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A STUDY OF THE SUBSTITUTION OF SOME FLUOROAROMATICS USING  
[Pb(EPh)<sub>3</sub>]<sup>-</sup> (E = S or Se) AS A SOURCE OF THE EPh<sup>-</sup> NUCLEOPHILE

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SUMMARY

A <sup>207</sup>Pb NMR study of Pb(SPh)<sub>2</sub>/DMF mixtures, which are known to act as a source of the SPh<sup>-</sup> nucleophile, suggests that they contain species with the Pb<sup>II</sup>S<sub>3</sub> kernel. To discover whether the carrier of SPh<sup>-</sup> could be [Pb(SPh)<sub>3</sub>]<sup>-</sup>, the room-temperature reactions of (AsPh<sub>4</sub>)[Pb(SPh)<sub>3</sub>] (**1**) with the representative substrates (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, 2,4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>F and C<sub>6</sub>F<sub>6</sub> in CHCl<sub>3</sub> (or CDCl<sub>3</sub>/CHCl<sub>3</sub>) have been investigated. The known compounds 4,4'-(C<sub>6</sub>F<sub>4</sub>(SPh))<sub>2</sub> and 2,4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>(SPh) are formed readily from the first and second substrates, but the conversion of C<sub>6</sub>F<sub>6</sub> to 4-C<sub>6</sub>F<sub>4</sub>(SPh)<sub>2</sub> is very slow under the conditions used. En-route to 4,4'-(C<sub>6</sub>F<sub>4</sub>(SPh))<sub>2</sub>, the new compound 4-C<sub>6</sub>F<sub>5</sub>.C<sub>6</sub>F<sub>4</sub>(SPh) is formed. For (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> and 2,4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>F, analogous but slower reactions are observed using (AsPh<sub>4</sub>)[Pb(SePh)<sub>3</sub>] (**2**), as a source of SePh<sup>-</sup>, but no reaction of C<sub>6</sub>F<sub>6</sub> with **2** was observed. In general, reactions of **2** are complicated by its ease of oxidation to Ph<sub>2</sub>Se<sub>2</sub>.

## INTRODUCTION

Although  $\text{Pb}(\text{SPh})_2$  in refluxing dimethylformamide (DMF) has been used as a source of the  $\text{SPh}^-$  nucleophile for the substitution of fluoroaromatics, the forms of the lead-containing and thiolate-containing species present in DMF remain unknown [1]. An X-ray crystal structure of  $\text{Pb}(\text{SPh})_2$  shows it to be extensively thiolate-bridged [2], which accounts for the poor solubility of the compound in many solvents and makes its relatively high solubility in DMF particularly noteworthy.

We report here the  $^{207}\text{Pb}$  NMR spectrum of a solution of  $\text{Pb}(\text{SPh})_2$  in DMF, which suggests ionization to species with a  $\text{Pb}^{\text{II}}\text{S}_3$  kernel. Accordingly, we postulate that  $[\text{Pb}(\text{SPh})_3]^-$  may be the carrier of  $\text{SPh}^-$  in  $\text{Pb}(\text{SPh})_2/\text{DMF}$ . To test this assertion, we have investigated the use of  $(\text{AsPh}_4)[\text{Pb}(\text{SPh})_3]$ , **1**, as a source of  $\text{SPh}^-$ . A particular advantage of this salt is its high solubility in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  at ambient temperature, which not only allows reactions to be studied under mild conditions but also allows for ready monitoring of reaction mixtures by  $^{19}\text{F}$  NMR. Three representative fluoroaromatic substrates have been investigated:  $\text{C}_6\text{F}_5\cdot\text{C}_6\text{F}_5$  (DFBP), 1-fluoro-2,4-dinitrobenzene (FDNB) and  $\text{C}_6\text{F}_6$  (HFB). In addition, we have extended our study to include  $(\text{AsPh}_4)[\text{Pb}(\text{SePh})_3]$ , **2**, as a source of  $\text{SePh}^-$ . In previous studies of nucleophilic substitution by  $\text{SePh}^-$ , alkali metal salts of the chalcogenate have been used, e.g. Ref. 3. ( $\text{Pb}(\text{SePh})_2$  has very poor solubility in DMF.)

## RESULTS

Lead-207 NMR spectrum of  $\text{Pb}(\text{SPh})_2$  in DMF

At 294 K, the  $^{207}\text{Pb}$  NMR spectrum of a saturated solution of  $\text{Pb}(\text{SPh})_2$  in DMF consists of a single broad resonance ( $\Delta\nu_{\frac{1}{2}} \approx 900$  Hz) with  $\delta_{\text{Pb}} \approx 2470$  (from external  $\text{PbMe}_4$  in toluene).

Reactions of 1 and 2 with (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, 2,4-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>F and C<sub>6</sub>F<sub>6</sub>

With a  $3.33 \times 10^{-2}$  M concentration of the various substrates, S, in CHCl<sub>3</sub> or CDCl<sub>3</sub>/CHCl<sub>3</sub> (1/2 v/v) at 294±3 K, the results summarized in Table 1 were obtained for reactions with [Pb(EPh)<sub>3</sub>]<sup>-</sup>.

TABLE 1

Reactions of [Pb(EPh)<sub>3</sub>]<sup>-</sup> with Various Substrates, S

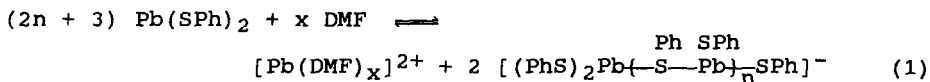
S	S/ 1 or 2	E	Time (h)	Comments
DFBP	3/1	S	24	Essentially complete reaction (by <sup>19</sup> F NMR); DFBP:4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SPh):4,4'-(C <sub>6</sub> F <sub>4</sub> {SPh}) <sub>2</sub> = 0.7:1:0.6.
	3/2	S	24	Close-to-complete reaction (by <sup>19</sup> F NMR); 4,4'-(C <sub>6</sub> F <sub>4</sub> (SPh)) <sub>2</sub> :4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SPh) = 7:1
	3/3	S	24	Major product (by <sup>19</sup> F NMR) remains 4,4'-(C <sub>6</sub> F <sub>4</sub> (SPh)) <sub>2</sub> .
	3/1	Se	24	Very little reaction (by <sup>19</sup> F NMR); DFBP:4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SePh) = 7:1
	3/2	Se	24	Incomplete reaction (by <sup>19</sup> F NMR); DFBP:4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SePh):4,4'-(C <sub>6</sub> F <sub>4</sub> {SePh}) <sub>2</sub> = 3.3:1:0.07.
	3/2	Se	168	Incomplete reaction (by <sup>19</sup> F NMR); DFBP:4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SePh):4,4'-(C <sub>6</sub> F <sub>4</sub> {SePh}) <sub>2</sub> = 1.1:1:0.2. Ph <sub>2</sub> Se <sub>2</sub> evident by TLC and <sup>77</sup> Se NMR.
	1/2	Se	168	Incomplete reaction (by <sup>19</sup> F NMR); DFBP:4-C <sub>6</sub> F <sub>5</sub> .C <sub>6</sub> F <sub>4</sub> (SePh):4,4'-(C <sub>6</sub> F <sub>4</sub> (SePh)) <sub>2</sub> = 0.5:1:0.6. Ph <sub>2</sub> Se <sub>2</sub> evident (TLC, <sup>77</sup> Se NMR)
FDNB	3/1 or 1/2	S	24	Complete reaction to C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> (SPh) (by TLC).
	3/1	Se	24	Incomplete reaction to C <sub>6</sub> H <sub>3</sub> (NO <sub>2</sub> ) <sub>2</sub> (SePh), with some formation of Ph <sub>2</sub> Se <sub>2</sub> (by TLC).
HFB	1/2	S	168	Incomplete reaction (by <sup>19</sup> F NMR); HFB:4-C <sub>6</sub> F <sub>4</sub> (SPh) <sub>2</sub> = 1:0.18.
	1/2	Se	168	No reaction (by <sup>19</sup> F NMR).

Although standard reaction times of 24 h, or 1 week, if necessary, were used, monitoring by  $^{19}\text{F}$  NMR shows that  $\geq 95\%$  of the  $[\text{Pb}(\text{SPh})_3]^-$  has reacted in ca. 1 h and  $\leq 30$  min for mixtures with  $\text{DFBP}/\underline{1} = 3/1$  and  $3/2$ , respectively. (Completion of reaction can be detected qualitatively by blanching of the pale yellow colour of  $[\text{Pb}(\text{SPh})_3]^-$ .) Reactions with FDNB appear to be even faster, as expected.

A white precipitate of, presumably,  $\text{PbF}_2$ , is particularly apparent when  $\text{DFBP}/\underline{1}$  mixtures react. In addition  $[\text{AsPh}_4]\text{F}$  can be isolated from such mixtures after equilibration.

## DISCUSSION

The  $^{207}\text{Pb}$  NMR signal found in  $\text{Pb}(\text{SPh})_2/\text{DMF}$  mixtures is in the general region expected for a  $\text{Pb}^{\text{II}}\text{S}_3$  kernel. For comparison, at 294 K  $\delta_{\text{Pb}} = 2881$  ( $\Delta\nu_{\frac{1}{2}} \approx 30$  Hz) for a solution containing 0.1 mol of  $\underline{1}$  per litre of DMF. (Under the same conditions,  $\delta_{\text{Pb}} = 3244$  ( $\Delta\nu_{\frac{1}{2}} \approx 160$  Hz) for  $\underline{2}$ .) The data for  $\underline{1}$  are close to values found for  $[\text{Pb}(\text{SPh})_3]^-$  in other solvents [4,5]. Also,  $\delta_{\text{Pb}} \approx 2457$  for  $[\text{Pb}(\text{SP}\{\text{C}-\text{C}_6\text{H}_{11}\})_3]^{2+}$  in  $\text{SO}_2$  at 203 K [6]. Thus the spectrum of  $\text{Pb}(\text{SPh})_2$  in DMF points to an ionization of the type shown in eqn.1. The large linewidth



suggests the presence of residual exchange-averaging, which would account for our inability to locate a line attributable to a cation - this may be very broad.

No evidence has yet been found for anions  $[\text{Pb}_{n+1}(\text{SPh})_{2n+3}]^-$  with  $n > 0$  [4,5]. Therefore we suggest that  $[\text{Pb}(\text{SPh})_3]^-$  is the important anion and  $\text{SPh}^-$ -carrier in  $\text{Pb}(\text{SPh})_2/\text{DMF}$ . In support of this assertion,  $\underline{1}$  causes substitution of DFBP, FDNB and HFB in  $\text{CHCl}_3$  or  $\text{CDCl}_3/\text{CHCl}_3$  as described above, though the reaction with HFB is incomplete even after one week at room temperature. The results with DFBP up to  $\text{DFBP}/\underline{1} = 3/2$ , and with  $\text{FDNB}/\underline{1} = 1/1$  show that  $[\text{Pb}(\text{SPh})_3]^-$  acts as a source of three  $\text{SPh}^-$ , as expected. As a result of the reactions,  $\underline{1}$  is converted into  $\text{PbF}_2$  and  $[\text{AsPh}_4]\text{F}$ .

Reactions of all three substrates with **2** are slower than their analogues with **1**, and in the extreme case of HFB as substrate, no product was discernable even after one week. Though solutions containing **2** were purged with Ar, some oxidation of  $[\text{Pb}(\text{SPh})_3]^-$  to  $\text{Ph}_2\text{Se}_2$  was found, particularly at long reaction times. Previously, exhaustive substitution of HFB with NaSPh was shown to give  $4\text{-C}_6\text{F}_2(\text{SPh})_4$  while that with NaSePh gave  $4\text{-C}_6\text{F}_4(\text{SePh})_2$  and copious amounts of  $\text{Ph}_2\text{Se}_2$  [3].

The compounds  $4,4'\text{-(C}_6\text{F}_4\{\text{SPh}\})_2$  (**3**),  $2,4\text{-C}_6\text{H}_3(\text{NO}_2)_2(\text{EPh})$  (E = S or Se) and  $4\text{-C}_6\text{F}_4(\text{SPh})_2$  are known [1,3,7,8]. Neither  $4\text{-C}_6\text{F}_5\text{.C}_6\text{F}_4(\text{EPh})$  (E = S or Se) nor  $4,4'\text{-(C}_6\text{F}_4\{\text{SePh}\})_2$  have been reported previously. The absence of significant concentrations of  $\text{C}_6\text{F}_5(\text{SPh})$  in **1**:HFB mixtures or of further substitution in **1**:**3** mixtures is consistent with earlier work using other sources of  $\text{SPh}^-$  [1,3].

The  $^{19}\text{F}$  NMR spectra of the substituted biphenyls (Table 2) were assigned on the basis of the known [9,10] spectrum of DFBP, the large magnitude of ortho effects in  $^{19}\text{F}$  NMR, e.g. Ref 11, relative intensities and the overall pattern of the changes that occur on substitution. In the series  $\text{C}_{12}\text{F}_{10-x}(\text{EPh})_x$ , the deshielding of  $^{19}\text{F}$  that occurs on ortho substitution varies with E in the order  $\text{Se} > \text{S}$  and is very similar in magnitude to values found for  $\text{C}_6\text{F}_{6-x}(\text{EPh})_x$  [3,12].

Overall, the properties of **1** as a source of the  $\text{SPh}^-$  nucleophile provide strong presumptive evidence for the importance of  $[\text{Pb}(\text{SPh})_3]^-$  as the source of  $\text{SPh}^-$  in  $\text{Pb}(\text{SPh})_2/\text{DMF}$ .

## EXPERIMENTAL

### Materials

Decafluorobiphenyl (PCR Inc), hexafluorobenzene (Aldrich) and 2,4-dinitrofluorobenzene (Eastman) showed no significant impurities by NMR and were used as received. Literature syntheses were used for  $\text{Pb}(\text{SPh})_2$  [13] and **1** and **2** [5].

TABLE 2

$^{19}\text{F}$  NMR chemical shifts of decafluorobiphenyl and some EPh-substituted derivatives in  $\text{CDCl}_3$  at 294 K

Compound	$\delta_{\text{F}}^{\text{a,b}}$					
	F <sub>4</sub>	F <sub>3,5</sub>	F <sub>2,6</sub>	F <sub>2',6'</sub>	F <sub>3',5'</sub>	F <sub>4'</sub>
$\text{C}_{12}\text{F}_{10}^{\text{c}}$	-150.2	-160.8	-137.9			
4- $\text{C}_6\text{F}_5$ . $\text{C}_6\text{F}_4$ (SPh)		-132.2	-137.5 <sup>d</sup>	-137.7 <sup>d</sup>	-160.8	-150.3
4- $\text{C}_6\text{F}_5$ . $\text{C}_6\text{F}_4$ (SePh) <sup>e</sup>		-126.7	-137.5 <sup>d</sup>	-137.5 <sup>d</sup>	-160.8	-150.5
4,4'-( $\text{C}_6\text{F}_4$ (SPh)) <sub>2</sub> <sup>f</sup>		-132.3	-137.4			
4,4'-( $\text{C}_6\text{F}_4$ (SePh)) <sub>2</sub> <sup>g</sup>		-126.9	-137.3			

<sup>a</sup>Estimated error  $\pm 0.1$  ppm or less.

<sup>b</sup>At 282.2 MHz, resonances are symmetrical multiplets except as noted.

<sup>c</sup>Lit:  $\delta_{\text{F}} = -138(\text{F}_{2,6})$ ,  $-161(\text{F}_{3,5})$ ,  $-150(\text{F}_4)$  [9];  $-137.5(\text{F}_{2,6})$ ,  $-161.4(\text{F}_{3,5})$ ,  $-150.3(\text{F}_4)$  [10] (both with conversion to current convention).

<sup>d</sup>Distorted multiplet indicating non-zero inter-ring F-F coupling.

<sup>e</sup> $^{77}\text{Se}$  NMR:  $\delta_{\text{Se}} = 293.2 \pm 0.1$  (triplet,  $J(^{77}\text{Se}-^{19}\text{F}) = 11 \pm 2$  Hz).

<sup>f</sup>Lit[1]:  $\delta_{\text{F}} = -130.0$ ,  $-135.3$  (with conversion to current convention), unassigned.

<sup>g</sup> $^{77}\text{Se}$  NMR:  $\delta_{\text{Se}} = 292.0 \pm 0.1$  (triplet,  $J(^{77}\text{Se}-^{19}\text{F}) = 12 \pm 1$  Hz).

### Spectroscopy

Carbon-13,  $^{19}\text{F}$  and  $^{77}\text{Se}$  NMR spectra were measured using a Varian XL-300 spectrometer system operating at 75.4, 282.2 and 57.2 MHz, respectively, with the samples in standard 5 mm od NMR tubes. The primary references were external TMS in  $\text{CDCl}_3$ , external  $\text{PhCF}_3$  in  $\text{CDCl}_3$  and external  $\text{Ph}_2\text{Se}_2$  in  $\text{CDCl}_3$ , respectively. For  $^{19}\text{F}$  and  $^{77}\text{Se}$ , chemical shifts were converted to the more normal  $\text{CFCl}_3$  and  $\text{Me}_2\text{Se}$  references using  $\delta_{\text{F}}(\text{external CFCl}_3 \text{ in } \text{CDCl}_3) = \delta_{\text{F}}(\text{external PhCF}_3 \text{ in } \text{CDCl}_3) - 63.23$  and  $\delta_{\text{Se}}(\text{external pure Me}_2\text{Se}) = \delta_{\text{Se}}(\text{external Ph}_2\text{Se}_2 \text{ in } \text{CDCl}_3) - 461.0$ . Lead-207 NMR spectra of DMF solutions of  $\text{Pb}(\text{SPh})_2$ , 1 and 2 in standard 10 mm od NMR tubes were measured on Varian XL-200

or XL-300 spectrometer systems operating at 41.7 or 62.6 MHz, respectively, at the external 1.0 M  $\text{Pb}(\text{NO}_3)_2(\text{aq})$  primary reference. Conversion to external  $\text{PbMe}_4$  in toluene as reference was made using  $\delta_{\text{Pb}}(\text{external PbMe}_4 \text{ in toluene}) = \delta_{\text{Pb}}(\text{external } 0.1 \text{ M Pb}(\text{NO}_3)_2(\text{aq})) - 2961$  [14]. Proton NMR spectra were measured on the XL-200 using samples in standard 5 mm od NMR tubes and internal TMS as reference.

Mass spectra were obtained using a Finnigan MAT8230C mass spectrometer.

### Reactions with 1 or 2

Samples to be used for  $^{19}\text{F}$  NMR directly were prepared in 5 mL glass vials having a polyethylene cap and equipped with a magnetic stirrer bar. The mixtures contained  $1.0 \times 10^{-4}$  mol of the organic substrate and the appropriate amount of the lead salt in 3 mL of  $\text{CDCl}_3/\text{CHCl}_3$  (1/2 v/v) as solvent. These mixtures were stirred at room temperature ( $294 \pm 3$  K) for a period of 24 h or 1 week. In trial reactions identical results were obtained with and without Ar-purging when 1 was used, so reactions involving 1 were normally run without Ar purging. However mixtures containing 2 were definitely  $\text{O}_2$ -sensitive, and for these Ar-purging was used routinely.

Preparative reactions were run in the same manner as for the NMR samples but with a scale ca. ten times larger and using  $\text{CHCl}_3$  as solvent.

Several reactions of DFBP with 1 were monitored continuously by  $^{19}\text{F}$  NMR, keeping the samples in 5 mm od NMR tubes in the probe of the NMR spectrometer.

### Isolation of components of reaction mixtures

#### (a) Fluoroaromatic compounds

Flash chromatography on silica (Merck, 230-400 mesh) was used for initial separation of portions of the mixtures derived from DFBP or DNFB. For mixtures derived from DNFB and 1 or 2, toluene was used as the eluent. The products of a mixture with

DFBP/1 = 3/1 were separated using hexane as eluent. Unreacted DFBP was eluted first, followed by the monosubstituted product then the disubstituted product. The products of a mixture with DFBP/2 = 1/1 were separated similarly but using hexane/toluene (5/1 v/v) as eluent.

The separated  $C_6H_3(NO_2)_2(EPh)$  were recrystallized from toluene/hexane (E = S) or MeOH (E = Se); their physical and  $^1H$  NMR spectroscopic properties coincided with those in the literature [7,8]. Similarly,  $4,4'-(C_6F_4\{SPh\})_2$ , recrystallized from MeOH, gave the reported [1]  $^{19}F$  NMR chemical shifts. The compounds  $4-C_6F_5.C_6F_4\{SPh\}$ , 4, and  $4,4'-(C_6F_4\{SePh\})_2$ , 5, were recrystallized from MeOH: m.p. 49-50 °C (4), 78-82 °C (5); m/e: obs/calc 423.996/423.997 (4), 609.896/609.898 (5). The compound  $C_6F_5.C_6F_4\{SePh\}$  was obtained as an oil: m/e obs/calc 471.943/471.941. The  $^{19}F$  NMR spectra of the various  $C_{12}F_{10-x}(EPh)_x$  are given in Table 2.

#### (b) Tetraphenylarsonium fluoride

The solvent from the mixture with DFBP/1 = 3/2, and  $[AsPh_4]F$  isolated from the residue by extraction with MeOH followed by recrystallization from toluene. Carbon-13 NMR in  $CDCl_3$ : 120.2( $C_1$ ), 132.8( $C_{2,6}$ ), 131.4( $C_{3,5}$ ), 134.9( $C_4$ ). Fluorine-19 NMR in  $CDCl_3$ : -131.4 ( $\Delta\nu_{\frac{1}{2}} \approx 16$  Hz).

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