

Pentafluorophenyl-Metal Chemistry II

Preparation and Characterization of Group III A Derivatives¹

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Unter Verwendung des Grignard-Reagenz von Brompentafluorbenzol wurde die vollständige Reihe der Tris-(pentafluorphenyl)-Verbindungen der Elemente der dritten Hauptgruppe in siedendem Toluol dargestellt und in Form der Ätherate charakterisiert. Bei der Sublimation ergaben die Bor- und die Thallium-Verbindungen die freien Derivate. Hingegen gelang es nicht, den 1:1-Ätherkomplex von Tris-(pentafluorphenyl)-aluminium zu spalten; ebenso schlugen alle Versuche fehl, die ätherfreie Verbindung direkt darzustellen.

Bei der Bereitung der Indium- und der Thallium-Derivate aus den Chloriden wurden die entsprechenden Bis-(pentafluorphenyl)-metallbromide als Nebenprodukte isoliert. Demnach muß ein Halogen austausch mit der Äthylierung in Konkurrenz stehen, da bei der Verwendung von Indiumtribromid nur Bis-(pentafluorphenyl)-indiumbromid erhalten wurde.

Bei den meisten Umsetzungen trat ein fluorhaltiger, aromatischer Kohlenwasserstoff als weiteres Nebenprodukt auf; derselbe wurde auch direkt aus Pentafluorphenylmagnesiumbromid in siedendem Toluol erhalten.

Several recent communications in the open literature treat briefly pentafluorophenyl derivatives of Group III A elements. STONE and his coworkers² synthesized tris-(pentafluorophenyl)-boron, which they did not fully characterize but successfully used as an intermediate for the preparation of some coordination compounds — the tetrakis-(pentafluorophenyl)-boronates of lithium, potassium, and tetraethyl ammonium among them.

Cleavage reactions of pentafluorophenyl-metal derivatives carried out with boron trihalides have yielded pentafluorophenyl-boron dibromide¹, as well as the difluoride³ and dichloride^{3,4}. The last compound is also included in a general F¹⁹-NMR spectra study by BOURN and coworkers⁵. Finally, DEACON and NYHOLM⁶ have prepared several stable bis-(pentafluorophenyl)-thallium salts, the F¹⁹-NMR spectra of which recently were reported by FENTON et al.⁷.

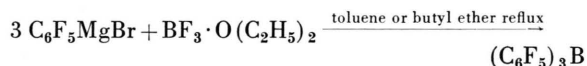
In this paper, we report the synthesis and characterization of the complete series of fully pentafluoro-

phenyl-substituted elements of Group III A as well as several related derivatives. In the following discussion, it is convenient to treat individual elements in the Group III A series as actually studied in our investigations. Where possible, relations in the series and with known phenyl analogues are brought out.

Discussion

Boron

Tris-(pentafluorophenyl)-boron was prepared from boron trifluoride etherate and pentafluorophenyl-magnesium bromide according to the following scheme:



Several experimental techniques were evaluated with yields ultimately exceeding 80 per cent. In view of the preparation of the phenyl analogue⁸

¹ Part I, see J. L. W. POHLMANN, F. E. BRINCKMAN, G. TESI, and R. E. DONADIO, Z. Naturforschg. **20 b**, 1 [1965].

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² A. G. MASSEY, A. J. PARK, and F. G. A. STONE, Proc. chem. Soc. [London] **1963**, 212.

³ R. D. CHAMBERS and T. CHIVERS, *ibid.* **1963**, 208.

⁴ P. M. TREICHEL, M. A. CHAUDHARI, and F. G. A. STONE, J. organometal. Chem. **1**, 98 [1963].

⁵ A. J. R. BOURN, D. G. GILLIES, and E. W. RANDALL, Proc. chem. Soc. [London], **1963**, 200.

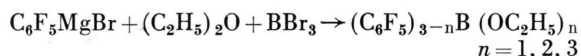
⁶ G. B. DEACON and R. S. NYHOLM, Chem. and Ind. **1963**, 1803.

⁷ D. E. FENTON, D. G. GILLIES, A. G. MASSEY, and E. W. RANDALL, Nature [London] **201**, 818 [1964].

⁸ G. WITTIG, G. KEICHER, A. RUECKERT, and P. RAFF, Liebigs Ann. Chem. **563**, 110 [1949].

and its well-known capability to form complexes^{9,10}, the magnesium salts precipitated were worked up carefully, but no evidence of tetrakis-(pentafluorophenyl)-boronates was found.

Boron trifluoride etherate is the most suitable starting material since it is not very sensitive toward the experimental conditions. Contrariwise when using boron tribromide, success depends very much on the experimental details as boron halides are able to cleave ethers¹¹. Thus, when an ether solution of pentafluorophenylmagnesium bromide was added cautiously at room temperature to a toluene solution of boron tribromide, a vigorous reaction was observed from which no tris-(pentafluorophenyl)-boron could be isolated. A mixture of air-sensitive liquids was obtained instead. After vacuum distillation infrared spectra were taken from the main fraction. Besides the characteristic C_6F_5 —frequencies (1640, 1460, and 950 cm^{-1}), C—H—stretching frequencies (3030 and 2325 cm^{-1}) were observed as well as B—O stretching frequencies^{12,13} (1415 and 1325 cm^{-1}). These findings indicate that ether cleavage is in competition with the anticipated substitution.



Working at low temperature might diminish the ether cleavage, but further efforts were discontinued.

Tris-(pentafluorophenyl)-boron crystallizes in white needles from n-hexane, m.p. $132^\circ - 134^\circ$; it can also be distilled or sublimed. It is soluble in hydrocarbons and in ether, but it is very sensitive to air and moisture. Tris-(pentafluorophenyl)-boron etherate also is a hygroscopic, white solid which can be crystallized from a very concentrated ether solution. *In vacuo* or above 60° it readily splits off its ether. In dilute benzene solution this 1 : 1 complex is partially dissociated (molecular weight determinations).

⁹ G. WITTIG and A. RUECKERT, *Liebigs Ann. Chem.* **566**, 101 [1950].

¹⁰ G. WITTIG and P. RAFF, *Liebigs Ann. Chem.* **573**, 195 [1951].

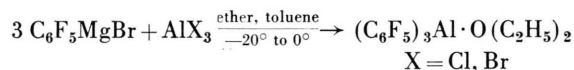
¹¹ H. RAMSER and E. WIBERG, *Ber. dtsch. chem. Ges.* **63**, 1136 [1930].

¹² E. W. ABEL, W. GERRARD, and M. F. LAPPERT, *J. chem. Soc. [London]* **1957**, 3833.

Aluminum

Aluminum derivatives generally form much stronger dative-bonded ether complexes than do boron compounds^{14,15}; therefore, careful consideration had to be given to the type of solvents used to carry out the reactions. Although our initial approach anticipated ether complexation, it was thought the donor would be fairly easily cleaved off as is reported for triphenylaluminum and other analogues.

Aluminum trihalides in ether reacted with pentafluorophenylmagnesium bromide at room temperature, but only dark tars were obtained. From one tar ($AlCl_3$ reaction), a crystalline material was separated, which after several recrystallizations could be sublimed, and yielded a white solid, m.p. 173° to 175° . Although attempts to sublime the crude material resulted in violent detonations, infrared and NMR spectra obtained with analytical data confirmed this compound as tris-(pentafluorophenyl)-aluminum etherate. The yield of the first successful run was only 6.5%, but upon repeating this reaction 67% was obtained by using a refined technique (see Experimental). In the same way, aluminium tribromide was reacted at -20° and yielded 67% almost pure tris-(pentafluorophenyl)-aluminium etherate.



Varied attempts were made to remove the ether from the aluminum complex, but none succeeded. When using the pyrolytic procedure worked out by WITTIG and WITTENBERG¹⁶ for the phenyl analogue, sublimation occurred on cautious heating *in vacuo*; but no free ether was detected. Heating the sample at a fast rate always resulted in violent decompositions.

All detonations left an appreciable amount of carbon black on the debris, but the generation of gases seemed to be rather low. It is reasonable to assume that the formation of Al—F bonds by either

¹³ W. J. LEHMANN, H. G. WEISS, and I. SHAPIRO, *J. chem. Physics* **30**, 1226 [1959].

¹⁴ F. G. A. STONE, *Chem. Reviews* **58**, 101 [1958].

¹⁵ G. E. COATES, "Organometallic Compounds", John Wiley and Sons, New York, 1960, page 136 and references cited therein.

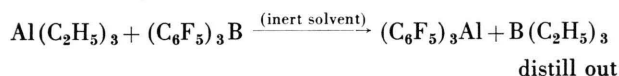
¹⁶ G. WITTIG and D. WITTENBERG, *Liebigs Ann. Chem.* **606**, 13 [1957].

intra- or inter-molecular F-abstraction processes is involved¹⁷. This could lead to intermediates of fluorobenzynes structure¹⁸ whose rapid decomposition may parallel that of the halo acetylides^{19, 20}.

Exchange reactions of diarylmercury with aluminum and reaction between triarylboron and triethylaluminum are two methods which lead directly to uncomplexed triphenylaluminum²¹. The employment of these methods were alternative routes for the preparation of uncomplexed tris-(pentafluorophenyl)-aluminum.

Excess aluminum wire was carefully activated and refluxed in toluene with bis-(pentafluorophenyl)-mercury. The amount of mercury produced after several days still was negligible. Activation with mercury halides, alkyl halides, or bromo-pentafluorobenzene did not show significant improvement. Carbon tetrachloride seemed to initiate a reaction, but only tar was ultimately recovered from the hydrocarbon solution.

The other exchange reaction should proceed according to the following scheme.



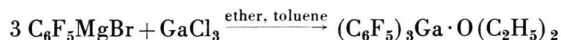
A first run without solvent led to an explosion as soon as the bath temperature reached 70°. When the experiment was repeated at 50° an air-sensitive liquid was collected in a trap. It gave a positive boron test, but its infrared spectrum did not completely agree with that of triethyl boron (C—F bonds). Thus, the liquid was believed to contain an ethylpentafluorophenylborane as impurity. From this reaction, however, no aluminum derivatives could be isolated. When the same exchange was performed in a hydrocarbon, mainly tar was obtained. Isolation of aryl aluminum compounds as trimethylamine complex in these experiments also failed.

¹⁷ F. G. A. STONE, private communication. Bis-(π -cyclopentadienyl)-bis-(pentafluorophenyl)-zirconium violently decomposed, when heated beyond its melting point. Such rapid decomposition at higher temperatures seems to be a more general behavior of pentafluorophenyl-substituted metals and not limited to aluminum only. Indeed, Stone has found that $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{F}_5)_2$ can undergo controlled pyrolysis at 150° to give small amounts of $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{F}_5)\text{F}$, see reference 4.

¹⁸ P. L. COE, R. STEPHENS, and J. C. TATLOW, J. chem. Soc. [London] **1962**, 3227.

Gallium

Revived interest in the chemistry of arylgallium derivatives is evidenced by the recent work of Russian authors²², who employed the Grignard route with success. Similar to their method, gallium trichloride was treated with pentafluorophenylmagnesium bromide to yield beautiful, colorless prisms which, after purification, gave the proper analysis for the etherate of tris-(pentafluorophenyl)-gallium, m.p. 169° – 171°.



This hygroscopic compound was readily sublimed without loss of ether. In benzene solutions, it displayed monomeric behavior.

Indium

The chemistry of indium has not yet been widely explored, although the most common organoindium derivatives are known. Triphenylindium was prepared by RUNGE and coworkers²³ from indium metal and diphenylmercury.

In order to synthesize the fluoro analogue, indium tribromide was treated with pentafluorophenylmagnesium bromide; a crystalline product similar to the aluminum and the gallium reactions resulted, but this contained halogen. Following sublimation, the reaction product was analyzed for bis-(pentafluorophenyl)-indium bromide and was found to be dimeric in benzene.

Interestingly enough, complete substitution on indium tribromide is not obtained on forcing the conditions—only a better yield of dimeric bis-(pentafluorophenyl)-indium bromide is achieved. In addition, an air-stable viscous fluoroaromatic oil was isolated; this was studied separately.

In sharp contrast, tris-(pentafluorophenyl)-indium etherate was obtained by rather mild treatment of indium trichloride with the Grignard solution of

¹⁹ W. J. MIDDLETON and W. H. SHARKEY, J. Amer. chem. Soc. **81**, 803 [1959].

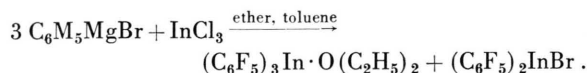
²⁰ H. G. VIEHE (Union Carbide), Dtsch. Pat. 1 126 388, 1 126 389, 1 126 390 C. A. **58**, 6860 c, 10235 d (1963).

²¹ J. R. SURTEES, Rev. pure appl. Chemistry **13**, 91 [1963] and references cited therein.

²² I. M. VICTOROVA, N. I. SHEVERDINA, E. D. DELINSKAYA, and K. A. KOCHVESHKOV, Doklady Akad. Nauk., SSSR **152**, 609 [1963].

²³ F. RUNGE, W. ZIMMERMANN, H. PFEIFFER, and I. PFEIFFER, Z. anorg. Chem. **267**, 39 [1951].

bromopentafluorobenzene. As coproduct, an amber fraction was distilled off *in vacuo*; the fraction crystallized immediately. This product was thought to be bis-(pentafluorophenyl)-indium chloride, but analysis proved that it was mainly the corresponding bromide.

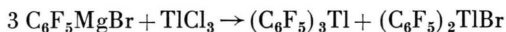


Therefore, a competitive halogen exchange must be operative and lead to the rather unreactive dimeric bis-(pentafluorophenyl)-indium bromide which, once formed like its corresponding thallium derivative⁶, is not affected by excess Grignard reagent.

Thallium

Until now, trisubstituted organothallium compounds were obtained by methods involving the use of organolithium reagents since all reactions with the less reactive Grignard reagent led only to very stable disubstituted thallium halides^{6, 24}.

For the special case where we reacted thallium trichloride with pentafluorophenylmagnesium bromide in a boiling hydrocarbon, a thallium compound was obtained which was free of halogen. Infrared spectrum and elemental analysis have verified this compound as tris-(pentafluorophenyl)-thallium. It is a very hygroscopic, white solid (m.p. 139°–141°) which readily sublimes *in vacuo*. In benzene solution, it displays monomeric behavior, and with ether it forms a 1 : 1 complex which is stable at room temperature but dissociates partially in benzene solution or completely upon heating up to 80°. From the resulting reaction mixture, bis-(pentafluorophenyl)-thallium bromide also was recovered;



As with indium, a competitive halogen exchange versus aryl substitution occurred but at such a rate that the tri-substitution of thallium seems to be the preferred route under the conditions employed.

²⁴ G. E. COATES, "Organometallic Compounds", John Wiley and Sons, New York 1960, page 155.

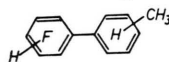
²⁵ E. F. P. FEAR, M. A. WHITE, and J. THROWER, Royal Aircraft Establishment, Report RAE TN CPM 26, August 1963; see also J. THROWER and M. A. WHITE, 148th Natl. Meeting Amer. chem. Soc. Sept. 1964, Chicago, Ill. USA, Abstr. p. 19k.

* Very recently the same reaction product was reported by VOROZHTSOV, BARKHASCH, IVANOVA, and PETROV in Tetrahedron Letters 47, 3575 [1964]. They also propose tetra-

Investigations of Side Products

Two types of side products resulted from all reactions—a volatile oil and a very viscous tar which was left as residue from sublimation. These amounts were negligible except in the more enforced reaction between indium tribromide and pentafluorophenylmagnesium bromide where the products seemed to be formed independently from the metal halide used (identical infrared spectra).

The Grignard solution of bromopentafluorobenzene was prepared and treated in the same fashion as done for all arylation reactions but without any metal halide present. A reaction mixture was obtained from which a volatile oil could be distilled off in a sharp fraction, and then a viscous glass could be isolated. The glass did not show any distinct boiling point since it was distilled in a very wide temperature range and contained bromine²⁵. Thus, efforts were concentrated on the fraction boiling first. Elemental analysis, cryoscopic molecular-weight determinations, and a mass spectrum of this material provided data for isomers whose formula, C₁₃H₈F₄, most likely is in accord with that of a methyl tetrafluoro diphenyl,



Infrared and NMR spectra appear to confirm this assumption. Repeated fractional distillations, although giving narrow boiling fractions, revealed a mixture of two isomers upon vapor-phase chromatographic analysis. Certainly an F-abstraction mechanism of formation cannot be ruled out, but separation of products and exact determination of structural features must await a more detailed examination of the course of this interesting reaction*.

Experimental

High-grade anhydrous metal halides were obtained from commercial suppliers (Alpha Inorganics, Beverly, Mass.) and directly used. Boron trifluoride etherate was

fluorobenzene as the reacting intermediate and a H-abstraction from toluene leading to methyl-2'.3'.4'.5'-tetrafluoro diphenyl, wherein the position of the methyl group is not specified. This is in good agreement with our findings, but as we definitely obtained two isomers a more general reaction mechanism occurs.

The abstraction of fluorine from the pentafluorophenyl group is not limited to magnesium only but also prevails with other electropositive metals; e.g. compare our findings for Al as well as STONE's results for Zr and Ti; ref. 1. c.¹⁷.

distilled prior to use and thallium trichloride was prepared by chlorination of thallium monochloride. solvents were distilled from sodium prior to use.

All reactions were carried out under an atmosphere of purified, dry nitrogen and conducted in standard laboratory glassware. All open manipulations such as weighing and transfer of material and sampling of organometals were carried out in an efficient recirculating drybox.

1. Tris-(pentafluorophenyl)-metal Compounds

A general working procedure for all tris-(pentafluorophenyl)-derivatives of Group IIIA is given in detail.

a) General Procedure

An ether solution (100 ml) containing 60 mmoles pentafluorophenyl-magnesium bromide was vigorously stirred in a cold bath. At -20° to 0° the anhydrous metal halide (20 mmoles) cautiously was added in n-hexane or toluene (slurry or solution). Immediate reaction was observed. Within 10 to 20 minutes the addition was completed and the cold bath was removed. Stirring was continued and heating was started after 1 hour. After another hour, absolute toluene was added and ether gradually distilled off, the reflux temperature being raised from about 35° to about 110° . At approximately 100° the black reaction mixture precipitated gray salts and the solution appeared to be brown or yellow. The mixture was generally refluxed for 1 to 3 hours, but refluxing was maintained for periods up to 19 hours when the solutions discolored slowly.

All precipitated salts were filtered from the hot solution and the solvent partially removed under reduced pressure. Crystals formed upon leaving the so-

lution overnight except in case of the boron product. A second or third crystal fraction was obtained after further concentration of the mother liquor. These fractions, in case of indium and thallium, consisted of disubstituted products only. The remaining residue was either treated with n-hexane, or attempts were made to sublime or distill it. Caution: If decomposition is observed, the heating has to be stopped immediately and the fractions discarded.

b) Purification

The raw product obtained was purified by vacuum sublimation, but where necessary the crude material was recrystallized from toluene/n-hexane in order to remove tarry impurities. All sublimations were carried out with quantities not to exceed 2 g; they were conducted *in vacuo* (0.05 mm Hg) at temperatures about 10° to 5° below the melting point of the substances. Tris-(pentafluorophenyl)-boron was distilled directly off the residue of its reaction solution. Its etherate as well as tris-(pentafluorophenyl)-thallium etherate was obtained in pure form by dissolving the uncomplexed compounds in small amounts of ether, evaporating excess solvent, and drying the precipitated crystals between filter paper.

c) Properties

Tris-(pentafluorophenyl)-derivates of Group IIIA elements are air-sensitive, hygroscopic, white solids. They are soluble in benzene, toluene and ether. Physical and analytical data are included in the Table. The results of the infrared spectra taken in fluorolube show an identical pattern for all metal compounds with these characteristic frequencies at 1645 cm^{-1} ($\text{C}=\text{C}$), 1520 cm^{-1} , and 1500 cm^{-1} diagnostic for the aromatic

Compound	Starting halide	Yield [%]	Melting point [$^{\circ}\text{C}$]	Mol. wt. ¹		Side products		Analysis ^{2, 3}			
				Calcd	Found	Compound	%	C	H	F	Metal
$(\text{C}_6\text{F}_5)_3\text{B} \cdot \text{O}(\text{C}_2\text{H}_5)_2$	— ⁴	quant.	dec.	586	(378) (374) (355)	—	—	45.08 44.81	1.72 1.74	48.62 48.89	1.84 2.09
$(\text{C}_6\text{F}_5)_3\text{Al} \cdot \text{O}(\text{C}_2\text{H}_5)_2$	AlCl_3	67	173—175	602	599	—	—	43.87	1.67	47.32	4.48
	AlBr_3	67			619	—	—	43.80	1.89	47.05	4.40
$(\text{C}_6\text{F}_5)_3\text{Ga} \cdot \text{O}(\text{C}_2\text{H}_5)_2$	GaCl_3	65	169—171	645	653	—	—	40.96	1.56	44.18	10.81
					659	—	—	41.22	1.72	44.10	10.51
$(\text{C}_6\text{F}_5)_3\text{In} \cdot \text{O}(\text{C}_2\text{H}_5)_2$	InCl_3	34	137—140 ⁵	690	684	$[(\text{C}_6\text{F}_5)_2\text{InBr}]_2$ ⁶	37	38.29	1.46	41.29	16.64
	InBr_3	0					43	38.34	1.45	41.38	16.74
$(\text{C}_6\text{F}_5)_3\text{Tl} \cdot \text{O}(\text{C}_2\text{H}_5)_2$	— ⁴	quant.	dec.	780	(482)	—	—	33.89	1.29	36.55	26.21
							—	33.82	1.33	36.60	25.99
$(\text{C}_6\text{F}_5)_3\text{B}$	$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$	88	132—134	512	529	—	—	42.23	—	55.66	2.11
							—	42.12	—	55.62	2.28
$(\text{C}_6\text{F}_5)_3\text{Tl}$	TlCl_3	56	139—141 ⁵	705	771 779	$[(\text{C}_6\text{F}_5)_2\text{TlBr}]_2$ ⁷	32	30.64 30.75	—	40.39 40.21	28.96 28.73

Table 1. Analysis of pentafluorophenyl metals. ¹ Determined cryoscopically in benzene. ² Top figures for C, H, F, and Metal denote % calculated; bottom figures for C, H, F, and Metal denote % found. ³ Microanalyses were carried out by Schwarzfopf Microanalytical Laboratory, Woodside, N. Y. ⁴ Prepared by recrystallization from concentrated ethyl ether solutions. ⁵ Sintering of crystals is observed 10° — 15° below the melting point. ⁶ Mol. wt. calcd, 529; found, 1022 in benzene. ⁷ Mol. wt. calcd, 618; found, 1209 by vapor pressure osmometer in toluene.

moiety²⁶, and at about 3000 cm⁻¹ in the etherates for the C—H bonds. Proton NMR spectra provided additional identification for the ether complexes of the heavier metals.

2. Bis-(pentafluorophenyl)-metal Bromides

a) Bis-(pentafluorophenyl)-indium Bromide

This compound was obtained with 43% yield as the only reaction product of indium tribromide and with 37% yield as a side product from the reaction of indium trichloride with pentafluorophenylmagnesium bromide. It is a white, hygroscopic solid and is moderately soluble in toluene. It can be purified by vacuum sublimation, m.p. 144°—147°, with sintering observed at lower temperature. In benzene solution it is dimeric.

	C	H	F	In	Br
Calcd for (C ₁₂ F ₁₀ InBr) ₂ :					
(1058)	27.25	0.00	35.92	21.71	15.11
Found:	1022	26.97	0.00	35.76	21.98
				14.84	

b) Bis-(pentafluorophenyl)-thallium Bromide

This compound was secured as a by-product (32%) from the reaction of thallium trichloride with pentafluorophenylmagnesium bromide. Molecular-weight determinations by the cryoscopic method are not possible because of the low solubility in cold benzene. Determinations with a vapor-pressure osmometer (in toluene) showed dimeric structure for the dissolved molecule, m.p. 225°—227°, with slow decomposition (lit.⁶ 215°—217° with decomposition).

3. Miscellaneous Reactions

a) Reaction of Bis-(pentafluorophenyl)-mercury With Aluminium

In 25 ml absolute toluene, 8.03 g (15 mmoles) bis-(pentafluorophenyl)-mercury was refluxed with 1.0 g (0.037 g atom) aluminium. After 2 hours no change was observed. On addition of one drop carbon tetrachloride, however, the solution turned dark red, and mercury droplets were observed within another hour of reflux.

After 2 days of reflux, 1.75 g (60% of theory) metallic mercury was obtained. Upon working up the red solution, a dark tar was found from which no compound could be isolated.

b) Reaction of Tris-(pentafluorophenyl)-boron With Triethylaluminium

In a closed and evacuated system, 7.50 g (14.7 mmoles) tris-(pentafluorophenyl)-boron was treated with 2.0 ml, 1.68 g (14.7 mmoles) triethylaluminium.

Some gas generation was observed. Heat was applied cautiously, but at a 70° bath temperature a violent detonation smashed the apparatus.

This experiment was repeated at a 50° bath temperature. A trace of a waterclear oil condensed into a trap, and after hydrolyzation it gave a positive boron test. From the tarry residue, no aluminium compound could be secured.

For another attempt, the reaction was carried out in boiling toluene. As toluene partially distilled off at 108°, a volatile boron compound could be detected. After 4 hours of reflux, the solvent was removed under reduced pressure. No aluminium compound could be separated from the remaining dark residue.

c) Reaction of Pentafluorophenylmagnesium Bromide With Toluene

In the same way as the metal derivatives were prepared, the Grignard reagent was reacted by itself with toluene. The magnesium salts and the solvent were removed, and a yellow, viscous oil was obtained. From this material a fraction could be distilled off before the distillate became viscous, high-boiling and yellow.

After refractionation, the lower boiling fraction was analyzed. It seemed to be a mixture of two isomeric methyltetrafluorodiphenyls, b.p. 79°/0.75 mm Hg.

		C	H	F
Calcd for C ₁₃ H ₈ F ₄ :	(240)	65.01	3.36	31.63
Found:	240	65.03	3.39	31.72

A mass spectrum run on the analyzed mixture revealed major peaks at m/e 240 (parent fragment), m/e 225 (—CH₃ loss), and m/e 202 (—loss of two F atoms).

Conclusions

The Grignard reagent of bromopentafluorobenzene can be used for the successful preparation of the trisubstituted pentafluorophenyl derivatives of all the Group III A elements. In all cases, the synthesis appears to afford the ether complexes; but because of the conditions of separation and purification, the boron and thallium compounds are secured in uncomplexed, monomeric form from which the 1 : 1 etherates can be prepared easily.

The relative order of stability toward dissociation of the tris-(pentafluorophenyl)-metal etherates appears to parallel that generally accepted for their phenyl analogues. It is likely, however, in the aluminium, gallium and indium complexes that the metal-oxygen dative bond is considerably stronger than with their comparable phenyl derivatives. Their etherates could be sublimed readily *in vacuo*, but all efforts to strip off the complexing solvent from

²⁶ D. A. LONG and R. T. BAILEY, *Trans Faraday Soc.*, **59**, 599 [1963] and references cited therein.

tris-(pentafluorophenyl)-aluminum etherate failed. Under enforced conditions, however, violent decompositions were experienced.

Some interesting deviations were found in the synthesis of the indium and thallium derivatives. Contrary to previous experience, indium indicates a significant stabilization in the dimeric bis-(pentafluorophenyl)-indium bromide since this is the only reaction product obtained from the treatment of indium tribromide with pentafluorophenylmagnesium bromide, and can be obtained as coproduct in considerable yield when indium trichloride is employed instead. In this regard, the preparation of the indium derivatives is dependent on the halide used and resembles that of thallium.

To our knowledge, we are the first to report the direct preparation of a trisubstituted organothallium compound by the Grignard route. A part

of the intermediate products underwent halogen exchange and resulted in the known, dimeric bis-(pentafluorophenyl)-thallium bromide. This novelty in the chemistry of organothallium compounds obviously is made possible by the significant thermal stability of pentafluorophenylmagnesium bromide. This reagent decomposes slowly in boiling toluene to form a variety of products of which only the lowest boiling product can be isolated. For these isomeric fluorine-containing aromatic hydrocarbons, the structures of methyltetrafluorodiphenyls are proposed.

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Polymerisation von Methacrylsäuremethylester unter stiller elektrischer Entladung

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Reiner Methacrylsäuremethylester (MM) kann unter stiller elektrischer Entladung bei Temperaturen polymerisiert werden, bei welchen eine thermische Polymerisation nicht möglich ist. Das gleiche gilt für MM, welchem Metallcarbonyle zugesetzt sind.

Zugabe von Metallcarbonylen und Tetrachlorkohlenstoff zu MM ermöglicht die entladungschemische Polymerisation bei 50° mit hohen Ausbeuten unter Bildung hochmolekularer Produkte.

Vinylmonomere $R_2C=CHX$ können kationisch, anionisch und radikalisch polymerisiert werden. Die radikalische Polymerisation kann entweder thermisch bei höheren Temperaturen erzwungen werden, wobei das Monomere die zur Initiierung notwendigen Radikale liefert oder man setzt dem Monomeren Substanzen zu, welche leicht in Radikale zerfallen. Weiterhin kann die radikalische Polymerisation auch photochemisch oder strahlenchemisch mit γ -Strahlen durchgeführt werden. Nun ist bekannt, daß organische Moleküle unter dem Einfluß der stillen elektrischen Entladung in Radikale der verschiedensten Arten aufgespalten werden¹, wobei sich die Bruchstücke vorwiegend in der Gasphase bilden.

Uns interessierte nun die Frage, ob Vinylmonomere, welche bei Raumtemperatur nicht polymerisie-

ren, unter dem Einfluß der bei einer stillen elektrischen Entladung gebildeten Radikale polymerisiert werden können, ohne daß zunächst eine Hilfskomponente als Initiator zugesetzt wird. Orientierende Versuche mit reinem Methacrylsäuremethylester (MM) ergaben eine glatte Polymerisation, welche im Gegensatz zu der photochemisch initiierten, langsam verläuft, so daß die Abführung der Reaktionswärme keine Schwierigkeit bereitet. Wir haben daher am MM die Polymerisation des Monomeren unter dem Einfluß der stillen elektrischen Entladung genauer untersucht und in Beziehung zur thermischen Polymerisation gesetzt.

Ein-Komponentensystem

Die Ergebnisse der thermischen und entladungschemischen Polymerisation von reinem MM sind in Tab. 1 zusammengefaßt. Die Grenzviskosität $[\eta]$ und der Erweichungspunkt $Schp$ des Polymeren nimmt

¹ Siehe z. B. TH. RUMMEL, Hochspannungsentladungschemie und ihre industrielle Anwendung. München 1951; Verlag von R. Oldenbourg und H. Reich, Verlag.