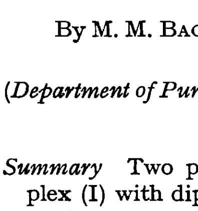
Carbene Insertion into a Carbon-Iron Bond

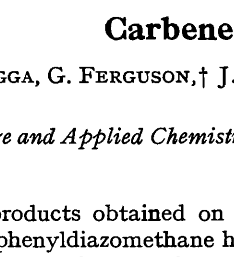
By M. M. Bagga, G. Ferguson,† J. A. D. Jeffreys,* Miss C. M. Mansell, P. L. Pauson, I. C. Robertson, and J. G. Sime†

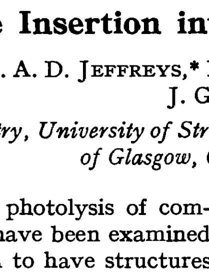
(*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1, and* †*Department of Chemistry, University of Glasgow, Glasgow, W.2*)

Summary Two products obtained on photolysis of complex (I) with diphenyldiazomethane have been examined by *X*-ray crystallography and shown to have structures (II) and (III).

In a recent communication,[1] Moritani, Yamamoto, and Konishi postulate insertion of a carbene into a carbon–nickel bond to account for the formation of ethyl penta-2,4-dienoate from bis(allylnickel bromide) and ethyl diazoacetate. We report here a reaction which apparently involves insertion of diphenylcarbene into a carbon–iron bond without destruction of the metal complex. In earlier communications[2] the photolysis of diphenyldiazomethane with pentacarbonyliron was shown to yield two complexes without loss of nitrogen from the diazo compound. At the same time one of us[3] studied the reaction of this diazo-compound with the readily-available complex (I).[4] Irradiation of 4 g of each component in benzene (400 ml.) for 5 h yielded a complex mixture from which two isomeric complexes were readily isolated on chromatography and crystallisation from light petroleum. These have now been characterised by *X*-ray crystallography. Complex (II) formed dark brown needles (0·2 g, 4%), m.p. 157°; monoclinic, space group $P2_1/c$, $a = 11{\cdot}76$, $b = 17{\cdot}60$, $c = 13{\cdot}66$ Å, $\beta = 119{\cdot}2°$, $U = 2466$ Å^3, $D_m = 1{\cdot}47$, $Z = 4$, $D_c = 1{\cdot}50$, $F(000) = 1136$. Intensities were estimated visually on Weissenberg photographs and the structure solved by the heavy atom method and refined by Fourier and least squares methods leading to a final $R = 0{\cdot}138$ based on 1527 reflections. The structure (II) shown can readily be understood as arising from the precursor (I) by carbene insertion into the Fe(1)–C(1) bond with rupture of this bond allowing rotation about C(1)–C(2) and then bonding of the oxygen atom to Fe (2·07 Å).


(I)


(II)


(III)

A very similar nitrene insertion has been observed on reaction of complex (I) with "dichloramine-T," p-MeC$_6$H$_4$-SO$_2$NCl$_2$; in this case the nitrogen atom becomes bonded to iron.[5] In the product (II) the Fe–Fe distance, 2·62 Å is well within the range considered as normal bonding distances in such compounds.[6] Fe(2) is now linked only to three carbons C(2)–C(4) forming a typical π-allyl group with Fe–C distances of 2·09, 2·07, and 2·09 Å. C(1) is displaced out of the plane of this allyl group by 0·87 Å away from Fe(2) [C(1)–Fe(2) = 2·96 Å].

Complex (III), studied by analogous methods, forms red monoclinic crystals, (0·3 g; 6%), m.p. 148°; space group $P2_1/c$, $a = 14{\cdot}75$, $b = 8{\cdot}95$, $c = 19{\cdot}58$ Å, $\beta = 108{\cdot}20°$, $U = 2455$ Å^3, $D_m = 1{\cdot}50$, $Z = 4$, $D_c = 1{\cdot}51$, $F(000) = 1136$, final $R = 0{\cdot}125$ based on 1547 reflections. Its formation is more difficult to account for as it involves a skeletal rearrangement, apparently by linkage of C(1) to C(4) [in (I)] with possible formation of an intermediate cyclobutadiene complex and either carbene insertion into a C–H bond or into a C–Fe bond followed by hydrogen migration. The final structure is closely similar to that of the precursor (I) (*cf.* ref. 7), with the formally co-ordinate

Fe–Fe bond having a length of 2·54 Å and distances from Fe(2) to C(1)–C(4) varying from 2·08—2·21 Å. Full structural details for both compounds will be reported elsewhere. The two methoxy-groups in complex (III) give rise to two singlet proton resonance signals at τ (CCl_4) 6·17 and 6·36 compared to 6·27 for complex (I) but in complex (II) only one methoxyl [presumably that on C(4)] gives a signal in the same region (6·10) while the other is displaced to 6·92.

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