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TRISPENTAFLUOROPHENYLINDIUM COMPOUNDS

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Although pentafluorophenylthallium compounds have been studied extensively (1), only three pentafluorophenylindium compounds have been reported (2,3) Both trispentafluorophenylindium etherate and bromobispentafluorophenylindium have been isolated from the reaction of indium trichloride with pentafluorophenylmagnesium bromide, whilst $(C_6F_5)_2InBr$ has also been obtained from the corresponding reaction of indium tribromide (2). Recently trispentafluorophenylindium has been prepared by the reaction between indium and bromobispentafluorophenylthallium, and has been isolated as the complex $(C_6F_5)_3\mathbf{In}.PPh_3$ (3). We now report further preparations of trispentafluorophenylindium derivatives, including the first isolation of "free" trispentafluorophenylindium and an exploratory study of the coordination derivatives of this compound.

Trispentafluorophenylindium was prepared by reaction of iodopentafluorobenzene with an excess of indium (2.67 gm.atoms/mole C_6F_5I).

$$3\ C_6F_5I + 4\ In \xrightarrow[6\ hr.]{160^{\circ}} (C_6F_5)_3In + 3InI \qquad a.$$

Sublimation of the reaction mixture gave the required compound (31%), m.p. 176-178° (Found: C,34.7; In,19.1; mol.wt. (by osmometry in benzene under nitrogen), 634 (2.15% solution, w/v). $C_{18}F_{15}In$ requires C,35.1; In,18.6%; mol. wt., 616). It is extremely sensitive to moisture, and gives pentafluorobenzene immediately on exposure to air. The infrared spectrum (4000-700 cm^{-1}) of the compound showed absorption of medium or greater intensity at 1644, 1511, 1470, 1377, 1371, 1264, 1080, 1072, 1010, 956, 788, and 718 cm^{-1}, characteristic (4) of a pentafluorophenyl organometallic, and no hydroxyl or water absorption, and similar features were observed for all other new compounds. When the stoichiometric amounts (equation a.) of iodopentafluorobenzene and indium were heated together, iodobispentafluorophenylindium, m.p. 136-140° (Found, C,24.5; I,22.2. $C_{12}F_{10}InI$ requires C,25.0; I,22.0%)*, was obtained in addition to $(C_6F_5)_3In$, and was separated by fractional sublimation. Trispentafluorophenylindium was also prepared by the reaction:

$$3(C_6F_5)_2Hg + 2In \xrightarrow[6\ days]{170^\circ} 2(C_6F_5)_3In + 3Hg$$

It was not obtained pure, but, after treatment of the reaction mixture with ether, analytically pure $(C_6F_5)_3In.OEt_2$ (38%) was isolated. The reaction of pentafluorophenylmagnesium chloride (5) with indium trichloride in tetrahydrofuran at 0° provided a further preparative route to $(C_6F_5)_3In$ derivatives. After treatment of the product with ether/dioxan, the complex $(C_6F_5)_3In.diox$ (diox =1,4-dioxan) was isolated in 41% yield. These conditions are far milder than those used (2) for the preparation of $(C_6F_5)_3In.OEt_2$ from pentafluorophenylmagnesium bromide.

The dioxan in the complex $(C_6F_5)_3In.diox$ may be readily replaced by other neutral ligands to form complexes such as $(C_6F_5)_3In.py$, $(C_6F_5)_3In.OAsPh_3$, $(C_6F_5)_3In(DMSO)_2$, and $[(C_6F_5)_3In]_2bipy$ (py = pyridine; DMSO = dimethylsulphoxide; bipy = 2,2'-bipyridyl). Similarly, the complex $(C_6F_5)_3In(THF)_2$ was prepared by reaction of tetrahydrofuran (THF) with $(C_6F_5)_3In.OEt_2$. The complexes are generally white, moisture-sensitive solids, soluble in organic solvents, and $(C_6F_5)_3In.py$, $(C_6F_5)_3In.OAsPh_3$, $(C_6F_5)_3In(DMSO)_2$, and $(C_6F_5)_3In(THF)_2$ are monomeric in benzene. Accordingly, the first two are considered to have four coordinate indium, and the last two, five coordinate indium.

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*Satisfactory analyses were also obtained for all other new compounds.

Both $[(C_6F_5)_3In]_2$bipy and $(C_6F_5)_3$In.diox are insufficiently soluble in benzene for molecular weight determinations. The former presumably contains a bridging bipyridyl molecule and four coordinate indium, whilst the latter may be polymeric with five coordinate indium.

Carbon-indium bond cleavage in $(C_6F_5)_3$In.diox has been shown to occur with reagents such as benzoic acid and 8-hydroxyquinoline.

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