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# PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XXI*. POLYFLUOROBENZOBARRELENE COMPLEXES OF IRON TRICARBONYL

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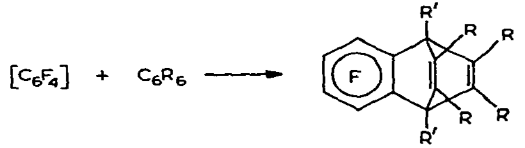
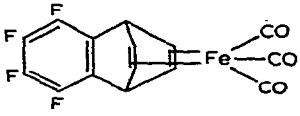
## SUMMARY

Bromine- and methyl-substituted analogues of tetrafluorobenzobicyclo-[2.2.2]octatriene (tetrafluorobenzobarrelene) react with triiron dodecacarbonyl to give complexes of the type $LFe(CO)_3$. Competition reactions, Mössbauer chemical shifts and proton NMR evidence all indicate that methyl groups on the olefinic carbon atoms of the ligands decrease the stability of the resulting complexes. The mass spectra of the complexes are discussed; arene–Fe and "butadiene"–iron complexes may be intermediates in the fragmentation processes.

Pentafluorophenyllithium and (pentafluorophenyl)magnesium bromide decompose thermally via loss of metal fluoride generating tetrafluorobenzyne in solution[2]. The benzyne can be trapped by the addition to the system of benzene or a substituted benzene:



When benzene is used the product of this trapping reaction is tetrafluorobenzobicyclo-[2.2.2]octatriene[3] (*i.e.* tetrafluorobenzobarrelene). When refluxed with triiron dodecacarbonyl in petrol ether, tetrafluorobenzobarrelene forms a complex $LFe(CO)_3$ which was given the structure:



on the basis of its proton nuclear magnetic resonance spectrum[4]. This structure has since been confirmed by X-ray diffraction studies on single crystals[5]. We now report the preparation and study of similar complexes in which some, or all, of the groups R and R′ on the ligand have been substituted by methyl, the remainder being hydrogen

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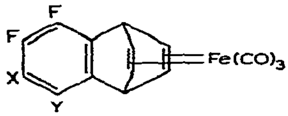
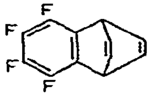
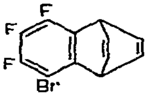
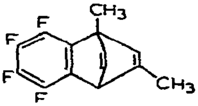
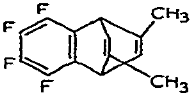
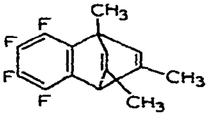
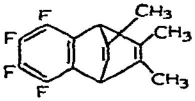
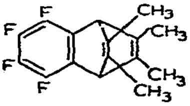
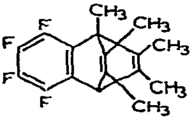
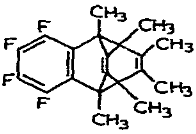
* For Part XX see ref. 1.

TABLE 1

BARRELENE–IRON TRICARBONYL COMPLEXES



| Barrelene ligand | Shortened notation used for complexes | M.p. | Analyses found (calcd.)(%) | | | Δ'$^a$ |
|---|---|---|---|---|---|---|
| | | | C | H | F | |
|  | $^{4F}$L(benzene)Fe(CO)$_3$ | 140–1° | 49.4<br>(49.2) | 1.8<br>(1.7) | 20.7<br>(20.8) | 3.50 |
|  | $\alpha$-$^{3F}_{Br}$L(benzene)Fe(CO)$_3$ | 135°(d) | 42.6<br>(42.15) | 1.5<br>(1.4) | ref. 8 | |
|  | $^{4F}$L(*m*-xylene)Fe(CO)$_3$ | 76–79°(d) | 51.95<br>(51.8) | 2.5<br>(2.5) | | 3.15<br>3.3 |
|  | $^{4F}$L(*p*-xylene)Fe(CO)$_3$ | 113°(d) | 51.7<br>(51.8) | 2.4<br>(2.5) | | 3.2 |
|  | $^{4F}$L(mesitylene)Fe(CO)$_3$ | 113.5–114.5° | 53.1<br>(53.1) | 2.9<br>(2.9) | | 3.03 |
|  | $^{4F}$L(tri-Me-benz)Fe(CO)$_3$ | 106°(d) | 53.3<br>(53.1) | 2.9<br>(2.9) | | 3.15 |
|  | $^{4F}$L(durene)Fe(CO)$_3$ | 134–137°(d) | 54.2<br>(54.05) | 3.3<br>(3.3) | | |
|  | $^{4F}$L(penta-Me-benz)Fe(CO)$_3$ | 135–138° (d) | 55.21<br>(55.04) | 3.63<br>(3.67) | | |
|  | $^{4F}$L(hexa-Me-benz)Fe(CO)$_3$ | 130–133°(d) | 56.1<br>(56.0) | 3.9<br>(4.0) | | |

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[a] $\Delta' = \delta'$(free ligand)$-\delta'$(complex) in ppm for the vinyl protons (when present).

atoms. There are two major effects to which methyl groups on the olefinic carbon atoms might contribute. These are:

(*a*) electron density will be increased in the C=C bonds by an inductive effect thus strengthening their interaction with the iron atom,

(*b*) adverse steric interaction between the methyl groups and the iron atom may prevent the metal from achieving the position of most favourable approach to the olefinic bonds.

Bridge-head methyl groups (position R′) can be expected to have little influence on either the bonding of the ligand to iron or steric interaction of the ligand with the iron. However, the change in symmetry of the ligand by having one R′ group as methyl will alter the molecular packing in the crystalline complexes and tend to lower their melting points.

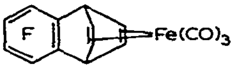
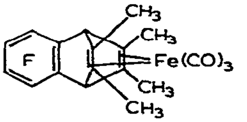
The complexes which have been prepared are summarised in Table 1 which also gives a shorthand notation used in this paper to describe a particular ligand. Competition reactions, in which two ligands are refluxed with a less than molar equivalent of triiron dodecacarbonyl in petrol ether, showed that the relative rates of reaction of four ligands were in the order,

$$^{4F}\mathrm{L(benz)} > {}^{4F}\mathrm{L(mesitylene)} \cong {}^{4F}\mathrm{L}(p\text{-xylene}) > {}^{4F}\mathrm{L(durene)}$$

As Table 2 illustrates the Mössbauer chemical shift, $\delta$, decreases significantly when the four vinyl hydrogen atoms in (tetrafluorobenzobarrelene)iron tricarbonyl are changed to four methyl groups in the complex $^{4F}$L(durene)Fe(CO)$_3$. This decrease in $\delta$ indicates that the *s* electron density at the iron nucleus is lower in the methyl complex, which in turn shows that the combined effect of the $\sigma$ and $\pi$ interactions of the $^{4F}$L(durene) ligand with the iron atom is smaller than that between $^{4F}$L(benzene) and iron. The complex $^{4F}$L(mesitylene)Fe(CO)$_3$ gave Mössbauer parameters lying between those of $^{4F}$L(benzene)Fe(CO)$_3$ and $^{4F}$L(durene)Fe(CO)$_3$ but the data are not collected in Table 2 as they were not measured with sufficient accuracy. The Mössbauer chemical shifts therefore suggest very strongly that the most stable complex is (tetrafluorobenzobarrelene)iron tricarbonyl, $^{4F}$L(benzene)Fe(CO)$_3$ and that methyl groups on the olefinic carbon atoms of the ligand decrease the stability of the resulting complexes, presumably by their adverse steric interaction with the metal. Such an inter-

TABLE 2

MÖSSBAUER SPECTRAL DATA FOR TWO BARRELENE–IRON TRICARBONYL COMPLEXES AT 80°K

| Complex | Chemical shift[a], $\delta$ | Quadrupole coupling[b], $\Delta$ |
|---|---|---|
|  | 0.284 | 2.141 |
|  | 0.262 | 2.619 |

[a] Relative to a single crystal of sodium nitroprusside with an error of ± 0.008 mm/sec. [b] In mm/sec; error ± 0.008 mm/sec.

action would be expected to cause some distortion of the symmetry about the iron and in agreement with this the two methyl substituted complexes have the larger values of the quadrupole splitting constant, Δ (the size of this constant is normally thought to reflect the amount of "distortion" around the iron atom).

Thus, although the competition reactions can be explained by kinetic effects, it is also possible that the reactivity sequence of the ligands given above may be governed in part by the thermodynamic stability of their respective complexes. It is interesting to note that many of the methyl-substituted complexes decompose rapidly on melting (Table 1). For all the complexes there is virtually no change in the position of the carbonyl stretching frequency in their infrared spectra probably indicating rather little change in both the Fe–CO and Fe–ligand π-bonding characteristics from complex to complex. The changes in thermodynamic stability noted are therefore presumably

TABLE 3

MASS SPECTRA OF (BENZOBARRELENE)IRON TRICARBONYL COMPLEXES

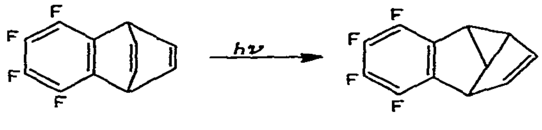
| Major ion fragments | Relative Intensities of Ions | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $^{4F}$L(benzene)Fe(CO)$_3$ | $^{3F}_{\alpha\text{-Br}}$L(benzene)Fe(CO)$_3$ | $^{4F}$L(*m*-xylene)Fe(CO)$_3$ | $^{4F}$(*p*-xylene)Fe(CO)$_3$ | $^{4F}$L(mesitylene)Fe(CO)$_3$ | $^{4F}$L(tri-Me-benz)Fe(CO)$_3$ | $^{4F}$L(durene)Fe(CO)$_3$ | $^{4F}$L(penta-Me-benz)Fe(CO)$_3$ | $^{4F}$L(hexa-Me-benz)Fe(CO)$_3$ |
| $[LFe(CO)_3]^+$ | 10 | 20 | 10 | 10 | 10 | 15 | 20 | 15 | 15 |
| $[LFe(CO)_2]^+$ | 25 | 35 | 30 | 30 | 20 | 30 | 40 | 25 | 30 |
| $[LFe(CO)]^+$ | 40 | 50 | 60 | 50 | 30 | 50 | 60 | 50 | 60 |
| $[LFe]^+$ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| $[LFe-H_2]^+$ | — | — | — | — | — | 70 | 110 | 65 | 150 |
| $[LFe-2H_2]^+$ | — | — | — | — | — | — | 35 | 20 | 40 |
| $[LFe-C_2H_2]^+$ | 85 | 75 | 15 | — | — | — | — | — | — |
| $[LFe-C_3H_4]^+$ | — | — | 90 | 70 | 120 | 30 | — | — | — |
| $[L-4(CH_3)]^+$ | — | — | — | — | — | <5 | <5 | <5 | <5 |
| $[L]^+$ | 70 | 1000 | 80 | 100 | 30 | 120 | 300 | 150 | 500 |
| $[L-CH_3]^+$ | — | — | 85 | 60 | 25 | 90 | 280 | 180 | 600 |
| $[L-2(CH_3)]^+$ | — | — | 15 | 10 | 7 | 20 | 60 | 30 | 250 |
| $[L-3(CH_3)]^+$ | — | — | — | — | <5 | 10 | 25 | 20 | 100 |
| $[L-4CH_3)]^+$ | — | — | — | — | — | — | <5 | 10 | 20 |
| $[L-C_2H_2]^+$ | 220 | 200 | 50 | — | — | — | — | — | — |
| $[L-C_3H_4]^+$ | — | — | 15 | 85 | 15 | 30 | — | — | — |
| $[L-C_4H_6]^+$ | — | — | — | — | — | 60 | 80 | 40 | 100 |
| $[L-C_2H_2-F_2]^+$ | 400 | 20 | 20 | — | — | — | — | — | — |
| $[L-C_3H_4-F_2]^+$ | — | — | 35 | 50 | 60 | 20 | — | — | — |
| $[L-C_4H_6F_2]^+$ | — | — | — | — | — | 25 | 10 | 20 | 30 |
| $[FeC_2H_2]^+$ | 800 | 50 | 20 | — | — | — | — | — | — |
| $[FeC_3H_4]^+$ | — | — | 100 | 150 | 95 | 80 | — | — | — |
| $[FeC_4H_6]^+$ | — | — | — | — | — | 110 | 100 | 100 | 60 |
| $[Fe]^+$ | 300 | 100 | 60 | 85 | 50 | 100 | 10 | 30 | 60 |

due to the decrease in $\sigma$-bonding brought about by the steric interference between the methyl groups and the iron; the adverse steric factor must outweigh the inductive effect of the methyl groups. This is the opposite conclusion reached from a comparative study of bis(duroquinone)nickel and bis(benzoquinone)nickel when the former complex is found to be more well-defined and more stable[6]. In the duroquinone ligand it is virtually impossible for the methyl groups to interact sterically with the nickel atom and the inductive effect of the four methyls is probably responsible for the observed increase in stability.

With the benzobarrelene we could detect no change (either way) in stabilities or reaction rates caused by the substitution of either one or two methyl groups in the bridge-head positions (*i.e.* $R' = CH_3$).

The proton nuclear magnetic resonance spectra of the free ligands and their iron complexes are deceptively simple, presumably due to second order effects. Without attempting to interpret the spectra we have calculated the difference in chemical shift between protons in the free ligand and those in the iron complexes, *i.e.* $\Delta' = \delta'(\text{ligand}) - \delta'(\text{complex})$ in ppm. Only for the vinyl protons did the value of $\Delta'$ appear to change significantly from complex to complex. When no methyl groups were on the olefinic carbon atoms the value of $\Delta'$ was 3.50 ppm and this decreased in a fairly regular manner as the number of vinylic methyl groups was increased; see final column in Table 1. Such a change in $\Delta'$ is consistent with weaker iron-to-olefin bonding as methyl groups are placed on the olefinic carbon atoms because this will result in a deshielding effect on the remaining vinylic protons.

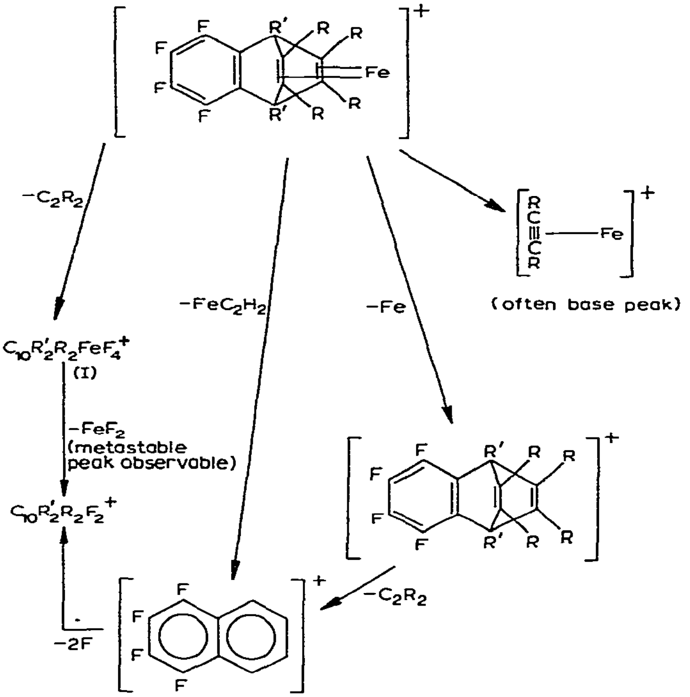
The thermal decomposition of (tetrafluorobenzobarrelene)iron tricarbonyl gave mainly carbon monoxide and tetrafluoronaphthalene[4]. Since the formation of tetrafluoronaphthalene occurred at a much lower temperature in the decomposition of the complex than when the free ligand itself was heated, it was suggested that perhaps the iron was in some way catalysing the loss of acetylene from the ligand[4]. We have now recorded the mass spectrum of this complex and find that the base peak (which is almost ten times more intense than any other in the spectrum) corresponds to the ion $FeC_2H_2^+$ which appears to substantiate the above suggestion of catalysis in the thermal decomposition of the complex. The complexes having several vinylic methyl groups on the ligand lose carbon monoxide on heating and the ligands become isomerised as they leave the iron atom; we have, as yet, been unable to identify the isomers which are produced but they may be methyl analogues of the compound formed when tetrafluorobenzobarrelene is photolysed[7]:



The fragmentation of these iron complexes in a mass spectrometer has proved to be rather interesting. In a typical spectrum peaks are observed for ions representing the loss of one, two and three carbon monoxide groups, metastable peaks being observed for all three stages of the process:

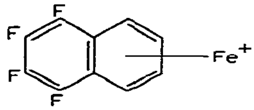
$$LFe(CO)_3^+ \xrightarrow{-CO} LFe(CO)_2^+ \xrightarrow{-CO} LFe(CO)^+ \xrightarrow{-CO} LFe^+$$

The decomposition of the ion $LFe^+$ depends quite markedly on the number and position of the methyl groups in the ligand, L. For a general case the main breakdown pattern follows the scheme shown below:



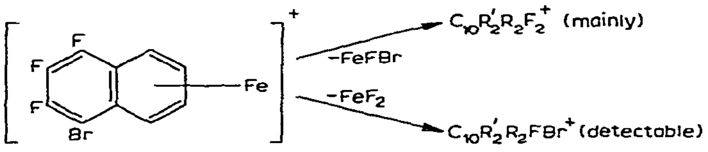
There are two main points of interest concerning this fragmentation scheme.

(*a*). The loss of $C_2R_2$ gives the ion $C_{10}R'_2R_2FeF_4^+$ which probably can be given a "sandwich" structure in which the iron atom is bonded to one half of a naphthalene molecule:

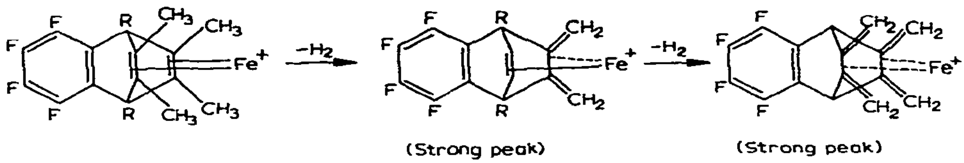


If this is the correct structure of the ion, it is the first instance of a transition metal forming a sandwich complex to an aromatic system containing several fluorine atoms. Fluoroaromatic ligands are relatively poor $\sigma$-donors (because of electron-withdrawal by the fluorine atoms) and normally increase the stability of their complexes by strong metal-to-ligand $\pi$-bonding. Since in sandwich complexes it is considered that back-bonding from metal to ligand is relatively unimportant, this would explain the non-existence of sandwich compounds such as $(C_6F_6)_2Cr$ and $C_6F_5C_6F_5Cr(CO)_3$.

A strong meta-stable peak representing the loss of $FeF_2$ shows that the ion $C_{10}R'_2R_2FeF_4^+$ decomposes largely via a carbon-to-metal fluorine shift. When a bromine atom is placed in the $\alpha$-position of the fluorinated ring, the loss of FeFBr is favoured by almost 80/1 compared to $FeF_2$ suggesting that it is the $\alpha$ carbon atoms which supply the halogen during the carbon-to-metal halogen shift,



(*b*). When the ligand has four methyl groups on the olefinic carbon atoms (positions R) two metastable peaks, each representing the loss of two hydrogen atoms (as $H_2$) from the ion $LFe^+$, can be distinguished. It is suggested that these metastable transitions indicate the formation of a type of butadiene–iron complex during the fragmentation processes. (The mass spectra of the free ligands do not show these metastable peaks.)



This idea finds support in the fact that a similar meta-stable peak is to be observed in the mass spectrum of the complex $^{4F}L$(tri-Me-benz)$Fe(CO)_3$, where two of the methyl groups are on the same double bond, but *not* in the spectra of complexes formed by ligands having two methyl groups on different olefinic double bonds, *e.g.* $^{4F}L$(mesitylene)$Fe(CO)_3$ and $^{4F}L$(*p*-xylene)$Fe(CO)_3$.

## EXPERIMENTAL

All reactions were carried out under dry, oxygen-free nitrogen; analyses were performed by the microanalytical department at Queen Mary College and by Dr. A. Bernhardt, Mülheim, Ruhr. We tank the Imperial Smelting Corporation for generous gifts of polyfluorobenzene derivatives.

### *Preparations of the ligands*

The ligands summarised in Table 1 were prepared in a manner similar to that used for tetrafluorobenzobicyclo[2.2.2]octatriene[4]. Most of the ligands have been described previously by Heaney and his co-workers using polyfluorophenyl Grignard reagents as the benzyne precurser; we used lithium reagents throughout this work.

### *Preparation of the iron tricarbonyl complexes*

The appropriate ligand and triiron dodecacarbonyl were refluxed in 80–100° petrol ether until the green colour of the iron carbonyl had been displaced. The solvent was then removed and the complex purified by either recrystallization or thin-layer chromatography on Kieselguhr. All the complexes are yellow or yellow-orange, air-stable solids which sublime without decomposition on heating in a vacuum.

## ACKNOWLEDGEMENTS

Dr. Edward Kostimer of Cornell University kindly recorded the Mössbauer data. One of us (D.M.R.) thanks the Science Research Council for a maintenance grant.

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