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ORGANOLANTHANOIDS

II.* PREPARATION AND IDENTIFICATION OF SOME ORGANOLANTHANOID SPECIES IN SOLUTION

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Summary

The organolanthanoid derivatives R_2M ($R = C_6F_5$, M = Yb or Eu; R = p-HC_6F_4 or PhCC, M = Yb) have been prepared by reaction of the corresponding diorganomercury compounds with ytterbium or europium metal in tetrahydrofuran at room temperature, and (o-$HC_6F_4)_2Yb$ has been obtained by an analogous reaction at 0°C. The compounds were identified by determination of the amounts of polyfluoroarene or phenylacetylene and lanthanoid ions formed on acidolysis of the filtered reaction mixtures. Reaction of samarium with bis(pentafluorophenyl)mercury and of ytterbium with bis-(2,3,4,5-tetrafluorophenyl)mercury at room temperature gives more complex products including RMF_2, MF_2 and RMF derivatives ($R = C_6F_5$, M = Sm; R = o-HC_6F_4, M = Yb), polyfluoropolyphenyls, and more complex organometallic species. These are considered to be derived from decomposition of initially formed $(C_6F_5)_2Sm$, $(C_6F_5)_3Sm$, and (o-$HC_6F_4)_2Yb$ derivatives. The decomposition paths include fluoride elimination to give polyfluoro-

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benzynes, reduction of polyfluoroaryl groups by lanthanoid(II) species, and hydrogen abstraction from tetrahydrofuran.

Introduction

The transmetallation reaction (1) has recently been developed as a route to divalent organoytterbium compounds, enabling the first fluorocarbon organolanthanoids, $R_2Yb(THF)_4$ ($R = C_6F_5$ or p-HC_6F_4; THF = tetrahydrofuran) [1, 2], and the phenylethynyl derivative, $(PhCC)_2Yb$ [3], to be isolated.

$$R_2Hg + M \longrightarrow R_2M + Hg\downarrow \qquad (1)$$

Several other reactions were observed, e.g. between bis(2,3,4,5-tetrafluorophenyl)mercury and ytterbium [1], but the products were either too unstable to be isolated or could not be crystallized. Even bis(2,3,5,6-tetrafluorophenyl)ytterbium could not be isolated analytically pure owing to thermal instability, and the composition was inferred from spectroscopic data. We have now investigated transmetallation reactions between mercurials and lanthanoid elements by detailed analysis of reaction mixtures rather than by product isolation.

Results and Discussion

(a) General Procedure

The reactions carried out are detailed in Table 1. They were normally effected using an excess of metal over that required by equation (1) in an attempt to ensure substantial consumption of the mercurial, since this simplified the analytical procedures. Following each reaction, the precipitate (mercury metal and unreacted lanthanoid element) was collected and analysed. The filtrate, which contained the organolanthanoid product, was treated with dilute sulphuric acid giving lanthanoid ions and the corresponding polyfluoroarene or phenylacetylene [see e.g. reaction (2)], which were determined quantitatively.

$$R_2M + H_2SO_4 \longrightarrow MSO_4{}^{*} + 2RH \qquad (2)$$

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[*] The divalent metal sulphates may then be oxidised partly or substantially into the trivalent sulphates, see e.g. reactions (6) and (7) below, and related discussion.

These data gave the ratios moles mercury precipitated/moles of organolanthanoid in solution [Hg_p/Ln_s], and moles of polyfluorobenzene (or PhCCH) formed on acidolysis/moles of organolanthanoid in solution [RH/Ln_s] (Table 1), from which the reaction stoichiometries and the nature of the products were determined. The observed reactions can conveniently be divided into three groups, depending on the thermal stability of the organolanthanoid and the complexity of the observed products.

(b) Formation of R_2M ($R = C_6F_5$, $M = Yb$ or Eu; $R =$ p-HC_6F_4 or PhCC, $M = Yb$) - Products of Moderate Thermal Stability in Tetrahydrofuran

Analytical data for the reactions of bis(pentafluorophenyl)mercury with ytterbium and europium and of bis(2,3,5,6-tetrafluorophenyl)mercury and bis(phenylethynyl)mercury with ytterbium in tetrahydrofuran indicated the formation of the corresponding diorganolanthanoids [$RH/Ln_s \simeq 2.0$ (Table 1)] by reaction (1) [$Hg_p/Ln_s \simeq 1.0$]. The results are consistent with isolation of $R_2Yb(THF)_4$ ($R = C_6F_5$ or p-HC_6F_4) [1, 2] and $(PhCC)_2Yb$ [3] from similar reactions, but also show that the yields of the diorganolanthanoids in solution are much higher than those (20-50% [1, 3]) of the isolated complexes. Addition of a little mercury was needed to initiate reaction between europium and bis(pentafluorophenyl)mercury (Table 1). Possibly amalgamation assists in exposing a fresh surface on the readily oxidised metal. Attempts to crystallize bis(pentafluorophenyl)europium were unsuccessful. The reaction between bis(pentafluorophenyl)mercury and ytterbium was also effected in ether (Table 1), but bis(phenylethynyl)mercury and ytterbium failed to react in this solvent.

For the systems considered in this section, some values of Hg_p/Ln_s and RH/Ln_s (Table 1) deviate from 1.00 and 2.00 respectively by slightly more than the maximum likely experimental error (4%). This indicates that side reactions occur, albeit to a very limited extent. In confirmation, the distillate following acidolysis of the products from reaction of ytterbium with bis(pentafluorophenyl)mercury in tetrahydrofuran contained a little 1,2,4,5-tetrafluorobenzene* (mole ratio C_6HF_5 : p-$H_2C_6F_4$, 19:1), and a trace of $C_{12}HF_9$ and $C_{12}H_2F_8$ besides the expected [reaction (2); $R = C_6F_5$, $M = Yb$] pentafluorobenzene. Less of the tetrafluorobenzene was obtained from

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* This compound was also detected on acidolysis of a sample of crystalline $(C_6F_5)_2Yb(THF)_4$ [1], which contained an impurity of a 2,3,5,6-tetrafluorophenylytterbium species.

TABLE 1

REACTIONS OF ORGANOMERCURIALS WITH LANTHANOID ELEMENTS IN TETRAHYDROFURAN

R_2Hg	mmol	Metal	mmol	Temp. (^oC)	Time (h)	Mole ratio[a] (Hg_p/Ln_s)	Mole ratio[b] (RH/Ln_s)	Products	R_2M (%)[c]	Hg (%)[c]	$MF_3.H_2O$ (%)[d]
$(C_6F_5)_2Hg$	3.02	Yb	6.68	18	4	1.07	2.15	$(C_6F_5)_2Yb$	92	98	
$(C_6F_5)_2Hg$[e]	2.53	Yb	6.50	0-2 15-18	2 2	1.02	2.20	$(C_6F_5)_2Yb$	90	90	
(*p*-$HC_6F_4)_2Hg$	2.73	Yb	6.35	18	4	1.03	1.86	(*p*-$HC_6F_4)_2Yb$	95	97	4
$(C_6F_5)_2Hg$	2.24[f]	Eu	4.60	0[g] 18	4 3.5	1.05	1.97	$(C_6F_5)_2Eu$	83	88	
$(PhCC)_2Hg$	3.00	Yb	5.67	19	4	0.97	1.94	$(PhCC)_2Yb$	98	96	
(*o*-$HC_6F_4)_2Hg$	3.00[h]	Yb	6.61	0	3	1.04	2.61	(*o*-$HC_6F_4)_2Yb$	84	88	3
(*o*-$HC_6F_4)_2Hg$	3.00	Yb	6.46	0-30	5	0.90	1.22	[i]		97	45
$(C_6F_5)_2Hg$	2.99	Sm	8.94	16[g]	4	1.26	0.98	[i]		90	64
$(C_6F_5)_3Bi$	2.66	Yb	4.12	55	168	> 10[l]				8[k]	

[a] Mole ratio, mercury precipitated/soluble organolanthanoid. Moles soluble organolanthanoid = moles lanthanoid ions determined on acidolysis of the filtered reaction mixture. [b] Mole ratio, polyfluorobenzene (or phenylacetylene)/soluble organolanthanoid, determined after acidolysis. [c] Based on initial organomercurial. [d] % Lanthanoid ions obtained as the trifluoride hydrate after acidolysis. [e] Solvent, diethyl ether. [f] 10% of the mercurial was recovered unchanged after the reaction. [g] Reaction induced by addition of mercury metal, and in the case of samarium by brief heating at 60°.

[h] 8% of the mercurial was unreacted and yielded mercury metal on acidolysis. [i] Complex mixture of products obtained.

[j] Bi_p/Ln_s. [k] % Bismuth precipitated based on initial $(C_6F_5)_3Bi$.

the same reaction system in ether (mole ratio C_6HF_5 : p-$H_2C_6F_4$, 50:1). The 1,2,4,5-tetrafluorobenzene contributes to the high RH/Ln_s ratios, since the amount of pentafluorobenzene was determined by ultraviolet spectrophotometry and the extinction coefficient of 1,2,4,5-tetrafluorobenzene (1650 at 264 nm) is larger than that of pentafluorobenzene (605 at 262 nm). Any polyfluorobiphenyls would probably have a similar effect, e.g. the extinction coefficient of 2-hydrononafluorobiphenyl is 4500 at 262 nm [4]. As discussed below [section (d)], the presence of 1,2,4,5-tetrafluorobenzene and polyfluorobiphenyls in the distillate can be attributed to thermal decomposition of the bis(polyfluorophenyl)lanthanoid. In the reaction of bis(2,3,5,6-tetrafluorophenyl)mercury with ytterbium, involatile polyfluoropolyphenyls, not volatile polyfluorobiphenyls, may be formed, as the RH/Ln_s ratio is somewhat lower than 2.00 (Table 1), and a very small residue of oil (fluorocarbon ?) remained after distillation. Ytterbium trifluoride was obtained in low yield on acidolysis, presumably formed by decomposition of a minor fluoroytterbium species [see section (d)].

High Hg_p/Ln_s ratios may arise from a slow lanthanoid catalysed decomposition of the mercurial [reaction (3)], and this would also contribute to high RH/Ln_s ratios.

$$R_2Hg \ (+ \ C_4H_8O) \xrightarrow{M} Hg\downarrow + \ 2RH \ (+ \ C_4H_6O \text{ or } C_4H_4O) \qquad (3)$$

Support for (3) was provided by the observation of slight catalytic decomposition of tris(pentafluorophenyl)bismuth by ytterbium in tetrahydrofuran. Bismuth was precipitated, even though no organoytterbium species could be detected (Table 1).

$$(C_6F_5)_3Bi \ (+ \ C_4H_8O) \xrightarrow{Yb} Bi\downarrow + \ 3C_6HF_5 \ (+ \ C_4H_6O \text{ or } C_4H_4O) \qquad (4)$$

Hydrogen abstraction from tetrahydrofuran, proposed in (3) and (4), has been shown to occur in the reaction of samarium with bis(pentafluorophenyl)mercury [section (d)], and has previously been observed during reaction of the dicarbonyl-η-cyclopentadienylferrate ion with halogenopentafluorobenzenes [5] and on dissolution of some methylruthenium(II) complexes in tetrahydrofuran [6]. G.c./m.s. of the distillate following acidification of the filtered $(C_6F_5)_3Bi$/Yb reaction mixture did not reveal any products from decomposition of tetrahydrofuran, but any furan or 2,3-dihydrofuran would have been decomposed during acidolysis [7].

Acidolysis of the filtered organolanthanoid solution from reaction of bis-

(phenylethynyl)mercury with ytterbium (Table 1) gave a mixture of phenylacetylene, styrene, and ethylbenzene (mole ratio, 79:20:1 respectively). Similar behaviour has been observed on acidolysis of crystalline bis(phenylethynyl)ytterbium, and it was shown that styrene formation results from hydrogenation on acidification [reaction (5)] not from cleavage of a styrylytterbium species [3].

$$2\,(PhCC)_2Yb + 3\,H_2SO_4 \longrightarrow 3\,PhCCH + PhCHCH_2 + Yb_2(SO_4)_3 \qquad (5)$$

Formation of styrene in addition to phenylacetylene does not affect determination of the RH/Ln_s ratio, since phenylacetylene and styrene have very similar extinction coefficients (1.39×10^4 and 1.37×10^4 respectively in ethanol) at the wavelength (245 nm) used for determination of phenylacetylene, and each coordinated phenylethynyl group gives either PhCCH or $PhCHCH_2$ on decomposition [reactions (2) (R = PhCC, M = Yb) and (5)]. Ethylbenzene is only a very minor product and it does not have significant absorption at 245 nm. Hydration of the triple bond giving acetophenone was not appreciable on acidolysis unless unreacted mercurial was present.

The ratio moles acid consumed on acidolysis/moles of organolanthanoid in solution [H^+/Ln_s] for the reaction of europium with bis(pentafluorophenyl)-mercury was 2.25 consistent with reaction (2) ($R = C_6F_5$, M = Eu) and only slight oxidation of europium(II) sulphate to europium(III) sulphate either by acid [reaction (6); M = Eu], or by air [reaction (7)] admitted subsequent to acidification. Complete oxidation would give $H^+/Ln_s = 3.00$. The result is consistent with the known slow oxidation of europium(II) sulphate by atmospheric oxygen or water [8]. For reactions of R_2Hg ($R = C_6F_5$ or p-HC_6F_4) with ytterbium, $H^+/Ln_s = 2.50 - 2.70$, consistent with the greater ease of oxidation of ytterbium(II) than europium(II) [9]. When ytterbium metal was dissolved in degassed sulphuric acid under nitrogen, and the residual acid was titrated immediately on exposure to air, the ratio moles acid consumed/moles metal dissolved was 2.51. Similar dissolution, standing at room temperature overnight, and heating under reflux in the presence of air for 40 min. gave a ratio of 2.84. The H^+/Ln_s ratio for the reaction of bis(phenylethynyl)mercury with ytterbium (3.01) is in agreement with the stoichiometry of reaction (5).

$$2\,MSO_4 + H_2SO_4 \longrightarrow M_2(SO_4)_3 + H_2 \qquad (6)$$

$$2\,MSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \longrightarrow M_2(SO_4)_3 + H_2O \qquad (7)$$

(c) Formation of Bis(2,3,4,5-tetrafluorophenyl)ytterbium – A Product of Low Thermal Stability in Tetrahydrofuran

When bis(2,3,4,5-tetrafluorophenyl)mercury was treated with ytterbium at 0°C, an orange solution characteristic [1] of a bis(polyfluorophenyl)-ytterbium compound was obtained, and the Hg_p/Ln_s ratio (Table 1) was consistent with formation of $(\underline{o}\text{-}HC_6F_4)_2Yb$ by reaction (1) [$R = \underline{o}\text{-}HC_6F_4$, $M = Yb$]. The apparently conflicting RH/Ln_s ratio (2.61) can be discounted, since interpretation of this value is not straightforward. Firstly, determination of 1,2,3,4-tetrafluorobenzene (RH) by ultraviolet spectroscopy gave a value somewhat greater than that for 100% yield [6.61 mmol obtained from 3.00 mmol of $(\underline{o}\text{-}HC_6F_4)_2Hg$], suggesting the presence of an impurity with a high extinction coefficient, e.g. a polyfluorobiphenyl [see $2\text{-}HC_{12}F_9$; section (b)]. In confirmation, g.c./m.s. of the volatile products following acidolysis showed a septafluorobiphenyl to be present. Secondly, the 1,2,3,4-tetrafluorobenzene was derived not only from acidolysis of the organolanthanoid, but also from reductive cleavage of unreacted bis(2,3,4,5-tetrafluorophenyl)mercury.*

$$(\underline{o}\text{-}HC_6F_4)_2Hg + H_2SO_4 + 2\,YbSO_4 \longrightarrow Hg\downarrow + Yb_2(SO_4)_3 + 2\,\underline{o}\text{-}H_2C_6F_4 \qquad (8)$$

Fluorocarbon mercurials are stable to direct cleavage by acid [10, 11, and see Experimental]. Evidence for reaction (8) was provided by precipitation of mercury during acidolysis of the organolanthanoid. Subtraction of $\underline{o}\text{-}H_2C_6F_4$ derived from this source, calculated from the amount of mercury precipitated, gives $RH/Ln_s = 2.42$. The remaining difference from 2.00 can be attributed to the presence of the septafluorobiphenyl, the origin of which is considered in section (d). The H^+/Ln_s ratio for the product (2.59) is comparable with those obtained on acidolysis of other bis(polyfluorophenyl)-ytterbium compounds [section (b)].

(d) Complex Transmetallation Reactions

1. The Nature of the Products

The reactions of bis(2,3,4,5-tetrafluorophenyl)mercury with ytterbium

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* An analogous reduction of unreacted $(C_6F_5)_2Hg$ was not observed in the reaction with europium (Table 1), presumably because Eu^{2+} is a less powerful reductant than Yb^{2+} [8, 9].

and of bis(pentafluorophenyl)mercury with samarium <u>at room temperature</u> were more complex than the transmetallation reactions previously discussed [sections (b) and (c)]. This was evident from the high yields of lanthanoid trifluorides (Table 1) and the mixture of fluorocarbons (see below) obtained on acidification of the tetrahydrofuran-soluble products.

Distillation of the products from acidolysis with H_2SO_4 of the filtered $(C_6F_5)_2Hg/Sm$ reaction mixture gave C_6HF_5 and $\underline{o}$-$H_2C_6F_4$ (mole ratio 7 : 1; the sole volatile polyfluoroaromatics detectable by ^{19}F n.m.r. spectroscopy), and left a residue of fluorocarbon gum containing $C_{18}HF_{13}$, $C_{18}H_2F_{12}$, $C_{18}H_3F_{11}$, and possibly $C_{12}HF_9$ and $C_{12}F_8$. To determine whether the hydrogen in these products was incorporated prior to or during acidolysis, the filtered reaction mixture was decomposed with deuterosulphuric acid. The fluorocarbon gum remaining after distillation was similar to that from decomposition with H_2SO_4, the only noticeable difference being the presence of $(C_6F_5C_6F_4)_2Hg$. No deuterated species could be detected. Thus, the hydrogen in the polyfluoroterphenyls must have been abstracted from tetrahydrofuran before acidification. The distillate after decomposition with D_2SO_4 contained C_6DF_5 and C_6HF_5 (main products; mole ratio 9 : 1 from mass spectrometry assuming comparable volatility and ability to carry the ion current), C_6HDF_4 and $C_6H_2F_4$ (mole ratio 1 : 8), $C_{12}DF_9$ and $C_{12}HF_9$ (mole ratio 1 : 2, three isomers of $C_{12}HF_9$ detected), $C_{12}H_2DF_7$, and possibly $C_{12}HD_2F_7$. Thus, the soluble organolanthanoid products included species with C_6HF_4Sm ($\xrightarrow{D_2SO_4}$ C_6HDF_4),* $C_{12}F_9Sm$ ($\xrightarrow{D_2SO_4}$ $C_{12}DF_9$), and $C_{12}H_2F_7Sm$ ($\xrightarrow{D_2SO_4}$ $C_{12}H_2DF_7$) groups in addition to those with C_6F_5Sm ($\xrightarrow{D_2SO_4}$ C_6DF_5) groups. ^{19}F n.m.r. data (above) for the distillate from acidolysis with H_2SO_4 suggest that the amounts of polyfluorobiphenyls, and hence the amounts of polyfluorobiphenylylsamarium species, must be very small.

The reaction of $(\underline{o}$-$HC_6F_4)_2Hg$ with ytterbium at 0-30° showed features similar to the reaction with samarium, although it was not studied in the same detail. After acidolysis, the distillate contained $C_{12}H_3F_7$ [see also (c)] as

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* Since $\underline{o}$-$H_2C_6F_4$ was the sole detectable tetrafluorobenzene on acidolysis with H_2SO_4 (above), only 2,3,4,5-tetrafluorophenylsamarium species were present.

well as o-$H_2C_6F_4$, and the residual fluorocarbon gum contained a variety of polyfluoropolyphenyls, e.g. $C_{30}H_6F_{16}$, $C_{30}H_7F_{15}$, $C_{24}H_5F_{13}$, $C_{18}H_4F_{10}$ (for a complete listing - see Experimental).

The lanthanoid trifluorides formed on acidolysis of the filtered reaction mixtures must be derived from decomposition of soluble fluorolanthanoid species, and the yields of the trifluorides indicate that the soluble species contained on average 1.9 fluorines per samarium and 1.3 fluorines per ytterbium. The amounts of polyfluorobenzenes (RH) determined by ultraviolet spectroscopy and hence the RH/Ln_s ratios [ca. 1.2 (Yb); ca. 1.0 (Sm) - Table 1] do not have strict quantitative significance, since the distillates contained polyfluorobiphenyls (above), which should enhance the ultraviolet absorption [section (b)]. For the $(C_6F_5)_2Hg$/Sm system, the two main polyfluoroaromatics in the distillate, C_6HF_5 and o-$H_2C_6F_4$, contribute to RH/Ln_s on an equivalent basis, as they have similar extinction coefficients [$\epsilon_{o\text{-}H_2C_6F_4}$, 593 at 260 nm; $\epsilon_{C_6F_5H}$, section (b)]. A reasonable interpretation of the RH/Ln_s values is that there is an average of ca. one o-HC_6F_4 group per ytterbium and less than one C_6F_5 (or o-HC_6F_4) group per samarium. On the basis of the analytical data, the tetrahydrofuran-soluble samarium containing products include $C_6F_5SmF_2$, SmF_2, probably C_6F_5SmF, o-$HC_6F_4SmF_2$, and possibly o-HC_6F_4SmF, together with minor amounts of analogous $C_{12}F_9Sm$- and $C_{12}H_2F_7Sm$- derivatives. Similarly, the ytterbium containing products include o-HC_6F_4YbF, o-$HC_6F_4YbF_2$, possibly YbF_2, and more complex species. Decomposition of the RMF_2 derivatives,

$$6\,RMF_2 + 3\,H_2SO_4 \rightarrow 6\,RH + 4\,MF_3\downarrow + M_2(SO_4)_3$$

and oxidation and rearrangement of fluorolanthanoid(II) species accounts for formation of lanthanoid trifluorides (Table 1 and above) on acidolysis.

Supporting evidence for the presence of lanthanoid(III) species in the reaction mixtures was obtained by visible/near infrared spectroscopy. Thus, near infrared absorptions of the Sm/$(C_6F_5)_2Hg$ reaction mixture at 1060-1095, 1220-1260, and 1380 nm correspond closely to characteristic maxima of aqueous samarium trichloride [12] and can be assigned to transitions from the ground state $^6H_{5/2}$ [9] to the states $^6F_{9/2}$, $^6F_{7/2}$, and $^6F_{5/2}$ respectively [13]. Samarium(II) does not absorb in this region [14]. The visible bands of the reaction mixture at 540 and 615 nm can be attributed to charge-transfer transitions of organosamarium species (see analogous bands of "PhSmI" [15]) overlapping a samarium(II) absorption [14, 16], whilst a feature at 400 nm can be assigned to f↔f transitions of both samarium(II) [14, 16] and samarium(III) [12, 13]. The visible/near infrared spectrum of the Yb/($\underline{o}$-$HC_6F_4)_2Hg$ reaction mixture shows a broad intense shoulder at 418 nm, attributable to 5d←4f transitions and/or metal←ligand charge transfer of a polyfluorophenylytterbium(II) species [1], and a much weaker double maximum at 978 and 980 nm, which may be assigned to ${}^2F_{5/2} \leftarrow {}^2F_{7/2}$ of an organoytterbium(III) species [17].

2. Routes to the Products

Since the reaction of ytterbium with bis(2,3,4,5-tetrafluorophenyl)-mercury at 0^oC yields ($\underline{o}$-$HC_6F_4)_2Yb$, it is probable that the products of the room temperature reaction [section (d).1] arise from thermal decomposition of the bis(polyfluorophenyl)ytterbium compound. The situation is more complex for the reaction of $(C_6F_5)_2Hg$ with samarium. The Hg_p/Ln_s ratio (1.26) is mid-way between the values for reactions (1) and (9) ($R = C_6F_5$, M = Sm).

$$3R_2Hg + 2M \rightarrow 2R_3M + 3Hg \qquad (9)$$

Transmetallations giving lanthanoid(III) compounds are known, e.g. reaction (9) (R = I, M = Sm [18]). Accordingly, it is possible that the observed products of the $(C_6F_5)_2Hg/Sm$ reaction are derived from thermal decomposition of both $(C_6F_5)_2Sm$ and $(C_6F_5)_3Sm$. The formation of many of the observed products can be explained by two main decomposition paths, (i) fluoride elimination and polyfluorobenzyne formation and (ii) reduction of polyfluoroaryl groups by lanthanoid(II) species. To simplify the following discussion, the decomposition steps have been formulated for $(C_6F_5)_2Sm$ [and $(C_6F_5)_3Sm$], but analogous reactions are also considered to occur on decomposition of ($\underline{o}$-$HC_6F_4)_2Yb$, and to explain formation of $C_{12}HF_9$, $C_{12}H_2F_8$, and $\underline{p}$-$H_2C_6F_4$ in the $(C_6F_5)_2Hg/Yb$ system [section (b)]. For convenience it has been assumed that (i) precedes (ii).

(i) Decomposition of polyfluorophenylsamarium compounds by fluoride elimination (10) – (12) explains the origin of three samarium containing products considered to be formed in the $(C_6F_5)_2Hg/Sm$ reaction [section (d).1].

$$(C_6F_5)_2Sm \rightarrow C_6F_5SmF + \underline{o}\text{-}C_6F_4 \qquad (10)$$

$$C_6F_5SmF \rightarrow SmF_2 + \underline{o}\text{-}C_6F_4 \qquad (11)$$

$$(C_6F_5)_3Sm \rightarrow C_6F_5SmF_2 + 2\,\underline{o}\text{-}C_6F_4 \qquad (12)$$

The origins of $C_{12}HF_9$, $C_{18}HF_{13}$, and $C_{12}F_9Sm$ compounds, detected by acidolysis with D_2SO_4 [section (d).1], are probably insertion reactions of tetrafluorobenzyne [from (10)-(12)] into polyfluoroarylsamarium bonds, e.g. (13), (14).

$$C_6F_5SmF + \underline{o}\text{-}C_6F_4 \rightarrow \underline{o}\text{-}C_6F_5C_6F_4SmF \qquad (13)$$

$$\underline{o}\text{-}C_6F_5C_6F_4SmF + \underline{o}\text{-}C_6F_4 \rightarrow \underline{o}\text{-}(\underline{o}\text{-}C_6F_5C_6F_4)C_6F_4SmF \qquad (14)$$

Perfluoroterphenylyl species [e.g. from (14)] are evidently completely decomposed into $C_{18}HF_{13}$ by hydrogen abstraction from tetrahydrofuran prior to acidolysis, whereas perfluorobiphenylylsamarium species are only partly decomposed into $C_{12}HF_9$. Tetrafluorobenzyne formation and insertion reactions, analogous to (10)-(13), have been observed on decomposition of pentafluorophenyllithium [19]. Formation of a polyfluorobenzyne on decomposition of a polyfluorophenyllanthanoid has been established by heating bis(pentafluorophenyl)ytterbium in the presence of furan (Experimental Section). After acidolysis of the reaction mixture, g.c./m.s. evidence was obtained for the presence of 5,6,7,8-tetrafluoronaphthalen-1-ol, which is formed [20] by acid-induced rearrangement of the product from addition of tetrafluorobenzyne to furan. This procedure has previously been used to trap tetrafluorobenzyne on decomposition of pentafluorophenyllithium [20]. Formation of $(C_6F_5C_6F_4)_2Hg$, detected following acidolysis with D_2SO_4 [section (d).1], can be attributed to insertion of tetrafluorobenzyne into C_6F_5-Hg bonds.

The preceding scheme only accounts for one of the three $C_{12}HF_9$ isomers detected. The other two could possibly be derived from unselective nucleophilic attack of pentafluorophenyl carbanions on pentafluorophenylsamarium compounds, followed by hydrogen abstraction from tetrahydrofuran.

$$C_6F_5^- + C_6F_5SmX \rightarrow F^- + \underline{m}\text{- or }\underline{p}\text{-}C_6F_5C_6F_4SmX \xrightarrow{THF} \underline{m}\text{- or }\underline{p}\text{-}HC_6F_4C_6F_5 \qquad (15)$$

An analogous substitution is observed when pentafluorophenylmagnesium bromide is treated with silicon tetrachloride in tetrahydrofuran [21], though only the _para_ position is attacked. In the case of pentafluorophenylsamarium(II) species, the electron donating character of samarium(II) (powerful reducing agent) could deactivate the _para_ position (the preferred position for nucleophilic substitution in most C_6F_5X compounds [22]) sufficiently for _meta_ substitution to become competitive.

(ii) The decomposition paths outlined in (10)-(15) do not account for the formation of $C_{12}H_2F_7Sm$ or $\underline{o}$-HC_6F_4Sm containing species, 1,2,3,4-tetrafluorobenzene, and polyfluorobiphenyls or polyfluoroterphenyls with more than one hydrogen substituent [section (d).1]. These products may be formed by reduction of polyfluoroaryl groups by samarium(II), followed by hydrogen abstraction from tetrahydrofuran and elimination of fluoride ions.

e.g. $$C_6F_5SmX + C_6F_5Y \rightarrow C_6F_5SmX^+ + YC_6F_5^{\dot{-}} \qquad (16)$$

X = F, C_6F_5, *o*-$C_6F_5C_6F_4$, etc.; Y = C_6F_5Sm, SmF, C_6HF_4, $C_{12}HF_8$, etc.

$$YC_6F_5^{\dot{-}} + C_4H_8O \rightarrow YC_6F_5H^{\bullet} + C_4H_7O^- \qquad (17)$$

$$C_6F_5SmX + YC_6F_5H^{\bullet} \rightarrow YC_6F_5H^- + C_6F_5SmX^+ \qquad (18)$$

$$YC_6F_5H^- \rightarrow YC_6F_4H + F^- \xrightarrow{C_6F_5SmX^+} C_6F_5SmFX \qquad (19)$$

The reaction scheme (16)-(19) is similar to that proposed [23, 24] for electrochemical reduction of polyfluoroaromatic compounds. Reduction of the fluorocarbon groups of polyfluoroarylsamarium(II) species may alternatively involve a similar intramolecular process. However, the reasons for regioselective formation of *o*-$H_2C_6F_4$ and *o*-HC_6F_4Sm compounds [section (d).1] are unclear. By contrast, a little 1,2,4,5-tetrafluorobenzene was obtained in addition to pentafluorobenzene on acidolysis of the products from reaction of ytterbium with bis(pentafluorophenyl)mercury [section (b)]. In electrochemical reduction of pentafluorobenzene [23] and pentafluorobenzoic acid [24], regioselective replacement of the fluorine *para* to hydrogen or or carboxyl occurs. The emergence of selectivity effects is of considerable interest, and is to be further investigated.

The ultimate fate of the deprotonated tetrahydrofuran is not entirely clear. There is evidence for the presence of C_4H_7DO in the products from treatment of the $(C_6F_5)_2Hg$/Sm reaction mixture with D_2SO_4, consistent with deuteration of $C_4H_7O^-$. Alternatively the carbanion may lose hydride ions giving 2,3-dihydrofuran, which would be decomposed during acidolysis [7].

Experimental

1. Reagents

Lanthanoid elements were from Koch-Light and Research Chemicals (Nucor). Ytterbium powder was used as supplied. Samarium powder was washed with dry benzene or hexane to remove adhering oil immediately before use. Europium, obtained as ingots under oil, was either hammered into discs (*ca*. 1 x 0.05 cm^2), which were washed with dry benzene, or was crushed in a mortar under dry hexane. Subsequently, samarium and europium were transferred under nitrogen to the reaction flasks. Polyfluoroaromatic compounds were from Bristol Organics and phenylacetylene was from Aldrich. Bis(polyfluorophenyl)mercurials [11, 25] and bis(phenylethynyl)-mercury [26] were prepared by the reported methods. Authentic lanthanoid trifluoride hydrates, MF_3 (0.5–1 H_2O) [27], were precipitated by addition of aqueous sodium fluoride to the lanthanoid trichlorides in water. Deuterosulphuric acid was prepared by absorption of sulphur trioxide in D_2O [28]. Furan (B.D.H.) was dried over anhydrous potassium carbonate, and was distilled from sodium under nitrogen. Benzene was dried over and distilled from sodium under nitrogen. Purification of other solvents and of nitrogen has been described in Part 1 [1].

2. Instrumentation

Mass spectra were obtained with AEI MS30 or VG Micromass instruments. Listed m/e values for mercury-containing ions are those for ^{202}Hg. Analytical g.l.c. separations were carried out with a Hewlett Packard 5750 or a Varian Aerograph 940 chromatograph. G.c./m.s. studies were carried out with a Perkin-Elmer 990 dual column chromatograph connected to a Hitachi RM50 mass spectrometer, or with a Pye 104 chromatograph interfaced to an AEI MS30 mass spectrometer via a Bieman frit separator. Tetrahydrofuran, phenylacetylene, styrene and ethylbenzene were separated on a 6' x 1/8" column packed with Carbowax 20M (15%) on 80–100 mesh Chromosorb W, nitrogen being the carrier gas, whilst acetophenone in this mixture was analysed with a 6' x 1/8" column containing silicone oil DC 200 (10%) on the same support. Mixtures of tetrahydrofuran and fluorocarbons were analysed with a 6' x 1/4" column packed with silicone oil SE 30 (3%) or Dexsil 300 (3%) on Chromosorb W. These separations generally used helium carrier gas and temperature programming from room temperature to 190^{o} at 10^{o}/min. Visible/near infrared spectra (300-1400 nm) of reaction mixtures were measured in a 1 mm silica cell, which was sealed onto a Quickfit flask fitted with a side arm tap for passage of nitrogen. After completion of reaction in the flask, precipitated mercury was allowed to settle, and the supernatant solution was decanted into the cell. Alternatively, solutions from other reaction vessels were transferred by syringe under nitrogen to the flask. The instrumentation for electronic and ^{19}F n.m.r. spectroscopy has been given in Part I [1]. X-ray powder photographs were obtained with a Philips Debye-Scherrer 114.6 mm powder camera using nickel-filtered CuKα radiation.

3. Reactions of Lanthanoid Elements with Mercurials

(i) General procedure and analytical methods. -

The reagents, solvents, and reaction conditions are given in Table.1. The reactions were carried out in 10 ml of solvent [8 ml for the $(C_6F_5)_2Hg$/Eu system] under purified nitrogen in Schlenk glassware. After reaction, the products were filtered through a celite pad to remove precipitated mercury and unreacted lanthanoid metal. The resulting organolanthanoid solution was treated with a known excess of degassed dilute H_2SO_4 (typically 0.6 mol/l; 10 ml) or dilute D_2SO_4 under nitrogen. The acidolysis reaction mixture was then distilled until the boiling point reached 100° (ca. 15 min), and the quantity of volatile polyfluoroarene (C_6F_5H, p-$H_2C_6F_4$, or o-$H_2C_6F_4$) or phenylacetylene and styrene in the distillate was determined by ultraviolet spectroscopy. In blank experiments, the recovery of C_6F_5H and PhCCH was ≥98%. Representative distillates were also examined by g.l.c., g.c./m.s., and/or ^{19}F n.m.r. spectroscopy (see below). After distillation, the resulting suspension or solution was extracted with ether to remove involatile organic products, and any oil or glue obtained on evaporation of the ether was examined by mass spectrometry. If any suspension remained in the aqueous layer, the solid was recovered by centrifugation, dried at 200°, and was identified by X-ray powder photography as substantially the corresponding hydrated lanthanoid trifluoride. In representative reactions, the aqueous layer was titrated with sodium hydroxide to determine the acid consumed on acidolysis. For determination of lanthanoid ions, the aqueous layer was buffered at pH 4.5 and titrated with sodium ethylenediaminetetraacetate using xylenol orange indicator [29]. Some solutions were treated with H_2S at pH 3 prior to titration, but no mercuric sulphide was precipitated. The celite pads containing precipitated mercury metal and unreacted lanthanoid metal were dried under vacuum to remove tetrahydrofuran and were dissolved in hot concentrated nitric acid (60 ml.). Concentrated sulphuric acid (3 ml) was added and the nitric acid was distilled off. The residue was dissolved in water (50 ml), the pH was adjusted to 3, mercury was precipitated as mercuric sulphide [30], and the lanthanoid ions in the filtrate were determined as above. Features of specific reactions follow.

(ii) The reaction of bis(pentafluorophenyl)mercury with ytterbium. -

The colour of the filtered solution of bis(pentafluorophenyl)ytterbium was orange. G.c./m.s. of the distillate after acidolysis revealed the presence of a tetrafluorobenzene (m/e 150), $C_{12}HF_9$ (m/e 316), and

$C_{12}H_2F_8$ (m/e 298), in addition to pentafluorobenzene (m/e 168). The ^{19}F n.m.r. spectrum of the distillate showed C_6HF_5 and p-$H_2C_6F_4$ to be present (mole ratio, 19:1 and 50:1 from reactions in tetrahydrofuran and ether respectively), but the polyfluorobiphenyls could not be detected by this technique.

(iii) The reaction of bis(2,3,5,6-tetrafluorophenyl)mercury with ytterbium. -

The filtered solution of bis(2,3,5,6-tetrafluorophenyl)ytterbium was orange in colour. The mass spectrum of the trace of oil remaining after acidolysis and distillation was uninformative. The only identifiable features were mercury containing clusters at m/e 450 ($C_{11}H_2F_6Hg^+$), 432 ($C_{11}H_3F_5Hg^+$), and 414 ($C_{11}H_4F_4Hg^+$).

(iv) The reaction of bis(pentafluorophenyl)mercury with europium. -

The reaction in Table 1 was carried out with europium discs [see 1. reagents], and was initiated with 0.130 g of metallic mercury. It was subsequently found that the alternative pretreatment of europium [1. reagents] permitted transmetallation to occur without initiation. After acidolysis of the green solution of bis(pentafluorophenyl)europium and distillation, white crystals were observed in the condenser and were identified as bis(pentafluorophenyl)mercury, m.p. 134-138°, mixed m.p. 138-140°, lit. [10] 142°. The crystals were combined with the product obtained by ether extraction of the aqueous suspension which remained after distillation. The amount of bis(pentafluorophenyl)mercury was determined by conversion into tetraiodomercurate(II) ions [11] by boiling with sodium iodide (2 g) and dilute HCl (1 mol/l; 1 ml) in ethanol (50 ml) for 10 min. The decomposition product was treated with sodium iodide (10 g), sodium metabisulphite (0.3 g), and sodium hydroxide (0.03 g) in ethanol (200 ml) and water (50 ml), and the tetraiodomercurate(II) ions were determined spectrophotometrically by comparison with a standard curve constructed from cleavage of a known amount of $(C_6F_5)_2Hg$. In a blank experiment, decomposition of $(C_6F_5)_2Hg$ under the acidolysis conditions was less than 1%.

(v) The reaction of bis(phenylethynyl)mercury with ytterbium. -

The resulting solution of bis(phenylethynyl)ytterbium was purple-black in colour. The mole ratio PhCCH : $PhCHCH_2$: $PhCH_2CH_3$ in the distillate after acidolysis [Results and Discussion (b)] was determined by g.l.c., the identification of the compounds being confirmed by g.c./m.s. The amount of acetophenone was <0.3%.

(vi) The reaction of bis(2,3,4,5-tetrafluorophenyl)mercury with ytterbium at 0°C.-

The ether-extracted involatile organic products [see 3(i) General procedure] from the reaction at 0°C (Table 1) gave the following mass spectrum (listing restricted to m/e > 200): m/e 670 (0.2% $C_{30}H_6F_{16}^+$), 652 (0.3%, $C_{30}H_7F_{15}^+$), 636 (0.2%, $C_{29}H_4F_{15}^+$), 540 (1% , $C_{24}H_5F_{13}^+$), 522 (2% , $C_{24}H_6F_{12}$), 504 (1%, $C_{24}H_7F_{11}^+$), 486 (0.4%, $C_{24}H_8F_{10}^+$), 429 (0.6%), 410 (5%, $C_{18}H_4F_{10}^+$), 392 (6%, $C_{18}H_5F_9^+$), 374 (4%, $C_{18}H_6F_8^+$), 280 (100%, $C_{12}H_3F_7^+$), 262 (35%, $C_{12}H_4F_6^+$), 244 (4%, $C_{12}H_5F_5^+$), 243 (3%, $C_{12}H_4F_5^+$), 242 (9%, $C_{12}H_3F_5^+$), 229 (5%, $C_{11}H_2F_5^+$), 211 (10%, $C_{11}H_3F_4^+$). G.c./m.s. analysis of the distillate after acidolysis showed a tetrafluorobenzene (m/e 150) and a septafluorobiphenyl (m/e 280) to be present. The last compound was contaminated with a little hexafluorobiphenyl (m/e 262). The ultraviolet spectrum of the distillate showed the distinctive features of 1,2,3,4-tetrafluorobenzene.

The reaction was repeated for 3 h. at 0°C with bis(2,3,4,5-tetrafluorophenyl)mercury (2.92 mmol) and ytterbium (6.64 mmol), and gave mercury metal (96%) and an orange solution of bis(2,3,4,5-tetrafluorophenyl)ytterbium (91%). The Hg_p/Ln_s and RH/Ln_s ratios were 1.06 and 2.43 respectively. The amount of $YbF_3.H_2O$ precipitated [see 3(i)] was 1.5% of the lanthanoid ions obtained on acidolysis. The amount of mercurial unreacted and recovered as mercury on acidification was 2.4%. Allowance for o-$H_2C_6F_4$ generated by reduction of unreacted mercurial gave an adjusted RH/Ln_s ratio of 2.38.

(vii) The reaction of bis(2,3,4,5-tetrafluorophenyl)mercury with ytterbium at > 0°C. -

In the reaction at 0-30°C (Table 1), the colour of the organolanthanoid product rapidly changed from orange [(o-$HC_6F_4)_2Yb$; section 3(vi)] to brown as the reaction mixture warmed from 0°C. The mass spectrum of the ether-soluble involatile organic products [see 3(i)] was similar to that of analogous products from the reaction at 0°C [3(vi)], except that peaks at m/e 410, 374, 280, 262, 229, and 211 had reduced intensity, whilst the rest (other than m/e 486) had increased intensity. G.c./m.s. of the distillate following acidolysis showed a tetrafluorobenzene and a septafluorobiphenyl to be present.

(viii) The reaction of bis(pentafluorophenyl)mercury with samarium.-

The reaction in Table 1 was initiated by addition of mercury (0.112 g) and brief heating at 60°C. An initial green colouration developed, and this became deep green-black after 4 h at 16°C. The ^{19}F n.m.r. spectrum of the distillate after acidolysis with H_2SO_4 showed pentafluorobenzene and 1,2,3,4-tetrafluorobenzene (mole ratio, 7 : 1) to be present. The ether-extracted involatile organic products had the following mass spectrum (restricted to m/e > 200): m/e 464 (1%, $C_{18}HF_{13}^+$), 446 (4%, $C_{18}H_2F_{12}^+$), 428 (5%, $C_{18}H_3F_{11}^+$), 369 (2%, $C_6F_5Hg^+$), 351 (1%, $C_6HF_4Hg^+$), 316 (2%, $C_{12}HF_9^+$), 315 (9%, $C_{12}F_9^+$), 296 (9%, $C_{12}F_8^+$), 265 (6%, $C_{11}F_7^+$), 223 (14%, $C_9HF_6^+$?), base peak 73 (100%, $C_4H_9O^+$). The mass spectrum of the corresponding products from acidolysis with D_2SO_4 was similar, but showed additional clusters at m/e 832 [$(C_6F_5C_6F_4)_2Hg^+$], 684 [$C_6F_5C_6F_4HgC_6F_5^+$], 517 [$C_6F_5C_6F_4Hg^+$]. G.c./m.s. of the distillate following D_2SO_4 acidolysis gave (a) a mixture of C_6DF_5 (m/e 169) and C_6HF_5 (m/e 168) (mole ratio, 9 : 1) with a smaller amount of C_6HDF_4 (m/e 151) and $C_6H_2F_4$ (m/e 150) (mole ratio, 1 : 8), (b) $C_{12}H_2DF_7$ (m/e 281) possibly containing a little $C_{12}HD_2F_7$ (m/e 282), (c) three separate mixtures of $C_{12}DF_9$ (m/e 317) and $C_{12}HF_9$ (m/e 316) (each with mole ratio $\simeq$ 1 : 2).

A blank experiment was carried out to test the ability of C_6HF_5 to exchange with D_2SO_4 under acidolysis conditions. Pentafluorobenzene (4.7 mmol), tetrahydrofuran (15.9 mmol), and D_2SO_4 (1.5 mol/l; 2 ml) were heated under reflux for 20 min, atmospheric moisture being excluded, and then the reaction mixture was distilled. The mole ratio, C_6HF_5 : tetrahydrofuran, determined by ^1H n.m.r. spectroscopy, in the distillate was similar to that in the reactants, hence a significant amount of C_6DF_5 was not formed.

The visible/near infrared spectrum of the filtered green-black reaction mixture had maxima at 325sh, 360sh, 405sh, 540w and 615w (on a broad feature at 500-650 nm), 1060-1080w (br), 1220-1260w (br), and 1380w (sp) nm. After evaporation of the reaction mixture to dryness, a Nujol mull of the residue showed only a weak sharp peak at 1378 nm in the region 300-1400 nm. The spectrum of a solution exposed to air revealed maxima at 645sh (br), 1075w (br), 1225w (br), and 1378w (sp) nm.

4. The Reaction of Tris(pentafluorophenyl)bismuth with Ytterbium. -

The procedure was similar to that used [3(i)] in reactions with mercurials. After reaction, the precipitate was mainly unreacted ytterbium with a little bismuth. Acidification of the filtered reaction mixture gave bismuth ions and no detectable ytterbium ions. The distillate after acidolysis contained pentafluorobenzene and 1,2,3,4-tetrafluorobenzene (mole ratio, 10:1 by ^{19}F n.m.r. spectroscopy). Bismuth was determined gravimetrically as Bi_2S_3 [31], which proved accurate to ±3%.

5. Decomposition of Bis(pentafluorophenyl)ytterbium in the Presence of Furan

A solution of bis(pentafluorophenyl)ytterbium was prepared by reaction of ytterbium (1.68 mmol) with bis(pentafluorophenyl)mercury (1.49 mmol) in ether (10 ml) for 4.5 h at 0-10°C, and was filtered through a celite pad, which was washed with ether. The volume was reduced to 5 ml, and furan (7.7 mmol) was added. The reaction mixture was refluxed for 2 h under nitrogen, dilute sulphuric acid (0.6 mol/l, 5 ml) was then added, and the mixture was extracted with ether. G.c./m.s. of the ether extract revealed the presence of 5,6,7,8-tetrafluoronaphthalen-1-ol (m/e 216), a nonafluorobiphenyl (m/e 316), and $C_{18}HF_{13}$ (m/e 464) [mole ratio (from g.l.c.), 45:24 :31].

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