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PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS—VI

FURTHER STUDIES OF THE 2-SUBSTITUTED NONAFLUOROBIPHENYLS

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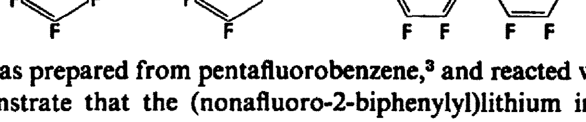
Abstract—The decomposition of pentafluorophenyllithium in the presence of C_6F_5X has been studied further and a mechanism proposed for the formation of 2-$XC_6F_4C_6F_5$ which involves the addition of pentafluorophenyllithium to tetrafluorobenzyne giving 2-$LiC_6F_4C_6F_5$, followed by Li/X exchange with C_6F_5X. The 2-bromononafluorobiphenyl has been used to prepare the organometallic compounds 2-$C_6F_4C_6F_5Mn(CO)_5$ and $(2\text{-}C_6F_4C_6F_5)_2Sn(CH_3)_2$. The F^{19} NMR spectra of 2-$BrC_6F_4C_6F_5$, 2-$IC_6F_4C_6F_5$ and 2-$HC_6F_4C_6F_5$ are described and chemical shifts and coupling constants given. Mass spectral data on four polyfluorobiphenyls are also presented.

THE reaction of pentafluorophenyllithium with a molar excess of bromo- or iodopentafluorobenzene has been shown previously to give 2-substituted nonafluorobiphenyls.[2] The position of substitution was deduced from H^1 and F^{19} NMR spectra and apparently supported by the reaction of 1,2-dibromotetrafluorobenzene and pentafluorophenyllithium. Following the work of Tamborski *et al.*,[3] we have now prepared 2-hydrononafluorobiphenyl from pentafluorobenzene. A mechanism, involving tetrafluorobenzyne as an intermediate, was proposed for the reaction, but it does not account for the 2-bromononafluorobiphenyl formed by reacting pentafluorophenyllithium with 1,2-dibromotetrafluorobenzene as direct coupling could also occur.

In an effort to understand the correct mechanism, an ether–hexane solution of pentafluorophenyllithium was allowed to warm to room temperature from −78°, and after standing for 30 minutes, was hydrolysed with distilled water. 2-Hydrononafluorobiphenyl was isolated in fair yield which strongly suggests that at a convenient temperature pentafluorophenyllithium is converted partially to tetrafluorobenzyne which interacts with unconverted pentafluorophenyllithium to give (nonafluoro-2-biphenylyl)lithium,[4,5] which acts as an intermediate in our reaction. Also pentafluorophenyllithium was prepared from pentafluorobenzene,[3] and reacted with C_6F_5X (X = Br, I) to demonstrate that the (nonafluoro-2-biphenylyl)lithium intermediate then



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[1] Part V: D. E. Fenton and A. G. Massey, *Chem & Ind.* 2100 (1964).
[2] D. E. Fenton, A. J. Park, D. Shaw and A. G. Massey, *J. Organometal. Chem.* **2**, 437 (1964).
[3] R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.* **29**, 2385 (1964).
[4] P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.* 3227 (1962).
[5] H. Gilman and R. D. Gorsich, *J. Amer. Chem. Soc.* **78**, 2217 (1956).

reacts with the pentafluoroaromatic derivative and not with any butyl halide also present; for example, in the case of iodopentafluorobenzene, 2-iodononafluorobiphenyl was isolated in a 67% yield.

$$\mathrm{LiBu} + \mathrm{C_6F_5H} \rightarrow \mathrm{LiC_6F_5} + \mathrm{BuH}$$

$$\mathrm{LiC_6F_5} + \mathrm{C_6F_5I} \rightarrow \text{2-}\mathrm{IC_6F_4C_6F_5}$$

Furthermore, metal–halogen exchange has been shown to occur when bromopentafluorobenzene was added to a solution of (nonafluoro-2-biphenylyl)lithium and, since hexafluorobenzene and methoxypentafluorobenzene do not give 2-substituted nonafluorobiphenyls under the same conditions, a criterion for nonafluorobiphenyl formation appears to be that the reactive group on the perfluoroaromatic ring must be capable of exchange with the lithium atom in (nonafluoro-2-biphenylyl)lithium.

Therefore the route by which we believe 2-substituted nonafluorobiphenyls to be formed is

$$\mathrm{LiC_6F_5} \rightarrow \text{2-}\mathrm{LiC_6F_4C_6F_5} \xrightarrow{\mathrm{C_6F_5X}} \text{2-}\mathrm{XC_6F_4C_6F_5} + \mathrm{LiC_6F_5}$$

and in the case of 1,2-dibromotetrafluorobenzene, perfluorobiphenyls of higher bromine content would also be expected.[6] High molecular weight fractions containing about 31% bromine have been isolated, but individual isomers have not yet been separated.

The reactivity of the bromine atom in 2-bromononafluorobiphenyl has been further exploited in the preparation of (nonafluoro-2-biphenylyl)manganese pentacarbonyl, a colourless crystalline solid, decomposing at 129–130°. This was prepared by treating 2-bromononafluorobiphenyl with sodium pentacarbonylmanganate(−1) in tetrahydrofuran at room temperature:

$$\mathrm{Mn_2(CO)_{10}} + \mathrm{Na/Hg} \rightarrow \mathrm{NaMn(CO)_5}$$

$$\mathrm{NaMn(CO)_5} + \text{2-}\mathrm{BrC_6F_4C_6F_5} \rightarrow \text{2-}\mathrm{C_6F_5C_6F_4Mn(CO)_5} + \mathrm{NaBr}$$

the product being identical to that which is obtained by using the possibly more standard reaction:

$$\mathrm{BrMn(CO)_5} + \text{2-}\mathrm{C_6H_5C_6F_4Li} \rightarrow \mathrm{LiBr} + \text{2-}\mathrm{C_6F_5C_6F_4Mn(CO)_5}$$

Treatment of sodium pentacarbonylmanganate(−1) with decafluorobiphenyl gave no fluoro-organometallic derivatives.

The high resolution IR spectrum of $\mathrm{C_6F_5C_6F_4Mn(CO)_5}$ in cyclohexane solution provides interesting evidence for 2-substitution. The spectra of $\mathrm{LMn(CO)_5}$ derivatives show three carbonyl (C≡O) fundamental bands. If the ligand, L, is not axially symmetric then the $2A_1$ and E modes are modified, the E vibration being split into a doublet and a low intensity B_1 transition being observed to give a five-line spectrum.[7] This occurs in (nonafluoro-2-biphenylyl)manganese pentacarbonyl (Fig. 1), where the E band splitting, Δ, is 9 cms.$^{-1}$. A splitting of this magnitude would not be expected for the 3-isomer whilst the 4-isomer is axially symmetric and thus Δ would be zero.

Bis(nonafluoro-2-biphenylyl)tindimethyl has been prepared by the reaction:

$$\text{2-}\mathrm{LiC_6F_4C_6F_5} + \mathrm{Cl_2Me_2Sn} \rightarrow (\text{2-}\mathrm{C_6F_4C_6F_5})_2\mathrm{SnMe_2}$$

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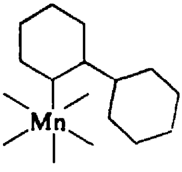
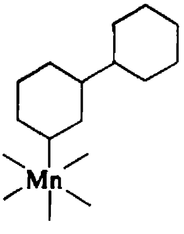
[6] P. L. Coe, private communication.

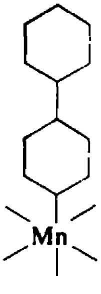
[7] J. B. Wilford and F. G. A. Stone, *J. Organometal. Chem.* **2**, 371 (1964).



2-isomer



3-isomer



4-isomer

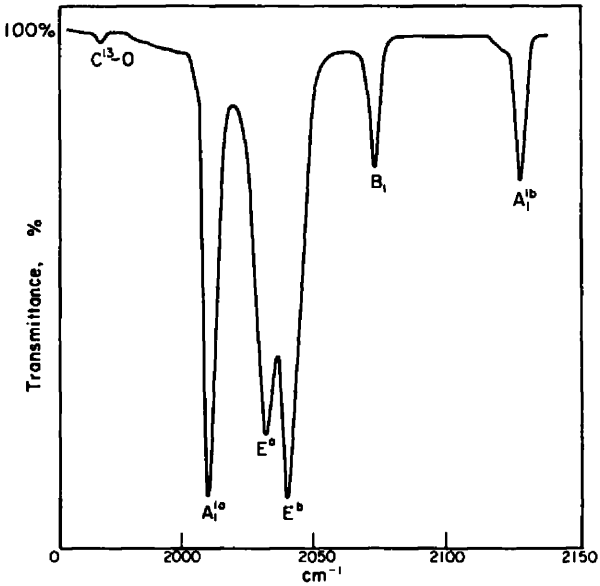


FIG. 1. *The Infrared Spectrum* (C≡O) *region of* (*Nonafluoro-2-biphenylyl*)*manganese Pentacarbonyl*

Spectrum taken of a cyclohexane solution. A_1^{1b} 2127 m, B_1 2072 m; E_b 2040 s; E_a 2031 A_1^{1a} 2010 s; ^{13}CO 1967, cm^{-1}.

It is a white, air-stable solid, m.p. 100–102°. The proton NMR spectrum of this compound was expected to show a long range coupling to the single fluorine in the 3-position.[8] However, only a single, relatively broad line downfield of tetramethylsilane was observed in the spectrum of the sample dissolved in carbon tetrachloride ($\delta_{TMS} = 0{\cdot}30 \pm 0{\cdot}02$ ppm; peak width at half height = 2 c/s).

We have grown single crystals of 2-bromononafluorobiphenyl and an X-ray structural analysis is being carried out on them.[9] Models have shown that there is considerable hindrance to rotation in nonafluorobiphenyls due to steric interaction in the 2,6 and 2′,6′ positions. Since biphenyl ($C_6H_5C_6H_5$) is known to be planar in the solid

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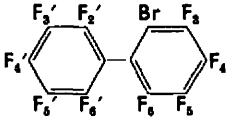
[8] A. G. Massey, E. W. Randall and D. Shaw, *Chem. & Ind.* 1244 (1963).

[9] J. W. Jeffery and R. W. Baker, private communication. The space groups and cell dimensions are also being calculated for $C_6F_5C_6F_5$, $C_6F_5C_6F_4H$ and $(C_6F_5C_6F_4)_2Hg$.

state,[10] these structural analyses are of great theoretical interest. The F^{19} NMR spectrum of decafluorobiphenyl in solution has shown that the rings take up an equilibrium position of 50° to each other,[11] and H^1 NMR of 2-hydrononafluorobiphenyl shows that the rings are not coplanar, as do the F^{19} spectra of 2-bromo, 2-iodo- and, 2-hydrononafluorobiphenyl, where 7 lines are observed in the spectrum, 9 being expected if the rings were planar.

It has been established by other workers that the coupling constants in the F^{19} NMR spectra of polyfluorobenzenes are in the order $J_o^{FF} > J_p^{FF} > J_m^{FF}$. Furthermore, it is known that the resonance due to the fluorine atoms *ortho* to the group X in C_6F_5X occurs at a lower field than that due to the *meta* or *para* fluorine atoms. Using this knowledge it has proved possible to assign completely all the peaks in the F^{19} NMR spectra of the 2-substituted nonafluorobiphenyls and in most cases to obtain the respective F—F and F—H coupling constants by treating these molecules as A_aX_x systems. The F^{19} NMR spectra can in no way be understood in terms of the 3- or 4-isomers.

The NMR spectrum of 2-bromononafluorobiphenyl, shown under low resolution in Fig. 2, consists of seven groups of lines due to the presence of seven types of fluorine atom in magnetically different environments.



Integration showed that the relative intensities of peak groups C and G were twice those of the remainder; clearly these two represent the resonances due to the 2′,6′ and 3′,5′ fluorine nuclei.

Group A. An eight-line multiplet. As this was the group of lines to lowest field it was assigned to F_3 since this fluorine atom is in the *ortho* position to the bromine.

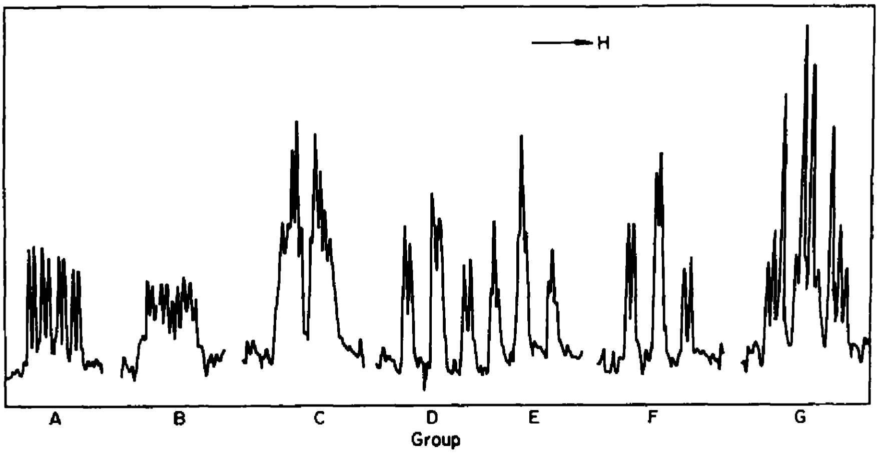


FIG. 2. Low Resolution ^{19}F NMR Spectrum of 2-bromononafluorobiphenyl.

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[10] J. E. Trotter, *Acta. Cryst.* 14, 1135 (1961).

[11] N. Boden J. W. Emsley, J. Feeney and L. H. Sutcliffe, *Mol. Physics* 8, 467 (1964).

Using the fact that $J_o^{FF} > J_p^{FF} > F_m^{FF}$ the following values of the coupling constants were deduced: $J_{3-4} = 21{\cdot}5$; $J_{3-5} = 3{\cdot}9$ and $J_{3-6} = 9{\cdot}8$ c/s.

Group B. Complex multiplet. This resonance was assumed to be due to F_6 since this fluorine atom is *ortho* to the C_6F_5 ring. The confidence with which we can assign peak-groups A and B depends on the fact that the spectrum as a whole can be understood having first made the postulate that the two groups to low field are due to fluorines which are *ortho* to the bromine and *ortho* to the C_6F_5 group; the coupling constants from peak A verify our choice as to which group is A or B. The latter group is broad and too complex to allow the calculation of the respective coupling constants; this complexity is probably due to further coupling of F_6 to $F_{2'}$ and $F_{6'}$.

Group C. This is one half of an AA'XX' system split further by F_4', and, from the arguments used above, arises from the fluorine atoms in the *ortho* position in the C_6F_5 ring; namely $F_{2'}$ and $F_{6'}$.

Group D. A triplet pattern. This is assigned to F_4 and the coupling constants evaluated as $J_{4-3} = 21{\cdot}5$; $J_{4-5} = 19{\cdot}6$; and $J_{4-6} = 4{\cdot}7$ c/s. The similarity of J_{4-3} and J_{4-5} of course account for the triplet appearance of this peak.

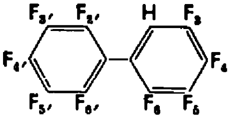
Group E. A triplet of triplets. From its shape this group of peaks can be assigned to fluorine nucleus $F_{4'}$, the *para* atom in the C_6F_5 ring. The coupling constants are $J_{4'-3'} = 20{\cdot}4$; and $J_{4'-2'} = 2{\cdot}5$ c/s.

Group F. A triplet pattern. From the high resolution spectrum a coupling of 19·6 c/s can be calculated; this is equal to the J_{4-5} coupling in group D and hence this group F probably arises from fluorine F_5. The coupling constants are then $J_{5-4} = 19{\cdot}6$; $J_{5-6} = 21{\cdot}3$; and $J_{5-3} = 3{\cdot}7$ c/s.

Group G. Complex multiplet. As this is of relative intensity two it can only arise from fluorine nucleii $F_{3'}$ and $F_{5'}$. This is the second half of the AA'XX' system (cf. peak C) split further by $F_{4'}$. As the coupling constant $J_{3'-4'} = 20{\cdot}4$ c/s is known from E the overlap at the centre of this group can be separated and the constants calculated using the method of Wiberg and Nist:[12] $J_{3'-2'} = J_{5'-6'} = \pm 21{\cdot}5$; $J_{5'-2'} = J_{3'-6'} = \mp 9{\cdot}2$; whilst $J_{2'-6'}$ and $J_{3'-5'}$ have the values 5·2 and 1·0 c/s although it is not possible to distinguish between the latter two coupling constants.

The NMR spectrum of 2-iodononafluorobiphenyl again consists of seven groups of lines and differs only slightly from that of the bromo-compound. The main point of interest is that the group of lines due to F_3 show a large shift downfield as is to be expected (from the C_6F_5I spectrum) for a fluorine atom in the *ortho* position to an iodine atom. The shifts of the various groups of lines are shown in Table 2 and the calculated coupling constants are listed in Table 1.

The F^{19} NMR spectrum of 2-hydrononafluorobiphenyl consists of only six groups of lines due to the fortuitous overlap of two of the expected seven groups; see Fig. 3—since it shows certain differences from the bromo or iodo case the spectrum will be reviewed in some detail. The H^1 NMR spectrum has been discussed in a previous communication.[2]



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[12] K. B. Wiberg and B. J. Nist, *Interpretation of NMR Spectra.* W. A. Benjamin (1962).

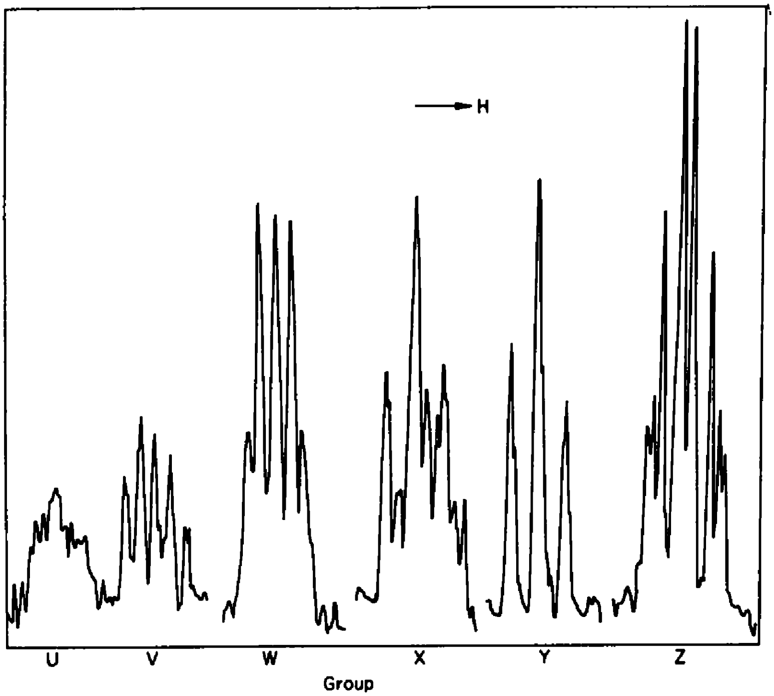

FIG. 3. The low resolution ^{19}F NMR Spectrum of 2-hydrononafluorobiphenyl.

Group U. Complex multiplet. The substitution of a proton for a bromine or iodine in the 2-position can be expected to cause changes in the chemical shift of the peak-group due to F_3. Thus group U, the one to lowest field, is found to be due to F_6; it is impossible however to calculate the respective coupling constants due to the broadening effect of the large number of couplings.

Group V. A thirteen-line multiplet due to F_3. As expected this group suffers the most change due to the *ortho effect* on changing a halogen atom for a proton in the 2-position. The eight-line pattern of the comparative group of peaks, A, in the spectrum of $2\text{-BrC}_6F_4C_6F_5$ and $2\text{-IC}_6F_4C_6F_5$ has now been modified due to changes in the coupling constants and to a proton-fluorine interaction. The coupling constants calculated are $J_{3-4} = 22{\cdot}4$; $J_{3-6} = 12{\cdot}4$; $J_{3-5} = 2{\cdot}7$ and $J_{3-H_1} = 10{\cdot}3$ c/s. This latter coupling constant agrees with the value of $J_{H_1-F_3}$ calculated from the H^1 NMR spectrum of $2\text{-HC}_6F_4C_6F_5$.

Group W. A complex multiplet of relative intensity two due to fluorines $F_{2'}$ and $F_{6'}$ which is part of an AA'XX' system.

Group X. A complex multiplet due to overlap of peaks arising from fluorine atoms F_5 and F_4. The chemical shift of F_5 has obviously been affected by substitution of H for either Br or I; the shift of a fluorine atom *para* to a substituent X is often quite sensitive to changes in substitution depending on whether the substituent X can interact with the π-electron cloud of the phenyl ring (e.g. X = Br or I) or not (e.g. X = H). The overlap of the two groups of lines does not allow the calculation of the coupling constants for these two fluorine nuclei.

Group Y. A triplet of triplets due to the *para* fluorine in the C_6F_5 ring, $F_{4'}$. The constants are $J_{4'-3'} = 19{\cdot}9$; and $J_{4'-2'} = 2{\cdot}7$ c/s.

Group Z. Complex multiplet of relative intensity two. This is the second half of the AA′XX′ system due to $F_{3'}$ and $F_{5'}$. Using the coupling constants available from group Y we can calculate that $J_{2'-3'} = J_{5'-6'} = \pm 22{\cdot}6$ and $J_{2'-5'} = J_{3'-6'} = \mp 8{\cdot}6$ c/s. Again $J_{2'-6}$ and $J_{3'-5'}$ are indistinguishable but have the values 3·7 and 1·5 c/s

The mass spectra of 2-iodo- and 2-bromononafluorobiphenyl show that very little fragmentation occurs until the halogen atom has been lost; for example peaks due to P–nF or P–nF–mC are normally less than one per cent as intense as the parent peak, whereas peaks due to P—X are among the strongest in the spectra. Having lost the halogen atom the molecules fragment by losing fluorine atoms and then carbon atoms in a stepwise manner, the number of fluorine atoms lost always being greater than or equal to the number of carbon atoms which have been lost; thus no peak can be definitely assigned as arising, at least in part, by loss of the 2-carbon atom. In all four cases peaks at mass number P/2 are present due to doubly charged ions, P^{2+}; the relative intensity of these peaks is about ten % and is probably a reflection of the stability of these molecules. The mass spectra of 2-hydrononafluorobiphenyl and decafluorobiphenyl show certain similarities; the proton obviously resists fragmentation as the peak due to P—H is of low intensity. Furthermore, several peaks in the spectrum of 2-hydrononafluorobiphenyl have a "doublet" appearance due to proton-loss giving a peak of unit mass lower down the spectrum, the ion containing the hydrogen atom usually being the more intense, e.g. $C_{11}F_6X^+$. The resistance towards fragmentation (coupled with the ready loss of halogen in $XC_6F_4C_6F_5$) made mass spectral analysis of little use in determining the structures of the 2-nonafluorobiphenyls, other than that of providing exact mol. wts to support the other analytical data.

TABLE 1. COUPLING CONSTANTS IN NONAFLUOROBIPHENYLS

Coupling, c/s $J_{F_x-F_y}$	$BrC_6F_4C_6F_5$	$IC_6F_4C_6F_5$	$HC_6F_4C_6F_5$
3–4	21·5	22·4	22·4
3–5	3·9	4·6	2·7
3–6	9·8	10·7	12·4
3–H_1	—	—	10·3*
4–3	21·5	22·4	—
4–6	4·7	5·0	—
4–5	19·6	19·1	—
4′–3′	20·4	20·0	19·9
4–2′	2·5	2·7	2·7
5–4	19·6	19·2	—
5–6	21·3	20·8	—
5–3	3·7	4·8	—
3′–2′ 5′–6′	± 21·5	± 21·5	± 22·6
5′–2′ 3′–6′	∓ 9·2	∓ 8·3	∓ 8·6
2′–6′	5·2 (1·0)	5·1 (1·0)	3·7 (1·5)
3′–5′	1·0 (5·2)	1·0 (5·1)	1·5 (3·7)

* $J_{H-F_3} = 10{\cdot}3$ (Ref. 2)

TABLE 2. CHEMICAL SHIFTS OF THE SEVEN MAGNETICALLY DIFFERENT TYPES OF FLUORINE ATOM IN THE NONAFLUOROBIPHENYLS: IN ppm RELATIVE TO CCl_3F

	F_3	F_6	$F_{2';6'}$	F_4	$F_{4'}$	F_5	$F_{3';5'}$
$BrC_6F_4C_6F_5$	126·2	133·6	137·8	149·6	150·6	154·3	161·2
$IC_6F_4C_6F_5$	111·4	132·4	138·1	149·8	151·4	153·6	161·6
$HC_6F_4C_6F_5$	138·0	136·7	139·7	152·3	154·3	—	161·8

TABLE 3. MASS SPECTRAL DATA ON THE NONAFLUOROBIPHENYLS

$IC_6F_4C_6F_5$	$BrC_6F_4C_6F_5$	$HC_6F_4C_6F_5$	$C_6F_5C_6F_5$	Peak Assignment
100·0	100.0	100·0	100·0	parent
1·4	1·5	7·1		$C_{12}F_8X$
—	0·7	7·1		$C_{12}F_7X$
—	—	3·1		$C_{11}F_7X$
—	—	23·2		$C_{11}F_6X$
—	—	4·7		$C_{11}F_5X$
38·0	13·6	0·9	10·0	$C_{12}F_9$
68·0	39·7	3·2	6·4	$C_{12}F_8$
4·4	3.3	—	—	$C_{12}F_7$
61·6	41·9	3·1	25·8	$C_{11}F_7$
15·0	10·6	1·0	1·7	$C_{11}F_6$
3·0	4·2	—	2·2	$C_{12}F_5$
3·6	5·5	—	5·6	$C_{10}F_6$
13·0	11·0	1·6	1·8	$C_{11}F_5$
10·0	8·8	8·7	10·4	parent^{2+}
6·0	4·2	—	2·1	$C_{10}F_5$
10·0	6·6	—	1·6	$C_{10}F_4$
3·4	2·2	—	0·6	$C_{10}F_3$
12·0	7·7	—	2·4	C_9F_3
3·6	7·0	—	1·4	C_9F_2
9·6	7·0	1·6	2·4	C_7F_3
3·9	2·8	—	1·0	C_7F_2
6·6	6·6	1·9	3·6	C_5F_3
3·3	2·6	—	0·6	C_7F_3
10·0	8·8	3·2	3·8	C_6F_3
3·4	2·0	—	0·8	C_5F

EXPERIMENTAL

The reactions were carried out under an atmosphere of dry, O_2-free N_2. Mol. wts were recorded in benzene at 30° using a Mechrolab vapour phase osmometer (model 301A) calibrated with benzil. Dr. A. Bernhardt of the Max-Planck-Institute, Mülheim, Germany performed the analyses. The IR spectrum of (nonafluoro-2-biphenylyl)manganesepentacarbonyl was kindly recorded by Mr. J. B. Wilford of Bristol University; we also thank Mr. Wilford for a discussion of the spectrum. Gifts of bromopentafluorobenzene and decafluorobiphenyl from the Imperial Smelting Corporation are gratefully acknowledged.

2-Hydrononafluorobiphenyl

Pentafluorophenyllithium was prepared by the addition of n-butyllithium (9 ml of a 15% solution in hexane) to pentafluorobenzene (3 g) in 50 ml ether at −78°. An excess of pentafluorobenzene (3 g) was then added and the reaction vessel allowed to warm up to room temp overnight. The ether–hexane mixture was evaporated *in vacuo* to leave a brown solid which afforded white 2-hydrononafluorobiphenyl on vacuum sublimation, m.p. 41–42°; yield 1·2 g. The product was characterized by its m.p., IR spectrum, VPC retention time and its H^1 and F^{19} NMR spectra.

2-Iodononafluorobiphenyl

Pentafluorophenyllithium was prepared in ether from butyllithium (9 ml) and pentafluorobenzene (3 g) at −78°. Iodopentafluorobenzene (5·25 g) was then added, the vessel warmed up to room temp overnight. The ether–hexane solvent was distilled off *in vacuo* and then the 2-iodononafluorobiphenyl was distilled over at 90° in high vacuum. The product solidified on standing to give a white solid (m.p. 33–34°); yield, 5·7 g. It was characterized by comparison with an authentic sample.

Reaction of 1,2-*dibromotetrafluorobenzene and pentafluorophenyllithium*

Iodopentafluorobenzene (8 g), 40 ml of ether and butyllithium were placed in a 3-necked flask at room temp. After 5 min 1,2-dibromotetrafluorobenzene was added and the mixture turned brown. On stirring overnight a black solid separated out; 2-bromononafluorobiphenyl (10% yield based on 1,2-dibromotetrafluorobenzene) was separated from the products by VPC. (Found: C, 36·6; H, 0·1; F, 43·3; Br, 20·1. Calc. for $C_{12}BrF_9$: C, 36·5; H, 0·0; F, 43·3; Br, 20·2%.) Spectral and VPC studies showed the compound was identical with that formed in the C_6F_5Li/C_6F_5Br reaction.

Pentafluorophenyllithium/bromopentafluorobenzene in hydrocarbon solvent.

Pentafluorophenyllithium was precipitated in a hexane–petrol ether mixture and reacted with excess of bromopentafluorobenzene at room temp to produce 2-bromononafluorobiphenyl in yields equivalent to those formed in an ether–hexane solvent; VPC showed that higher mol. wt. fractions were present but these have not yet been studied.

Decomposition of pure pentafluorophenyllithium

Exact mole ratios of bromopentafluorobenzene and butyllithium were mixed at −78° and then warmed to room temp for 30 min; the addition of distilled water produces 2-hydrononafluorobiphenyl in fair yield; if the pentafluorophenyllithium is left at room temp for much longer than 30 min before hydrolysis the yield of 2-hydrononafluorobiphenyl falls off, due no doubt to the thermal instability of 2-nonafluorobiphenyllithium from which it arises.

Reaction of 2-*nonafluorobiphenyllithium with bromopentafluorobenzene*

(Nonafluoro-2-biphenylyl)lithium was prepared in the usual way from iodononafluorobiphenyl and allowed to interact with bromopentafluorobenzene at −78°: after hydrolysis at low temp, 2-bromopentafluorobiphenyl and pentafluorobenzene (from hydrolysis of C_6F_5Li) were shown to be formed by IR and VPC studies.

(Nonafluoro-2-biphenyl)manganesepentacarbonyl

Dry mercury (25 ml) was placed in a 3-necked flask fitted with a stirrer, N_2 inlet, dropping funnel and a wide-bore tap fused to the middle of the base (this allowed removal of the Hg at a later stage). Sodium (0·45 g) was added under N_2, 0·1 g at a time and after the vigorous formation of NaHg had subsided, tetrahydrofuran (100 ml) and then manganese pentacarbonyl (3 g) were added and the solution stirred for 1 hr at room temp until a grey solution was obtained. The excess Hg was run off and the sodium pentacarbonylmanganate (−1) washed with a small quantity of dry Hg to remove any traces of Na-metal. The solution was split into two portions; to one was added decafluorobiphenyl (2·3 g) and to the other 2-bromononafluorobiphenyl (3·2 g).

(i) *Decafluorobiphenyl reaction.* The mixture was stirred for 60 hr to yield a yellow solution from which only decafluorobiphenyl and manganese pentacarbonyl could be isolated.

(ii) 2-*Bromononafluorobiphenyl reaction.* The mixture was stirred for 4 hr to yield a yellow solution. After removal of the tetrahydrofuran *in vacuo*, sublimation under high vacuum gave manganese pentacarbonyl and traces of 2-bromononafluorobiphenyl. Further sublimation at 40° gave a pale yellow sublimate; the unsublimed residue was ether-extracted and chromatographed (fluorosil 60/100 mesh) from which a further amount of pale yellow solid was obtained (the IR spectrum of this compound and the pale yellow sublimate showed the presence of manganese pentacarbonyl impurity). A fractional crystallization from ether gave white crystals, decomposition point 129–130°, of (nonafluoro-2-biphenylyl)manganesepentacarbonyl. (Found: C, 40·1; F, 33·3; H, 0·00; mol. wt., 532. Calc for $C_{17}F_9MnO$: C, 40·1; F, 33·5; H, 0·00%; mol. wt., 510.) The compound is soluble in ether, cyclohexane, benzene and tetrahydrofuran.

IR spectrum in nujol and hexachlorobutadiene mulls (cm^{-1}). Low resolution: 2123 m, 2056 m, 2044 s, 2012 s, 2012 s, 1985 s, 1655 m, 1624 m, 1610 m, 1588 m, 1520 m, 1282 wk, 1170 wk, 1152 wk, 1132 wk, 1101 wk, 1083 s, 1024 s, 987 s, 939 m, 773 m, 753 s, 728 b, 711 b, 669 sh, 656 s.b, 647 s.b, 643 s.b, 606 b.

Bis(2-nonafluorobiphenyl)tindimethyl

2-bromononafluorobiphenyl (4·3 g) was dissolved in 30 ml dry ether using a 3-necked flask fitted with a N_2 inlet, stirrer and serum cap; butyllithium was added at −78° and the solution left for 1 hr (a green colour was observed during this period). Dimethyltin dichloride (1·11 g in 30 ml dry ether) was added and the stirred mixture allowed to rise to room temp overnight. A white precipitate formed which settled on standing to give a clear ether solution. On evaporation of the ether a pale yellow viscous liquid remained which was extracted with pet. ether (30/40) to give a white crystalline solid, m.p., 100–102°; yield 12%. (Found: C, 40·2; H, 0·9; F, 43·7; Sn, 14·5; mol. wt., 778. Calc. for $C_{26}H_6F_{18}Sn$: C, 40 0; H, 0·7; F, 43·9; Sn, 15·2%; mol. wt., 783.) The compound is soluble in CCl_4, $CHCl_3$, pet. ether, ether, benzene and acetone. IR spectrum in nujol and hexachlorobutadiene mulls (cm^{-1}). 3128 w, 3006 w, 1651 m, 1622 m, 1595 m, 1519 s, 1291 m, 1264 m, 1150 wk, 1096 s, 1042 m, 1036 s, 988 s, 940 w, 806 w, 790 m, 772m, 767 m, 714 s, 539 b.

The ^1H NMR spectrum of the compound dissolved in CCl_4 was of a single peak centred at 0·30 ± 0·02 ppm downfield from tetramethylsilane. Satellite lines due to tin-proton coupling were also observed with $J_{Sn-H} = 62$ c/s.

Spectra. The ^{19}F NMR spectra were recorded at 56·4 Mc/s on a Perkin–Elmer spectrometer by Dr. E. Mooney of the Northern Polytechnic. The 2-substituted nonafluorobiphenyls were run as 15% solutions in a trichlorofluoromethane–ether mixture using a decade shift and calibrated chart paper. All the resonances were found to lie up-field relative to trichlorofluoromethane. The mass spectra were recorded on an MS9 A.E.I. instrument by Dr. A. H. Jackson of Liverpool University and the main peaks (only those peaks of relative intensities greater than 3·0% are recorded) are given in Table 3. Since Br has two isotopes, mass 87 and 89, mass peaks containing Br atoms appear as doublets; in order to compare all the spectra, the intensities of Br-containing doublet peaks have been added to give the relative intensities quoted in Table 3.

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