Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOTHALLIUM COMPOUNDS
VI*. REACTIONS OF BROMOBIS(PENTAFLUOROPHENYL)THALLIUM(III) WITH MAIN GROUP ELEMENTS**

G. B. DEACON AND J. C. PARROTT
Chemistry Department, Monash University, Clayton, Victoria (Australia)

(Received October 22nd, 1969)

SUMMARY

Bromobis(pentafluorophenyl)thallium(III) reacts with many main group elements on heating in the absence of a solvent to give pentafluorophenyl derivatives of these elements. The compounds C_6F_5M (M=Cl, Br, or I), $(C_6F_5)_2M$ (M=Zn, Cd, Hg, S, Se or Te), $(C_6F_5)_3M$ (M=In, P, As, or Sb), and $(C_6F_5)_4M$ (M=Ge or Sn) have been prepared by this method. Substantial decomposition of $(C_6F_5)_2TlBr$ occurs on reaction with aluminium, gallium, lead and bismuth, but pentafluorophenyl derivatives of these elements are not obtained.

INTRODUCTION

Transmetallation reactions of organomercury compounds:

$$n\,R_2Hg + 2\,M \rightarrow n\,Hg + 2\,MR_n$$

are an important synthetic route to organometallic compounds[3]. Isoelectronic relationships ($Hg^{2+} \rightarrow Hg^0$ with $Tl^{3+} \rightarrow Tl^+$) suggest that diorganothallium(III) halides may undergo analogous reductive exchange reactions,

$$n\,R_2TlX + 2\,M \rightarrow n\,TlX + 2\,MR_n \qquad (1)$$

but such reactions have been carried out only when M is mercury or an halogen[4]. We now report that pentafluorophenyl derivatives of many main group elements can be prepared from bromobis(pentafluorophenyl)thallium(III) by this method. The possibility of using reaction (1) for these syntheses was suggested by the ready reduction of bromobis(pentafluorophenyl)thallium(III) by iodide ions in various solvents[1], *e.g.*:

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

and by iodine in ethanol[1]:

---

* For Part V see ref. 1.

** For a preliminary report, see ref. 2.

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

Recent preliminary reports[5] have described another method for the preparation of pentafluorophenyl organometallics from bromobis(pentafluorophenyl)thallium(III), *viz.* reduction by compounds in low oxidation states (generally transition metal derivatives), *e.g.*:

$$Ph_3PAuCl + (C_6F_5)_2TlBr \rightarrow TlBr + cis\text{-}(C_6F_5)_2Au(Ph_3P)Cl$$

RESULTS AND DISCUSSION

Bromobis(pentafluorophenyl)thallium(III) was found to react with many main group elements on heating in the absence of a solvent. Reactions with halogens occurred at room temperature. Reactants, reaction conditions, and the principle pentafluorophenyl compound identified in each case are given in Table 1. For most elements, the observed reaction may be represented by eqn. (2). Thallous bromide

TABLE 1

REACTIONS OF BROMOBIS(PENTAFLUOROPHENYL)THALLIUM(III) WITH MAIN GROUP ELEMENTS

Element	(mg-atom)	$(C_6F_5)_2TlBr$ (mmole)	Reaction conditions		Product $(C_6F_5)_nM$[a]	Yield (%)
			Temp. (°C)	Time (days)		
Zn (*i*)	0.502	0.503	180	0.5	$(C_6F_5)_2Zn$	19
(*ii*)	0.528	0.527	185	0.5	$(C_6F_5)_2Zn$[c]	44
Cd	0.498	0.498	160	5	$(C_6F_5)_2Cd$	53
Hg (*i*)	0.743	0.743[d]	130	7	$(C_6F_5)_2Hg$	67
(*ii*)	0.715	0.716[b]	130	7	$(C_6F_5)_2Hg$	77
Al	0.345	0.517	190	4	[e]	
Ga	0.347	0.521	190	4	[e]	
In	0.502	0.752	160	1	$(C_6F_5)_3In$[f]	28
Si	0.256	0.512	190	13	$(C_6F_5)_2TlBr$	61
Ge	0.503	1.01	190	7	$(C_6F_5)_4Ge$	33
Sn	0.293	0.586	190	7	$(C_6F_5)_4Sn$	54
Pb	0.245	0.490	190	14	$(C_6F_5)_2TlBr$	19
P	0.423	0.635	190	4	$(C_6F_5)_3P$	70
As	0.394	0.591	190	6	$(C_6F_5)_3As$	31
Sb	0.683	1.02	190	0.75	$(C_6F_5)_3Sb$	23
Bi	0.343	0.514	190	7	$(C_6F_5)_2$	43
S	0.496	0.496	190	5	$(C_6F_5)_2S$	55
Se	0.504	0.504	190	3	$(C_6F_5)_2Se$	50
Te	0.494	0.494	190	3	$(C_6F_5)_2Te$	18
Cl_2	*ca.* 3	0.500	*ca.* 20	5	C_6F_5Cl	92
Br_2	1.99	0.500	*ca.* 20	1	C_6F_5Br	100
I_2	0.946	0.473	*ca.* 20	5	C_6F_5I	96
(*i*)		0.500	190	14	$(C_6F_5)_2TlBr$	66
(*ii*)		0.500	280	0.5	C_6F_5Br	19
					$(C_6F_5)_2$	*ca.* 3

[a] Or $(C_6F_5)_2$, or $(C_6F_5)_2TlBr$ recovered. [b] Using $(C_6F_5)_2TlBr$, m.p. 223° (slight dec.). [c] Isolated as the complex with 2,2'-bipyridine. [d] Using $(C_6F_5)_2TlBr$, m.p. 217–221° (dec.). [e] Gross decomposition to tar was observed; at 160°, no reaction occurred. [f] Isolated as the complex with triphenylphosphine.

$$n\,(C_6F_5)_2TlBr+2\,M \rightarrow n\,TlBr+2\,M(C_6F_5)_n \tag{2}$$

$n=1$; $M=I$

$n=2$; $M=Zn, Cd, Hg, S, Se$, or Te

$n=3$; $M=In, P, As$, or Sb

$n=4$; $M=Ge$ or Sn

was identified as a product from representative reactions. Reactions with chlorine and bromine were carried out using an excess of halogen over that required in eqn. (2) and thallic salts were obtained.

$$(C_6F_5)_2TlBr+2\,X_2 \rightarrow TlBrX_2+2\,C_6F_5X \qquad (X=Cl \text{ or } Br)$$

The pentafluorophenyl derivatives obtained by these reactions have previously been prepared by other methods, generally reactions of element halides with Grignard or organolithium reagents[6,7] or reactions of elements with bis(pentafluorophenyl)mercury[7-11] or iodopentafluorobenzene[7,11-13]. Tris(pentafluorophenyl)indium has previously been obtained only as the etherate[14], $(C_6F_5)_3In \cdot Et_2O$, which sublimes under vacuum without loss of ether suggesting that removal of the donor molecule is difficult. The present method enables tris(pentafluorophenyl)indium to be prepared in the absence of a donor solvent. Hexane solutions of the compound have been obtained from the reaction mixtures as indicated by the precipitation of pure tris(pentafluorophenyl)(triphenylphosphine)indium(III) on addition of triphenylphosphine to such a solution. A significantly lower yield of bis(pentafluorophenyl)zinc was obtained when the compound was isolated directly from the reaction mixture by sublimation than when the compound was isolated as bis(pentafluorophenyl)(2,2′-bipyridine)zinc. This may be related to the observation that on standing bis(pentafluorophenyl)zinc is converted into an unsublimable form[15]; the reaction conditions used in the present study may have caused partial conversion into this form.

We have found that to obtain satisfactory and reproducible reactions with elements at 180–190°, it is necessary to use highly purified bromobis(pentafluorophenyl)thallium(III) (see *Experimental*). However, use of less pure $(C_6F_5)_2TlBr$ in reactions with mercury at 130° caused only slight lowering of the yield of bis(pentafluorophenyl)mercury (Table 1). Highly purified $(C_6F_5)_2TlBr$ has reasonable thermal stability at 190° as it was recovered in good yield after prolonged heating at this temperature. At 280°, the compound underwent complete decomposition with the formation of bromopentafluorobenzene, decafluorobiphenyl, higher molecular weight perfluoroaromatic compounds which may include a perfluoroterphenyl and a perfluoroquaterphenyl (see *Experimental*), thallous bromide, and probably thallous fluoride.

Pentafluorophenyl derivatives of aluminium, gallium, silicon, lead, and bismuth were not isolated after heating these elements with bromobis(pentafluorophenyl)thallium(III). In the case of silicon, the thallium compound was recovered in similar yield to that obtained when it was heated alone under comparable conditions (Table 1), hence no reaction occurred between this element and $(C_6F_5)_2TlBr$. However, none of the thallium compound was recovered from reactions with aluminium, gallium, and bismuth, and only a low yield from the reaction with lead. Possibly these elements catalyse thermal decomposition of $(C_6F_5)_2TlBr$. Alternatively, pentafluorophenyl derivatives of these elements may have been formed and then been thermally decomposed. This is certainly possible for aluminium, since (pentafluorophenyl)aluminium compounds have fairly low thermal stability[14,16], especially when impure[14], but is much less likely for lead as (pentafluorophenyl)lead compounds have high thermal stability[17,18], *e.g.* tetrakis(pentafluorophenyl)lead is not decomposed[18] at 260°. The fairly high yield of decafluorobiphenyl in the reaction of $(C_6F_5)_2TlBr$ with bismuth suggests formation and decomposition of a (pentafluorophenyl)bismuth compound, since decafluorobiphenyl was obtained only in very low yield on thermal decomposition of $(C_6F_5)_2TlBr$ (Table 1). Nothing has been reported about (pentafluorophenyl)bismuth compounds except for the comment that preliminary experiments suggest tris(pentafluorophenyl)bismuth decomposes on exposure to air[19].

From reactions with some elements, products were isolated in addition to thallous bromide and the pentafluorophenyl derivatives given in Table 1. Thus, the reaction with germanium gave, in addition to tetrakis(pentafluorophenyl)germane, decafluorobiphenyl, one or more higher molecular weight perfluoroaromatic compounds possibly including a perfluoroterphenyl and a perfluoroquaterphenyl, and a (pentafluorophenyl)germanium compound, probably tris(pentafluorophenyl)germanium fluoride [not $(C_6F_5)_3GeBr$], which was hydrolysed in air to tris(pentafluorophenyl)germanol (see *Experimental*). From the reaction with selenium, bis(pentafluorophenyl) diselenide was obtained, whilst a perfluoroaromatic compound, probably a perfluoroterphenyl, was detected in the reaction with tellurium. It is probable that similar minor products were formed in other reactions and would be detectable with different isolation procedures.

Besides the method used in the present study, the direct conversion of certain elements into their pentafluorophenyl derivatives may be achieved by heating the elements with bis(pentafluorophenyl)mercury[7-11] or iodopentafluorobenzene[7,11-13]. Reactions with the mercurial have less scope than those with bromobis(pentafluorophenyl)thallium(III), since the former does not give pentafluorophenyl compounds of zinc, cadmium, and phosphorus on reaction with these elements[8] and at this stage only derivatives of germanium[7], tin[8], sulphur[8], selenium[8], tellurium[11], bromine[9], and iodine[10] have been obtained by this method. Moreover, reactions of elements with bis(pentafluorophenyl)mercury generally require more severe conditions than the corresponding reactions with $(C_6F_5)_2TlBr$. By contrast, all the pentafluorophenyl derivatives obtained in the present study, except tris(pentafluorophenyl)indium and tris(pentafluorophenyl)arsine, have been prepared by reaction of iodopentafluorobenzene with the appropriate elements[7,11-13]. In general, reactions of iodopentafluorobenzene require higher temperatures than the corresponding reactions of $(C_6F_5)_2TlBr$, but the commercial availability of the former favours its use. The high thermal stability of most pentafluorophenyl organometallics[6,7] makes possible their synthesis from elements at elevated temperatures.

EXPERIMENTAL

Microanalyses were by the Australian Microanalytical Service, Melbourne, and Dr. A. Bernhardt, Mülheim, Germany. Zinc was determined volumetrically with ethylenediaminetetraacetic acid[20] and cadmium gravimetrically as $\{Cd[SC(NH_2)_2]_2\}[Cr(NH_3)_2(NCS)_4]$[21]. For metal analyses, bis(pentafluorophenyl)zinc and bis(pentafluorophenyl)cadmium were decomposed by dilute sulphuric and nitric acids, respectively. Infrared spectra and X-ray powder photographs were obtained as described previously[1]. Mass spectra were obtained with an Hitachi Perkin–Elmer RMU-6E spectrometer, samples being introduced by direct evaporation. Gas–liquid chromatography was carried out using an Aerograph Model A-700 instrument with a silicon gum SE30 column, helium carrier gas, and column temperatures of 80–160°. Compounds were chromatographed as solutions in cyclohexane, the error in yields determined by this method being *ca.* 5%. The products from reactions with Zn, Cd, In, Sb, and Bi, and from the decomposition of $(C_6F_5)_2TlBr$ at 280° were manipulated under nitrogen in a dry box.

Bromobis(pentafluorophenyl)thallium(III) was prepared by the reported method[19], and was recrystallized from benzene in the presence of activated charcoal until the compound melted in the range 223–226° with only slight decomposition, lit. m.p. 217–220° (dec.)[19], slow dec. at 150°, 225–227° (slight dec.)[14]. Some preliminary experiments were carried out with a sample crystallized from benzene alone and having m.p. 217–221° (dec.), but, although this was satisfactory for the reaction with mercury (Table 1), further purification was necesaary to obtain satisfactory and reproducible reactions with elements at 180–190°.

Reactions of bromobis(pentafluorophenyl)thallium(III) with elements

Reactions were carried out in sealed evacuated thick-walled pyrex tubes. Except in reactions with chlorine, bromine, and phosphorus, the element (generally as a powder or filings) and bromobis(pentafluorophenyl)thallium(III) were thoroughly mixed at room temperature before evacuation and sealing. Chlorine was condensed onto $(C_6F_5)_2TlBr$ at $-196°$ under vacuum, bromine was added to the compound at $-45°$ under nitrogen, and phosphorus (yellow) was added under nitrogen as a standard solution in benzene, the solvent being removed *in vacuo* before the tube was sealed. (The Reaction of $(C_6F_5)_2TlBr$ with iodine at room temperature was sufficiently slow—no reaction detectable for 0.5 h—to obviate the need for cooling). Quantities of reagents and reaction conditions are given in the Table. The formation of a pale-yellow solid was observed in most reactions; this was identified as thallous bromide by X-ray powder photography from reactions with Hg, Sn, S and I_2. The separation, purification, and characterization of the products of the various reactions are described below.

Zinc. Reaction (*i*) (*Table 1*): Sublimation (110°, 5×10^{-3} mm) of the reaction product gave bis(pentafluorophenyl)zinc, m.p. 94–96°, lit.[22,15] m.p. 91–93°; 106–108°. (Found: Zn, 17.0. $C_{12}F_{10}Zn$ calcd.: Zn, 16.4%.) *Reaction* (*ii*) (*Table 1*): Addition of a solution of 2,2′-bipyridine (0.53 mmole) in benzene to a benzene extract of the product precipitated bis(pentafluorophenyl)(2,2′-bipyridine)zinc, m.p. *ca.* 245–260° (dec.), lit.[23] m.p. *ca.* 250° (dec.). Infrared absorption (1700–400 cm^{-1}): *1635*s, 1613m, 1603s, 1580m, 1570w, 1531w, *1503*vs,br, 1482m, *1450*vs,br, 1442sh, 1425sh, *1372*m, 1342w, 1333 and 1323s, *1281*w, 1257s, 1177m, 1159m, 1108w, 1099w, *1065* and *1045*vs,br, 1028m, 1019m, 977w, *948*vs,br, 897w, 762vs, 736vs, *712*m, 653m, 634m, *600* and *592*m, *482*w, and 418m cm^{-1}. The frequencies *in italics* are attributable to the pentafluorophenyl group[9,24–27], and the others are closely related to those observed for complexes of 2,2'-bipyridine[19,28,29].

Cadmium. Sublimation (125°, 10^{-3} mm) gave bis(pentafluorophenyl)cadmium, m.p. 154–155°, lit.[30] m.p. 156–158°. (Found: Cd, 26.0. $C_{12}CdF_{10}$ calcd.: Cd, 25.2%.) The infrared spectrum of the product showed the principle peaks reported[30] (a full spectrum was not given).

Mercury. Reaction (*i*) (*Table 1*): Ether extraction gave bis(pentafluorophenylmercury), m.p. 140–141°, lit.[9] m.p. 142°. (Found: C, 27.2; F, 35.4. $C_{12}F_{10}Hg$ calcd.: C, 26.95; F, 35.5%.) *Reaction* (*ii*) (*Table 1*): A similar procedure gave bis(pentafluorophenyl)mercury, m.p. 140–141°, mixed m.p. [with product from (*i*)] 140–141°. The infrared spectra of the mercurials from (*i*) and (*ii*) were identical with that of an authentic sample obtained by the Grignard method[9].

Aluminium and gallium. Hydrolysis of the brown tar obtained in each case gave no pentafluorobenzene (gas–liquid chromatography), hence significant amounts of (pentafluorophenyl)aluminium or -gallium compounds were not present[16].

Indium. The reaction product was extracted with dry hexane, which was filtered into a solution of triphenylphosphine (0.751 mmole) in hexane. On concentrating the solution, precipitation occurred and the mixture was allowed to stand under nitrogen for 1 day. The precipitate was then collected, washed with hexane, and dried under vacuum yielding tris(pentafluorophenyl)(triphenylphosphine)indium(III), m.p. 222–224°. (Found: C, 48.9; H, 2.1; P, 3.8. $C_{36}H_{15}F_{15}InP$ calcd.: C, 49.2; H, 1.7; P, 3.5%.) Infrared absorption (1700–400 cm^{-1}): *1637*m, *1505*vs, *1464*vs, 1440s [ν(CC)], *1372*, *1365*, and *1357*s, *1266*m, *1131*w, 1099m ["X-sens" *q*], *1073*s, *1053*s, *ca.* 1005w,br [β(CH) and ring mode], *957*vs, *783*m, 749vs [γ(CH)], *713*m, [and "X-sens" *r*], 695s [Φ(CC)], *601*m, 525s and 495s ["X-sens" *y*], and 444m ["X-sens" *t*] cm^{-1}. The frequencies *in italics* are characteristic of a pentafluorophenyl organometallic[9,26,27]. The remaining frequencies can be attributed to modes of triphenylphosphine[31], as indicated. The complex can be exposed to air for limited periods without hydrolysis. Free $(C_6F_5)_3In$ readily underwent hydrolysis under dry box conditions used for the isolation of the highly moisture sensitive[22,30] $(C_6F_5)_2Zn$ and $(C_6F_5)_2Cd$.

Silicon and lead. The reaction mixtures contained the element, $(C_6F_5)_2TlBr$, and no decafluorobiphenyl. In the case of lead, a red tar was also obtained.

Germanium. Fractional sublimation gave the following products: (*i*) At 0–20°, 5×10^{-2} mm, −78° probe, decafluorobiphenyl (0.036 g, 11%) was obtained, m.p. 67–68°, mixed m.p. (with an authentic sample from Imperial Smelting Corporation), 68–69°, lit.[32] m.p. 68–69° (infrared identification). (*ii*) At 75°, 5×10^{-3} mm, 0° probe, a white solid (0.049 g) was obtained, m.p. *ca.* 57–116°. The mass spectrum showed weak peaks at *m/e* 630 [$C_{24}F_{18}^+$], 594 [$(C_6F_5)_3GeF^+$]*, and 427 [$(C_6F_5)_2GeF^+$], and a strong peak at *m/e* 482 [$C_{18}F_{14}^+$]. The first and last of these may be parent ions of a perfluoroquarterphenyl and a perfluoroterphenyl, respectively (though $C_{18}F_{14}^+$ may arise from breakdown of $C_{24}F_{18}^+$). The infrared spectrum of the sublimate was similar to that of decafluorobiphenyl, except for additional bands at 831w, 771m, and 648m cm^{-1}. The ion $(C_6F_5)_3GeF^+$ may be the parent ion of tris(pentafluorophenyl)germanium fluoride. The germanium containing compound was probably not tetrakis(pentafluorophenyl)germane, since this did not sublime until a much

---

* The correct isotope pattern was observed for peaks attributed to germanium containing ions. The *m/e* value for the ion containing ^{74}Ge is given.

higher temperature (below). Moreover $(C_6F_5)_3GeF^+$ is not a significant fragment in the breakdown of $(C_6F_5)_4Ge$[33]. The mass spectrum showed no peaks attributable to ions containing bromine. On prolonged exposure of the sublimate to air, or on dissolution of the sublimate in ether with exposure to air followed by evaporation to dryness, the resulting solids gave similar mass spectra with peaks at *m/e* 630 $[C_{24}F_{18}^+]$, 592 $[(C_6F_5)_3GeOH^+]$, 575 $[(C_6F_5)_3Ge^+]$, 482 $[C_{18}F_{14}^+]$, 425 $[(C_6F_5)_2GeOH^+]$, and 424 $[(C_6F_5)_2GeO^+]$ consistent with hydrolysis of $(C_6F_5)_3GeF$ in the original product to tris(pentafluorophenyl)germanol. The infrared spectrum of the ether-treated product was again similar to that of decafluorobiphenyl but also showed an hydroxyl absorption at *ca.* 3400br, lit.[34] ν(OH) of $(C_6F_5)_3GeOH$ 3378br cm^{-1}. (*iii*) At 160°, 10^{-3} mm, a pale yellow sublimate was obtained, which on crystallization from benzene yielded white crystals of tetrakispentafluorophenylgermane, m.p. 241–243°, lit.[34] m.p. (sealed tube) 246–248°, (Found: C, 39.2; F, 51.5. $C_{24}F_{20}Ge$ calcd.: C, 38.9; F, 51.3%.) The infrared spectrum of the compound corresponded closely to the reported spectrum[34], except that a strong band at 1557 cm^{-1} was not observed.

Tin. Extraction with boiling acetone and crystallization from cyclohexane gave tetrakis(pentafluorophenyl)tin, m.p. 221°, lit.[26] m.p. 221°. (Found: C, 36.9; F, 48.6. $C_{24}F_{20}Sn$ calcd.: C, 36.6; F, 48.3%.) The infrared spectrum was identical with the reported spectrum[26].

Phosphorus. Ether extraction, and sublimation (80°, 10^{-1} mm) of the resulting solid gave tris(pentafluorophenyl)phosphine, m.p. 115–117°, mixed m.p. (with an authentic sample obtained by the Grignard method[35]), 115–117°, lit.[35] m.p. 116–117°. (Found: C, 41.1; F, 53.9; P, 6.7; mol.wt. by mass spectrometry, 532. $C_{18}F_{15}P$ calcd.: C, 40.6; F, 53.55; P, 5.8%; mol.wt., 532.) The infrared spectrum of the product was identical with that of the authentic compound, and the mass spectrum corresponded closely to that reported[36].

Arsenic. Ether extraction and sublimation (80–95°, 10^{-2} mm) gave tris(pentafluorophenyl)arsine, m.p. 104–106°, lit.[37] m.p. 106°. (Found: C, 37.15; F, 49.5. $C_{18}AsF_{15}$ calcd.: C, 37.5; F, 49.5%.) The infrared spectrum showed the intense features reported[37] (a complete spectrum was not given). The most intense peaks in the mass spectrum were at *m/e* 576 $[(C_6F_5)_3As^+]$, 557 $[(C_6F_5)_2AsC_6F_4^+]$, 409 $[(C_6F_5)_2As^+]$, 296 $[C_{12}F_8^+]$, 277 $[C_{12}F_7^+]$, 261 $[C_6F_5AsF^+]$, 242 $[C_6F_5As^+]$, 129 $[C_6F_3^+]$, 117 $[C_5F_3^+]$, 113 $[AsF_2^+]$, and 110 $[C_6F_2^+]$.

Antimony. Ether extraction and sublimation (60°, 10^{-2} mm, probe at 0°) yielded tris(pentafluorophenyl)stibine, m.p. 77–79°, lit.[37] m.p. 74°. (Found: C, 34.7; F, 45.6. $C_{18}F_{15}Sb$ calcd.: C, 34.7; F, 45.75%.) The infrared spectrum of the product contained the principle bands reported[37].

Bismuth. Ether extraction and sublimation (*ca.* 20°, 10^{-2} mm, probe at 0°) gave decafluorobiphenyl, m.p. 68–69°, mixed m.p. 68–69° (infrared identification).

Sulphur. Ether extraction and sublimation (80°, 10^{-2} mm) gave bis(pentafluorophenyl) sulphide, m.p. 83–86°, lit.[8,11] m.p. 84–85°. (Found: C, 39.25; F, 50.9; S, 9.2. $C_{12}F_{10}S$ calcd.: C, 39.4; F, 51.9; S, 8.8%.) The infrared spectrum of the product was identical with the reported spectrum[38].

Selenium. Crystallization of the product from ethanol at −24° gave bis(pentafluorophenyl) selenide, m.p. 77–78°, lit.[8] m.p. 73–74°. (Found: C, 34.7; F, 45.9. $C_{12}F_{10}Se$ calcd.: C, 34.9; F, 46.0%.) The infrared spectrum (1700–650 cm^{-1}) showed absorption at 1638m, 1512vs, 1492vs, 1395m, 1088vs, 980 and 972 vs, and 818s cm^{-1} characteristic[9,27,26] of a pentafluorophenyl organometallic. Evaporation of the filtrate to dryness yielded a yellow solid (8 mg), m.p. 39–41°, considered to be impure bis(pentafluorophenyl) diselenide, lit.[11] m.p. 46–48°. The mass spectrum showed a parent ion at *m/e* 494 $[(C_6F_5)_2Se_2^+]$. (The characteristic pattern for the selenium isotopes was observed. The *m/e* value for $^{80}Se_2$ is given).

Tellurium. Ether extraction and sublimation (*ca.* 20°, 5×10^{-3} mm, probe at 0°) gave bis(pentafluorophenyl) telluride as a pale-yellow solid, m.p. 54–55°, lit.[11] m.p. 50–51°. (Found: C, 32.0; F, 42.2. $C_{12}F_{10}Te$ calcd.: C, 31.2; F, 41.15%.) The infrared spectrum (1700–650 cm^{-1}) showed absorption at 1637s, 1508vs, 1484vs, 1383m, 1083vs, 971vs, and 793s cm^{-1} characteristic[9,26,27] of a pentafluorophenyl organometallic. Further sublimation (70°, 5×10^{-3} mm, 0° probe) gave an orange oil (0.012 g), the infrared spectrum of which differed slightly from that of $(C_6F_5)_2Te$. No bis(pentafluorophenyl) ditelluride nor a significant amount of any tellurium compound with a molecular weight greater than that of $(C_6F_5)_2Te$ could be detected by mass spectrometry. However, a peak was observed at *m/e* 482 $(C_{18}F_{14}^+)$ suggesting the presence of a perfluoroterphenyl.

Chlorine, bromine and iodine. The halogenopentafluorobenzenes were identified by gas–liquid chromatography; authentic samples used for comparison were from Imperial Smelting Corporation. The formation of thallic salts in reactions with chlorine and bromine was established by reactions of aqueous solutions of the solid products with aqueous sodium iodide followed by base[1], or with acidified boiling aqueous sodium sulphite[39].

Thermal decomposition of bromobis(pentafluorophenyl)thallium(III)

Reaction (i) (Table 1). No decafluorobiphenyl was detected. Crystallization of the product from benzene/hexane gave $(C_6F_5)_2TlBr$.

Reaction (ii) (Table 1). A brown tar was obtained and was extracted with cyclohexane. Bromopentafluorobenzene was detected in the extract (gas–liquid chromatography). Extraction of the residue with ether and evaporation of the combined ether and cyclohexane extracts gave tar, which on sublimation gave firstly (22°, 0.13 mm, probe at −78°) impure decafluorobiphenyl m.p. 59–60° (infrared identification), and then (70°, 5×10^{-2} mm, 0° probe) a white solid (0.021 g) m.p. *ca.* 59–98°. The infrared spectrum was similar to that of decafluorobiphenyl. The mass spectrum showed a weak peak at *m/e* 630 $(C_{24}F_{18}^+)$ and a strong peak at *m/e* 482 $(C_{18}F_{14}^+)$ consistent with the presence of a perfluoroquaterphenyl and a perfluoroterphenyl. The X-ray powder photograph of the ether insoluble residue was identical with that of thallous bromide except for the presence of additional faint lines, two of which corresponded closely to the two most intense lines in the powder photograph of thallous fluoride[40]. At 280°, the residue on the bottom of the reaction tube appeared to contain black metallic specks, but the powder photograph showed no evidence for the presence of thallium metal.

ACKNOWLEDGEMENTS

We are grateful to the Australian Research Grants Committee for support, to Mr. F. Lawson for the use of X-ray facilities, and to Dr. S. Middleton for assistance with the mass spectra.

REFERENCES

1 G. B. Deacon and J. C. Parrott, *J. Organometal. Chem.*, 15 (1968) 11.
2 G. B. Deacon and J. C. Parrott, *J. Organometal. Chem.*, 17 (1969) P17.
3 L. G. Makarova and A. N. Nesmeyanov, *The Organic Compounds of Mercury*, North Holland Publ. Co., Amsterdam, 1967, p. 381.
4 A. N. Nesmeyanov and R. A. Sokolik, *The Organic Compounds of Boron, Aluminium, Gallium, Indium, and Thallium*, North Holland Publ. Co., Amsterdam, 1967, p. 586; K. Yasuda and R. Okawara, *Organometal. Chem. Rev.*, 2 (1967) 255.
5 R. S. Nyholm and P. Royo, *Chem. Commun.*, (1969) 421.
6 R. D. Chambers and T. Chivers, *Organometal. Chem. Rev.*, 1 (1966) 279.
7 S. C. Cohen and A. G. Massey, in press.
8 J. Burdon, P. L. Coe and M. Fulton, *J. Chem. Soc.*, (1965) 2094.
9 R. D. Chambers, G. E. Coates, J. G. Livingstone and W. K. R. Musgrave, *J. Chem. Soc.*, (1962) 4367.
10 P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1962) 3227.
11 S. C. Cohen, M. L. N. Reddy and A. G. Massey, *J. Organometal. Chem.*, 11 (1968) 563.
12 J. M. Birchall, R. Hazard, R. N. Haszeldine and W. W. Wakalski, *J. Chem. Soc., C*, (1967) 47.
13 S. C. Cohen, M. L. N. Reddy and A. G. Massey, *Chem. Commun.*, (1967) 451.
14 J. W. L. Pohlmann and F. E. Brinkman, *Z. Naturforsch., B*, 20 (1965) 5.
15 P. Sartori and M. Weidenbruch, *Chem. Ber.*, 100 (1967) 3016.
16 R. D. Chambers and J. A. Cunningham, *J. Chem. Soc., C*, (1967) 2185.
17 D. E. Fenton and A. G. Massey, *J. Inorg. Nucl. Chem.*, 27 (1965) 329.
18 C. Tamborski, E. J. Soloski and S. M. Dec, *J. Organometal. Chem.*, 4 (1965) 446.
19 G. B. Deacon, J. H. S. Green and R. S. Nyholm, *J. Chem. Soc.*, (1965) 3411.
20 C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. 1B, Elsevier, Amsterdam, 1960, p. 348.
21 C. L. Rulfs, E. P. Przybylowicz and C. E. Skinner, *Anal. Chem.*, 26 (1954) 408.
22 J. G. Noltes and J. W. G. van den Hurk, *J. Organometal. Chem.*, 1 (1964) 377.
23 J. G. Noltes and J. W. G. van den Hurk, *J. Organometal. Chem.*, 3 (1965) 222.
24 D. A. Long and D. Steele, *Spectrochim. Acta*, 19 (1963) 1947, 1955.
25 I. J. Hyams, E. R. Lippincott and R. T. Bailey, *Spectrochim. Acta*, 22 (1966) 695.
26 R. D. Chambers and T. Chivers, *J. Chem. Soc.*, (1964) 4782.
27 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 24A (1968) 1125.
28 W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, 26 (1964) 15, 21.
29 A. J. Canty and G. B. Deacon, *Aust. J. Chem.*, 21 (1968) 1757.
30 M. Schmeisser and M. Weidenbruch, *Chem. Ber.*, 100 (1967) 2306.
31 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta*, 24A (1968) 845.
32 E. Nield, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, (1959) 166.
33 J. M. Miller, *Can. J. Chem.*, 47 (1969) 1613.
34 D. E. Fenton, A. G. Massey and D. S. Urch, *J. Organometal. Chem.*, 6 (1966) 352.
35 L. A. Wall, R. E. Donadio and W. J. Pummer, *J. Amer. Chem. Soc.*, 82 (1960) 4846.
36 J. M. Miller, *J. Chem. Soc., A*, (1967) 828.
37 M. Fild, O. Glemser and G. Christoph, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 801.
38 *Documentation of Molecular Spectroscopy, Infrared and Raman Spectral Cards, Part* 1, Butterworths, London, Spectrum No. 13440.
39 A. I. Vogel, *Textbook of Quantitative Inorganic Analysis*, Longmans, London, 3rd Ed., 1961, p. 549.
40 *X-ray Powder Data File*, American Society for Testing Materials, Philadelphia, Pa., Special Publication No. 48K, 1961.

J. Organometal. Chem., 22 (1970) 287–295