# Iron Complexes from Diaryldiazomethanes

By M. M. Bagga, P. E. Baikie, O. S. Mills,* and P. L. Pauson

(*Department of Chemistry, University of Manchester; Department of Pure and Applied Chemistry, University of Strathclyde and Anorganisch-Chemisches Laboratorium der Technischen Hochschule München, West Germany)

The metal-containing products obtained by irradiation of diaryldiazomethanes with pentacarbonyliron contain nitrogen and are not derived from the diarylcarbenes expected as intermediates. Indeed, the same products are formed by thermal reaction using dodecacarbonyltri-iron under conditions where carbene formation is inherently unlikely. Both diphenyl- and di-*p*-tolyl-diazomethanes yielded two iron complexes, whereas neither phenylbenzoyl- nor phenyl-diazomethane gave stable products under the same conditions.

From diphenyldiazomethane a black complex (I), m.p. 170°, and an orange complex (II), m.p. 167°, were obtained, both by irradiation (8 hr.) in benzene solution with an equimolar amount of the pentacarbonyl and by stirring for 4 hr. at 70—75° with the higher carbonyl. The former method was employed to obtain analogous black (I′) and orange (II′) complexes, m.p. 158 and 165—165·5° respectively, from di-*p*-tolyldiazomethane. The black complexes (I, I′), which were formed in greater yield, showed three carbonyl stretching frequencies at 2010, 2035, and 2055 cm.$^{-1}$ and 2018, 2042, and 2060 cm.$^{-1}$, respectively ($CCl_4$ solutions), but were too involatile for mass-spectroscopic examination. Whilst their proton resonance spectra were rather poor, there was no indication of protons other than those of the aryl groups.

The mass spectrum† of the orange compound (II) gave a parent ion peak at *m/e* 670 corresponding to $C_{32}H_{22}Fe_2N_4O_6^+$ and although both compounds (II, II′) gave somewhat high carbon analysis values, the corresponding molecular formula (II′), $C_{36}H_{30}Fe_2N_4O_6$, is fully confirmed by the *X*-ray analysis. Successive loss of 6 × 28 mass units (6 CO groups) allows the formula of the former compound to be written as $[(C_6H_5)_2CHN_2Fe(CO)_3]_2$. The n.m.r. peaks, which occur in (II) ($C_6F_6$ solution) at $\tau$ 2·45, 3·36, and 4·14 and in (II′) at $\tau$ 3·0, 4·4, 5·48 and 7·7 in the approximate ratios of 20 : 1 : 1 and 16 : 1 : 1 : 12 respectively, agree with this formulation, especially in confirmation of the presence of two additional (possibly solvent-derived) protons. The latter are nonequivalent and their chemical shifts are most readily compatible with two nonequivalent NH groups in each case.

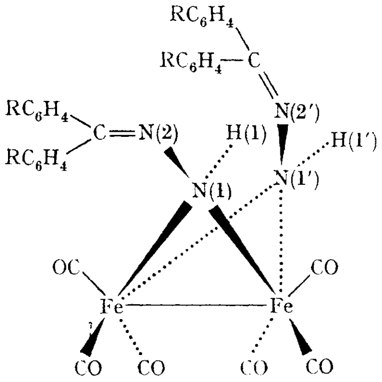
In continuation of our studies[1-3] of the molecular geometry of nitrogen–metal complexes, the orange *p*-tolyl complex (II′) has been examined by *X*-ray methods. The compound crystallises in the monoclinic system with $a = 17{\cdot}64$, $b = 12{\cdot}17$, $c = 17{\cdot}36$ Å and $\beta = 101° 35'$. Systematic absences correspond to the spacegroup $P2_1/c$ (No. 14, $C_{2h}^5$). The calculated density, based on the molecular formula $C_{36}H_{30}Fe_2N_4O_6$, ($M = 726{\cdot}3$) and $Z = 4$, is $1{\cdot}32 \pm 0{\cdot}01$ g. cm.$^{-3}$ in

---

† We thank Mr. F. J. Preston and Dr. R. I. Reed for this determination.

agreement with the observed value 1·32 ± 0·1 g. cm.$^{-3}$ The asymmetric unit is thus the whole molecule. The structure, shown in the Figure, has been deduced from 1143 reflexions by the usual heavy-atom method and the current *R*-factor is 11%.

It is apparent that the reactions proceed with remarkable little change of the skeleton of the ligand although the bonding between the atoms is much altered. The terminal nitrogen atom of the diazomethane bridges the iron atoms in a manner similar to that found for the Schiff-base complex $C_6H_4{\cdot}CH_2{\cdot}NC_6H_4{\cdot}MeFe_2(CO)_6$ (III)[1] and $\mu$-semidinatobis(tricarbonyliron) (IV)[2] where the nitrogen can be regarded as $sp^3$-hybridised and contributing three electrons to the binding. We have previously noted that in the examples (III) and (IV) as well as in di-$\mu$-(4,4′-dimethylbenzophenoniminato)bis(tricarbonyliron)[3] the presence of such bridging nitrogens is associated with short Fe–Fe distances and the present compound also exhibits a similar short value of 2·40 Å. The four independently determined Fe–N distances lie between 1·99 and 2·02 Å and compare well with those determined in other $sp^3$-hybridised nitrogen bridged complexes. They are indicative of essentially single Fe–N bonds. Likewise the N–N distances, average 1·40 Å, are consistent with a single-bond formulation in contrast with the much shorter value, 1·12 Å, found in free diazomethane.[4] The N–C distances, average 1·26 Å, however, suggest a double bond in accord with the formulation shown in the Figure. The atoms N(2), N(2′) occupy different environments and so must the atoms H(1), H(1′) whose positions are inferred (they have not at the present been observed in the *X*-ray analysis) from the stereochemistry around N(1), N(1′) and from the mass spectrum. This accords with the above inference from the n.m.r. spectrum. The complex is thus bis-($\mu$-4,4′-dimethylbenzophenonehydrazonatotricarbonyliron).



(II) R=H
(II′) R=*p*-Me

FIGURE

This work was supported in part by a grant from the N.A.T.O.

(*Received, September 4th,* 1967; *Com.* 946.)

---

[1] P. E. Baikie and O. S. Mills, *Chem. Comm.*, **1966**, **707**.

[2] P. E. Baikie and O. S. Mills, *Inorg. Chim. Acta*, **1967**, **1**, 55.

[3] D. Bright and O. S. Mills, *Chem. Comm.*, **1967**, **245**.

[4] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, **1958**, **181**, 1157.