The Reaction of Pentacarbonyliron with Phenyl- and Methyl-lithium; a Crystal Structure Analysis of a Two-atom Bridged Complex

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THE addition of phenyl- or methyl-lithium to Group VI metal carbonyls leads to the formation of metallates (I), which can also be isolated as their tetramethylammonium salts. Subsequent methylation to yield the neutral carbene complexes (II) can be achieved by treatment with diazomethane after acidification or, better, by reaction with trimethyloxonium tetrafluoroborate.[1–3] We now report the corresponding reactions with pentacarbonyliron.

The analogous tetracarbonyliron species (III) can also be isolated as their tetramethylammonium salts.[4] The reaction of the methyl-lithium adduct with trimethylammonium tetrafluoroborate does not lead to the desired mononuclear carbene complex, but to a number of products, the main component being $(C_5H_3O_4Fe)_2$.† The analogous compound (IV) $(C_{10}H_5O_4Fe)_2$ is best prepared by the reaction of the phenyl-lithium adduct with trityl chloride, a method also applicable to the methyl-lithium adduct. The i.r. spectrum of (IV) shows absorptions at 2083, 2040, 2008, and 1972 cm.$^{-1}$ (hexane), typical for the terminal carbonyl stretching region, and at 1497 cm.$^{-1}$ (KBr disc). The n.m.r. spectrum (pentane) shows a single absorption at τ 3·35 for the phenyl protons. The complex is polar (μ = 3·71 D in cyclohexane) and melts with decomposition at ~98°. These observations could be consistent with a structure such as (V) provided that the central 6-ring is non-planar.

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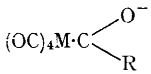
† All new compounds reported have yielded satisfactory total analyses.

Crystals of (IV) have been examined by *X*-ray diffraction methods. Crystal data: $C_{20}H_{10}O_8Fe_2$, $M = 490{\cdot}0$, orthorhombic, $a = 12{\cdot}54$, $b = 17{\cdot}79$, $c = 8{\cdot}82$ Å, $U = 1967$ Å^3, $D_c = 1{\cdot}65$, Z = 4, space group either *Pnma* (No. 62, D_{2h}^{16}) or $Pna2_1$ (No. 33, C_{2v}^{9}) by systematic absences. The former space group requires that the molecule contains a mirror plane of symmetry, the alternative of a centre of symmetry is inconsistent with the observed finite dipole moment, whereas the latter space group places no restriction on the molecular shape. Some 793 non-zero, three-dimensional intensities were estimated visually and the structure was solved by Patterson and Fourier methods. Although both space groups were continually considered throughout the analysis, we were able to refine the structure to $R = 5{\cdot}6\%$ (full-matrix, least-squares refinement with anisotropic temperature parameters only for the metal atoms) within the symmetry *Pnma* and since the individual temperature parameters are very reasonable we conclude that this is the correct space group.

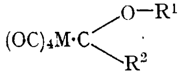
The structure found, (VI), is novel and surprising in that although in the anion the carbene atom is attached to the metal, in the dimer both these carbon atoms are attached to the same metal atom. The two iron atoms lie in the crystallographic mirror plane and the Fe–C–O–Fe–O–C ring is boat-shaped. The Fe–Fe vector (2·57 Å), although bridged by two pairs of atoms whose interatomic vectors [C–O 1·26(1) Å) are parallel to the Fe–Fe direction, unexpectedly lies within the range (2·46—2·64 Å) found when a single carbon atom is the bridging function. The carbon atom of the bridging group is coplanar, within 0·001 Å, with its three nearest neighbours, an arrangement common to all the carbene complexes of the Group VI metals so far examined.[5–8] The phenyl group is twisted 29° out of this plane. The Fe(2)–C distance, 1·95(1) Å, is significantly longer than the other Fe–CO distances. The Fe(1)–O distance is 1·97(1) Å and the C–Ph distance 1·49(1) Å, typical of that involving two sp^2-hybridised carbon atoms.

Two alternative descriptions for the molecule seem currently feasible. The first involves a phenylferroxycarbene description. Since the Fe–O bond would be expected to have considerable ionic character, the C–O distance should be compared with that in an ionic carbene complex rather than a neutral complex and indeed the observed value is marginally closer to that reported[9] for $(C_5H_5)Mn(CO)_2CPhO^-$ than to those for either of the methoxy-carbene complexes. Although it is very difficult to ascribe a reliable radius to Fe(O), we note that the Fe–C distance observed must imply much less double-bond character than is present in the Fe–CO bonds. The difference in length between these bonds (0·17 Å) is identical, within experimental error, to that observed in the chromium compounds.[5,6] The second description involves that of a benzoyl complex. The major difference is that the C–O bond is now regarded principally as a double bond so that the observed length should be compared with that of a oxo-group (1·23 Å). This description requires the oxygen atom of the oxo-group to co-ordinate with Fe(1) and would be the first example of such an interaction.

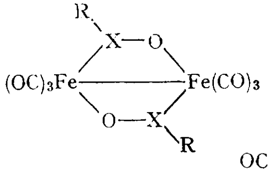


(I) M=CrCO, WCO; R=Ph, Me

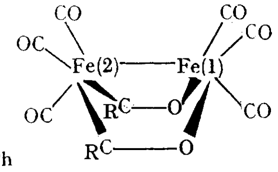
(III) M=Fe; R=Ph, Me



(II) M=CrCO, WCO; R^1=Me; R^2=Ph, Me



X	R
(V) C	Ph
(VII) N	Ph
(VIII) N	*p*-MePh
(IX) N	*p*-MeOPh
(X) N	*o*-Me,*m*-ClPh



(VI) R=Ph

We have noted that the mode of bridging causes non-equivalence of the two Fe atoms and this is clearly shown in the Mössbauer spectrum, measured at room and liquid nitrogen temperatures. In both cases we found a well-resolved 4-peak spectrum which arises from the superposition of two quadrupole-split spectra. Although the structure (VI) is novel, structures analogous to the closely related (V) have been proposed for some nitrosobenzene complexes.[10] Although the two sets of compound involve very different methods of preparation, we have examined the possibility that the nitroso-compounds‡ [(VII)—(X)] may also have structures similar to (VI) by studying their Mössbauer spectra. In every case the spectrum was found to consist of a quadrupole-split doublet with quadrupole splitting ~0·95 mm./sec., isomer shift (relative to sodium nitroprusside) of +0·25 mm./sec. and line width at half-height of less than 0·30 mm./sec., and we conclude that there is no evidence for a structure

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‡ We thank Dr. E. Koerner for supplying us with samples of these complexes.

similar to (VI) for these compounds. A diffraction study of these compounds should determine their structures definitely.

In addition to the methyl and phenyl complexes (IV), we have also prepared a number of derivatives in which one CO is substituted to yield compounds of the general formula $Fe_2(CO)_5R^1(COR^2)_2$ ($R^1 =$ $H_2N{\cdot}NHPh$, NC_5H_5, NC_5H_{11}; $R^2 =$ Me, Ph). The Mössbauer spectra of these derivatives are being studied.

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