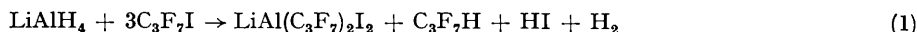


## Perfluorophenylaluminium Complexes

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VERY few compounds having fluorocarbon groups bonded to aluminium are known.<sup>1</sup> The unusual behaviour of perfluoroalkyl halides with ethereal solutions of lithium aluminium hydride has been reported.<sup>2</sup> These reactions lead to unstable perfluoroalkylaluminium complexes according to the overall stoichiometry of equation (1).



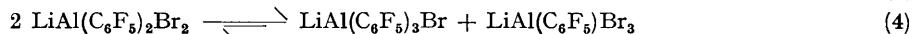
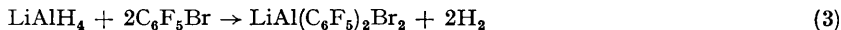
The aluminium complex could not be isolated from solution. Independently, the trimethylamine adduct of tris(perfluorovinyl)aluminium has been obtained<sup>3</sup> by the reaction (2).



This complex can be kept at  $-20^\circ$ , but undergoes decomposition at room temperature.

We now report a remarkably stable perfluorophenylaluminium complex prepared by treatment of a tetrahydrofuran solution of lithium aluminium hydride with bromopentafluorobenzene. Unlike the similar reactions with perfluoroalkyl halides (equation 1), almost all the hydrogen is evolved as molecular hydrogen in this treatment.

Under nitrogen, a solution of bromopentafluorobenzene in tetrahydrofuran was slowly added to a stirred solution of lithium aluminium hydride



in tetrahydrofuran at  $-78^\circ$ . A vigorous evolution of hydrogen occurred. After 30 min., the mixture

was allowed to warm to room temperature and was subsequently refluxed for 2 hr. Evaporation of tetrahydrofuran left a white sludge which solidified when heated *in vacuo* at  $120^\circ$ . Lithium tris(perfluorophenyl)bromoaluminate,  $\text{LiAl}(\text{C}_6\text{F}_5)_3\text{Br}$ , was obtained as an air-sensitive white solid by extraction of the solid residue with

cold benzene and subsequent evaporation of the benzene. The solid can be recrystallised from boiling cyclohexane. It will sublime at  $160^\circ$  *in vacuo*, but simultaneous decomposition is observed. The

complex was characterised by elemental analysis and its spectroscopic properties. The infrared spectrum in the range  $1500\text{--}750 \text{ cm.}^{-1}$  is very similar to those of other perfluorophenyl-metal compounds,<sup>4</sup> and the fluorine-19 magnetic resonance spectrum (20% in benzene) shows three peaks centred at 44.6, 73.7, and 83.0 p.p.m. relative to trifluoroacetic acid as reference.

Other perfluorophenylaluminium compounds are formed in the reaction, but these are not so easily purified. The following reaction stoichiometry seems to be indicated

The overall yield of the tris(perfluorophenyl) complex is approximately 30%.

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<sup>3</sup> B. Bartocha and A. J. Bilbo, *J. Amer. Chem. Soc.*, 1961, **83**, 2202.

<sup>4</sup> P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometallic Chem.*, 1963, **1**, 98; 1964, **2**, 206.