

## Tripoly-bridging Nitrogen: a Trinuclear Iron Carbonyl Complex from Diphenyldiazomethane

By P. E. BAIKIE and O. S. MILLS\*†

(Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, West Germany)

THE preparation of two types of complex, one black and the other orange, from the reaction of diaryldiazomethanes with pentacarbonyliron under irradiation conditions or by heating with dodecacarbonyltri-iron, has recently been reported.<sup>1</sup> The structure of the orange complex, specifically that obtained from di-*p*-tolylidiazomethane, was shown to correspond to bis-( $\mu$ -4,4'-dimethylbenzophenone-hydrazone-tricarbonyliron) (I) but the black complexes gave poor proton resonance spectra and were too involatile for mass spectroscopic examination. The infrared spectra were characterised by three absorptions in the terminal carbonyl region.

We have determined the structure of one of the black complexes, that from diphenyldiazomethane, by *X*-ray methods and have shown the formula to correspond to (diaryldiazomethane)<sub>2</sub>[Fe(CO)<sub>3</sub>]<sub>3</sub>.†

*Crystal data.* C<sub>35</sub>H<sub>20</sub>Fe<sub>3</sub>N<sub>4</sub>O<sub>9</sub>, *M* = 808.1, *triclinic*, *a* = 10.61, *b* = 13.40, *c* = 13.51 Å,  $\alpha$  = 96.97°,  $\beta$  = 99.16°, and  $\gamma$  = 111.57°. *U* = 1729 Å<sup>3</sup>. *Z* = 2, space group either *P*1 (*C*<sub>1</sub><sup>1</sup>, No. 1) or  $\bar{P}1$  (*C*<sub>1</sub><sup>1</sup>, No. 2) 1533 independent three-dimensional intensities were collected by film methods (precession photographs taken with Mo-*K*<sub>α</sub> radiation).

The structure was solved and refined within the symmetry of the space group  $\bar{P}1$ , which imposes no restriction upon the molecular symmetry. No assumptions were made about the molecular

formula which was deduced only from the analysis. The three-dimensional Patterson synthesis was interpretable in terms of three iron atoms at the corners of a triangle and the determination of the light atoms followed by the application of the heavy-atom method. Refinement by least-squares methods has reduced the value of *R* to 9.5% at present. The formula which we find is in agreement with the analytical data.<sup>2</sup>

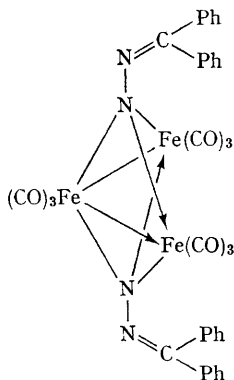
The principle feature of this new type of structure lies in the now demonstrated capacity of nitrogen to bridge, simultaneously and equally, three metal atoms. Thus the six Fe-N distances lie within the range 1.91–1.98 Å with mean 1.95 Å, a value not significantly different from the mean of four values, 1.97 Å, found for the orange complex<sup>1</sup> (I) where the organic ligand bridges, through the terminal nitrogen, two iron atoms.

The condition that the bridging nitrogen atoms should be equidistant from the three metal atoms imposes only the condition that the iron atoms form an isosceles triangle; we find two Fe-Fe distances, 2.43 and 2.46 Å, much shorter than the third, 3.06 Å. At the present we regard this as a null metal-metal bond whilst the other two are represented by single metal-metal bonds. These latter are again found to have short distances as is apparently always the case when nitrogen bridges

† Present address: Department of Chemistry, University of Manchester, Manchester 13.

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are present.<sup>3-5</sup> Diamagnetic behaviour can be rationalised by the formal structure shown in the Figure. In accord with this, the N-N distances, average 1.39 Å, in good agreement with the corresponding bond in the orange complex, indicate a



FIGURE

single bond whilst the N-C distances, mean 1.31 Å, are in keeping with double bonds.

The complex can be regarded as a bridging hydrazone complex in which both terminal hydrogens have been substituted by metal atoms and is to be compared with the orange complex where only one such substitution has occurred. Since both complexes are formed, however, not from the parent hydrazone, but from the diazo-reagent, the black compound, which occurs in greater yield, seems more likely to be an intermediate in the formulation of the orange complex which requires the loss of a Fe(CO)<sub>3</sub> fragment and the capture of two protons.

From this analysis and our earlier ones, it is now clear that nitrogen is capable of co-ordination to polynuclear metal systems in ways at least as varied as carbon and these variants may yet be involved in some nitrogen fixation compounds.

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<sup>1</sup> M. M. Bagga, P. E. Baikie, O. S. Mills, and P. L. Pauson, *Chem. Comm.*, 1967, 1106.

<sup>2</sup> P. L. Pauson, personal communication.

<sup>3</sup> P. E. Baikie and O. S. Mills, *Chem. Comm.*, 1966, 707.

<sup>4</sup> P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, 1967, **1**, 55.

<sup>5</sup> D. Bright, and O. S. Mills, *Chem. Comm.*, 1967, 245.