

## Preliminary Note

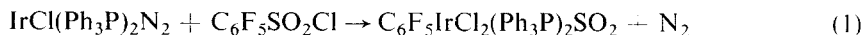
### The formation of organometallic compounds by sulphur dioxide elimination reactions of the pentafluorobenzenesulphinate ion

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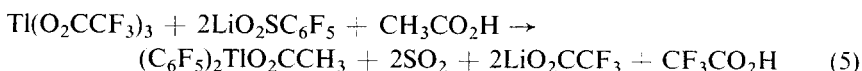
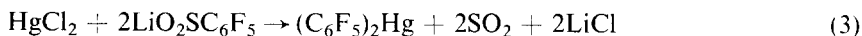
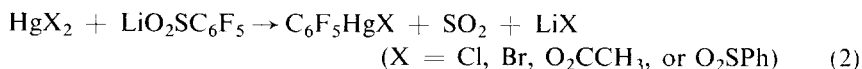
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Only two preparations of pentafluorophenylorganometallics by sulphur dioxide elimination reactions have been reported. Thermal decomposition of the *S*-sulphinato complex  $C_6F_5SO_2Fe(\pi-C_5H_5)(CO)_2$  gives  $C_6F_5Fe(\pi-C_5H_5)(CO)_2^1$ , and a pentafluorophenyliridium compound has been prepared by the reaction<sup>2</sup>:



We now report preparations of several pentafluorophenylmercurials and the first synthesis of an organothallium compound (or any Group III organometallic\*) by sulphur dioxide elimination reactions [equations (2)–(5); Table 1].



The compounds  $C_6F_5HgX$  ( $X = Cl, Br, O_2CCH_3, \text{ or } O_2SPh$ ) were precipitated on addition of aqueous lithium pentafluorobenzenesulphinate<sup>9</sup> to an aqueous solution ( $X = Cl, Br, \text{ or } O_2CCH_3$ ) or suspension ( $X = O_2SPh$ ) of the mercuric salt at room temperature. Bispentafluorophenylmercury was isolated by partial evaporation of the reaction solvent (Table 1). Acetato-bis(pentafluorophenyl)thallium(III) was precipitated on pouring the reaction mixture into water. The mercurial  $C_6F_5HgO_2SPh$  was recrystallized from chloroform/hexane, and the other compounds were dissolved in ether (mercurials) or methanol

\* The compound  $Ph_3In \cdot SO_2$ , formulated as diphenylindium benzenesulphinate, which decomposes on mild heating into triphenylindium and sulphur dioxide<sup>3</sup>, is now considered to be a sulphur dioxide adduct<sup>4</sup>.

TABLE 1  
 REACTIONS OF MERCURIC AND THALIC SALTS WITH LITHIUM PENTAFLUOROBENZENESULPHINATE AT AMBIENT TEMPERATURE (ca. 25°)

Metal salt	(mmol)	LiO <sub>2</sub> SC <sub>6</sub> F <sub>5</sub> (mmol)	Solvent	Volume (ml)	Reaction time (min)	Product	Yield (%)	m.p. <sup>a</sup> (°C)
HgCl <sub>2</sub>	2.1	1.0	H <sub>2</sub> O	60	Immed.	C <sub>6</sub> F <sub>5</sub> HgCl	43	164
HgBr <sub>2</sub>	1.1	1.0	H <sub>2</sub> O	90	2	C <sub>6</sub> F <sub>5</sub> HgBr	49	155–156
Hg(O <sub>2</sub> CCH <sub>3</sub> ) <sub>2</sub>	2.1	1.0	H <sub>2</sub> O	50	Immed.	C <sub>6</sub> F <sub>5</sub> HgO <sub>2</sub> CCH <sub>3</sub>	51	182–183
Hg(O <sub>2</sub> SPh) <sub>2</sub>	1.0	1.2	H <sub>2</sub> O	50	30	C <sub>6</sub> F <sub>5</sub> HgO <sub>2</sub> SPh	20	dec. <sup>b</sup>
HgCl <sub>2</sub>	0.55	2.1	t-BuOH/H <sub>2</sub> O <sup>c</sup>	55	5	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Hg	66	137
C <sub>6</sub> F <sub>5</sub> HgCl	0.35	1.3	t-BuOH/H <sub>2</sub> O <sup>c</sup>	55	10	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> Hg	92	138
Tl(O <sub>2</sub> CCF <sub>3</sub> ) <sub>3</sub>	0.50	1.1	CH <sub>3</sub> CO <sub>2</sub> H/H <sub>2</sub> O <sup>d</sup>	24	20	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> TlO <sub>2</sub> CCH <sub>3</sub>	24	220–240 <sup>e</sup>
Tl(O <sub>2</sub> CCH <sub>3</sub> ) <sub>3</sub>	0.50	1.1	CH <sub>3</sub> CO <sub>2</sub> H/H <sub>2</sub> O <sup>d</sup>	24	20	(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> TlO <sub>2</sub> CCH <sub>3</sub>	Trace	

<sup>a</sup> Reported values (°C): 165 (C<sub>6</sub>F<sub>5</sub>HgCl) <sup>5</sup>; 155 (C<sub>6</sub>F<sub>5</sub>HgBr) <sup>5</sup>; 178 (C<sub>6</sub>F<sub>5</sub>HgO<sub>2</sub>CCH<sub>3</sub>) <sup>6</sup>; 165 (C<sub>6</sub>F<sub>5</sub>HgO<sub>2</sub>SPh) <sup>7</sup>; 142 [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Hg] <sup>5</sup>; 224–240 (dec.) [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TlO<sub>2</sub>CCH<sub>3</sub>] <sup>8</sup>.

<sup>b</sup> Decomposition temperature and melting point dependent on rate of heating and immersion temperature; reported melting point <sup>7</sup> is considered incorrect.

<sup>c</sup> 8:3, v/v.

<sup>d</sup> 5:1, v/v.

<sup>e</sup> Decomposition temperature.

$[(C_6F_5)_2TiO_2CCH_3]$ , and, after filtration, were recovered on evaporation of the solvent. The infrared spectra of the products were identical with those of the authentic compounds prepared by reported methods, viz. re-distribution reactions of bispentafluorophenylmercury for  $C_6F_5HgX$  ( $X = Cl^{10}$ ,  $Br^5$ , or  $O_2SPh^7$ ), mercuration of pentafluorobenzene for  $C_6F_5HgO_2CCH_3^6$  and  $(C_6F_5)_2Hg^{11}$ , and reaction of  $(C_6F_5)_2TiBr$  with sodium acetate for  $(C_6F_5)_2TiO_2CCH_3^8$ .

Mercuric salts undergo sulphur dioxide elimination reactions more readily with the pentafluorobenzenesulphinato ion than the benzenesulphinato ion. By contrast with the results of Table 1, benzenesulphinato ions react with aqueous mercuric chloride at room temperature to give  $(PhSO_2HgCl)_2HgCl_2^{12}$  and with mercuric acetate to give  $Hg(O_2SPh)_2^{13}$ . These *S*-sulphinato complexes undergo sulphur dioxide elimination in boiling water to give  $PhHgCl$  and  $Ph_2Hg$  respectively<sup>12,13</sup>, and at  $80^\circ$   $Hg(O_2SPh)_2$  gives  $PhHgO_2SPh^{13}$ . Similarly, benzenesulphonyl chloride reacts with  $IrCl(Ph_3P)_2N_2$  to yield  $PhSO_2IrCl_2(Ph_3P)_2$ , which gives  $PhIrCl_2(Ph_3P)_2SO_2$  on being heated, whereas pentafluorobenzenesulphonyl chloride gives the pentafluorophenyliridium analogue directly<sup>2</sup> [equation (1)].

Other possible organometallic syntheses using the pentafluorobenzenesulphinato ion are being investigated.

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