

The Structure of Diphenylvinylideneoctacarbonyldi-iron

By O. S. MILLS and A. D. REDHOUSE

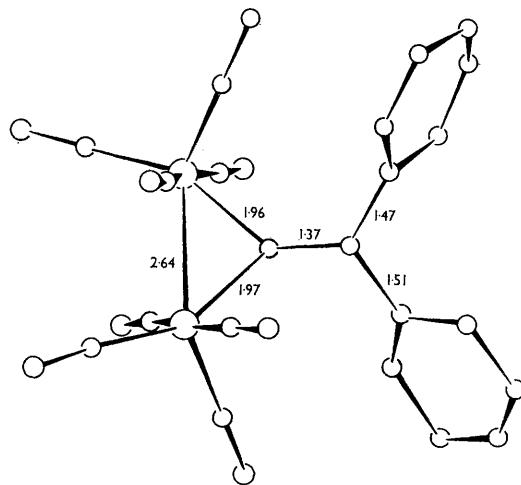
(Department of Chemistry, University of Manchester, Manchester, 13)

ALTHOUGH the most direct method for the preparation of carbene adducts of metal carbonyls would seem to be by liberation of carbene in presence of the carbonyl, the photolysis of diazomethanes under these conditions leads not to the desired products but to nitrogen-containing complexes.¹ An alternative source of carbenes is from the photolysis of ketens. Recently the photolysis of diphenylketen in various solvents has been explained, though admittedly incompletely, in terms of diphenylcarbene,² whilst the synthesis of tetramesitylethylene by the photolysis of dimesitylketen is considered to proceed *via* dimesitylcarbene.³

Irradiation of a solution of diphenylketen and iron pentacarbonyl in benzene, a solvent inert to diphenylketen and photochemically derived species therefrom,² leads to an air-stable, orange complex (I) of composition $C_{22}H_{10}Fe_2O_8$.⁴ The crystals are monoclinic with $a = 37.08$, $b = 8.67$, $c = 13.35 \text{ \AA}$, and $\beta = 90^\circ 14'$. Systematic absences correspond to space-groups Cc and $C2/c$. There are eight formula units per unit cell. The structure, deduced from 1372 reflections and the latter space-group, is shown in the Figure ($R = 11.9\%$). It consists of two $Fe(CO)_4$ groups bridged by a single ligand, the organic fragment Ph_2CC . It therefore appears that either the primary photolysis product is not Ph_2C or that the carbene attacks the $MC=O$ bond. Isotopic labelling experiments are to be performed to decide whether the bridging carbon atom arises from the keten or from the carbonyl.

The structure contains the following novel features. It is a binuclear iron complex which contains a single bridging group; this group has not hitherto been reported; the two $Fe(CO)_4$ groups have not previously been reported joined in this fashion. The co-ordination around each iron atom, though distorted, is closer to trigonal bipyramidal than to square pyramidal or to

octahedral if the latter is considered when the metal-metal direction is included. Although the Fe-Fe distance, 2.64 \AA , is larger than in any other carbon-bridged iron complex,⁵ save $Fe_3(CO)_{12}$, the angle subtended at the bridging carbon is 84° which lies in that small range ($80-87^\circ$) which appears to be independent both of the element(s) bonded to the bridging carbon atom (*e.g.*, carbon here, oxygen in carbonyl, nitrogen in isonitrile, or carbon and oxygen in a lactone ring) and of the metal atoms (iron, cobalt, nickel, ruthenium, or rhodium). Two extreme descriptions of the bonding of the organic



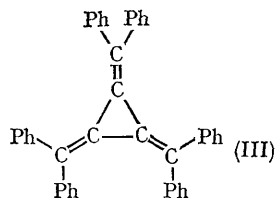
FIGURE

group within the molecule seem possible. In one, the carbon makes two single Fe-C bonds and one double bond and the complex can be regarded as a substituted ethylene; in the other the ligand is considered to be a bridging carbene. These

extremes have analogies in the bridging by carbon monoxide and isonitriles but differ in that these latter ligands are stable in the free state.

This formulation deduced from the X-ray analysis is in agreement with the mass spectrum.⁷ Decomposition of the complex in the ion source or on the probe occurs without additional heating (*ca.* 150°) at a temperature slightly greater than the melting point. Additional to the parent-ion peak at $m/e = 514$ and peaks corresponding to the successive stripping of eight CO groups, peaks at 178, 179, and 180 are indicative of diphenylvinylidene (II), and of $\text{Ph}_2\text{C}=\text{CH}$ and Ph_2CCH_2 . A further strong peak at 356 corresponds to tetraphenylbutatriene whilst a trimer peak at 534, which in some spectra is more intense than the parent molecular ion, could arise from attack by (II) on the central double bond of the cumulene to yield

(III). The peak at highest m/e -value detected occurs at 636 and together with six CO stripped fragments indicates the presence of tetraphenylbutatrienehexacarbonyldi-iron.⁶ These observations indicate that (I) may prove to be a useful source of unsaturated carbene (II) and further experiments to verify this prediction are intended.



(Received, June 6th, 1966; Com. 381.)

¹ P. L. Pauson and M. M. Bagga, personal communication.

² H. Nozaki, M. Nakano, and K. Kondo, *Tetrahedron*, **1966**, **22**, 477.

³ H. E. Zimmerman and D. H. Paskovich, *J. Amer. Chem. Soc.*, **1964**, **86**, 2149.

⁴ Our thanks are due to Professor P. L. Pauson for permission to refer to this unpublished preparation.

⁵ J. Lewis, "VIIIth International Conference on Co-ordination Chemistry," Vienna, 1964. (Butterworths, London, 1965.)

⁶ D. Bright and O. S. Mills, unpublished structure determination.

⁷ We thank Dr. J. M. Wilson for these measurements.