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PRELIMINARY COMMUNICATION

ELEMENT INTERCHANGE REACTIONS OF BROMOBIS(PENTAFLUOROPHENYL)-THALLIUM(III)

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Diorganothallium(III) halides, R_2TlX (X = Cl, Br, or I) are potential sources of organic derivatives of other elements by reductive exchange reactions of the type,

$$n\ R_2TlX + M \rightarrow n\ TlX + MR_{2n} \quad (1)$$

but such reactions have only been demonstrated when M is mercury or an halogen[1]. The ready reduction of bis(pentafluorophenyl)thallium(III) compounds by iodide ions in various solvents[2],

$$e.g.\ (C_6F_5)_2TlBr + 2I^- + H_2O \rightarrow 2C_6F_5H + TlI + OI^- + Br^-$$

and of bromobis(pentafluorophenyl)thallium(III) by iodine in ethanol[2]:

$$(C_6F_5)_2TlBr + I_2 \rightarrow 2C_6F_5I + TlBr$$

has led us to investigate element interchange reactions [as in reaction (1)] of bromobis-(pentafluorophenyl)thallium(III). Preliminary results suggest that pentafluorophenyl derivatives of mercury, zinc, tin, germanium, arsenic, phosphorus, sulphur, iodine, and bromine can be prepared by this method.

The reactions were carried out in sealed Carius tubes, using stoicheiometric amounts [in terms of reaction (1)] of bromobis(pentafluorophenyl)thallium(III) and the appropriate element. No solvent was added. Details of reactions with six elements are given in Table 1. In addition to these examples, reactions of zinc, germanium, and arsenic with bromobis(pentafluorophenyl)thallium(III) at 190°, yielded $(C_6F_5)_2Zn$ (isolated as the complex with 2,2'-bipyridyl[8]), $(C_6F_5)_4Ge$, and $(C_6F_5)_3As$, respectively, the compounds being identified by their melting points [8-10] and infrared spectra[9,10] However, further investigations of these reactions are being carried out, as, so far, only low yields have been obtained. At the highest reaction temperature used (190°), bromobis-(pentafluorophenyl)thallium(III) has reasonable thermal stability; after 14 days at 190°, the compound was recovered in 66% yield.

Attempts are being made to prepare pentafluorophenyl derivatives of other elements by this method.

TABLE 1

REACTIONS OF BROMOBIS(PENTAFLUOROPHENYL)THALLIUM(III) WITH VARIOUS ELEMENTS

Element	Reaction		Product	Yield
	Temp.(°C)	Time(days)	$(C_6F_5)_nM$	(%)
Hg	130	7	$(C_6F_5)_2Hg^b$	67
Sn	190	7	$(C_6F_5)_4Sn^b$	54
P	190	4	$(C_6F_5)_3P^b$	70
S	190	5	$(C_6F_5)_2S^b$	55
I_2	*ca.* 25	5	$C_6F_5I^c$	96
$Br_2{}^a$	*ca.* 25	1	$C_6F_5Br^c$	100

[a] Mole ratio, $Br_2/(C_6F_5)_2TlBr$ 2/1 used in this reaction. [b] The products were characterized by melting points[3-6], microanalyses, and infrared spectra [3-5,7]. Analyses indicated the phosphine was not quite pure, but the identification by melting point, mixed melting point (with an authentic sample prepared from C_6F_5MgBr[5]), and comparison of the infrared spectrum with that of the authentic compound, was unambiguous. [c] The compounds were identified by vapour phase chromatography.

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