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Preliminary Note

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

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

$$IrCl(Ph_3P)_2N_2 + C_6F_5SO_2Cl \rightarrow C_6F_5IrCl_2(Ph_3P)_2SO_2 + N_2 \qquad (1)$$

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].

$$HgX_2 + LiO_2SC_6F_5 \rightarrow C_6F_5HgX + SO_2 + LiX$$
$$(X = Cl,\ Br,\ O_2CCH_3,\ \text{or}\ O_2SPh) \qquad (2)$$

$$HgCl_2 + 2LiO_2SC_6F_5 \rightarrow (C_6F_5)_2Hg + 2SO_2 + 2LiCl \qquad (3)$$

$$C_6F_5HgCl + LiO_2SC_6F_5 \rightarrow (C_6F_5)_2Hg + SO_2 + LiCl \qquad (4)$$

$$Tl(O_2CCF_3)_3 + 2LiO_2SC_6F_5 + CH_3CO_2H \rightarrow$$
$$(C_6F_5)_2TlO_2CCH_3 + 2SO_2 + 2LiO_2CCF_3 + CF_3CO_2H \qquad (5)$$

The compounds C_6F_5HgX ($X = Cl$, Br, O_2CCH_3, or O_2SPh) were precipitated on addition of aqueous lithium pentafluorobenzenesulphinate[9] to an aqueous solution ($X = Cl$, Br, 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

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[*] The compound $Ph_3In{\bullet}SO_2$, formulated as diphenylindium benzenesulphinate, which decomposes on mild heating into triphenylindium and sulphur dioxide[3], is now considered to be a sulphur dioxide adduct[4].

TABLE 1

REACTIONS OF MERCURIC AND THALLIC SALTS WITH LITHIUM PENTAFLUOROBENZENESULPHINATE AT AMBIENT TEMPERATURE (*ca.* 25°)

Metal salt	(mmol)	$LiO_2SC_6F_5$ (mmol)	Solvent	Volume (ml)	Reaction time (min)	Product	Yield (%)	m.p. [a] (°C)
$HgCl_2$	2.1	1.0	H_2O	60	Immed.	C_6F_5HgCl	43	164
$HgBr_2$	1.1	1.0	H_2O	90	2	C_6F_5HgBr	49	155–156
$Hg(O_2CCH_3)_2$	2.1	1.0	H_2O	50	Immed.	$C_6F_5HgO_2CCH_3$	51	182–183
$Hg(O_2SPh)_2$	1.0	1.2	H_2O	50	30	$C_6F_5HgO_2SPh$	20	dec. [b]
$HgCl_2$	0.55	2.1	t-BuOH/H_2O [c]	55	5	$(C_6F_5)_2Hg$	66	137
C_6F_5HgCl	0.35	1.3	t-BuOH/H_2O [c]	55	10	$(C_6F_5)_2Hg$	92	138
$Tl(O_2CCF_3)_3$	0.50	1.1	CH_3CO_2H/H_2O [d]	24	20	$(C_6F_5)_2TlO_2CCH_3$	24	220–240 [e]
$Tl(O_2CCH_3)_3$	0.50	1.1	CH_3CO_2H/H_2O [d]	24	20	$(C_6F_5)_2TlO_2CCH_3$	Trace	

[a] Reported values (°C): 165 (C_6F_5HgCl) [5]; 155 (C_6F_5HgBr) [5]; 178 ($C_6F_5HgO_2CCH_3$) [6]; 165 ($C_6F_5HgO_2SPh$) [7]; 142 [$(C_6F_5)_2Hg$] [5]; 224–240 (dec.) [$(C_6F_5)_2TlO_2CCH_3$] [8].

[b] Decomposition temperature and melting point dependent on rate of heating and immersion temperature; reported melting point [7] is considered incorrect.

[c] 8:3, v/v.

[d] 5:1, v/v.

[e] Decomposition temperature.

$[(C_6F_5)_2TlO_2CCH_3]$, 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 $(C_6F_5)_2TlBr$ with sodium acetate for $(C_6F_5)_2TlO_2CCH_3$[8].

Mercuric salts undergo sulphur dioxide elimination reactions more readily with the pentafluorobenzenesulphinate ion than the benzenesulphinate ion. By contrast with the results of Table 1, benzenesulphinate 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[12,13], and at 80° $Hg(O_2SPh)_2$ 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[2] [equation (1)].

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

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REFERENCES

1 R. L. Downs, *Ph. D. Thesis*, Ohio State University, (1968). See also M. I. Bruce and A. D. Redhouse, *J. Organometallic Chem., 30* (1971) C78.
2 M. Kubota and B. M. Loeffler, *Inorg. Chem., 11* (1972) 469.
3 A. T. T. Hsieh, *J. Organometallic Chem., 27* (1971) 293.
4 A. T. T. Hsieh, personal communication.
5 R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc.*, (1962) 4367.
6 G. B. Deacon and F. B. Taylor, *Austral. J. Chem., 21* (1968) 2675.
7 G. B. Deacon and P. W. Felder, *Austral. J. Chem., 22* (1969) 549.
8 G. B. Deacon, *Austral. J. Chem., 20* (1967) 459.
9 W. A. Sheppard and S. S. Foster, *J. Fluorine Chem., 2* (1972/1973) 53.
10 G. E. Coates and D. Ridley, *J. Chem. Soc.*, (1964) 166.
11 G. B. Deacon, H. B. Albrecht and M. J. Osborne, *Inorg. Nuclear Chem. Letters, 5* (1969) 985.
12 J. R. Brush, P. G. Cookson and G. B. Deacon, *J. Organometallic Chem., 34* (1972) C1.
13 G. B. Deacon, *Austral. J. Chem., 20* (1967) 1367; P. G. Cookson and G. B. Deacon, *Austral. J. Chem., 24* (1971) 1599.