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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

XXVIII*. SOME REACTIONS OF FLUORO-AROMATIC ACETYLENES

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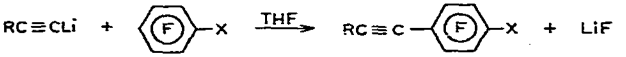
SUMMARY

Reactions between caesium fluoride, bromine, palladium chloride, triiron dodecacarbonyl, dicobalt octacarbonyl, nickelocene, cyclopentadienylmanganese tricarbonyl or decaborane with acetylenes containing one highly fluorinated aromatic group are described. The products mainly resembled those obtained from analogous experiments involving diphenylacetylene, although in the case of the $PdCl_2$ reaction no intermediate derivatives could be isolated.

INTRODUCTION

Previously[2] we have described a simple and convenient method for the preparation of a series of acetylenes containing one highly fluorinated aromatic group



(1)

(I)

$X = F, Cl, C_6F_5, C{\equiv}CR;$
$R = C_6H_5, C_3H_7, C_4H_9$

Several other syntheses are also available [3]. In this paper we discuss a variety of reactions displayed by these compounds, as exemplified in the Scheme 1.

RESULTS AND DISCUSSION

When either pentafluorobenzene or iodopentafluorobenzene is used in the above preparation no isolable products are formed, probably because Li/H and Li/I exchange processes greatly complicate the reaction. (In contrast, a 7% yield of phenyl(pentafluorophenyl)acetylene is obtained when phenylethynylmagnesium bromide is treated with iodopentafluorobenzene.) The chlorine atom in 1-(phenylethy-

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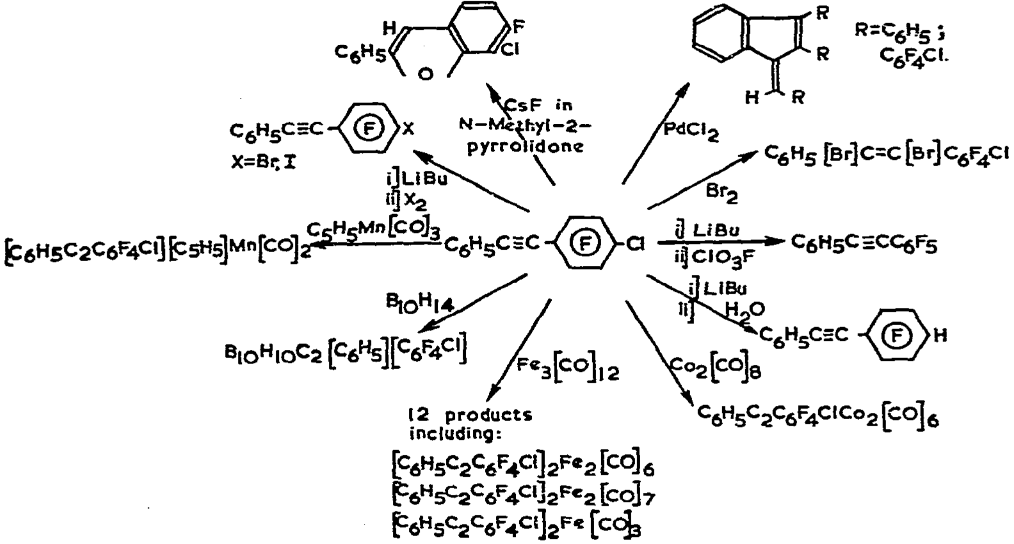
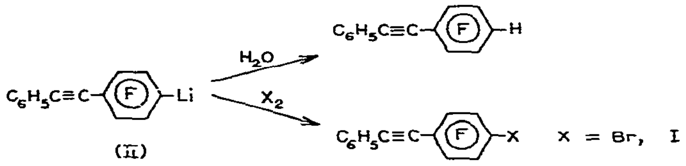
* For Part XXVII see ref. 1.

SCHEME 1

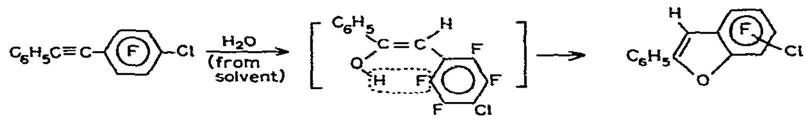


nyl)-4-chlorotetrafluorobenzene (I; $R = C_6H_5$, $X = Cl$) can be lithiated very easily and in high yield by butyllithium at −78° in ether, which makes it a useful source of other acetylenes[4].



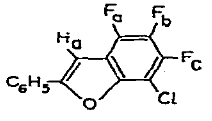
Since 1-(phenylethynyl)-4-chlorotetrafluorobenzene is much more readily accessible via reaction (1) than the synthetically useful phenyl(pentafluorophenyl)acetylene (I; $R = C_6H_5$, $X = F$) we searched for a method of substituting the chlorine atom by fluorine. The best small scale method of achieving this Cl/F exchange (in 70–80% yield of $C_6F_5C{\equiv}CC_6H_5$) is to first prepare the lithium derivative (II) and then to treat this with perchloryl fluoride. A minor product of this reaction was always obtained in too small an amount for analysis. Its mass spectrum showed a cluster of peaks at *m/e* 322–325, the relative intensities of the component peaks agreeing with the values calculated for the isotopes in $C_{14}Cl$; other ions were observed for the loss of O_3 and Cl. These facts suggest that the compound was probably 1-(phenylethynyl)-4-perchloryltetrafluorobenzene and in agreement with this the infrared spectrum, in addition to the usual adsorptions of 1-(phenylethynyl)-4-chlorotetrafluorobenzene, showed a strong, poorly-resolved doublet at 1260 cm^{-1} attributable to the ClO_3 group[5].

The direct exchange of the chlorine atom in 1-(phenylethynyl)-4-chlorotetrafluorobenzene with potassium fluoride did not appear to occur in the absence of solvents up to 420°, at which temperature the acetylene decomposed rapidly. In sulpholane at 210° a 5% yield of phenyl(pentafluorophenyl)acetylene was obtained after six hours but the reaction was accompanied by extensive charring. Caesium fluoride in *N*-methyl-2-pyrrolidone at 150° reacted with 1-(phenylethynyl)-4-chlorotetrafluorobenzene to give a white solid, (III), m.p. 115–117°, in about 90% yield; the reaction vessel showed considerable signs of etching presumably due to hydrogen fluoride formed during the reaction. The mass spectrum of (III) showed a parent ion cluster at *m/e* 282–285, attributable to ^{12}C, ^{13}C, ^{35}Cl and ^{37}Cl isotopes; an accurate mass determination on the peak at *m/e* 282 gave a value 282.0063 ± 0.0005. A computer search based on the elements C, H, F, Cl, O and N established that the only formulation which gives a mass within the above limits of error is $^{12}C_{14}H_6F_3O$-^{35}Cl (mass 282.0059). Metastable peaks visible in the mass spectrum corresponded to the loss of Cl, CO (or CHO) and COCl from the parent ion. The infrared spectrum of (III) had, in particular, peaks at 987 cm^{-1} (C–F), 879 cm^{-1} (C–Cl), 760 and 685 cm^{-1} (C_6H_5) and 1640 cm^{-1} (C=C); there were no peaks attributable to –C=O, –OH or –C≡C– absorptions. The proton NMR spectrum of (III) dissolved in carbon tetrachloride showed three groups of resonance absorptions corresponding to 1, 3 and 2 protons at 7.13 (doublet, coupling constant 2.7 Hz), 7.4 (complex) and 7.8 (complex) ppm respectively, from tetramethylsilane as internal standard. There was little difference between the UV spectra of (III) and 1-(phenylethynyl)-4-chlorotetrafluorobenzene. These facts are consistent with the following reaction sequence, although we were unable to isolate any product resembling (IV). Somewhat similar ring closures involving fluoro-aromatic groups are known[6,7].



(IV) (III)

Although the production of (III) by the above ring closure is interesting in itself, a further unexpected facet to the reaction is that the chlorine atom apparently undergoes a migration in the presence of a reasonably high concentration of fluoride ions! Evidence of this migration comes from the ^{19}F NMR spectrum of (III) dissolved in fluorotrichloromethane; three groups of lines were observed which integrated in the ratio 1/1/1. The lines in group 1, which appeared at 142.0 ppm upfield from $CFCl_3$, had the appearance of a doublet of doublets split further by a coupling of 2.7 Hz (presumably an H–F coupling, compare to the proton spectrum above); the F–F coupling constants were 17.3 and 3.8 Hz. Group 2 consisted of a doublet of doublets at a chemical shift of 145.1 ppm and with coupling constants 19.5 and 3.8 Hz. The third group was also a doublet of doublets with coupling constants 19.6 and 17.3 Hz, and occurred at 147.9 ppm. Normally coupling constants in fluoro-aromatic compounds are of the order J_{ortho} 20 Hz, J_{meta} 8 Hz and J_{para} 2.5 Hz[8]; this suggests that two "*ortho*" couplings occur in this molecule and, in particular, the fluorine atom responsible for the peaks around 147.9 ppm has two fluorine atoms *ortho* to it (F_b in the formula below). The H–F coupling presumably occurs between H_a and F_a which enables



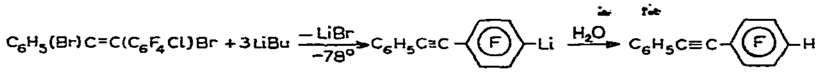
(III)

the group of lines at 142.0 ppm to be assigned to F_a and those at 145.1 ppm to F_c. Chambers[9] has reported a similar migration of C_3F_7 groups round a pyridine ring in the presence of potassium fluoride.

When 1-(phenylethynyl)-4-iodotetrafluorobenzene was heated to 150° in dimethylsulphoxide with potassium fluoride, a 70% yield of 1-(phenylethynyl)-2,3,5,6-tetrafluorobenzene (I; X=H) was obtained; part of the solvent was converted to dimethyl sulphide during the process.

Diphenylacetylene is known to react with lithium in ether solution to give 1,4-dilithio-1,2,3,4-tetraphenylbutadiene[10]. No reaction between lithium and several of these fluoro-aromatic acetylenes could be induced. Similarly, sulphur did not react with 1-(phenylethynyl)-4-chlorotetrafluorobenzene on heating although bis(pentafluorophenyl)acetylene reacts with sulphur at 190° to give tetrakis(pentafluorophenyl)thiophene[11]. A low yield of the carborane $B_{10}H_{10}C_2(C_6H_5)(C_6F_4Cl)$, m.p. 97–101°, was obtained when 1-(phenylethynyl)-4-chlorotetrafluorobenzene was treated with decaborane-14; the yields in such carborane syntheses are very sensitive to the acetylene used and are as low as 2% for phenylacetylene.

One mole of bromine adds to 1-(phenylethynyl)-4-chlorotetrafluorobenzene when the two are heated to 110° in a sealed tube. Attempts to lithiate this dibromo derivative using a slight excess of butyllithium at −78° gave 1-(phenylethynyl)-2,3,5,-6-tetrafluorobenzene (I; X=H) in almost quantitative yield on hydrolysis:

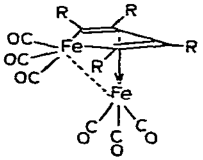


In investigations of these acetylenes with transition metal complexes, 1-(phenylethynyl)-4-chlorotetrafluorobenzene was most often used because of its more ready synthesis and the fact that the ^{35}Cl and ^{37}Cl isotopes proved useful when investigating products by mass spectral analysis. 1-(Phenylethynyl)-4-chlorotetrafluorobenzene reacts with π-cyclopentadienylmanganese tricarbonyl when the two are irradiated with UV light in hexane solution to give the air-sensitive compound $(C_6H_5C_2C_6F_4Cl)(C_5H_5)Mn(CO)_2$. The infrared spectrum of this compound has carbonyl absorptions which are shifted by 15 cm^{-1} to lower frequency than in $(\pi\text{-}C_5H_5)Mn(CO)_3$, and a C≡C absorption some 20 cm^{-1} lower than in 1-(phenylethynyl)-4-chlorotetrafluorobenzene. Hence this spectrum, and the stoichiometry of the product, suggest a simple replacement of one CO group by a molecule of acetylene. Rather few such complexes are known for other acetylenes except hexafluoro-2-butyne[12] and diphenylacetylene[13].

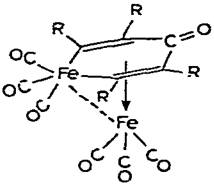
A dark green, slightly air-sensitive, complex analysing as $C_6H_5C_2C_6F_4Cl(NiC_5H_5)_2$ is formed when nickelocene and 1-(phenylethynyl)-4-chlorotetrafluorobenzene are heated for 30 hours in a sealed tube; the compound decomposes rapidly on chromatographic plates and was therefore purified by fractional sublimation. The acetylene probably bridges the two nickel atoms as suggested for other acetylene–nickelocene complexes having this stoichiometry[14].

The acetylenes (I; $R=C_6H_5$; $X=Cl$, C_6F_5, $C{\equiv}CC_6H_5$) all react with dicobalt octacarbonyl simply on stirring for some hours at room temperature in a hydrocarbon solvent; the products are red oils or solids which have the stoichiometry, $Co_2(CO)_6A$, generally expected of acetylene–cobalt carbonyl derivatives; the acetylene molecule bridges two $Co(CO)_3$ groups[15].

A complex mixture of at least twelve products is obtained when 1-(phenylethynyl)-4-chlorotetrafluorobenzene is refluxed in benzene with triiron dodecacarbonyl. The main product, formed in about 70% of the total isolable products, is the complex $(C_6H_5C_2C_6F_4Cl)_2Fe_2(CO)_6$ which is an orange solid melting at 136°. Its infrared spectrum in the carbonyl region is very similar to the diphenylacetylene[16] and bis(pentafluorophenyl)acetylene[11] analogues which have the structure:

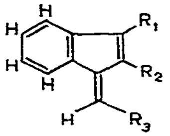


The complex obtained in this experiment can exist as four structural isomers; it was not soluble enough in any solvents for a high resolution ^{19}F NMR spectrum to be recorded, although from the weak, low resolution spectrum it appeared that more than one type of fluoro-aromatic group was present in solution. Only two other products could be isolated by TLC in sufficient quantities for identification by mass spectrometry. The fifth band to elute gave an orange solid which showed, in its infrared spectrum, three terminal CO stretching frequencies around 2000 cm^{-1} and an absorption at 1683 cm^{-1} due to a $-C{=}O$ group. The mass spectrum had a parent ion cluster centred at *m/e* 876 and peaks due to the "step-wise" loss of seven CO groups could be observed. There seems little doubt that this is the analogue of $(Ph_2C_2)_2Fe_2(CO)_7$ reported by Hubel and Braye[16]:



The last band to elute which contained sufficient material to allow isolation of the component gave a dark red-orange solid which, from its mass spectrum, was identified as $(C_6H_5C_2C_6F_4Cl)_2Fe(CO)_3$. Similar results were obtained when the acetylenes (I; $R{=}C_6H_5$; $X{=}C_6F_5$) and (I; $R{=}C_6H_5$; $X{=}F$) were treated with triiron dodecacarbonyl.

Phenyl(pentafluorophenyl)acetylene produces a yellow solution when stirred for a few days at room temperature with an ethanolic solution of palladium dichloride. Thin-layer chromatography produced four yellow bands, but only two of these contained sufficient material to warrant collection. The band nearest the solvent front was present in the largest amount and on collection proved to contain a mixture of two compounds which could only be separated by crystal picking: pale yellow needles, m.p. 140–141°, and orange plates, m.p. 169–170°. The component next nearest the solvent front was a yellow solid, m.p. 123.5–126.5°. Analyses and mass spectra showed all three compounds to be dimers of the original acetylene; their colours and UV spectra are very similar to the phenyl-substituted benzofulvenes made by pyrolysis of palladium dichloride complexes derived from diphenylacetylene[17]. Their infrared spectra also showed absorptions at about 1600 cm^{-1} and 1360 cm^{-1} attributable to the exocyclic double bond and which are characteristic of fulvenes. Obviously the donor ability of phenyl(pentafluorophenyl)acetylene is too low to allow the formation of a stable palladium complex but the products suggest, in relation to the work of Maitlis[17], that such a complex formed initially and then decomposed to give a variety of isomeric benzofulvenes.



$R_1, R_2, R_3 = I\ C_6F_5, C_6H_5, C_6F_5I$

The same mixture of products was obtained when $(CH_3CN)_2PdCl_2$ was used in lieu of palladium dichloride.

EXPERIMENTAL

Reaction of 1-*(phenylethynyl)*-4-*lithiotetrafluorobenzene and perchloryl fluoride*

1-(Phenylethynyl)-4-lithiotetrafluorobenzene was prepared under an atmosphere of dry nitrogen in ether solution at −78° by adding n-butyllithium (1.4 ml of hexane solution, 0.0018 mole) to 1-(phenylethynyl)-4-chlorotetrafluorobenzene (0.6 g, 0.0018 mole). After stirring for 30 min, the reaction flask was cooled in liquid nitrogen to −196°, connected to a vacuum line and an excess of perchloryl fluoride was allowed to distil in. A nitrogen atmosphere was re-introduced into the flask and the temperature allowed to rise to ambient overnight. The reaction mixture then consisted of a yellow solution and white precipitate; the latter was filtered off and gave positive tests for both Li^+ and ClO_3^-. The ether was removed from the filtrate under reduced pressure to leave a yellow solid which on sublimation at 100°/10^{-3} mmHg yielded a white solid. TLC separated this into two components; that which was nearest the solvent front was phenyl(pentafluorophenyl)acetylene. (Found: C, 62.9; H, 2.2. $C_{14}H_5F_5$ calcd.: C, 62.7; H, 1.9%.) The other component appeared, from its mass spectrum, to be 1-(phenylethynyl)-4-perchloryltetrafluorobenzene. On this scale of reaction the phenyl(pentafluorophenyl)acetylene is obtained in yields of 70–80%.

Reaction of 1-*(phenylethynyl)*-4-*chlorotetrafluorobenzene with caesium fluoride in N-methyl*-2-*pyrrolidone*

Caesium fluoride (0.5 g) and 1-(phenylethynyl)-4-chlorotetrafluorobenzene (0.5 g) were held at 150° for 12 h in 30 ml of *N*-methyl-2-pyrrolidone (unpurified commercial sample). The reaction mixture turned orange almost immediately at room temperature but after reaction was a dark brown colour (the orange colour appeared to be due to the interaction of caesium fluoride with the solvent). The reaction mixture was poured into cold water (100 ml) and left for two days to allow the precipitate to coagulate; the precipitate was then collected, dried and sublimed at 80°/10^{-3} mmHg to give a white solid, (III). An analytical sample, m.p. 115–117°, was obtained by crystallization from petrol. (Found: C,59.9, 60.4; H, 2.4, 2.1; F, 19.4. $C_{14}H_6ClF_3O$ calcd.: C, 59.3; H, 2.1; F, 20.1%.) The corresponding tetrafluoro derivative[7] has a melting point of 114.5–115.5°.

1-(Phenylethynyl)-4-chlorotetrafluorobenzene was recovered in over 90% yield after being heated alone in *N*-methyl-2-pyrrolidone for 5 h (the same work-up procedure as described above was followed for this recovery).

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and decaborane*-14

Decaborane-14 (0.22 g, 0.002 mole) was refluxed for 1 h in 20 ml of acetonitrile; 1-(phenylethynyl)-4-chlorotetrafluorobenzene (0.5 g, 0.0018 mole) was then added and the mixture further refluxed for 3 h. After the acetonitrile had been distilled off under vacuum the residue was subjected to fractional sublimation, the white product subliming at 120°/10^{-3} mmHg being collected (25 mg). The sample, m.p. 97–101°, was identified via its mass spectrum. The relative intensities of the peaks in the ion cluster formed by the parent ion were in close agreement with those computed for the ion $B_{10}C_{14}H_{15}F_4Cl^+$: *m/e* 398 calcd. intensity 1.6 (observed 0.4%); 399, 2.9 (1.7); 400, 7.6 (5.9); 401, 15.2 (14.2); 402, 22.9 (23.4); 403, 23.1 (25.2); 404, 15.9 (17.1); 405, 7.2 (8.1); 406, 3.1 (3.4); 407, 0.6 (0.4).

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and bromine*

Bromine (0.3 g, 0.0019 mole) and 1-(phenylethynyl)-4-chlorotetrafluorobenzene (0.5 g, 0.0018 mole) were heated at 110° for 6 h in a sealed, evacuated tube. After opening the tube, the contents were extracted with ether and the excess of bromine destroyed by aqueous sodium thiosulphate; the ether layer was separated, dried with magnesium sulphate and the ether removed under vacuum to leave a brown, gummy solid. Sublimation of this solid at 80°/10^{-3} mmHg yielded the pale yellow solid 1-phenyl-1,2-dibromo-2-(chlorotetrafluorophenyl)ethylene (0.6 g, m.p. 65–66°). (Found: C, 37.9; H, 1.1; Br, 35.9; Cl, 7.9; F, 17.3. $C_{14}H_5Br_2ClF_4$ calcd.: C, 37.8; H, 1.1; Br, 35.9; Cl, 8.0; F, 17.1%.) The conformation of the molecule was not determined.

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and π-cyclopentadienylmanganese tricarbonyl*

1-(Phenylethynyl)-4-chlorotetrafluorobenzene (0.42 g, 0.00147 mole) and π-cyclopentadienylmanganese tricarbonyl (0.3 g, 0.0015 mole) were dissolved in hexane and irradiated with ultraviolet light until 43 ml of carbon monoxide has been evolved. The solution was filtered under nitrogen and the hexane distilled off under reduced pressure to leave a brown solid; this was held at 100°/10^{-3} mmHg and the unreacted starting materials which sublimed away were collected on a cold finger at −78°. The deep red solid which remained in the flask was extracted with hexane, filtered under nitrogen and the solution evaporated down to give 0.6 g of π-cyclopentadienyl[1-(phenylethynyl)-4-chlorotetrafluorobenzene]manganese dicarbonyl. (Found: C, 54.9; H, 2.8. $C_{21}H_{10}ClF_4MnO_2$ calcd.: C, 54.7; H, 2.2%.) The compound is air-sensitive and decomposes rapidly in contact with oxygen to give a brown solid.

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and nickelocene*

Nickelocene (0.165 g, 0.008 mole, purified by sublimation) and 1-(phenylethynyl)-4-chlorotetrafluorobenzene (0.5 g, 0.018 mole) were heated at 100° for 30 h in a sealed, evacuated tube. After opening the tube and extracting the dark-green residue with hexane, the mixture was filtered and the hexane removed under vacuum. Fractional sublimation yielded at 70°/10^{-3} mmHg, a dark-green solid which was twice resublimed, m.p. 163–168° (decomp). Analyses for C and H gave inconsistent results but the nickel content and the mass spectrum were satisfactory. (Found: Ni, 21.8; 21.8, 21.8. $C_{24}H_{15}ClF_4Ni_2$ calcd.: 22.1%.) In the mass spectrum the parent ion cluster of peaks, centred at *m/e* 532, had an intensity of about 13% relative to the base peak which was due to $C_6H_5C_2C_6F_4Cl^+$; the peak due to $(P-Ni_2)$ had a relative intensity of about 8%. The peaks making up the parent ion cluster had intensities (relative to each other) which were close to the theoretical values computed from the known abundances of the isotopes of C, Ni and Cl: *m/e* 530 calcd. 26.3 (observed 25.8%); 531, 7.4 (6.9); 532, 29.9 (29.7); 533, 9.1 (8.7); 534, 14.7 (14.2); 535, 4.5 (6.1); 536, 4.8 (6.4); 537, 1.4 (2.0); 538, 1.2 (1.1).

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and dicobalt octacarbonyl*

Dicobalt octacarbonyl (1.2 g, 0.035 mole) and 1-(phenylethynyl)-4-chlorotetrafluorobenzene (1.0 g, 0.035 mole) were refluxed in 60 ml of benzene for 3 h. After removing the benzene under reduced pressure 40–60, petroleum ether (40 ml) was added to extract the products; the solution was then filtered and the mixture separated by large scale TLC using 60–80 petroleum ether as eluant. Four components were observed of which the two nearest the solvent front were the starting materials; the slowest-moving band was in too small an amount to isolate and identify, but the intermediate component was collected, 0.9 g, and found to be a dark red oil. (Found: C, 42.1; H, 1.1; F, 13.1. $C_{20}H_5ClCo_2F_4O_6$: C, 42.1; H, 0.9; F, 13.3%.)

A similar product (dark red solid, m.p. 125° with some decomposition) was obtained using 4-(phenylethynyl)nonafluorobiphenyl. (Found: C, 44.4; H, 1.2; F, 24.4. $C_{26}H_5Co_2F_9O_6$ calcd.: C, 44.5; H, 0.7; F, 24.4%.) The diacetylene 1,4-bis(phenylethynyl)tetrafluorobenzene gave a complex, as a dark red oil, in which one triple bond was interacting with a $Co_2(CO)_6$ unit. (Found: 52.5; H, 2.4; F, 11.7. $C_{28}H_{10}Co_2F_4O_6$ calcd.: C, 52.8; H, 1.6; F, 11.9%.) Two other unidentified complexes were also formed in low yield.

Reaction of 1-(*phenylethynyl*)-4-*chlorotetrafluorobenzene and triiron dodecacarbonyl*

This reaction seemed to proceed in the same manner if carried out in refluxing benzene, in refluxing 80–100 petroleum ether or in sealed evacuated tubes in the absence of solvents. The latter procedure is the most simple, the two reactants being held at 105° for 18 h in a vessel of about 500 ml capacity. TLC analysis of the products showed that at least twelve components were present, not including possible isomers. The compound $(PhC{\equiv}CC_6F_4Cl)_2Fe_2(CO)_6$, m.p. 156°, was the main product and accounted for some 70% of the isolated material. For some reason the analysis of the iron carbonyl derivatives proved troublesome and the various components were best identified by their mass spectra; the computed and observed peak intensities in the various ion clusters allow very positive identification of the species giving rise to the ion clusters. Furthermore the carbon monoxide molecules were lost from the complexes in a "step-wise" manner so that the number of carbonyl groups initially present could be readily counted. The above complex had the following carbonyl frequencies in the infrared spectrum (hexane solution): 2089, 2068, 2024, 2020, 1960 cm^{-1}.

Reaction of phenyl(*pentafluorophenyl*)*acetylene and palladium chloride*

The two reactants were stirred for five days at room temperature in absolute ethanol. Over this period the solution slowly acquired an orange colour and deposited a reddish-grey solid. The mixture was filtered and the solvent removed under reduced pressure to leave a brown residue; this was taken up in a 5% acetone/95% petroleum ether (60–80°) mixture and separated into four yellow components by TLC. Only the first two bands to elute contained sufficient material for analysis; furthermore, the first band proved to be a mixture of two compounds 1A, orange plates m.p. 169–170°, and 1B, fine yellow needles m.p. 140–141°, which could only be separated by crystal-picking "techniques". Compound 2 was yellow, crystalline, and melted at 123.5–126.5°. All three compounds analysed as dimers of the starting acetylene: Compound 1A: (Found: C, 62.7; H, 2.0%; *m/e*, 536.) Compound 1B: (Found: C, 62.5; H, 2.0%; *m/e*, 536.) Compound 2: (Found: C, 62.9; H, 1.8%; *m/e*, 536. $C_{28}H_{10}F_{10}$ calcd.: C, 62.7; H, 1.9%; mol. wt., 536.) Major peaks in the mass spectra were due to P^+, $(P-F)^+$, $(P-C_6F_5)^+$, P^{++}, $(P-2C_6F_5)^+$, $C_8H_9^+$ and $C_6H_5^+$, where P is the parent ion. UV spectra: Compound 1A, 318 nm (ε, 4.1 × 10³); 253 (8.2 × 10³) and 217 (1.3 × 10³); compound 1B, 321 (3.0 × 10³) and 261 (6.4 × 10³); compound 2, 325 (4.9 × 10³) and 260 (7.9 × 10³).

4-(Phenylethynyl)nonafluorobiphenyl reacted with palladium chloride in a similar fashion; the first, second and third yellow bands to elute after the solvent front were collected: Compound 1 (11.3% yield), m.p. 170–173°. (Found: C, 58.2; H, 1.2; F, 40.8%; *m/e*, 832.) Compound 2 (very low yield): not analysed; m.p. 169–180°. Compound 3 (4.3% yield), m.p. 247–250°. (Found: C, 58.2; H, 1.2; F, 41.1%; *m/e*, 832. $C_{40}H_{10}F_{18}$ calcd.: C, 57.7; H, 1.2; F, 41.1%; mol. wt., 832.)

When the products of the reaction between palladium chloride and 1-(phenylethynyl)-4-chlorotetrafluorobenzene were subjected to TLC the first band to elute again contained two compounds one of which consisted of yellow needles, the other of orange plates; in this case no attempt was made to separate the two for analysis by crystal picking. Only bands 1 and 2 were collected of the six yellow ones which were visible. Compound 1. (Found: C, 58.8; H, 1.8%.) Compound 2, m.p. 175–176°. (Found: C, 58.7; H, 1.8; $C_{14}H_5ClF_4$ calcd.: C, 59.0; H, 1.8%.) UV spectra: Compound 1A, 325 nm (4.0 × 10³); 260 (7.9 × 10³) and 218 (1.0 × 10³); compound 1B, 328 (3.2 × 10³) and 262 (7.1 × 10³); compound 2, 331 (3.5 × 10³) and 250 (8.9 × 10³).

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