Polyfluoroaryl Organometallic Compounds. Part IV.[1,2] Fluorocarbon Derivatives of Tricovalent Aluminium

By **R. D. Chambers** and **J. A. Cunningham**, University Science Laboratories, South Road, Durham

Pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide have been prepared by cleavage of methylpentafluorophenylmercury with aluminium tribromide. The bromides are both essentially dimeric in benzene and the stability of the compounds, formally three-covalent, is attributed to a combination of bromine bridging and internal p–π bonding; the latter is indicated by ^{19}F n.m.r. measurements. Pentafluorophenylaluminium dibromide can be sublimed, with some disproportionation, but no Al–F bonds are formed, although at higher temperatures explosive decomposition occurs. Some reactions of pentafluorophenylaluminium dibromide are described, as well as unsuccessful attempts to prepare tris(pentafluorophenyl)aluminium.

EARLIER work in this Series included a study of pentafluorophenylboron derivatives and it was concluded that, unlike polyfluoro-alkyl or -vinyl boron compounds, the polyfluoroaryl derivatives do not decompose by a process involving ready migration of fluorine from carbon to boron.[3] This increased stability was partly attributed to internal saturation of the fourth covalency of boron by p–π bonding between boron and pentafluorophenyl.[1,3] Clearly then, an analogous process should stabilise polyfluoroaryl aluminium compounds.

The literature on fluorocarbon derivatives of aluminium is sparse, presumably because of the tendency for fluorine to migrate from carbon to aluminium. No fluoroalkyl derivative of three-covalent aluminium is known, although complexes involving four-covalent aluminium have been described[4] (*e.g.*, $Li[(C_3F_7)_2AlI_2]$, and even these compounds are unstable) and tris(trifluorovinyl)aluminium has been isolated in co-ordination with trimethylamine, $(CF_2{:}CF)_3Al{\cdot}NMe_3$.[5] We have prepared some derivatives of formally three-covalent aluminium; pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide, by utilising the easy electrophilic cleavage of methylpentafluorophenylmercury,[3] in this case by aluminium tribromide and by pentafluorophenylaluminium bromide. The former

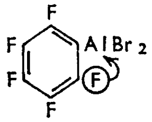
$$C_6F_5HgMe + AlBr_3 \longrightarrow C_6F_5AlBr_2 + MeHgBr$$

$$C_6F_5HgMe + C_6F_5AlBr_2 \xrightarrow{\text{petroleum}} (C_6F_5)_2AlBr + MeHgBr$$

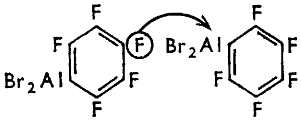
reaction was carried out by mixing the reagents neat and using an excess of aluminium tribromide; pentafluorophenylaluminium dibromide is the only component of the mixture of products which is soluble in petroleum and can be extracted. However, bis(pentafluorophenyl)aluminium bromide as usually obtained contains methylpentafluorophenylmercury, since an excess of the latter is necessary in the reaction to avoid obtaining an inseparable mixture of mono- and di-bromide; a pure product is only obtained by prolonged high vacuum evaporation of the remaining mercurial. Like alkyl- and aryl-derivatives of aluminium, these compounds are extremely air- and moisture-sensitive; they can inflame in air and explode during uncontrolled hydrolysis. They were characterised by analysis for bromine after careful hydrolysis, and by gravimetric analysis for aluminium. Also, controlled hydrolysis gave a quantitative amount of pentafluorobenzene from pentafluorophenylaluminium dibromide, but hydrolysis of bis(pentafluorophenyl)aluminium bromide was always accompanied by charring and the yield in this case was not quantitative.

These are the first fluorocarbon derviatives of three-covalent aluminium to be characterised; an attempt was made to establish the limits of their thermal stability:

(*a*) The dibromide was heated slowly, under vacuum, to 140° during three hours while the compound melted (69°) and slowly sublimed on to a cold finger (80—90°) as a white solid. The melting point of this solid was lower (59—60°) than that of the starting material and it has a higher bromine content. However, although some disporoportionation obviously occurs, this result shows that the compound can be sublimed without significant intramolecular (A) or intermolecular (B) migration of fluorine from carbon to aluminium.



(A)



(B)

(*b*) There was no sign of general decomposition when the dibromide was heated to 100° for twelve hours, under vacuum, in a sealed tube; after twentyfour hours at 160° the liquid became deep red, and at 180° carbonisation occurred within thirty minutes.

(*c*) When the dibromide was heated rapidly, under vacuum, in a sealed tube, violent explosion occurred at 195°.

These results, coupled with the fact that boron compounds disproportionate,[3] $2C_6F_5BF_2 \longrightarrow (C_6H_5)_2BF + BF_3$, suggest that the decomposition occurs through an initial disproportionation at high temperature, $3C_6F_5AlBr_2 \longrightarrow Al(C_5F_5)_3 + 2AlBr_3$, under conditions where the tris(pentafluorophenyl)aluminium is unstable. Other workers have observed explosions when attempting to obtain the latter compound unco-ordinated,[6] and

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[1] Part III, R. D. Chambers, T. Chivers, and D. A. Pyke, *J. Chem. Soc.*, 1965, 5144.

[2] Preliminary Communication, R. D. Chambers and J. A. Cunningham, *Tetrahedron Letters*, 1965, 2389.

[3] R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 1965, 3933; *Organometallic Chem. Rev.*, 1966, **1**, 279.

[4] M. Hauptschein, A. J. Saggiomo, and C. S. Stokes, *J. Amer. Chem. Soc.*, 1956, **78**, 680.

[5] B. Bartocha and A. J. Bilbo, *J. Amer. Chem. Soc.*, 1961, **83**, 2202.

[6] J. L. W. Pohlmann and F. E. Brinkmann, *Z. Naturforsch.*, 1965, **20***b*, 5.

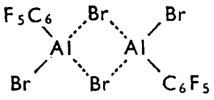
their observations and our own (see later) indicate that it will be very difficult to obtain. Even the classical method of heating a diaryl mercurial, $(C_6F_5)_2Hg$, with aluminium powder was unsuccessful.[7] It may eventually be possible to isolate tris(pentafluorophenyl)-aluminium by a very careful disproportionation of bis-(pentafluorophenyl)aluminium bromide, $3(C_6F_5)_2AlBr \longrightarrow 2(C_6F_5)_3Al + AlBr_3$, but we have not yet investigated this system sufficiently.

Both pentafluorophenylaluminium dibromide and bis(pentafluorophenyl)aluminium bromide were shown to be essentially dimeric in benzene solution. Bridging by fluorine in the pentafluorophenyl group, $-C_6F_4-F-Al\equiv$, although unlikely, can be discounted because of the similarity of the ^{19}F n.m.r. spectra for the mono- and di-bromides and for the etherate (see Table), where bridging will be absent. We cannot distinguish between structures (I) and (II) for pentafluorophenylaluminium dibromide, although we prefer (I).

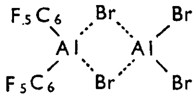
^{19}F Chemical shifts for pentafluorophenylaluminium compounds

Compound	*ortho*	*meta*	*para*
$(C_6F_5AlBr_2)_2$*	−41	−2·8	−15·1
$C_6F_5AlBr_2,OEt_2$ ...	−41	−1·3	−10·8
$(C_6F_5)_2AlBr$*	−41	−2·6	−13·8

* Solution in petroleum.



(I)



(II)

The *para*-fluorine chemical shift is very dependent on resonance interaction of a substituent with the aromatic ring[8,9] and we concluded from the large (*ca.* 10 p.p.m.) difference in *para*-fluorine shift between the three- and four-covalent pentafluorophenylboron compounds[3] that $p-\pi$ overlap is involved in the former. There is a *para*-fluorine shift of *ca.* 5 p.p.m. between pentafluorophenylaluminium dibromide and the corresponding etherate and this means that the system is also stabilised by internal $p-\pi$ bonding from aluminium to pentafluorophenyl as well as the bromine bridging. Also, $p-\pi$ bonding accounts for the order, towards high field, of the *para*-fluorine shifts: $C_6F_5AlBr_2 < (C_6F_5)_2AlBr < C_6F_5AlBr_2,OEt_2$. Donation from the ring would be greatest in the first of the series and insignificant in the last.

Reaction between a large excess of methylpentafluorophenylmercury and aluminium tribromide produced mixtures which were difficult to separate; preparation of the monobromide is only possible by the two-step procedure already described because the one-step reaction $AlBr_3 + 2MeHgC_6F_5 \longrightarrow (C_6F_5)_2AlBr + 2MeHgBr$ does not give a pure product. Similarly, we were unable to obtain complete reaction leading to tris(pentafluorophenyl)aluminium this way, or from the monobromide. We have also investigated the reaction

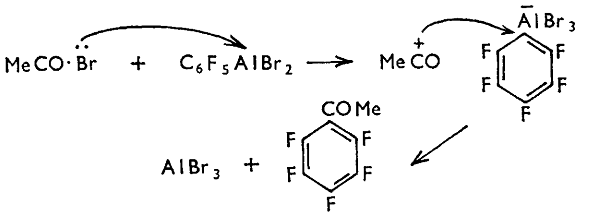
$$MeHgC_6F_5\text{ (excess)} + AlBr_3 \longrightarrow Al(C_6F_5)_3 \longleftarrow (C_6F_5)_2AlBr + MeHgC_6F_5$$

of aluminium tribromide with pentafluorophenyllithium and found, like other workers,[6] who used pentafluorophenylmagnesium bromide that with ether as solvent, tris(pentafluorophenyl)aluminium etherate, from which we were unable to remove ether, is formed. With pentafluorophenyl-lithium in hydrocarbon solvents, we could not isolate any pentafluorophenyl derivatives; this suggests that tris(pentafluorophenyl)-aluminium, a very strong acceptor, reacts preferentially when formed with pentafluorophenyl-lithium to give salts of the type isolated previously from reaction between lithium aluminium hydride and bromopentafluorobenzene,[10] *e.g.*, $Li[Al(C_6F_5)_3Br]$.

$$\begin{tikzcd}
C_6F_5Li + AlBr_3 \arrow[r] & Li[C_6F_5AlBr_3] \arrow[r, "C_6F_5Li"] & Li[(C_6F_5)_3AlBr] \arrow[d] \\
 & & Li[(C_6F_5)_4Al]
\end{tikzcd}$$

The white solid residues contained pentafluorophenyl (infrared), but no material could be extracted with a variety of solvents including benzene, in which the complexes isolated by Dickson[10] were soluble. We conclude that these routes are not suitable for the isolation of uncomplexed tris(pentafluorophenyl)-aluminium.

Reactions.—Pentafluorophenylaluminium dibromide forms co-ordination complexes with ether and with trimethylamine; it does not react with carbon dioxide and only forms a co-ordination complex with benzophenone, which when hydrolysed gives quantitative recovery of benzophenone. However, with acid halides, *i.e.*, acetyl bromide and benzoyl chloride, the corresponding pentafluorophenyl ketones are formed. These last reactions can probably be regarded as Friedel–Crafts reactions with the substrate acting as its own 'catalyst.' Results of some reactions with olefins and acetylenes will be published later.



It is difficult at this stage to compare adequately the pentafluorophenyl- and phenyl-aluminium compounds since relatively little is known about phenylaluminium

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[7] J. Burdon, P. L. Coe, and M. Fulton, *J. Chem. Soc.*, 1965, 2094.

[8] R. W. Taft and J. W. Rakshys, *J. Amer. Chem. Soc.*, 1964, **87**, 4387, and references therein.

[9] I. J. Lawrenson, *J. Chem. Soc.*, **1965**, **1117**.

[10] R. S. Dickson, *Chem. Comm.*, 1965, 68; *Austral. J. Chem.*, 1966, **19**, 2073.

dihalides.[11] However, the instability of unco-ordinated tris(pentafluorophenyl)aluminium is a pointer to greater electron accepting powers of the latter than of triphenylaluminium.

The cleavage reactions described involved methylpentafluorophenylmercury, which was most satisfactory because it could easily be sublimed off. However, in some cleavage reactions ethylpentafluorophenylmercury is useful because of its long-term stability. Although the equilibrium, $Me_2Hg + (C_6F_5)_2Hg \rightleftharpoons 2MeHgC_6F_5$, lies well to the right,[12,13] dimethylmercury can slowly be lost and disproportionation occurs. Diethylmercury, with a lower vapour pressure, is less easily lost from the system and, consequently, ethylpentafluorophenylmercury is more stable. Previous work [12] indicated that bis(pentafluorophenyl)mercury is resistant to electrophilic cleavage. In agreement with this, an equimolar mixture of this compound and aluminium tribromide only reacted at elevated temperatures, to give an inseparable mixture of $C_6F_5AlBr_2$ and $(C_6F_5)_2AlBr$.

EXPERIMENTAL

The aluminium compounds described are extremely oxygen- and moisture-sensitive and, consequently, the operations described, including weighing, were carried out with the aid of a glove-box through which was circulated oxygen-free nitrogen dried in traps at liquid-air temperature. ^{19}F n.m.r. measurements were obtained (by D. Dyson) with an A.E.I. RS2 spectrometer.

Pentafluorophenylaluminium Dibromide.— Methylpentafluorophenylmercury [12] (6·6 g., **17** mmoles) was melted through a narrow funnel into a previously constricted Carius tube with a ground-glass joint. The tube was then evacuated and introduced into a glove-box where freshly-sublimed aliminium tribromide (5·3 g., 20 mmoles) was ground-up and carefully added to the mercurial in the tube. The tube was again evacuated and cooled in liquid air; any adhering aluminium tribromide was sublimed away from the constriction before the tube was sealed under high vacuum. When warmed to room temperature the mercurial melted and the mixture became a viscous mass. The tube was then heated in an oil-bath at 70° for 5 days. The hard crystalline product was extracted with several small volumes (*ca.* 5 × 20 ml.) of dry petroleum, b. p. 40°, and the combined extracts were filtered (sinter) into a dry, weighed, two-necked 250 ml. flask which was then closed by means of a tap and joint (containing a sinter) and connected to a vacuum system. The solvent was removed by vacuum transfer (the sinter prevented splashing of reactive aluminium compounds into the vacuum system) and a viscous liquid remained. This was kept under vacuum for several hours during which time any remaining methylpentafluorophenylmercury sublimed, and the residue solidified to give *pentafluorophenylaluminium dibromide* (5·8 g., 97%), m. p. 69—71° (Found: Al, 7·7; Br, 45·6. $C_6AlBr_2F_5$ requires Al, 7·6; Br, 45·2%). The residue, which was insoluble in petroleum, was methyl mercury bromide (6·0 g., 100%).

Characterisation of Pentafluorophenylaluminium Dibromide.—Aluminium was estimated gravimetrically. A long-necked silica flask (150 ml.) was heated strongly for 1 hr. in a bunsen flame and cooled in a desiccator (P_2O_5). Platinum wire was fixed around the neck of the flask for suspension both from the balance and for heating. After 1 hr. the aluminium compound was weighed out into the flask in the glove-box. The compound was then exposed to air for 30 min., and the derivative began to decompose. Distilled water (*ca.* 1 ml.) was added dropwise, to effect hydrolysis, followed by a mixture of concentrated sulphuric and nitric acids (1 ml.). The temperature of the mixture was gradually increased to distil off all volatile material and, finally, the flask was ignited for 1 hr. The flask was cooled in a desiccator and reweighed.

Quantitative hydrolysis was also effected with a vacuum system. Pentafluorophenylaluminium dibromide (0·64 g., 1·8 mmoles) in a dry 200 ml. flask was transferred under nitrogen to a vacuum system where water (0·14 g., 8 mmoles) was condensed on to it. At this stage the flask was cooled in liquid air; a vigorous reaction took place as it was warmed slowly to room temperature. When reaction was complete, all volatile material was transferred to a second trap containing phosphorus pentoxide. Dry volatile products were collected in a weighed evacuated bulb and weighed; the product was shown to be pentafluorobenzene (0·229 g., 99%) by its infrared spectrum and by gas chromatography.

Bromine was estimated by careful hydrolysis of a sample and use of the Vieböck method. Molecular weights were determined by a cryoscopic technique adapted for air- and moisture-sensitive compounds. A mean value of 650 was recorded for the molecular weight in benzene ($C_6F_5AlBr_2$ requires 354).

Bis(pentafluorophenyl)aluminium Bromide.—By techniques similar to those described, a solution of methylpentafluorophenylmercury (5·7 g., 15 mmoles) in petroleum (*ca.* 10 ml.) was introduced into a Carius tube and pentafluorophenylaluminium dibromide (3·0 g., 8 mmoles) was added. The tube was then sealed under vacuum and heated in an oil-bath for 96 hr. at 45°. The product was filtered (sinter) into a weighed 100 ml. flask. The residue was extracted with solvent (5 × 10 ml.) and the extracts were filtered into the flask. The solvent was then removed by vacuum transfer, to leave a light brown viscous liquid, which was kept under high vacuum for 8 hr. during which time the excess of methylpentafluorophenylmercury sublimed and the *bis(pentafluorophenyl)aluminium* bromide (2·8 g., 80%) slowly crystallised (Found: Al, 6·2; Br, 18·1. $C_{12}AlBrF_{10}$ requires Al, 6·1; Br, 18·1%). Aluminium was estimated as before. Attempts at controlled hydrolysis were unsuccessful; charring occurred under all conditions used and only *ca.* 80% of the theoretical amount of pentafluorobenzene was recovered. Molecular weight 730 (mean value) [$(C_6F_5)_2AlBr$ requires 441].

Reactions of Pentafluorophenylaluminium Dibromide.—(a) *With trimethylamine*. Trimethylamine (2·0 g., 34 mmoles) was condensed from a vacuum system into pentafluorophenylaluminium dibromide (3·0 g., 8·4 mmoles). An exothermic reaction took place when the mixture warmed to room temperature and, after several hours, the excess of amine was pumped off to leave *pentafluorophenylaluminium dibromide–trimethylamine*, m. p. 42° with loss of trimethylamine (Found: Al, 6·2; Br, 38·4. $C_9H_9AlBr_2F_5N$ requires Al, 6·5; Br, 38·8%).

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[11] J. R. Surtees, *Rev. Pure Appl. Chem.*, 1963, **13**, 91; R. Koster and P. Binger, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 263, and references therein.

[12] R. D. Chambers, G. E. Coates, J. G. Livingstone, and W. K. R. Musgrave, *J. Chem. Soc.*, 1962, 4367.

[13] M. D. Rausch and J. Van Wazer, *Inorg. Chem.*, 1964, 761.

(b) *With benzophenone.* A mixture of pentafluorophenylaluminium dibromide (1·45 g., 4 mmoles) in hexane (*ca.* 25 ml.) and benzophenone (0·73 g., 4 mmoles) was stirred for 12 hr. and the solvent was removed under vacuum. A viscous oil remained which crystallised after it was warmed to 70° under vacuum. Hydrolysis of an aliquot of the solid gave pentafluorobenzene (infrared) and a quantitative amount of benzophenone. The same result was obtained by heating the reactants to 100° for 96 hr.

(c) *Acetyl bromide.* A solution of acetyl bromide (1·0 g., 8 mmoles) in hexane (*ca.* 5 ml.) was added dropwise to pentafluorophenylaluminium dibromide (1·0 g., 3 mmoles) in hexane (20 ml.) under nitrogen. The mixture turned red immediately and was heated under reflux for 15 min. It was then hydrolysed with ice–water and the organic layer was separated and dried ($MgSO_4$). The solvent was removed to leave pentafluoroacetophenone (0·5 g., 80%) characterised by comparison of its infrared spectrum with that of an authentic sample prepared from pentafluorophenylmagnesium bromide and acetyl chloride[14] (Found: C, 46·0; F, 45·5. Calc. for $C_8H_3F_5O$: C, 45·7; F, 45·2%).

(d) A mixture of benzoyl chloride (0·88 g., 6 mmoles) and pentafluorophenylaluminium dibromide (2·2 g., 6 mmoles) was heated in a sealed, evacuated Carius tube to 80° for 96 hr. A red colour was produced when the reactants were mixed and progressive darkening occurred on heating The mixture was then poured into ice–water and neutralised with sodium hydrogen carbonate. Extraction with ether and removal of the solvent after drying ($MgSO_4$) gave a viscous liquid from which 2,3,4,5,6-pentafluorobenzophenone (1·2 g., 70%) was sublimed under high vacuum, m. p. 33° (lit.,[14] 33—34°) (Found: C, 57·2; H, 2·1. Calc. for $C_{13}H_5F_5O$: C, 57·4; H, 1·9%).

Attempted Preparation of Pentafluorophenylaluminium Derivatives from Aluminium Tribromide and Pentafluorophenyl-lithium.—Aluminium tribromide (1·6 g., 6 mmoles) suspended in hexane (15 ml.) was added to a solution of pentafluorophenyl-lithium (6 mmoles), in hexane (20 ml.) at −65°, formed from n-butyl-lithium (2 ml., 6 mmoles) and pentafluorobenzene (1·0 g., 6 mmoles). After 0·5 hr. at −65°, the mixture was left to warm to room temperature and filtered in a glove-box; solvent was removed by vacuum transfer to leave a little viscous yellow oil which did not contain pentafluorophenyl (infrared). Extraction of the solid residue with benzene, toluene, or light petroleum also did not yield a pentafluorophenyl derivative. However, the infrared spectrum of the residue showed the presence of pentafluorophenyl. Similar reactions with an excess of pentafluorophenyl-lithium and benzene as a co-solvent for the aluminium tribromide gave the same result. With hexane–ether as solvent an etherate was isolated (cf. ref. 6) from which the ether could not be removed.

Pentafluorophenyl Derivatives from Ethylpentafluorophenylmercury.—Ethylpentafluorophenylmercury (3·7 g., 9·3 mmoles) was placed in a previously constricted Carius tube, which was then evacuated. Boron trichloride (2·0 g., 17 mmoles) was condensed into the tube by standard vacuum techniques, and the tube was sealed under vacuum. After 2 days at room temperature the tube was opened into a vacuum system and the contents fractionated through a trap cooled to −78°, into a liquid-air trap. The trap at −78° contained a colourless liquid which was identified as pentafluorophenylboron dichloride (2·1 g., 91%) by comparison with an authentic sample. Excess of boron trichloride collected in the liquid-air trap, and the solid residue in the Carius tube was ethylmercury chloride (2·38 g., 97%).

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[14] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.