of the plane (III) by 50°. The rotation, away from the adjacent cyclopentadienyl group, prevents short nonbonded approaches between this group and the phenyl group. The cyclopentadienyl groups (and terminal carbonyls) are arranged *cis*. If we neglect the phenyl group the remainder of the molecule contains an approximate plane of mirror symmetry (non-crystallographic), *i.e.* normal to the Fe-Fe vector and passing through the mid-point of this bond. This is in contrast to the *trans*-arrangement found⁶ in crystalline bis(dicarbonylcyclopentadienyliron) where this mid-point is a crystallographic centre of symmetry, and as a consequence the two carbons of the bridging carbonyls and the two iron atoms are strictly coplanar. Although the coincidence of crystal symmetry and molecular symmetry cannot arise in the less-symmetrical (I), nevertheless, deviation of this four-atom arrangement from coplanarity, though real, is comparatively small; the observed dihedral angle, the fold about the Fe-Fe vector, of 166° is much larger than those found in Fe₂(CO)₉ and Co₂(CO)₈.

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⁶ O. S. Mills, *Acta Cryst.*, 1958, **11**, 620.