Structures of Two Nitrogen-containing Organometallic Complexes

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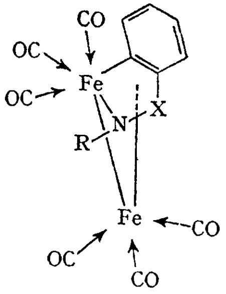
RECENTLY[1] structures of type (I) have been proposed for complexes of composition $L(CO)_6Fe_2$ (where L = ligand) formed by the reaction of iron enneacarbonyl with either Schiff bases (*e.g.*, I; X = CHMe, R = Ph) or azobenzene (I; X = NH, R = Ph). These structures closely resemble those already found in $(MeCCOH)_2(CO)_6Fe_2$[2] (II) and $(PhC)_2(CO)_6Fe_2$[3] (III) which involve a stable ferracyclopentadiene ring π-bonded to a second iron atom. In the case of Pt and Pd, stable five-membered rings occur without this additional bonding.[4,5]



(I)

When the Schiff base is that formed from *p*-toluidine and benzaldehyde, we have verified that a structure of type (I) does occur. The complex, $C_{20}H_{13}NO_6Fe_2$, crystallises in the monoclinic system, $a = 8{\cdot}67 \pm 0{\cdot}02$, $b = 19{\cdot}47 \pm 0{\cdot}03$, $c = 12{\cdot}14 \pm 0{\cdot}03$Å, $\beta = 92°25'$, $M = 475{\cdot}0$, $U = 2047$ Å^3, $Z = 4$ and space-group $P2_1/n$. The current R-value for 1237 unique reflexions is 10·4%. The structure is shown in Figure 1. There are significant differences between this and structures (II) and (III). For these, the ferracyclopentadiene ring is essentially flat and the four carbons are equidistant from the π-bonded iron atom; this is not so in the Schiff-base complex. Although the carbons of the phenyl group which form part of the ring are equidistant from the iron (2·3 Å), the methylene group, which cannot participate in bonding with the metal, is bent away (2·6 Å) whilst the nitrogen moves towards the iron so that it lies equidistant from both iron atoms (1·96 Å). The metal–metal distance, 2·43 Å, is shorter than those found in (II) and (III) and is in accord with our findings on other nitrogen-bridged complexes of iron. If we assume that the nitrogen atom acts as a three-electron donor then simple valence-bond structures can be written which account for the symmetrical bridging by the nitrogen.

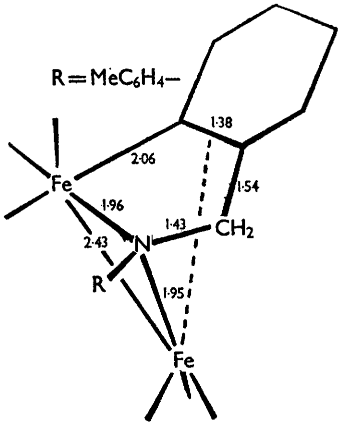


FIGURE 1

In the case of the complex formed from azobenzene, a different structure occurs; the reaction with iron is thus different from those with nickel, platinum, and palladium. We find that the complex $C_{18}H_{10}N_2O_6Fe_2$ crystallises in the triclinic system, $a = 8{\cdot}59 \pm 0{\cdot}02$, $b = 13{\cdot}92 \pm 0{\cdot}03$, $c = 7{\cdot}85 \pm 0{\cdot}02$ Å, $\alpha = 92°14'$, $\beta = 93°24'$ and $\gamma = 90°24'$, $M = 462{\cdot}0$, $U = 937{\cdot}1$ Å^3, $D_m = 1{\cdot}65$ g.cm.$^{-3}$ by flotation, $D_c = 1{\cdot}65$ g. cm.$^{-3}$, $Z = 2$ and space-group $P\bar{1}$. The R-value for 1915 independent non-zero reflexions is 8·02%. The structure is shown in Figure 2. Both nitrogen atoms bridge the two $Fe(CO)_3$ groups which are themselves arranged in an eclipsed configuration. The complete bridging group N–C_6H_4–N-(*o*) lies accurately perpendicular to the Fe–Fe vector. The Fe–Fe distance, 2·37 Å, is the shortest yet reported.

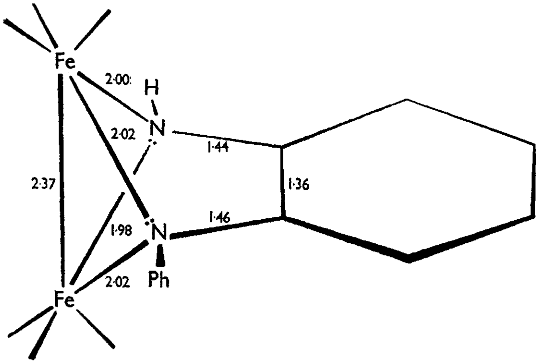


FIGURE 2

The formation of this complex thus involves the rupture of the –N=N– bond with rearrangement to form the *o*-semidine skeleton[6] which is released by reduction with lithium aluminium hydride.[1] Neither phenyl group participates in bonding with the metal atoms. The central group of six atoms, $C_2N_2Fe_2$, forms a bicyclo[2,1,1]-system. All ten hydrogen atoms, including that transferred from the ring to the nitrogen atom, have been determined. A thirty-six-electron structure can be rationalised on the supposition that each nitrogen acts as a three-electron donor. The Fe–N–Fe angle is 73°; the compression of this angle from the tetrahedral value is of the same magnitude as is found in bridging carbonyl groups. This small value is of particular significance since in every other bridged binuclear iron complex the metal atoms are further apart and this supports the view that it is the nature and number of the bridging groups which determine the metal separation.

Finally we mention that the complex formed from benzophenone azine and iron enneacarbonyl[1] does not correspond to either of these structures.[7]

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[2] A. A. Hock and O. S. Mills, *Acta Cryst.*, 1961, **14**, 139.

[3] M. Van Meerssche, P. Piret, J. Meunier-Piret, and Y. Degrève, *Bull. Soc. chim. belges.*, 1964, **73**, 724.

[4] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

[5] J. P. Kleiman and M. Dubeck, *J. Amer. Chem. Soc.*, 1963, **85**, 1544.

[6] This kind of arrangement had been discussed between Professor Pauson and ourselves prior to the above Communication.

[7] D. Bright and O. S. Mills, unpublished work.