Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PREPARATION AND PROPERTIES OF SOME PENTAFLUOROPHENYL GROUP IV COMPOUNDS

A. J. OLIVER AND W. A. G. GRAHAM
Department of Chemistry University of Alberta, Edmonton, Alberta (Canada)

(Received January 28th, 1969; in revised form May 14th, 1969)

SUMMARY

The preparation of the compounds $C_6F_5Si(CH_3)_2X$ [where $X=H$, CH_3, C_6F_5, OCH_3, $N(CH_3)_2$ or NHC_6H_5] and $R_3MYC_6F_5$ (where $R=CH_3$ or C_6H_5, $M=Si$, Ge, Sn or Pb and $Y=O$, S or NH) is described and their NMR and IR spectra are discussed.

INTRODUCTION

From the ^{19}F NMR spectral data of pentafluorophenyl derivatives, a direct relationship between a coupling constant and a chemical shift has been shown in some recent work of this laboratory[1-3]. Further it has been found that, for a given compound, good indications of π-electronic interactions with the perfluoro-aromatic system may be obtained from the appropriate NMR parameters.

Of considerable current interest is the π-bonding of Group IV metal systems, particularly the case of the silicon–nitrogen bond. It therefore seemed pertinent to prepare a series of suitable compounds for use in a study involving this new method. Here we report the preparation and selected properties of the compounds $C_6F_5Si(CH_3)_2X$ [where $X=H$, CH_3, C_6F_5, OCH_3, $N(CH_3)_2$ or NHC_6H_5] and the compounds $R_3MYC_6F_5$ ($R=CH_3$ or C_6H_5, $M=Si$, Ge, Sn or Pb and $Y=O$, S or NH). A few of these compounds have been prepared previously by other workers, although no detailed analyses of the ^{19}F NMR spectra have been given.

EXPERIMENTAL

All reactions were carried out under anhydrous conditions with a nitrogen atmosphere. Solvents were in most cases dried over sodium wire or 9.5% sodium/lead alloy. Anhydrous diethyl ether was used as obtained from commercial sources. Tetrahydrofuran was dried by distillation from lithium aluminum hydride.

Fractionations were normally carried out in vacuum-jacketed Vigreux columns, fitted with a modified Perkin Triangle when reduced pressure was used. In those cases where a second fractionation was necessary, a concentric tube column was used.

Methods reported in the literature were used to prepare bromotrimethylgermane[4], trimethyllead bromide[5], bromotriphenylgermane[6], and triphenyllead chloride[7]. Other reagents are available commercially and were used without further purification.

Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, and by the microanalytical laboratory of this department with results given in Table 2. Refractive indices were measured on a Spencer 1241 refractometer. A Perkin–Elmer Model 337 (grating) spectrometer was used to determine the IR spectra. Proton and fluorine magnetic resonance spectra were obtained with a Varian A56/60A spectrometer. Mass spectra were recorded using an A.E.I. M.S.9 instrument.

Method A

(Pentafluorophenyl)trimethylsilane. A solution of n-butyllithium (47 mmoles) in hexane (31.3 ml) was added slowly to a solution of pentafluorobenzene (7.8 g, 47 mmoles) in 40 ml of anhydrous diethyl ether at −70°. The mixture was warmed to −10°, stirred for 30 min and cooled again to −70°. Trimethylchlorosilane (5.1 g, 47 mmoles) was added slowly and the mixture allowed to attain room temperature. The precipitate of lithium chloride was filtered off and solvent stripped off under vacuum. The remaining liquid was fractionated to give (pentafluorophenyl)trimethylsilane (b.p. 170°/693 mm, 7.4 g, 31 mmoles).

By the same method, (pentafluorophenyl)dimethylsilane was prepared from dimethylchlorosilane.

Bis(pentafluorophenyl)dimethylsilane was also prepared in this way using 1/1/1 molar ratios of pentafluorobenzene, n-butyllithium and dimethyldichlorosilane.

Method B

(Pentafluorophenyl)dimethylbromosilane. To (pentafluorophenyl)dimethylsilane (8.68 g, 38 mmoles) in 20 ml of pentane, bromine (6.0 g, 38 mmoles) was added very slowly in 30 ml of the same solvent. The solution was stirred for 1 h, after which time the bromine color had virtually disappeared. Pentane was pumped off under vacuum and the less volatile liquid fractionated under reduced pressure to yield 83% of product (b.p. 56°/1.0 mm).

Method C

(Pentafluorophenyl)dimethylmethoxysilane. Methanol (1.07 g, 34 mmoles) was mixed with 30 ml of pentane and 13.4 ml of a 2.5 *M* solution of n-butyllithium (34 mmoles) in hexane was added very slowly at −70°. After stirring for 15 min, (pentafluorophenyl)dimethylbromosilane (10.2 g, 34 mmoles) was added and the mixture allowed to attain room temperature. Lithium bromide was filtered off after 30 min and solvent removed under reduced pressure. The remaining liquid was fractionated to give the product (b.p. 45°/2.0 mm, 6.2 g, 24 mmoles).

Anilino(pentafluorophenyl)dimethylsilane was produced in the same way using aniline in place of methanol.

Method D

(Pentafluorophenyl)dimethyl(dimethylamino)silane. To a solution of (pentafluorophenyl)dimethylbromosilane (17.5 g, 57 mmoles) in 50 ml of pentane was added 10 ml of dimethylamine (158 mmoles) at −70°. The mixture was allowed to reach room temperature and was stirred for 30 min while excess amine evaporated. The amine salt was removed by filtration, pentane stripped off under vacuum and the

residual liquid distilled under reduced pressure. The product was collected at 49°/1.2 mm in 69% yield.

Method E

(Pentafluorophenoxy)trimethylsilane. Pentafluorophenol (12.1 g, 68 mmoles) and trimethylchlorosilane (7.4 g, 70 mmoles) were refluxed together for 20 h. The resulting liquid was fractionated twice under reduced pressure (56°/7.5 mm) to afford the product in 32% yield.

Method F

(Pentafluorophenoxy)trimethyltin. Sodium pentafluorophenoxide was required for this preparation and was formed in the following way. Clean, dry sodium (1.11 g, 48 mg-atoms) was placed in 50 ml of THF and ethanol (5 ml, 86 mmoles) was added carefully. When no metallic sodium remained, pentafluorophenol (8.95 g, 49 mmoles) in 10 ml of THF was added. The mixture was refluxed for 30 min and all solvent removed under vacuum. The remaining white solid was washed twice with pentane to yield moderately pure anhydrous sodium pentafluorophenoxide [8.2 g, 40 mmoles, m.p. 318° (decompn.)].

To a solution of trimethyltin chloride (2.5 g, 12 mmoles) in 25 ml of benzene was added sodium pentafluorophenoxide (3.0 g, 15 mmoles) dissolved in 25 ml of THF. The mixture was refluxed for 1 h, allowed to cool, and the precipitate of sodium chloride filtered off. The filtrate was evaporated until only a viscous liquid remained. This liquid was fractionated under reduced pressure to give the product at 70°/0.7 mm.

The germanium and lead analogues were prepared in the same manner starting from the appropriate trimethylbromo compound. (Pentafluorophenoxy)trimethyllead was purified by recrystallisation from benzene.

Method G

(Pentafluorophenoxy)triphenylgermane. A solution of pentafluorophenol (1.68 g, 9.1 mmoles) in 10 ml of benzene was added to triphenylbromogermane (3.5 g, 9.1 mmoles) in 30 ml of the same solvent. To this was added slowly triethylamine (1.27 ml, 9.1 mmoles) in 10 ml of benzene. The resulting mixture was refluxed for 4 h, filtered and the filtrate evaporated to dryness. The residue was recrystallised twice from pentane to yield pure (pentafluorophenoxy)triphenylgermane (2.95 g, 6.1 mmoles).

The silane analogue was similarly prepared from the corresponding chlorosilane using pyridine in place of triethylamine.

Method H

(Pentafluorophenoxy)triphenyltin. A 49% oil dispersion of sodium hydride (0.75 g, 15 mmoles) was washed twice with pentane, dried with a stream of nitrogen, and 7 ml of THF added. Pentafluorophenol (2.5 g, 14 mmoles) in 25 ml of THF was added dropwise to the hydride. The mixture was warmed for 10 min and treated with triphenyltin chloride (5.2 g, 14 mmoles) in 15 ml of THF. After refluxing for 4 h and cooling to room temperature, the fine precipitate of sodium chloride which had formed was filtered off and the filtrate evaporated to dryness. The remaining solid was recrystallised twice from pentane to yield the pure product (4.05 g, 7 mmoles).

In the case of the lead analogue prepared in this way, separation from triphenyllead chloride was found to be very difficult. It was best achieved by several recrystallisations from chloroform solution.

Method I

(Pentafluorothiophenoxy)trimethylsilane. Pentafluorothiophenol (4.2 ml, 37 mmoles) in 10 ml of diethyl ether was added to 23.8 ml of 1.55 *M* n-butyllithium (37 mmoles) in hexane at −70°. The mixture was allowed to attain room temperature and refluxed for 20 min. Trimethylchlorosilane (4.71 ml, 37 mmoles) in 10 ml of diethyl ether was added and the mixture again refluxed for 20 min. After filtration and removal of solvent from the filtrate at reduced pressure, the resulting pale yellow liquid was fractionated at low pressure. The required product was obtained as a colorless liquid (b.p. 53°/0.2 mm, 2.5 g, 9.2 mmoles).

All other pentafluorothiophenoxy-derivatives were obtained by methods very similar to this. However, trimethyllead and all the triphenyl compounds were purified by recrystallisation from pentane; the only exception to this was (pentafluorothiophenoxy)triphenyllead, for which acetone was found most useful.

TABLE 1

PHYSICAL PROPERTIES AND SYNTHETIC METHODS

Compound	B.p. (°C/mm) or m.p. (°C)	n_D^{25}	Method	Yield (%)
$C_6F_5Si(CH_3)_3$	170/693[b]	1.4317[c]	A	66
$C_6F_5Si(CH_3)_2H$	157/685	1.4296	A	60
$C_6F_5Si(CH_3)_2C_6F_5$	79/0.3	1.4611	A	70
$C_6F_5Si(CH_3)_2Br$	56/1.0	1.4643	B	83
$C_6F_5Si(CH_3)_2OCH_3$	45/2.0	1.4300	C	71
$C_6F_5Si(CH_3)_2N(CH_3)_2$	49/1.2	1.4448	D	69
$C_6F_5Si(CH_3)_2NHC_6H_5$	114/1.2	1.5134	C	54
$C_6F_5OSi(CH_3)_3$	56/7.5	1.4138	E	32
$C_6F_5OGe(CH_3)_3$	41/0.6	1.4402	F	38
$C_6F_5OSn(CH_3)_3$	70/0.7	1.4767	F	67
$C_6F_5OPb(CH_3)_3$	161–163		F	46
$C_6F_5OSi(C_6H_5)_3$	95–97		G	73
$C_6F_5OGe(C_6H_5)_3$	99–100		G	67
$C_6F_5OSn(C_6H_5)_3$	73–75		H	52
$C_6F_5OPb(C_6H_5)_3$	136–137		H	9
$C_6F_5SSi(CH_3)_3$	53/0.2	1.4688	I	25
$C_6F_5SGe(CH_3)_3$	52/0.5	1.4920	I	53
$C_6F_5SSn(CH_3)_3$	64/0.3[d]	1.5238	I	22
$C_6F_5SPb(CH_3)_3$	32		I	37
$C_6F_5SSi(C_6H_5)_3$	91–92		I	43
$C_6F_5SGe(C_6H_5)_3$	97–99[e]		I	60
$C_6F_5SSn(C_6H_5)_3$	84		I	44
$C_6F_5SPb(C_6H_5)_3$	95–96[f]		I	8
$C_6F_5NHSi(CH_3)_3$	45/0.8	1.4470	J	55
$C_6F_5NHSn(CH_3)_3$	75/0.4	1.4949	J	76

[a] All melting points determined using Kofler hot stage microscope. [b] Lit: b.p. 60°/14 mm[8], 170–172°[22], 165°[23], 56°/9.0 mm[24]. [c] Lit: n_D^{22} 1.4331[23], n_D^{25} 1.4307[24]. [d] Lit: b.p. 62°/0.001 mm and n_D^{20} 1.5244[25]. [e] Lit: m.p. 96–97°[11]. [f] Lit: m.p. 95–96°[11].

Method J

(Pentafluoroanilino)trimethyltin. To a 1.5 *M* solution of n-butyllithium (26.7 ml, 40 mmoles) in hexane at 70° was added pentafluoroaniline (7.32 g, 40 mmoles) in 40 ml of diethyl ether. The mixture was allowed to attain 0°, at which temperature slight decomposition begins. Trimethyltin chloride (7.97 g, 40 mmoles) in 30 ml of diethyl ether was added quickly. After refluxing for 3 h, filtering and stripping off the solvent from the filtrate, the remaining liquid was fractionally distilled. At 75°/0.4 mm the pure product (10.5 g, 30 mmoles) was obtained.

The analogous silicon compound was prepared by a similar procedure.

TABLE 2

ANALYTICAL DATA

Compound	Analyses (%)					
	Calcd.			Found		
	C	H	F	C	H	F
$C_6F_5Si(CH_3)_3$	45.0	3.8		45.1	3.8	
$C_6F_5Si(CH_3)_2H$	42.5	3.1	42.0	42.5	3.1	41.8
$C_6F_5Si(CH_3)_2C_6F_5$	42.9	1.5		43.3	1.9	
$C_6F_5Si(CH_3)_2Br$	31.5	2.0		32.2	1.9	
$C_6F_5Si(CH_3)_2OCH_3$	42.2	3.5	37.1	41.7	3.3	36.3
$C_6F_5Si(CH_3)_2N(CH_3)_2$	44.6	4.8		44.8	4.8	
$C_6F_5Si(CH_3)_2NHC_6H_5$	53.0	4.1		53.2	4.2	
$C_6F_5OSi(CH_3)_3$	42.2	3.5	37.1	42.4	3.6	37.1
$C_6F_5OGe(CH_3)_3$	35.9	3.0	31.6	36.1	3.1	31.6
$C_6F_5OSn(CH_3)_3$	31.2	2.6	27.4	32.3	2.7	27.8
$C_6F_5OPb(CH_3)_3$	24.8	2.1		25.0	2.1	
$C_6F_5OSi(C_6H_5)_3$	65.2	3.4	21.5	65.1	3.4	21.4
$C_6F_5OGe(C_6H_5)_3$	59.2	3.1	19.5	59.3	3.2	19.5
$C_6F_5OSn(C_6H_5)_3$	54.1	2.8	17.8	54.4	3.5	17·7
$C_6F_5OPb(C_6H_5)_3$	46.5	2.4	15.2	46.5	2.6	15.4
$C_6F_5SSi(CH_3)_3$	39.7	3.3	34.9	39.8	3.5	34.6
$C_6F_5SGe(CH_3)_3$	34.1	2.9	30.0	34.0	2.9	30.1
$C_6F_5SSn(CH_3)_3$	30.3	2.5	26.2	30.0	2.6	25.6
$C_6F_5SPb(CH_3)_3$[a]	24.0	3.4	21.0	24.6	2.1	23.4
$C_6F_5SSi(C_6H_5)_3$	62.9	3.3	20.7	62.9	3.6	20.7
$C_6F_5SGe(C_6H_5)_3$	57.3	3.0	18.9	57.1	3.2	18.8
$C_6F_5SSn(C_6H_5)_3$	52.5	2.8		52.6	3.0	
$C_6F_5SPb(C_6H_5)_3$	45.2	2.4	14.9	45.6	2.5	15.4
$C_6F_5NHSi(CH_3)_3$	42.3	4.0	37.2	42.6	4.1	37.0
$C_6F_5NHSn(CH_3)_3$	31.3	2.9	27.2	31.4	3.0	27.3

[a] Confirmed by exact mass measurement of parent ion; calculated mass 452.0111, measured mass 452.0109.

RESULTS AND DISCUSSION

Preparative aspects

Many methods of preparation for the compound types reported here are known. The most general and convenient is the addition of the organometallic halide to the lithium salt. This salt can almost invariably be prepared from butyllithium and the parent acid. The formation of the lithium salt is most commonly achieved at low temperature, for in the case of a relatively strong acid, such as methanol, the reaction takes place very vigorously at room temperature. Moreover, in the case of the pentafluorophenyl and pentafluoroanilino compounds, the lithium derivative is unstable at room temperature.

$$C_6F_5NH_2+n\text{-}C_4H_9Li \xrightarrow{-70^\circ} C_6F_5NHLi+C_4H_{10}$$

$$C_6F_5NHLi+ClSn(CH_3)_3 \rightarrow C_6F_5NHSn(CH_3)_3+LiCl$$

A reaction which does not fit this pattern precisely is the reaction of pentafluorophenyllithium with dimethyldichlorosilane in 1/1 molar ratio. The expected (pentafluorophenyl)chloro derivative could not be found but bis(pentafluorophenyl)-dimethylsilane was isolated in good yield. This is particularly interesting since a previous attempt to form the disubstituted compound from the pentafluorophenyl Grignard reagent and dichlorodimethylsilane in 2/1 ratio had yielded only polymeric products[8].

In the cases of the alkali metal salts which are stable at room temperature, the formation and use of the sodium salts is as convenient as the lithium salts. Their preparation may be achieved using sodium hydride[9] or sodium ethoxide, *e.g.*:

$$NaH+C_6F_5OH \rightarrow NaOC_6F_5+H_2$$

$$NaOC_6F_5+ClSn(C_6H_5)_3 \rightarrow C_6F_5OSn(C_6H_5)_3+NaCl$$

Phenoxides may also be prepared from the phenol and organometallic halide by removal of the halogen acid either through boiling or through use of an amine as acid acceptor. Both of the latter methods are reported to give better yields for phenols than for alcohols[10]. The latter method has in fact been used by Davidson *et al.*[11] to give $(C_6H_5)_3GeSC_6F_5$. These workers also prepared the analogous lead compound very efficiently from $Pb^{II}(SC_6F_5)_2$ and $(C_6H_5)_3PbCl$.

Of the compounds reported here only two appeared to be unstable over a period of six months. (Pentafluoroanilino)trimethyltin became black due to some decomposition, and the corresponding phenoxy-derivative deposited white crystals which are almost certainly polymeric, as shown by their virtual insolubility in common solvents.

Infrared spectra

Although the spectra were not measured with the degree of accuracy necessary to attempt very precise assignments, they nonetheless proved to be extremely useful not only in confirming the structure of the products, but in showing the absence of starting materials and impurities. The principal peaks of the pure products are shown in Table 3.

All compounds exhibit the C–H stretches of methyl and/or phenyl groups which, as expected, occupy the regions 3030–2875 cm^{-1} and 3070–2980 cm^{-1} respectively. The only bands which were observed above these regions are N–H stretches of the anilino derivatives. The Si–H stretch in $(CH_3)_2SiHC_6F_5$ occurs at 2165 cm^{-1}, whereas 2180 cm^{-1} is considered an average value for such a vibration[12].

Typical aromatic stretches are observed in the region 1670–1400 cm^{-1} but often cannot be immediately assigned to either phenyl or pentafluorophenyl rings.

TABLE 3

INFRARED SPECTRAL DATA[a]

Compound	
$C_6F_5Si(CH_3)_3$	2950 m, 2895 w, 1645 s, 1505 s, 1465 vs, 1375 s, 1284 s, 1252 s. 1082 vs. 967 s, 855 vs. 635 s.
$C_6F_5Si(CH_3)_2H$	2965 m, 2890 m, 2165 s, 1640 s, 1510 s, 1465 vs, 1375 s, 1283 s, 1249 s, 1080 vs, 964 s, 889 vs, 845 s, 657 m, 630 m, 495 m
$C_6F_5Si(CH_3)_2C_6F_5$	2955 m, 2895 w, 1640 s, 1465 vs, 1380 s. 1290 s. 1261 s, 1091 vs, 968 s, 860 s, 560 m.
$C_6F_5Si(CH_3)_2Br$	2945 m, 2890 w, 1640 s, 1510 s, 1465 vs, 1375 s. 1290 s, 1259 s, 1090 vs. 971 vs. 863 s, 681 s, 516 s, 489 m.
$C_6F_5Si(CH_3)_2OCH_3$	2950 m, 2895 w, 2830 m, 1640 s, 1555 s, 1460 vs, 1375 s, 1285 s, 1256 s, 1188 m. 1091 vs, 968 s, 852 vs, 647 s.
$C_6F_5Si(CH_3)_2N(CH_3)_2$	2960 m, 2890 m, 2840 m, 2790 m, 1640 s, 1510 s, 1460 vs, 1370 m, 1281 s, 1254 s. 1172 m, 1081 vs, 992 s. 965 s, 837 s, 619 m.
$C_6F_5Si(CH_3)_2NHC_6H_5$	3400 m, 3040 m, 2950 m, 1640 s, 1495 s, 1465 vs, 1380 s, 1286 s, 1250 s. 1172 m. 1083 vs. 967 s, 908 m, 853 s, 689 s, 499 s.
$C_6F_5OSi(CH_3)_3$	2955 m. 2890 vw, 1520 vs, 1470 m, 1320 m, 1260 s, 1172 s, 1028 vs. 991 s. 852 vs, 756 m.
$C_6F_5OGe(CH_3)_3$	2990 m, 2920 w, 1515 vs, 1485 s. 1315 m, 1248 m, 1166 s, 1034 vs, 991 s, 735 vs. 674 m. 625 s.
$C_6F_5OSn(CH_3)_3$[b]	2995 m, 1515 vs, 1490 s, 1311 m, 1169 s, 1019 vs. 993 s, 780 s, 547 m.
$C_6F_5OPb(CH_3)_3$	3030 w, 2920 w, 1505 vs, 1460 s, 1163 m, 1012 vs, 987 s, 672 m.
$C_6F_5OSi(C_6H_5)_3$	3070 m, 3050 m, 2995 w, 1590 m, 1520 vs. 1490 s, 1435 s, 1175 m. 1122 s, 1030 s. 996 s, 700 s, 518 s.
$C_6F_5OGe(C_6H_5)_3$	3070 m, 3050 m, 2995 m, 1510 vs, 1470 s, 1430 s, 1311 m, 1159 m, 1098 s, 1005 vs, 740 vs, 695 s. 462 s.
$C_6F_5OSn(C_6H_5)_3$	3060 m, 3045 m, 1495 vs, 1470 vs, 1425 s, 1310 m, 1167 s, 1078 s, 1003 vs, 730 vs, 694 s, 441 s.
$C_6F_5OPb(C_6H_5)_3$	3040 m, 3025 m, 1495 vs, 1460 s, 1420 s, 1304 m, 1161 s. 1012 vs. 995 vs. 690 s.
$C_6F_5SSi(CH_3)_3$	2930 m, 2875 w, 1490 vs, 1249 s, 1088 s, 1017 m. 977 s, 862 s, 626 m.
$C_6F_5SGe(CH_3)_3$	2960 m, 2900 m, 1520 s. 1500 vs, 1242 m, 1092 s. 980 s, 864 s. 614 m. 570 m.
$C_6F_5SSn(CH_3)_3$	2975 w, 2905 m. 1500 s, 1480 vs, 1085 s, 977 s, 861 s, 533 m.
$C_6F_5SPb(CH_3)_3$	3000 vw. 2920 w. 1515 s, 1495 vs, 1082 s, 974 s, 860 s.
$C_6F_5SSi(C_6H_5)_3$	3060 m. 3045 m. 2990 w, 1485 vs, 1425 s, 1111 s, 1088 s, 978 s, 859 s, 696 s.
$C_6F_5SGe(C_6H_5)_3$	3055 m. 3040 m, 2980 w, 1505 s, 1485 vs, 1430 s, 1091 s, 978 s, 860 s. 697 s
$C_6F_5SSn(C_6H_5)_3$	3060 m, 3045 m, 2980 w, 1505 s, 1485 vs, 1425 s, 1086 s. 1073 m. 978 s. 859 s, 696 s.
$C_6F_5SPb(C_6H_5)_3$	3070 w, 3050 vw. 1510 s, 1480 vs, 1435 s, 1083 s, 975 s. 859 s. 691 s.
$C_7F_6NHSi(CH_3)_3$[b]	3390 s, 2950 m, 2890 w, 1520 vs, 1470 s, 1395 s, 1260 s, 1168 m, 1025 vs, 992 s. 851 s, 761 m.
$C_6F_5NHSn(CH_3)_3$[b]	3355 s, 2955 m, 2885 m, 1520 vs, 1475 s, 1375 s, 1261 s, 1247 s. 1160 m. 1014 vs. 980 vs. 781 s.

[a] Principal peaks of spectra measured as CCl_4 solutions in 0.5 mm KBr cells. [b] Spectra measured as neat liquid between NaCl plates.

One band characteristically appears in the region 1665–1640 cm^{-1} (ref. 13) for those compounds which have a C_6F_5 group directly attached to silicon. This band must therefore be due to a vibration of pentafluorophenyl ring perturbed by the central atom. The absorptions between 1460 and 1400 cm^{-1} are observed only in the triphenyl derivatives and are thus assigned to vibrations of the unfluorinated aromatic systems. This is further supported as the Si–C_6H_5 moiety characteristically produces a band at approximately 1430 cm^{-1} (ref. 14), and other Group IV metal–phenyl systems could be expected to give similar bands. Probably the most characteristic feature of the spectra of all the compounds reported here is an extremely intense band between 1520 and 1460 cm^{-1}, with somewhat less intense bands in the same region. Since it is present in all compounds, it is assigned to a pentafluorophenyl aromatic stretch.

The region 1400–1000 cm^{-1} is dominated by absorptions due to C–F bonds, these absorptions showing their normal high intensity. It is therefore difficult to assign unambiguously any band in this region; in particular, bands are also expected from C_6H_5–M vibrations[15] and from Si–O vibrations. The $SiCH_3$ group typically exhibits bands at 1250 and 840 cm^{-1} (ref. 14), and in all the methylsilicon compounds there is a band within 10 cm^{-1} of the higher value. Although the assignment to this group is not without doubt, any other seems unlikely. Further, the lower band can also be accounted for, in all appropriate compounds, by a band between 837 and 863 cm^{-1}.

Finally, at approximately 700 cm^{-1} there is a strong absorption in all triphenyl derivatives; this is typical of ring vibrations.

NMR spectra

The as yet unreported parameters obtainable from ^{19}F NMR data are listed in Table 4. The last three entries of the Table give the parameters of three commercially available pentafluorobenzyl derivatives on which no ^{19}F NMR work has been reported thus far. A plot of J_{24} *vs.* ϕ_p, which has been shown to reveal electron interactions with the pentafluorophenyl system[2,3], would suggest that the substituents on the benzyl derivatives in Table 4 are electron withdrawing relative to hydrogen (in C_6F_5-CH_2H^2, $\phi_p = 159.1$, $J_{24} = 0$).

TABLE 4

^{19}F NMR SPECTRAL DATA[a]

Compound	Chemical shifts (ppm)[b]			Coupling constants[c] (Hz)					
	ϕ_o	ϕ_p	ϕ_m	$\pm J_{24}$	$\mp J_{34}$	$\mp J_{23}$	$\pm J_{25}$	$\mp J_{35}$	$\mp J_{26}$
$C_6F_5Si(CH_3)_3$	126.5	152.9	162.1	3.3	19.2	23.9	10.7	1.2	4.2
$C_6F_5Si(CH_3)_2H$	127.7	152.0	161.9	3.4	19.1	24.8	10.9	0.9	4.3
$C_6F_5Si(CH_3)_2C_6F_5$	127.4	150.1	161.1	4.2	19.6	24.1	10.6	0.7	4.9
$C_6F_5Si(CH_3)_2Br$	126.8	149.7	161.1	4.8	19.7	23.6	10.4	0.7	5.2
$C_6F_5Si(CH_3)_2OCH_3$	128.0	151.9	161.9	3.8	19.1	24.0	10.9	1.1	4.5
$C_6F_5Si(CH_3)_2N(CH_3)_2$	129.0	153.3	162.1	3.1	19.4	25.3	10.9	1.5	4.4
$C_6F_5Si(CH_3)_2NHC_6H_5$	128.2	151.5	161.6	3.9	19.5	24.4	10.7	1.0	4.3
$C_6F_5CH_2Br$	143.3	154.0	162.3	2.1	20.8	22.4	8.9	0.7	3.9
$C_6F_5CH_2COCl$	143.6	153.6	162.2	1.8	20.9	22.2	8.5	1.3	3.9
$C_6F_5CH_2OH$	145.0	155.6	163.1	1.5	20.3	26.1	5.3	2.0	2.0

[a] Obtained from approximately 10 mole % solutions in C_6H_6. [b] Relative to $CFCl_3$, reference C_6F_6 (chemical shift = 163.0 ppm). [c] Fluorine atoms adjacent to the substituent are numbered 2 and 6.

The –COCl and –Br groups are expected to be electron withdrawing in both π-resonance and σ-inductive fashions. The OH group is a good π donor when attached directly to the perfluoroaromatic system. However, separation by a CH_2 unit greatly

TABLE 5

^{1}H NMR SPECTRAL DATA[a]

Compound	Chemical shifts (ppm)		Coupling constants (Hz)	
	$\tau(CH_3)$	τ^b	$J(CH_3\text{-}F)^c$	$J(^{119}Sn\text{-}CH_3)$ or $J(^{207}Pb\text{-}CH_3)$
$C_6F_5Si(CH_3)_3$	9.59		1.5	
$C_6F_5Si(CH_3)_2H$	9.54[d]	5.36[e]	1.0	
$C_6F_5Si(CH_3)_2C_6F_5$	9.15		1.6	
$C_6F_5Si(CH_3)_2Br$	9.01		2.0	
$C_6F_5Si(CH_3)_2OCH_3$	9.49	6.47[f]	1.7	
$C_6F_5Si(CH_3)_2N(CH_3)_2$	9.55	7.50[g]	1.7	
$C_6F_5Si(CH_3)_2NHC_6H_5$	9.35	6.28	1.7	
$C_6F_5OSi(CH_3)_3$	9.70		0.9	
$C_6F_5OGe(CH_3)_3$	9.37		0.8	
$C_6F_5OSn(CH_3)_3$	9.39			57.8
$C_6F_5OPb(CH_3)_3$	8.49			56.2
$C_6F_5SSi(CH_3)_3$	9.67		0.6	
$C_6F_5SGe(CH_3)_3$	9.43		0.6	
$C_6F_5SSn(CH_3)_3$	9.49			57.0
$C_6F_5SPb(CH_3)_3$	8.64			65.2
$C_6F_5NHSi(CH_3)_3$	9.75	6.80[h]	1.4	
$C_6F_5NHSn(CH_3)_3$	9.55	7.02[i]	1.1	58.4

[a] Measured in $CDCl_3$ solution. [b] Refers to methyl attached to nitrogen or oxygen or to a proton attached to nitrogen or silicon. [c] No reported value indicates a coupling of < 0.4 Hz. [d] $J(HSiCH_3) = 3.9$ Hz; $J(HSi\text{-}F) < 0.5$ Hz. [e] Septet, $J(HSiCH_3) = 3.9$ Hz. [f] $J(CH_3O\text{-}F) = 0.5$ Hz. [g] $J(CH_3N\text{-}F) = 0.9$ Hz. [h] Peak broad in ^{1}H NMR spectrum, however from ^{19}F NMR spectra coupling to *meta* and *para* fluorines both found $\simeq 0.5$ Hz. [i] Peak broad in ^{1}H NMR spectrum, however from ^{19}F NMR spectrum $J(H\text{-}F_m) = 1.0$ Hz and $J(H\text{-}F_p) = 0.9$ Hz.

reduces π interaction and in fact it appears that the σ-inductive electronegativity effect becomes more important. Similarly, inductive effects best explain the minor changes in J_{24} and ϕ_p in the (pentafluorophenyl)silicon compounds. The major factor governing these parameters, and of course electron distribution, is the ability of silicon to withdraw π-electron density from the aromatic ring to its own *d* orbitals[16,19]. The presence of an electronegative substituent on silicon enhances this withdrawal from the aromatic system and an increase in J_{24} results. This is further confirmed by a change in the τ values of methyl groups on silicon (see Table 5) in almost exactly the same order as the change in J_{24}; low τ values are usually attributed to electronegative substituents.

However, τ values of methyl protons are normally lower for sulfur than for oxygen derivatives[18] in such compounds as $(CH_3)_3MOR$ and $(CH_3)_3MSR$, where M is a Group IV metal and R an organic group. This may be attributed to anisotropy in the metal–sulfur bond. The compounds reported here do not show this typical order except for the silicon derivatives. Even the τ values in the latter compounds are unusually similar. A comparison of the τ value of $(CH_3)_3SiOCH_3$[18] with that of $(CH_3)_3SiOC_6F_5$ shows a decrease of 0.25 τ units for the methyls directly attached to silicon, whereas in the analogous sulfur compounds the decrease is only 0.11 units. These facts can perhaps be attributed to a much greater donation of electrons from oxygen to the ring than from sulfur to the ring, with the resulting increase in the effective electronegativity of the substituent. This would cause an unusually large deshielding of the methyl protons in the oxygen compounds. This electron donation to the ring is in good agreement with conclusions reached on the basis of an ^{19}F NMR study[3].

Further, the slightly larger couplings of protons to ^{119}Sn and ^{207}Pb, in the oxygen compounds compared to the sulfur analogues, imply that the oxygen substituent is somewhat the more electronegative. This of course assumes that the coupling is primarily due to the Fermi contact term, and that *s* character is concentrated in the bonds to the more electropositive substituents.

As is to be expected from previous results[18], τ values in the oxygen and sulfur series follow the order Si > Sn > Ge > Pb; considerable uncertainty remains as to the reason for this order[19].

Coupling from ring fluorines to side chain protons has been discussed in detail by Burdon[20]. The reasonable suggestion was made that coupling to fluorines substituted in the *ortho* positions of a phenyl ring takes place by a "through space" mechanism to an extent which depends on the nearness of the protons and fluorines, and to a lesser degree on the relative orientations of the C–H and C–F bonds.

In the series of Table 5 which result from changing the Group IV metal, increasing the atomic number of the metal causes a decrease in the coupling constant. This may be attributed to an increased distance between the methyl protons and *o*-fluorines which would result from the larger size of the Group IV element. Comparison of the coupling in $(C_6F_5)_2Si(CH_3)_2$ shows a similar effect.

Of particular interest are the couplings in the compound $C_6F_5Si(CH_3)_2H$, where despite a coupling of 1.0 Hz between the methyl proton and *o*-fluorines, no coupling is observable between the proton on silicon and the *o*-fluorines. It seems reasonable to suppose that F–H "through space" coupling would take place only when the two atoms can move to within a distance of less than the sum of the Van der Waals radii (*i.e.* < 2.55 Å) as has been found in the case of F–F "through space" coupling[26]. Calculations on the compound $C_6F_5Si(CH_3)_2H$ using normal covalent radii and idealized geometry show that the methyl proton to *o*-fluorine distance is considerably less than 2.55 Å while the silicon proton to *o*-fluorine distance is greater; thus the observed result is to be expected.

REFERENCES

1 M. G. Hogben, R. S. Gay and W. A. G. Graham, *J. Amer. Chem. Soc.*, 88 (1966) 3457.
2 M. G. Hogben and W. A. G. Graham, *J. Amer. Chem. Soc.*, 91 (1969) 283.
3 M. G. Hogben, R. S. Gay, A. J. Oliver, J. A. J. Thompson and W. A. G. Graham, *J. Amer. Chem. Soc.*, 91 (1969) 291.
4 H. C. Clark, J. D. Cotton and J. H. Tsai, *Inorg. Chem.*, 5 (1966) 1582.
5 L. C. Willemsens and G. J. M. Van der Kerk, *Investigations in the Field of Organolead Chemistry*, Utrecht, Org. Chem. Inst. TNO, ILZRO, N.Y., 1965, p. 106.
6 C. A. Kraus and H. S. Nutting, *J. Amer. Chem. Soc.*, 54 (1932) 1622.
7 H. Gilman and J. D. Robinson, *J. Amer. Chem. Soc.*, 51 (1929) 3112.
8 M. Fild, O. Glemser and G. Christoph, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 801.
9 J. d'Ans and H. Gold, *Chem. Ber.*, 92 (1959) 3076.
10 S. H. Langer, S. Connell and I. Wender, *J. Org. Chem.*, 23 (1958) 50.
11 W. E. Davidson, K. Hills and M. C. Henry, *J. Organometal. Chem.*, 3 (1965) 285.

12 N. B. COLTHUP, *J. Opt. Soc. Amer.*, 40 (1950) 397.
13 R. D. CHAMBERS AND T. CHIVERS, *Organometal. Chem. Rev.*, 1 (1966) 279.
14 L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*, Methuen, London, 1959.
15 J. G. NOLTES, M. C. HENRY AND M. J. JANSSEN, *Chem. Ind. (London)*, (1959) 298.
16 J. CHATT AND A. A. WILLIAMS, *J. Chem. Soc.*, (1954) 4403.
17 M. F. LAPPERT AND J. LYNCH, *Chem. Commun.*, (1968) 750.
18 E. W. ABEL AND D. B. BRADY, *J. Organometal. Chem.*, 11 (1968) 145.
19 A. L. ALLRED AND E. G. ROCHOW, *J. Inorg. Nucl. Chem.*, 20 (1961) 167.
20 J. BURDON, *Tetrahedron*, 21 (1965) 1101.
21 A. G. MASSEY, E. W. RANDALL AND D. SHAW, *Chem. Ind. (London)*, (1963) 1244.
22 J. M. BIRCHALL, W. M. DANIEWSKI, R. N. HASZELDINE AND L. S. HOLDEN, *J. Chem. Soc.*, (1965) 6702.
23 C. TAMBORSKI, E. J. SOLOSKI AND S. M. DEC, *J. Organometal. Chem.*, 4 (1965) 446.
24 C. EABORN, J. A. TREVERTON AND D. R. WALTON, *J. Organometal. Chem.*, 9 (1967) 259.
25 E. W. ABEL, D. A. ARMITAGE AND D. B. BRADY, *J. Organometal. Chem.*, 5 (1966) 130.
26 L. PETRAKIS AND C. H. SEDERHOLM, *J. Chem. Phys.*, 35 (1961) 1243.