

## PENTAFLUOROPHENYL ORGANOMETALLIC COMPOUNDS OF GROUP IV ELEMENTS

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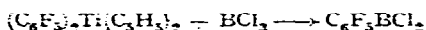
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### INTRODUCTION

Since the first successful synthesis of the organometallic intermediates pentafluorophenylmagnesium bromide<sup>1,2</sup> and pentafluorophenyllithium<sup>3</sup>, research interest in the preparation of numerous pentafluorophenyl organometallic compounds has been extensive. Pentafluorophenyl derivatives of Zn<sup>4</sup>, Hg<sup>3,5,29</sup>, B<sup>6,7,8,9,10</sup>, Si<sup>11,12,\*</sup>, Ge<sup>13</sup>, Sn<sup>7,14,15</sup>, Pb<sup>28</sup>, P<sup>11,12</sup>, As<sup>12</sup>, Sb<sup>12</sup>, and Tl<sup>16,29</sup> representing a  $\sigma$  bond between the metal and pentafluoroaryl group have been reported. Other investigators have prepared pentafluorophenyl derivatives of transition elements Mn<sup>6,17</sup>, Fe<sup>6,17,18</sup>, and Ti<sup>6,17,19</sup> also representing a  $\sigma$  bond between the metal and the pentafluoroaryl group. Interest in these pentafluoroaryl organometallics has been varied and includes studies as thermal stability, infrared studies, nuclear magnetic resonance studies and reactions toward various reagents.

The reaction between the pentafluorophenyl Grignard and pentafluorophenyllithium reagents with the appropriate metallic halides have been most often used in preparation of other pentafluorophenyl organometallic compounds. Other less frequently used procedures for introducing a pentafluorophenyl group onto a metal are cleavage reactions<sup>6,7</sup>:



and reactions of the sodium salt of transition metal anions with fluoroaromatic compounds<sup>18</sup>:



The last two procedures appear to be applicable only to a few specific reactions and are not as versatile as the Grignard or organolithium reactions for introducing pentafluorophenyl groups.

We now wish to report our studies on the synthesis of pentafluorophenyl containing group IV elements by use of the pentafluorophenyllithium and penta-

\* Fild *et al.*<sup>12</sup> reported  $(\text{CH}_3)_2\text{SiC}_6\text{F}_5$ , b.p.  $60^\circ/14$  mm, yield 42%. Tamborski and Soloski<sup>12</sup> prepared  $(\text{CH}_3)_2\text{SiC}_6\text{F}_5$ , b.p.  $165^\circ$ ,  $n_D^{25}$  1.4331, from  $\text{C}_6\text{F}_5\text{MgBr} + (\text{CH}_3)_2\text{SiCl}$  in 94% yield.

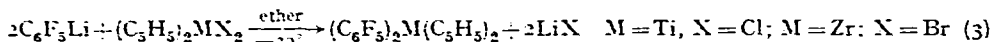
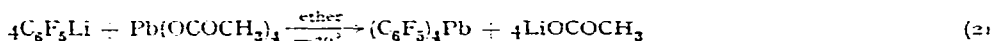
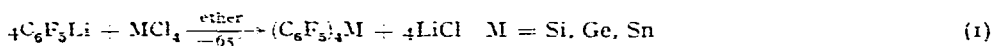
fluorophenylmagnesium reagents. With a few exceptions, little attention has been paid in literature to the method of preparing and using these useful intermediates. In many instances, these intermediates were used for synthesis of other organometallic compounds by techniques similar to their hydrogenic analog phenyllithium and phenylmagnesium bromide. Coe, Stephens and Tatlow<sup>3</sup> who first prepared and studied pentafluorophenyllithium noted the instability of this organometallic under certain temperature conditions. We, also, have studied the stability of the pentafluorophenyllithium as well as the pentafluorophenyl Grignard under various temperature and solvent conditions. It is no wonder that some of the previous investigators wishing to synthesize pentafluorophenyl organometallics have experienced unusually low yields of products.

We have found in our studies that the pentafluorophenyllithium intermediate in diethyl ether has advantages over the pentafluorophenyl Grignard either in diethyl ether or tetrahydrofuran, in the synthesis of pentafluorophenyl organometallic compounds\*. Generally, higher yields of products are obtained by the use of the lithium intermediate. The reaction can be carried out at very low temperatures ( $-65^{\circ}$ ) thus avoiding the by-products that are usually formed by use of the pentafluorophenyl Grignard at higher temperatures\*\*.

From our studies on the stability of the pentafluorophenyllithium and Grignard reagents, it has been found that both the organolithium and Grignard are more stable in ether than in tetrahydrofuran. At higher temperatures both will decompose to yield high melting intractable polymeric materials. It is these competing reactions that must be avoided or minimized in order to obtain higher yields of various derivatives of pentafluorophenyllithium and pentafluorophenylmagnesium bromide.

#### DISCUSSION

We have prepared the pentafluorophenyl derivatives of Si, Ge, Sn, Pb, Ti and Zr by the following reactions:



With the exception of  $(\text{C}_6\text{F}_5)_4\text{Pb}$  all the other members of Group IV were easily prepared in ether between  $-20$  and  $-65^{\circ}$  by conventional methods of reacting an organolithium intermediate with a metallic halide. An attempted synthesis of the

\* In the preparation of  $(\text{C}_6\text{F}_5)_3\text{B}$ , it has been found that oxygen containing solvents as diethyl ether are difficult to remove from the boron compound. In these instances a hydrocarbon solvent as *n*-hexane offers advantages as a reaction medium over diethyl ether solvent, see ref. 8.

\*\* Wall *et al.*<sup>11</sup> in their original work on the synthesis of tetra(pentafluorophenyl)silane via the Grignard reagent, obtained a 32% yield of product plus a solid by-product of unknown composition. Recently, Fear *et al.*<sup>20</sup> have reported on the decomposition of pentafluorophenylmagnesium bromide in refluxing tetrahydrofuran to yield polyfluorophenylenes of high molecular weight.

(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Pb compound by the reaction between C<sub>6</sub>F<sub>5</sub>Li and PbCl<sub>2</sub> was unsuccessful. The synthesis of (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Si, (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Ge, (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Sn and (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Pb were also studied through the reaction between the Grignard C<sub>6</sub>F<sub>5</sub>MgBr and the appropriate metallic halide in tetrahydrofuran. In this solvent the (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Si (68.9%) and (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Ge (72.5%) were easily prepared. The (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Sn (13.5%) and (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Pb (1-3%) were prepared only in low yields with the major product as an intractable high melting material suspected by infrared analysis to be a polyfluorophenylene polymer similar to that reported by Fear *et al.*<sup>20</sup>

Many of the prepared pentafluorophenyl derivatives were subjected to the following studies: infrared and vapor phase chromatography analysis, acid and base hydrolysis, thermal stability and reactions with bromine and lithium.

(a) *Infrared analysis.* The infrared spectra of the pentafluorophenyl derivatives have been recorded on a Perkin-Elmer Model 102 spectrophotometer. The spectra were determined on the samples in KBr pellets and are reported in Table I.

TABLE I  
INFRARED SPECTRA OF PENTAFLUOROPHENYL COMPOUNDS

Compound	C-F stretch		Benzene ring	C <sub>3</sub> H <sub>5</sub> ring	C-H deformation	C-H stretch	Others
(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> Si	1379 (s) 1140 (wsh) 1023 (w)	1292 (s) 1098 (s) 970 (s)	1641 (m) 1516 (s) 1466 (s)				
(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> Ge	1411 (s) 1140 (m) 1087 (s) 970 (s)	1313 (s) 1106 (msh) 1015 (w)	1671 (m) 1539 (s) 1479 (s)				818 (m)
(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> Sn	1378 (s) 1137 (m) 1077 (ssh) 964 (s)	1281 (m) 1087 (s) 1015 (m)	1640 (m) 1509 (s) 1479 (s)				803 (m)
(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> Pb	1375 (s) 1134 (w) 1075 (msh) 963 (s)	1275 (m) 1078 (s) 1005 (m)	1632 (m) 1509 (s) 1469 (s)				782 (m)
(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Ti(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	1373 (m) 1252 (m) 950 (s)	1262 (msh) 1055 (s)	1635 (m) 1505 (s)	1427 (s)	1020 (m) 847 (sh) 835 (s) 827 (ssh)	3150 (w) 3137 (w) 3130 (w) 3119 (w)	745 (m) 1337 (m)
(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Zr(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	1363 (w) 1246 (m) 942 (s)	1260 (wsh) 1041 (s)	1629 (m) 1500 (s)	1431 (s) 1420 (s)	1015 (m) 827 (msh) 804 (s) 785 (m)	3125 (w) 3100 (w)	725 (s) 1325 (w)
(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> TiCl <sub>2</sub>				1435 (s)	1011 (m) 864 (m) 813 (s)	3100 (m)	

\* s = strong; m = medium; w = weak; sh = shoulder.

In the hydrogenic series of tetraphenyl group IV elements  $(C_6H_5)_4M$ , a useful characteristic absorption band for the phenyl-M bond has been reported<sup>21</sup> as  $C_6H_5-Si$ , 9.05  $\mu$ ;  $C_6H_5-Ge$ , 9.18  $\mu$ ;  $C_6H_5-Sn$ , 9.34  $\mu$ ; and  $C_6H_5-Pb$ , 9.45  $\mu$ . This band has been suggested as due to a phenyl group vibration perturbed by the central atom (M). In the corresponding fluorine series no characteristic bands of a  $C_6F_5-M$  bond are apparent. Since the pentafluorophenyl group should have different infrared characteristics than the phenyl group, it is possible that a  $C_6F_5-M$  characteristic absorption band lies in the far infrared region of the spectrum. Studies along this line are in progress.

(b) *Vapor phase chromatography.* The presence of a number of pentafluorophenyl groups on a metal or metalloidal atom enhances the volatility of the compound. Many of the  $(C_6F_5)_4M$  compounds could be easily sublimed as compared to the hydrogen analogs. In addition, the  $(C_6F_5)_4Si$ ,  $(C_6F_5)_4Ge$  and  $(C_6F_5)_4Sn$  could be analyzed by vapor phase chromatography techniques whereas the hydrogen analogs, under comparable conditions, could not. The  $(C_6F_5)_4Pb$  compound under these analytical conditions could not be detected. Since the lead compound has a low order of thermal stability, it is possible that under different analytical conditions, the  $(C_6F_5)_4Pb$  could be analyzed by vapor phase chromatography techniques. The retention time for the compounds determined are  $(C_6F_5)_4Si$ , 2.3 min.;  $(C_6F_5)_4Ge$ , 3.0 min.; and  $(C_6F_5)_4Sn$ , 4.1 min. Column conditions used: isothermal, 275°, 6 ft. ( $\frac{1}{4}$ " O.D.) Apiezon L column on chromasorb P (60-80 mesh), helium flow rate 100 ml/min, F & M 500 instrument.

(c) *Hydrolysis.* Hydrolysis<sup>22</sup> of fluoroalkyl-silanes, -germanes and -tin compounds have been previously studied. In general, the fluoroalkyl groups attached to these metals can be cleaved under basic hydrolysis conditions. In some cases, hot water alone is sufficient to cleave a perfluoroalkyl group from tin.

Results of our hydrolysis studies on tetrakis(pentafluorophenyl)silane, -germane, -tin and -lead compounds are shown in Table 2. Apparently the pentafluorophenyl organometallic derivatives are more stable to hydrolysis than the perfluoroalkyl

TABLE 2

## HYDROLYSIS OF PENTAFLUOROPHENYL COMPOUNDS

N.R. = no reaction, absence of  $C_6F_5H$ ; C = cleavage, as indicated by presence of  $C_6F_5H$ ; R.T. = room temperature.

Conditions	Si	Ge	Sn	Pb	Ti*
HCl (6 N), reflux 5 h	N.R.	N.R.	N.R.	N.R.	
HCl (6 N) + THF, reflux 5 h	C	N.R.	C	C	
NaOH (10%), reflux 5 h	N.R.	N.R.	C	C	
NaOH (10%) + THF, reflux 5 h	C	C	C		
H <sub>2</sub> O-acetone, R.T., initial	N.R.	N.R.	N.R.	N.R.	
H <sub>2</sub> O-acetone, R.T., 2 days	C	N.R.	N.R.	N.R.	
H <sub>2</sub> O-acetone, R.T., 5 days	C	N.R.	N.R.	N.R.	
H <sub>2</sub> O-acetone, R.T., 26 days	C	N.R.	N.R.	N.R.	
Recovered starting material	0	100%	100%	80%	
NaOH (20%), 100°, 8 days					N.R.
HCl (gas), 150°					C
HCl (aq.) + THF, reflux					C

\* Data obtained from ref. 19.

compounds. In a heterogeneous acid hydrolysis (6 *N* HCl) medium, the silane, germane, tin and lead compounds are unaffected at reflux temperature. The silane and germane are also stable to a basic hydrolysis (6 *N* NaOH) in a heterogeneous system at reflux temperature but the tin and lead compounds are hydrolyzed. In a homogeneous hydrolysis (tetrahydrofuran solution) medium under acid and base conditions, the only compound resistant to hydrolysis was the germane whereas the silane, tin and lead were unstable. There seems to be no apparent reason at this time why the germane should show this anomaly.

The silane can be hydrolyzed at room temperature by wet acetone alone whereas under the same conditions the germane, tin and lead are unaffected. The hydrolysis studies were carried out by analyzing for one of the expected cleavage products pentafluorobenzene by vapor phase chromatography. No attempt was made to identify any other products of hydrolysis.

Dicyclopentadienylbis(pentafluorophenyl)titanium has recently been prepared and some of its reactions studied<sup>19</sup>. This compound was stable to basic hydrolysis in a heterogeneous mixture at 100°. Acid hydrolysis in a tetrahydrofuran solution, however, resulted in cleavage of the pentafluorophenyl group.

(d) *Thermal stability*. An indication of thermal stability for the pentafluorophenyl organometallic compounds prepared has been obtained by measuring their decomposition temperatures<sup>23</sup>. Table 3 indicates the comparison of the fluorocarbon versus

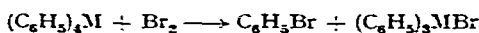
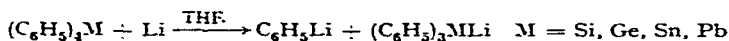
TABLE 3  
RELATIVE THERMAL STABILITIES OF GROUP IV COMPOUNDS

Compounds	Decomposition temperature (°C)*	
	Ar = C <sub>6</sub> H <sub>5</sub>	Ar = C <sub>6</sub> F <sub>5</sub>
Ar <sub>2</sub> Si	468	382
Ar <sub>2</sub> Ge	421	416
Ar <sub>2</sub> Sn	352	399
Ar <sub>2</sub> Pb	232	> 260
Ar <sub>2</sub> Ti(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	105 (ref. 24)	> 260
Ar <sub>2</sub> Zr(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>		256 m.p. (dec.)

\* Decomposition temperature defined as the temperature at which the compound decomposes at the rate of 1 mole %, per hour. See ref. 23.

the hydrocarbon derivatives. In earlier studies Wall *et al.*<sup>11</sup> qualitatively determined the greater stability of (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Si over the (C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>Si. As can be seen from the decomposition temperature values, the silicon member of the fluorocarbon series is less thermally stable, however, the other members of the series have equal or increased stability over their hydrocarbon analogs. Recently, Stone *et al.*<sup>19</sup> have pyrolyzed dicyclopentadienylbis(pentafluorophenyl)titanium *in vacuo* at 150°. One of the decomposition products identified was dicyclopentadienyl(pentafluorophenyl)titanium fluoride. This compound was formed by fluorine migration from a pentafluorophenyl group to the titanium metal, a mode of decomposition characteristic of other fluorocarbon-metal compounds<sup>22</sup>. It is quite conceivable that by an analogous procedure the perfluorophenyl derivatives of the group IV elements decompose in the same fashion.

(c) *Reactions of  $(C_6F_5)_4M$ .* Attempts were made at cleaving a  $C_6F_5$  group from a metal atom with either metallic lithium or bromine. The hydrogenic analogs under similar experimental conditions yield functional compounds according to the following equations:



In this manner useful organometallic intermediates can be prepared for the synthesis of other compounds. Unfortunately, the perfluoroaryl analogs (Si, Ge, Sn) do not react with lithium or bromine. This observation may not be too surprising in view of some of the findings of Eaborn<sup>25</sup> in his studies on rates of cleavage of various substituted aryl silicon compounds. Electron-withdrawing groups (*e.g.* *p*-F and *p*-NO<sub>2</sub>) retarded cleavage of the phenyl group by electrophilic reagents. The fluorine atoms in the  $(C_6F_5)_4M$  compounds would act in a similar manner placing a positive charge on the metal and thus inhibiting an electrophilic attack on the metal atom.

#### EXPERIMENTAL

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. All melting points are uncorrected.

##### *Pentafluorophenyl-metal compounds*

*Pentafluorophenyllithium.* Pentafluorophenyllithium was prepared<sup>26</sup> by the addition of an ether solution of pentafluorobenzene to *n*-butyllithium\* at  $-65^\circ$ .

*Tetrakis(pentafluorophenyl)silane.* Silicon tetrachloride (4.25 g, 0.025 mole) dissolved in 20 ml of diethyl ether was added to a solution of pentafluorophenyllithium (prepared from 16.8 g, 0.10 mole pentafluorobenzene, 0.10 mole of *n*-butyllithium and 130 ml of diethyl ether) at  $-65^\circ$  over an 8 min period. After 3 h of stirring at  $-65^\circ$  the Color Test I<sup>27</sup> was negative indicating absence of pentafluorophenyllithium.

The reaction mixture was allowed to warm up to room temperature and the precipitate filtered. The filtrate was aspirated to dryness. The crude solid plus the precipitate were combined and recrystallized from hot benzene. From the benzene solution was obtained tetrakis(pentafluorophenyl)silane (13.0 g, 75% yield), m.p.  $245-246^\circ$  (lit.<sup>11</sup> reported  $248-250^\circ$ ). (Found: C, 41.22; F, 54.39; Si, 4.31; C<sub>24</sub>F<sub>20</sub>Si calcd.: C, 41.40; F, 54.57; Si, 4.03%.)

In a similar manner as described above via the pentafluorophenyllithium intermediate the following compounds were prepared, tetrakis(pentafluorophenyl)germane, 88.0% yield, m.p.  $246.5-247.5^\circ$  (lit.<sup>13</sup> reported sublimation  $224-230^\circ$ ); tetrakis(pentafluorophenyl)tin, 91.4% yield, m.p.  $220-222^\circ$  (lit.<sup>14</sup> reported  $221^\circ$ ); tetrakis(pentafluorophenyl)lead, (prepared from lead tetraacetate and pentafluorophenyllithium), 15.5% yield, m.p.  $204-206^\circ$  (lit.<sup>28</sup> reported  $199-200^\circ$ ).

*Dicyclopentadienylbis(pentafluorophenyl)zirconium.* Bis(cyclopentadienyl)zirconium dibromide (6.48 g, 0.017 mole) was added directly to pentafluorophenyllithium

\* Commercially prepared in *n*-hexane, Foote Mineral Co., Exton, Pennsylvania, U.S.A.

(prepared from 5.72 g, 0.034 mole pentafluorobenzene, 0.034 mole of *n*-butyllithium and 100 ml of diethyl ether) at  $-65^{\circ}$ . The reaction was allowed to warm up to  $-20^{\circ}$  during 3.5 h. After this time Color Test I<sup>±</sup> was negative indicating an absence of pentafluorophenyllithium. The white precipitate was filtered and the filtrate aspirated to dryness. The crude material was combined and recrystallized from warm benzene yielding 2.54 g (26.9%) pure dicyclopentadienylbis(pentafluorophenyl)zirconium, m.p.  $257^{\circ}$  (dec.) and 1.93 g of an unidentified white crystals, m.p.  $> 340^{\circ}$ . The product was identified by elemental and infrared analysis. (Found: C, 47.49; H, 2.74;  $C_{22}H_{10}F_{10}Zr$  calcd.: C, 47.56; H, 1.81%.)

*Dicyclopentadienylbis(pentafluorophenyl)titanium*. Prepared by a similar procedure as described above, 52% yield, m.p.  $228-229^{\circ}$  (lit.<sup>19</sup> reported  $228-230^{\circ}$ ).

*Tetrakis(pentafluorophenyl)germane via pentafluorophenylmagnesium bromide*. Pentafluorophenylmagnesium bromide was prepared by the addition of pentafluorobromobenzene (123.6 g, 0.5 mole) dissolved in 250 ml of tetrahydrofuran to magnesium (12.2 g, 0.5 g-atom) turnings in 500 ml tetrahydrofuran. The addition required 75 min during which time the mixture changed from colorless to a clear brown solution. The temperature rose to a maximum of  $38^{\circ}$  during the addition. Titration indicated an 87% yield of Grignard reagent. The Grignard was cooled to  $-10^{\circ}$  and germanium tetrachloride (21.4 g, 0.1 mole) dissolved in 170 ml of tetrahydrofuran was added to the Grignard over a period of 60 min. The reaction was slightly exothermic and a precipitate soon developed. After an additional 60 min of stirring at  $-10^{\circ}$ , Color Test I<sup>±</sup> was negative. The precipitate was filtered and recrystallized from benzene to yield 57.90 g (72.5%) of tetrakis(pentafluorophenyl)germane, m.p.  $244-246^{\circ}$ .

In a similar manner as described above via the Grignard intermediate, tetrakis(pentafluorophenyl)silane (68.9%), tetrakis(pentafluorophenyl)tin (13.5%) and tetrakis(pentafluorophenyl)lead (1-3%) were prepared.

#### *Hydrolysis studies*

(a) *HCl (heterogeneous)*. A 5.0 g sample of tetrakis(pentafluorophenyl)silane, tetrakis(pentafluorophenyl)germane, tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)lead were individually treated with 6 N HCl (40 ml) under reflux for 5 h. On cooling the starting materials were recovered in each case quantitatively.

(b) *HCl (in tetrahydrofuran)*. Tetrakis(pentafluorophenyl)silane (3.0 g) was treated with 6 N HCl (40 ml) and tetrahydrofuran (40 ml) for 5 h at reflux temperature. The solution was cooled and extracted with 5-100 ml portions of diethyl ether. A VPC analysis of the dried ether extract indicated only pentafluorobenzene. Evaporation of the ether extract yielded none of the tetrakis(pentafluorophenyl)silane.

Tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)lead were similarly treated with VPC analysis indicating pentafluorobenzene. Tetrakis(pentafluorophenyl)germane under the above hydrolysis conditions was resistant to cleavage. The tetrakis(pentafluorophenyl)germane was recovered quantitatively.

(c) *NaOH (heterogeneous)*. Tetrakis(pentafluorophenyl)silane (5.0 g) and tetrakis(pentafluorophenyl)germane (5.0 g) when individually refluxed for 5 h in NaOH (40 ml, 10% solution) were recovered quantitatively. Tetrakis(pentafluorophenyl)tin and tetrakis(pentafluorophenyl)lead when treated under the same hydrolysis conditions indicated by VPC analysis the presence of pentafluorobenzene.

(d) *NaOH (in tetrahydrofuran)*. Tetrakis(pentafluorophenyl)silane (5.0 g),

tetrakis(pentafluorophenyl)germane (5.0 g) and tetrakis(pentafluorophenyl)tin (5.0 g) when individually refluxed in NaOH (40 ml, 10 % solution) and tetrahydrofuran (40 ml) for 5 h yielded none of the starting material. VPC analysis indicated pentafluorobenzene.

*Attempted cleavage of  $(C_6F_5)_4M$*

(a) *Bromine.* A slurry of tetrakis(pentafluorophenyl)tin (3.93 g, 0.005 mole) in ethylene dibromine (50 ml) was added to a solution of bromine (0.50 g, 0.005 mole) in ethylene bromide (50 ml) plus a catalytic amount of aluminum bromide. After refluxing for 6 h the reaction mixture was cooled to room temperature. The reaction was treated with potassium sulfite solution. The organic layer was washed with water and dried. A sample of this solution was analyzed by VPC and indicated no pentafluorobromobenzene. After aspirating the solution to dryness, the crude solid material was recrystallized from chloroform-methanol. Tetrakis(pentafluorophenyl)tin (3.35 g) was recovered in 85.2 % yield.

In a similar manner as described above, tetrakis(pentafluorophenyl)silane and tetrakis(pentafluorophenyl)germane showed no cleavage of the pentafluorophenyl group.

(b) *Lithium.* A paste of tetrakis(pentafluorophenyl)silane (3.48 g, 0.005 mole) in a few milliliters of tetrahydrofuran and dispersed lithium (0.02 mole) was rapidly stirred for approximately 20 h at room temperature. No apparent reaction took place. The reaction was heated for an additional 8 h without any indication of reaction. To this mixture was added diethyl ether (30 ml) and the Color Test I which was taken was negative indicating no organometallic formation. The reaction mixture was hydrolyzed, the ether layer was separated and dried over magnesium sulfate. Aspiration of the ether solution left crude tetrakis(pentafluorophenyl)silane (3.35 g, 96.2 %).

In a similar manner as described above the tetrakis(pentafluorophenyl)germane and tetrakis(pentafluorophenyl)tin showed no apparent reaction with dispersed lithium.

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#### SUMMARY

The synthesis of pentafluorophenyl group IV elements  $(C_6F_5)_4Si$ ,  $(C_6F_5)_4Ge$ ,  $(C_6F_5)_4Sn$ ,  $(C_6F_5)_4Pb$ ,  $(C_5H_5)_2Ti(C_6F_5)_2$  and  $(C_5H_5)_2Zr(C_6F_5)_2$  is reported. The above compounds are prepared through the reaction of the appropriate metal halide and pentafluorophenyllithium. The various pentafluorophenyl derivatives were subjected to the following studies: infrared and vapor phase chromatography analysis, acid and base hydrolysis, thermal stability and reactions with bromine and lithium.



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