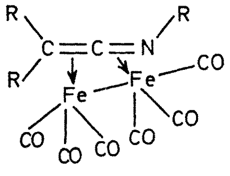
Molecular Structure of Hexacarbonyl-(4,4-diphenyl-2-azabuta-2,3-diene)di-iron, $(Ph_2C:C:NMe)Fe_2(CO)_6$

By K. OGAWA, A. TORII, H. KOBAYASHI-TAMURA, and T. WATANABÉ
(*College of General Education, Osaka University, Toyonaka*)
T. YOSHIDA and SEI OTSUKA
(*Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan*)

Summary An *X*-ray analysis of the title compound revealed a novel co-ordination scheme of a heterocumulene system.

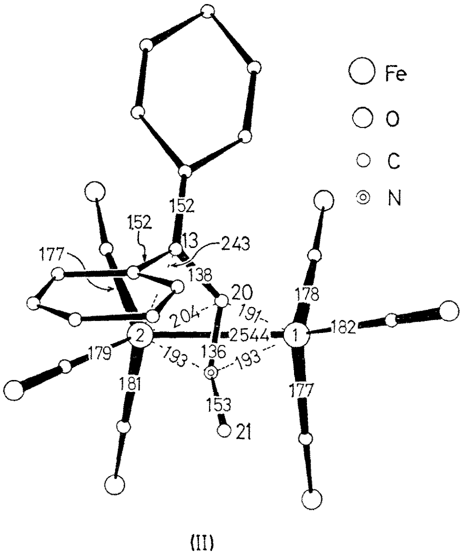
FROM spectroscopic evidence the molecular structure of the title compound[1] was assigned (I), but a single crystal *X*-ray



(I)

study now shows that it must be revised to structure (II) depicted in the Figure.

$(Ph_2C:C:NMe)Fe_2(CO)_6$ formed dark red crystals, m.p. 219—221° (from benzene–heptane). *Crystal data:* $C_{21}H_{13}Fe_2NO_6$: *M*, 423; orthorhombic; $a = 12{\cdot}41$, $b = 14{\cdot}64$, $c = 11{\cdot}81$ Å, $U = 2145{\cdot}67$ Å^3; $Z = 4$, $D_c = 1{\cdot}309$; $F(000) = 984$; space group $P2_12_12_1$, Co-K_α ($\lambda = 1{\cdot}791$ Å), iron-filtered Nonius Weissenberg camera. About 1500 independent



(II)

FIGURE. *Perspective view with relevant bond lengths in* $(Ph_2C:CNMe)Fe_2(CO)_6$

intensities were measured by visual methods. The structure was solved by the heavy atom method, and refined by block-diagonal least-squares with anisotropic thermal parameters to $R = 10{\cdot}7\%$. Hydrogen atoms were not included in the refinement.

One iron atom Fe(1) is bonded to C(20) and N while the other atom Fe(2) is co-ordinated to three atoms C(13), C(20), and N which form a bent (127·5°) delocalised system analogous to an allyl system. This allyl plane forms an angle of 22° with the Fe(1) and Fe(2) vector. The bond distances C(20)–C(13) and C(20)–N are longer than those for unco-ordinated C=C and C=N bonds, but are significantly shorter than the C–C distances (1·45—1·41 Å) found in the related μ-allyl complexes $(CH_2{\cdot}C{:}CH_2)Fe_2(CO)_6(PPh_3)$[2] and $C_{11}H_{18}Fe_2(CO)_7$[3] ($C_{11}H_{18}$ = cyclic C_{11} allene). This may imply less effective back-bonding to the nitrogen atom-containing allyl system. However, the nitrogen of the three allylic atoms is closest to Fe(2).

The two iron atoms are linked by a metal–metal bond (2·54 Å) and each acquires a closed shell configuration. Fe(1) may be regarded as being co-ordinated with one-electron donor ligand C(20) and with the lone-pair electrons on the nitrogen atom, while Fe(2) is co-ordinated with the three-electron ligand. This bonding scheme, however, seems oversimple. The plane defined by C(20), N, and C(21) nearly bisects the Fe(1)–Fe(2) bond and makes an angle of 84° with this bond. The two iron atoms lie equidistant from the nitrogen atom, and the angle C(20)–N–C(21) is 129·6°. This geometry around the nitrogen atom does not favour the above bonding scheme, but instead suggests a hybridization similar to that in the azomethine complex $(MeN{:}NMe)Fe_2(CO)_6$[4] or the benzo[*c*]quinoline complex $(C_{12}H_8N_2)Fe_2(CO)_6$.[5] All these aspects suggest that the metal–nitrogen bond has considerable σ-bond character, an assumption consistent with the up-field shift of the *N*-methyl proton resonance in comparison with that for the free ligand.[1]

(*Received, June 8th,* 1971; *Com.* 981.)

---

[1] S. Otsuka, A. Nakamura, and T. Yoshida, *J. Organometallic Chem.*, 1967, **7**, 339.
[2] R. E. Davis, *Chem. Comm.*, 1968, 248.
[3] P. F. Lindley and O. S. Mills, *J. Chem. Soc.* (*A*), 1970, 38.
[4] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 2709.
[5] R. J. Doedens, *Inorg. Chem.*, 1970, **9**, 429.

Printed by W Heffer & Sons Ltd Cambridge England