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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS XI*. METAL CARBONYL DERIVATIVES OF TETRAFLUOROBENZOBICYCLO[2.2.2]OCTATRIENE[1]

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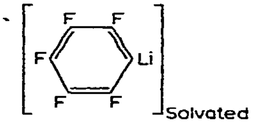
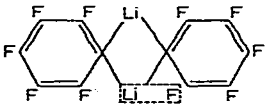
Pentafluorophenyllithium is a useful reagent not only for the synthesis of simple pentafluorophenyl–metal derivatives but also for the preparation of 4-substituted[2], or 2-substituted[2,3] nonafluorobiphenyls and tetrafluorobenzobicyclo[2.2.2]octatriene[4]. The latter compounds all arise from the pentafluorophenyllithium via a fluorine shift from carbon to lithium, the process being strongly influenced by the choice of solvent. In an ether solvent where the pentafluorophenyllithium might be expected to be partially solvated as monomers, (I), there is a possibility of nucleophilic attack in the 4-position on neighbouring pentafluorophenyl compounds, *e.g.*[2]:



(I)



Hypothetical dimer(II)

$$C_6F_5Li(\text{solvated}) + C_6F_5X \xrightarrow[5\text{ days}]{-40°} 4\text{-}XC_6F_4C_6F_5 \qquad (X = \text{Li or Br})$$

If the fluorine shift is allowed to occur at higher temperatures in an ether, ether/hydrocarbon or hydrocarbon solvent then the main product is 2-lithiononafluorobiphenyl. This may be explained by assuming that a faster intermolecular loss of lithium fluoride occurs mainly within a dimer species such as (II) (phenyllithium is known to be present as dimers in ether solution but the thermal instability of pentafluorophenyllithium makes molecular weight determinations very difficult in this case) leaving the remnants suitably positioned for the formation of 2-lithiononafluorobiphenyl without the actual presence of "free" tetrafluorobenzyne which has been postulated previously. In benzene the pentafluorophenyllithium monomer will probably again be solvated (in this case, sandwich-fashion[4], *cf.* the compound between hexafluorobenzene and benzene[5]) which will hinder the addition of pentafluorophenyllithium to any tetrafluorobenzyne by intramolecular loss of lithium fluoride; the benzyne in this case will attack the (suitably orientated) solvent[4] to give mainly tetrafluorobenzobicyclo[2.2.2]octatriene although the concurrent formation of some 2-lithiononafluorobi-

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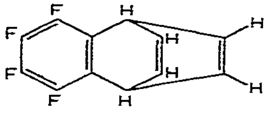
* For Part X see ref. 1.

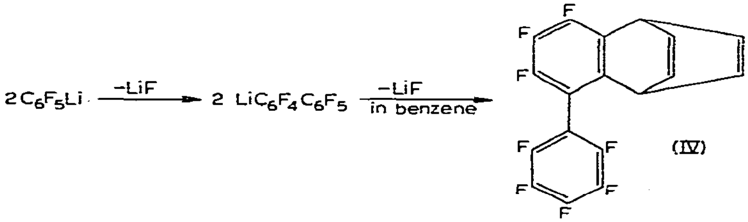
phenyl is evidenced by the isolation of small quantities of 1-(pentafluorophenyl)-2,3,4-trifluorobenzobicyclo[2.2.2]octatriene (see *Experimental Section*). A similar mechanism may well account for the tetrafluorobenzyne addition products formed[6] with substituted benzenes, furan, pyridine and thiophene when pentafluorophenylmagnesium bromide is used to generate the benzyne.

Since the molecular shape of tetrafluorobenzobicyclo[2.2.2]octatriene (III) is rather similar to that of norbornadiene we investigated the possible synthesis of metal carbonyl derivatives of this triene in order to determine whether its coordinating ability would be reduced or increased, compared to norbornadiene, by the rather electron-withdrawing tetrafluorobenzene nucleus.



(III)

The ligand (III) was synthesised in 50–55% yield by allowing pentafluorophenyllithium to decompose at 0° in benzene solution; small amounts of impurity were shown to arise from a side-reaction in which 2-lithiononafluorobiphenyl eliminated lithium fluoride and then gave a benzene adduct:

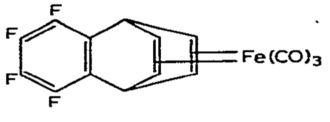


$$2C_6F_5Li \xrightarrow{-LiF} 2\ LiC_6F_4C_6F_5 \xrightarrow[\text{in benzene}]{-LiF}$$

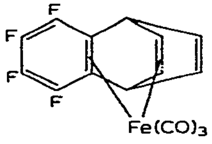
(IV)

When tetrafluorobenzobicyclo[2.2.2]octatriene is refluxed with an excess of iron pentacarbonyl, an orange-yellow solid analysing as $Fe(CO)_3C_6F_4C_6H_6$ can be isolated in about 40% yield; triiron dodecacarbonyl is also obtained as a by-product in this reaction and is removed by sublimation and recrystallisation. If triiron dodecacarbonyl is refluxed with a small excess of tetrafluorobenzobicyclo[2.2.2]octatriene in a petrol ether solvent until all the iron carbonyl has either reacted or decomposed, a 20% yield of the same complex is obtained. The solid complex appears to be air-stable at room temperature and decomposes by less than 1% at 120° after 12 days in an evacuated, sealed tube. Under these conditions the orange-yellow microcrystalline solid slowly grows into large orange-red crystals without any accompanying change in the infrared or ^1H NMR spectra, the colour change being apparently due to the change in crystal size. Between 150° and 200° decomposition is more rapid and produces carbon monoxide, 1,2,3,4-tetrafluoronaphthalene, tetrafluorobenzobicyclo-[2.2.2]octatriene (III) and a black solid (which contained some free iron since it was attracted by a magnet). The 1,2,3,4-tetrafluoronaphthalene no doubt arises from decomposition of the triene ligand because Heaney[4] has shown that tetrafluorobenzobicyclo[2.2.2]octatriene loses acetylene at 300° to give high yields of this tetrafluoronaphthalene; at 150° we could detect no loss of acetylene from the free triene ligand after 24 hours. It is possible that the iron carbonyl derivatives present in the $Fe(CO)_3C_6F_4C_6H_6$ decomposition vessel catalyse the removal of acetylene (perhaps as complexes) from tetrafluorobenzobicyclo[2.2.2]octatriene as it breaks away from the iron atom.

As iron carbonyls are notorious reagents for isomerising olefins we considered the possibility that tetrafluorobenzobicyclo[2.2.2]octatriene may isomerise in some way before forming the iron carbonyl complex; however, the presence of free triene ligand among the decomposition products of the complex suggests that no such isomerisation had taken place, in which case there are two possible structures for the iron carbonyl complex:



(V)



(VI)

The proton NMR spectrum of the complex shows that the four olefinic protons are equivalent and therefore proves that the structure is as in (V). The resonance due to the olefinic protons moved up field by 3.55 ppm (compared to free triene ligand) due to the deshielding effect of bonding to the iron. The magnitude of this up-field shift can perhaps be envisaged as a qualitative measure of the strength of the ligand–iron bond. The up-field shift of the olefinic protons in norbornadieneiron tricarbonyl compared to free norbornadiene is 3.06 ppm[7] and accordingly tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl can be refluxed, or heated in a sealed tube, with a very large excess of norbornadiene without any occurrence of ligand exchange. (Such a correlation for the chemical shifts can only be expected to hold true for those olefins which undergo little steric change on coordination to a metal.)

The ^{19}F NMR spectrum of tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl is rather complex and we have been unable to obtain the respective coupling constants because very weak lines expected to occur in the wings of the spectrum could not be detected; however, the spectrum is almost superposable on that of free tetrafluorobenzobicyclo[2.2.2]octatriene (allowing for a small down-field shift) showing that the coupling constants in the two molecules are virtually identical. This is further strong evidence against isomerisation of the ligand when coordinated to the iron and is also in agreement with structure (V). The presence of only two carbonyl stretching frequencies in the infrared spectra of non-conjugated diene–iron tricarbonyls is usually indicative of non-isomerisation to a conjugated diene system[8]; however, tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl shows three carbonyl frequencies in the spectrum of a solid mull and, although two bands are observed for solution spectra, the one at longer wavelength is particularly broad. Hence, the infrared spectral evidence is of little structural help in the case of this particular complex.

Chromium hexacarbonyl and tetrafluorobenzobicyclo[2.2.2]octatriene react together when refluxed in a hydrocarbon solvent giving an air-stable yellow solid complex, $Cr(CO)_4C_6F_4C_6H_6$, analogous to the iron complex (V). [Attempts to make $Cr(CO)_2(C_6F_4C_6H_6)_2$ by using an excess of the triene have so far failed.] The similar complexes formed by molybdenum and tungsten are fairly air-sensitive, especially in solution, but appear to be stable when stored under nitrogen or in a vacuum at room temperature. We have so far been unable to make the diene complex, hexafluoro-Dewar-benzenechromium tetracarbonyl either by subjecting chromium hexacarbonyl and hexafluorobenzene to UV radiation in sealed pyrex or quartz vessels, or by heating the two together at about 150°; no hexafluorobenzenechromium tricarbonyl was obtained under any of these conditions and, indeed, on heating some attack of the C–F bonds by the chromium appeared to take place.

EXPERIMENTAL

Reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Analyses were performed by A. Bernhardt, Mülheim, Ruhr and molecular weights determined by Miss B. Harman of this department using a Mechrolab vapour phase osmometer, model 301A. We thank the Imperial Smelting Corporation for generous gifts of bromopentafluorobenzene.

Preparation of tetrafluorobenzobicyclo[2.2.2]octatriene

A mixture of bromopentafluorobenzene (8 g), 20 ml of a 15% solution of butyllithium in hexane and 100 ml of benzene was stirred at 0° for 2 h. After removal of the solvent under vacuum, the residue afforded 4 g of tetrafluorobenzobicyclo[2.2.2]octatriene (m.p. 70–71°) on sublimation at 60° under high vacuum; yield 55%. (Found: C, 63.6; H, 2.6; F, 33.8; mol.wt., 239. $C_{12}H_6F_4$ calcd.: C, 63.7; H, 2.7; F, 33.6; mol.wt., 226.) On sublimation of the residues at 90° a small amount of very pale yellow solid, m.p. 153–155°, was obtained and shown by analysis and proton NMR studies to be 1-(pentafluorophenyl)-2,3,4-trifluorobenzobicyclo[2.2.2]octatriene, (IV). (Found: C, 57.8; H, 1.6; F, 40.7. $C_{18}H_6F_8$ calcd.: C, 57.8; H, 1.6; F, 40.6%.)

Decomposition of tetrafluorobenzobicyclo[2.2.2]octatriene in a sealed tube

Tetrafluorobenzobicyclo[2.2.2]octatriene (526 mg) was held at 325° for 3 days in an evacuated, sealed Pyrex tube. An infrared examination of the gaseous products showed that acetylene, a trace of ethylene, and silicon tetrafluoride (from attack of the reaction vessel) were present. On vacuum sublimation of the residue at 65° 407 mg of 1,2,3,4-tetrafluoronaphthalene (88% yield) were obtained, identified by its melting point and infrared spectrum.

Preparation of tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl

(*a*) *From $Fe(CO)_5$.* Tetrafluorobenzobicyclo[2.2.2]octatriene (1.52 g) was refluxed with a large excess of iron pentacarbonyl (100 ml) for 24 h. The unreacted iron pentacarbonyl was evaporated off under vacuum to leave a mixture of a yellow solid and the dark green, triiron dodecacarbonyl; fractional crystallisation from 40–60° petrol ether gave 1.06 g of the pure yellow-orange solid, tetrafluorobenzobicyclo-[2.2.2]octatrieneiron tricarbonyl; yield 43%. (Found: C, 49.4; H, 1.8; F, 20.7; mol.wt., 356. $C_{15}H_6F_4FeO_3$ calcd.: C, 49.2; H, 1.65; F, 20.8%; mol.wt., 366.)

(*b*) *From $Fe_3(CO)_{12}$.* Triiron dodecacarbonyl (300 mg) and tetrafluorobenzobicyclo[2.2.2]octatriene (650 mg; mole ratio *ca.* 1:4 respectively) were refluxed in 80–100° petrol ether (100 ml) for several hours until the dark green colour of the iron carbonyl had dispersed; the solvent was evaporated and the yellow complex either sublimed in vacuum or recrystallised from 60–80° petrol ether. Yield 120 mg; 17% based on the triiron dodecacarbonyl. When the reaction was carried out in a sealed evacuated tube at 100° in the absence of solvent yields of up to 30% could be achieved.

Attempts to remove the coordinated olefin

(*a*) *With triphenylphosphine.* Tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl (220 mg) was refluxed with more than a 3-fold excess of triphenylphosphine in petrol ether (60–80°) for 20 h. After this time it was possible to recover about 150 mg of the pure complex but no free tetrafluorobenzobicyclo[2.2.2]octatriene could be detected.

(*b*) *With norbornadiene.* After being refluxed at 75° with a large excess of norbornadiene for 20 h, the complex could be isolated unchanged. When the experiment was carried out in a sealed tube at 80° for 3 days, no free tetrafluorobenzobicyclo-[2.2.2]octatriene could be detected whilst the original complex could be recovered from the liquid norbornadiene.

(*c*) *With iodine.* When the iron complex was heated with iodine at 95–100° in a sealed, evacuated tube, carbon monoxide was released but the free ligand was not isolated from among the products since it underwent further reaction by the addition of iodine giving an unidentified solid, m.p. 143°. (Found C, 30.3; H, 1.1; F, 16.0; I, 52.8. "$C_{12}H_6F_4I_2$" calcd.: C, 30.0; H, 1.3; F, 15.8; I, 52.9%.) The same compound was obtained on heating the free triene with iodine at 100°.

Thermal decomposition of tetrafluorobenzobicyclo[2.2.2]*octatrieneiron tricarbonyl*

(*a*) *At* 95–100°. Tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl (184.5 mg) was placed in a sealed, evacuated Pyrex vessel and held at between 95 and 100° in an oven. Over a period of 12 days the only change noted was that the yellow-orange starting material gave way to large, transparent, orange-coloured crystals. The tube was opened to a vacuum apparatus and the carbon monoxide (0.013 mmole, 0.9%) measured with a Töpler pump. Infrared and proton NMR spectral studies showed the orange crystals (which were yellow when crushed) were unchanged starting material (total recovered, 182 mg or 98.7%).

(*b*) *At* 150°. In this experiment 206.0 mg of the iron complex was heated, in a similar vessel to that used above, to 150° for 96 h. A metallic mirror appeared on parts of the vessel and a mixture of yellow and white crystals could be seen inside; 0.22 mmole of carbon monoxide was present in the gas phase (equivalent to about 13% decomposition of the complex). The yellow crystals (143.0 mg) proved to be unchanged starting material and the white crystals (15.0 mg) were 1,2,3,4-tetrafluoronaphthalene.

(*c*) *At* 220°. At this temperature decomposition appeared to be quite rapid and after about 24 h no unchanged complex remained. About 60% of the available carbonyl groups appeared as free carbon monoxide and again 1,2,3,4-tetrafluoronaphthalene was the major decomposition product; only a few per cent of free tetrafluorobenzobicyclo[2.2.2]octatriene could be recovered.

Preparation of tetrafluorobenzobicyclo[2.2.2]*octatrienechromium tetracarbonyl*

Chromium hexacarbonyl (0.48 g) and tetrafluorobenzobicyclo[2.2.2]octatriene (0.5 g) were refluxed in 125 ml of petrol ether (100–120°) for 24 h. The solvent was evaporated off in a vacuum and the yellow residue recrystallised from petrol ether (40–60°) to give 0.25 g (29% yield) of tetrafluorobenzobicyclo[2.2.2]octatrienechromium tetracarbonyl. (Found: C, 49.5; H. 1.7; F, 19.7; mol.wt., 381. $C_{16}H_6F_4CrO_4$ calcd.: C, 49.2; H, 1.55; F, 19.5; mol.wt., 390.) Only a trace of the complex was formed after 5 days when the reaction was attempted in a sealed, evacuated tube at 100° in the absence of solvent.

The reactions of molybdenum and tungsten hexacarbonyls with the olefin in petrol ether were entirely analogous to the chromium case and the products, yellow solids, had virtually identical infrared spectra to tetrafluorobenzobicyclo[2.2.2]octatrienechromium tetracarbonyl. When the latter chromium complex was heated to 190° for 4 days in a sealed tube, complete decomposition to a black solid, carbon monoxide, chromium hexacarbonyl and 1,2,3,4-tetrafluoronaphthalene occurred.

No bis(tetrafluorobenzobicyclo[2.2.2]octatriene)chromium dicarbonyl could be isolated by refluxing an excess of olefin with chromium hexacarbonyl in petrol ether (100–120°) for 20 h.

Infrared spectra

These were recorded on a Grubb-Parsons double beam grating spectrophotometer (in Nujol and hexachlorobutadiene mulls).

$C_{12}H_6F_4$: 3074 w, 3003 w, 1626 w, 1577 w, 1492 s, 1408 m, 1389 s, 1373 m, 1324 s, 1305 m, 1282 s, 1266 m, 1238 w, 1224 m, 1149 w, 1124 m, 1104 m, 1093 msh, 1070 s, 1034 s, 992 w, 944 m, 923 w, 913 msh, 909 m, 888 s, 854 s, 746 ssh, 739 s, 732 msh, 718 wsh, 687 s, 683 msh, 665 w, 635 w, 513 w.

$C_{12}H_6F_4Fe(CO)_3$: 2035 s, 1970 s, 1940 s, 1491 s, 1464 m, 1437 w, 1402 vw, 1373 m, 1370 msh, 1342 wsh, 1317 w, 1302 m, 1247 w, 1182 m, 1123 m, 1093 m, 1068 w, 1038 s, 992 vw, 947 wsh, 943 m, 928 vw, 900 w, 891 m, 845 m, 816 vw, 799 vw, 730 w, 722 wsh, 686 m, 668 vw, 649 m, 620 s, 596 s, 567 msh, 560 s, 501 m.

$C_{12}H_6F_4Cr(CO)_4$: 2014 s, 1959 m, 1940 s, 1912 s, 1496 s, 1475 wsh, 1429 vw, 1381 m, 1366 wsh, 1333 vw, 1323 vw, 1300 w, 1274 vw, 1245 w, 1199 m, 1120 m, 1092 w, 1085 wsh, 1064 vw, 1040 s, 952 w, 939 m, 912 w, 890 m, 855 m, 784 w, 775 w, 769 w, 738 w, 721 w, 682 w, 673 s, 669 ssh, 658 m, 629 s, 620 s, 549 w, 527 wsh, 522 m.

$C_{12}H_6F_4Mo(CO)_4$: 2959 w, 2030 s, 1968 wsh, 1949 s, 1904 s, 1527 wsh, 1492 s, 1471 msh, 1458 wsh, 1429 vw, 1379 m, 1359 wsh, 1321 w, 1297 m, 1258 s, 1247 wsh, 1196 w, 1116 m, 1093 msh, 1086 m, 1081 msh, 1070 m, 1036 s, 1015 m, 995 wsh, 965 vw, 946 w, 930 s, 904 w, 883 m, 851 m, 800 m, 745 w, 737 w, 721 w, 705 vw, 680 wsh, 675 w, 653 w, 618 s, 567 s, 535 w.

$C_{12}H_6F_4W(CO)_4$: 3096 vw, 3072 vwsh, 2959 m, 2924 w, 2853 vw, 2029 s, 1942 s, 1901 s, 1873 msh, 1493 s, 1468 msh, 1431 vw, 1410 vw, 1381 m, 1322 vw, 1299 m, 1259 s, 1192 m, 1119 m, 1086 s, 1070 s, 1036 s, 1018 s, 948 w, 931 m, 905 w, 882 m, 850 m, 800 s, 767 w, 746 w, 737 w, 715 w, 704 w, 678 w, 667 vw, 655 vw, 604 m, 567 m, 536 w.

NMR spectra

These were measured in $CDCl_3$ solution. Chemical shifts for protons are in ppm from Me_4Si, for ^{19}F atoms in ppm (± 0.5) from $CFCl_3$.

Tetrafluorobenzobicyclo[2.2.2]octatriene[4]: vinyl-H at 6.8 ppm (rel. int. 4), tert-H at 5.2 ppm (rel. int. 2), 1- and 4-F at 169.0 ppm, 2- and 3-F at 156.5 ppm.

Tetrafluorobenzobicyclo[2.2.2]octatrieneiron tricarbonyl: vinyl-H at 3.3

ppm (rel. int. 4), tert-H at 5.0 ppm (rel. int. 2), 1- and 4-F at 165.5 ppm, 2- and 3-F at 152.2 ppm.

1-(Pentafluorophenyl)-2,3,4-trifluorobenzobicyclo[2.2.2]octatriene: vinyl-H at 6.85 ppm (rel. int. 4), tert-H at *ca.* 4.6 ppm (rel. int. 1) and *ca.* 5.3 ppm (rel. int. 1).

1,2,3,4-Tetrafluoronaphthalene: 1- and 4-F at 165.5 ppm, 2- and 3-F at 156.5 ppm.

The Cr, Mo, and W triene derivatives were too unstable in solution for their spectra to be obtained.

ACKNOWLEDGEMENTS

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SUMMARY

On treatment with various metal carbonyls tetrafluorobenzobicyclo[2.2.2]-octatriene (which is formed when pentafluorophenyllithium decomposes in the presence of benzene) gives complexes of the type triene $M(CO)_n$ when $M = Fe$, $n = 3$ or $M = Cr$, Mo, W, $n = 4$; the bonding of the triene to the metal is shown to occur via the aliphatic C=C bonds. Thermal decomposition of these complexes gives mainly carbon monoxide and 1,2,3,4-tetrafluoronaphthalene with only a trace of free triene ligand.

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