The Structure of Di-μ-(4,4′-dimethylbenzophenoniminato)bis(tricarbonyliron)

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THE preparation of a number of organometallic complexes with nitrogen-containing organic ligands has been reported,[1] and structural determinations have shown two classes of structure.[2] We now report the structure of a third class of complex.

The orange complex, $C_{36}H_{28}N_2O_6Fe_2$, formed from the reaction of 4,4′-dimethylbenzophenone azine (I) with iron pentacarbonyl, crystallises in the orthorhombic system, $a = 17{\cdot}84 \pm 0{\cdot}05$, $b = 17{\cdot}25 \pm 0{\cdot}05$, $c = 22{\cdot}60 \pm 0{\cdot}06$ Å, $M = 696{\cdot}3$, $U = 6955$ Å^3, $D_m = 1{\cdot}33$ (by flotation in aq. KI), $D_c = 1{\cdot}33$ g. cm.$^{-3}$, $Z = 8$, and space-group *Pbca*. The asymmetric unit contains 46 atoms other than hydrogen. 1795 reflexions were visually estimated from Weissenberg photographs taken with Co-K_α radiation. The solution of the structure was complicated because both iron atoms had very nearly equal x and z co-ordinates which had the pseudo-special values of 1/4 and 1/6 respectively. Additionally their y co-ordinates were such that their sum was 1/4. Thus these atoms did not contribute to those reflexions for which $k = 2n + 1$ or for which $k = 2n$ when $k/2 + l = 2n + 1$. When these reflexions are ignored, the resulting Fourier synthesis of electron density contained, in addition to the normal space-group symmetry, spurious mirror planes perpendicular to a at $x = 1/4$ and to b at $y = 1/8$. The solution proceeded by a careful selection of peaks from the superimposed pattern and the structure was refined by least-squares methods. The final R factor was 11·6%.

The structure, shown in the Figure, contains two 4,4′-dimethylbenzophenoniminato-groups which bridge two $Fe(CO)_3$ units. These ligands bridge through the nitrogen atoms and the reaction product is thus di-μ-(4,4′-dimethylbenzophenoniminato)bis(tricarbonyliron). From this it is clear that rupture of the =N–N= bond in (I) occurs during the reaction. Splitting of the N–N bond also occurs in the reaction of azobenzene with iron

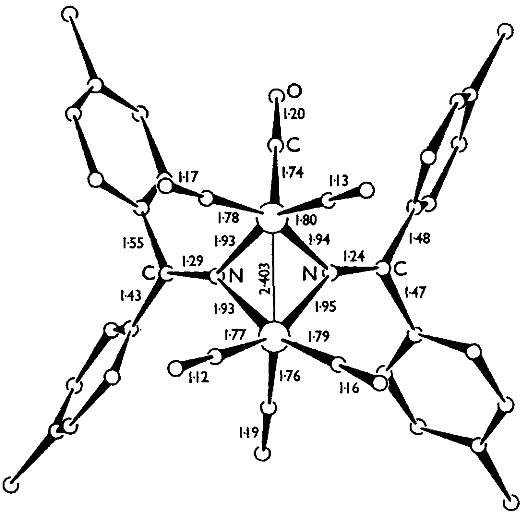

FIGURE. *Molecule viewed along the idealised 2-fold direction.*
Average standard deviation of Fe–Fe = 0·006 Å;
Average standard deviation of Fe–N = 0·012 Å;
Average standard deviation of C–N = 0·016 Å.

carbonyl,[2] but whereas in that case rearrangement occurs to form the *o*-semidine skeleton here both moieties are trapped in the complex separately. In accord with these findings, the mass spectrum fragmentation pattern* shows no evidence of peaks with *m/e* values of 416, corresponding to (I), though peaks at 208 and 209 were observed.

The molecule has idealised 2-fold symmetry. The tricarbonyl groups are eclipsed and the nitrogen and iron atoms form a tetrahedron. The central portion of the molecule is thus similar in shape to that of $Co_2(CO)_8$. The Fe–Fe distance is short when compared with carbon-bridged binuclear complexes and can be compared with the value 2·37 Å found in the *o*-semidine complex. The averaged Fe–N distance is 1·94 Å, which is shorter than those reported in the previous structures. In the present structure the nitrogen atoms can be considered to be sp^2 hybridised whereas in these other structures with Fe–N distances of 1·97—200 Å the hybridisation would be sp^3. In all these cases the nitrogen atoms can be regarded as three-electron donors.

(*Received, January* 10*th*, 1967; *Com.* 031.)

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* We thank Dr. J. M. Wilson for mass spectra.

[1] M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Comm.*, 1965, 543.
[2] P. E. Baikie and O. S. Mills, *Chem. Comm.*, 1966, 707.