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A STUDY OF THE SUBSTITUTION OF SOME FLUOROAROMATICS USING $[Pb(EPh)_3]^-$ (E = S or Se) AS A SOURCE OF THE EPh^- NUCLEOPHILE

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SUMMARY

A ^{207}Pb NMR study of $Pb(SPh)_2$/DMF mixtures, which are known to act as a source of the SPh^- nucleophile, suggests that they contain species with the $Pb^{II}S_3$ kernel. To discover whether the carrier of SPh^- could be $[Pb(SPh)_3]^-$, the room-temperature reactions of $(AsPh_4)[Pb(SPh)_3]$ (1) with the representative substrates $(C_6F_5)_2$, $2,4\text{-}C_6H_3(NO_2)_2F$ and C_6F_6 in $CHCl_3$ (or $CDCl_3/CHCl_3$) have been investigated. The known compounds $4,4'\text{-}(C_6F_4\{SPh\})_2$ and $2,4\text{-}C_6H_3(NO_2)_2(SPh)$ are formed readily from the first and second substrates, but the conversion of C_6F_6 to $4\text{-}C_6F_4(SPh)_2$ is very slow under the conditions used. En-route to $4,4'\text{-}(C_6F_4\{SPh\})_2$, the new compound $4\text{-}C_6F_5.C_6F_4(SPh)$ is formed. For $(C_6F_5)_2$ and $2,4\text{-}C_6H_3(NO_2)_2F$, analogous but slower reactions are observed using $(AsPh_4)[Pb(SePh)_3]$ (2), as a source of $SePh^-$, but no reaction of C_6F_6 with 2 was observed. In general, reactions of 2 are complicated by its ease of oxidation to Ph_2Se_2.

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INTRODUCTION

Although $Pb(SPh)_2$ in refluxing dimethylformamide (DMF) has been used as a source of the 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 $Pb(SPh)_2$ 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}Pb NMR spectrum of a solution of $Pb(SPh)_2$ in DMF, which suggests ionization to species with a $Pb^{II}S_3$ kernel. Accordingly, we postulate that $[Pb(SPh)_3]^-$ may be the carrier of SPh^- in $Pb(SPh)_2$/DMF. To test this assertion, we have investigated the use of $(AsPh_4)[Pb(SPh)_3]$, 1, as a source of SPh^-. A particular advantage of this salt is its high solubility in $CHCl_3$ and CH_2Cl_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}F NMR. Three representative fluoroaromatic substrates have been investigated: $C_6F_5.C_6F_5$ (DFBP), 1-fluoro-2,4-dinitrobenzene (FDNB) and C_6F_6 (HFB). In addition, we have extended our study to include $(AsPh_4)[Pb(SePh)_3]$, 2, as a source of $SePh^-$. In previous studies of nucleophilic substitution by $SePh^-$, alkali metal salts of the chalcogenate have been used, e.g. Ref. 3. ($Pb(SePh)_2$ has very poor solubility in DMF.)

RESULTS

Lead-207 NMR spectrum of $Pb(SPh)_2$ in DMF

At 294 K, the ^{207}Pb NMR spectrum of a saturated solution of $Pb(SPh)_2$ in DMF consists of a single broad resonance ($\Delta\nu_{\frac{1}{2}} \approx$ 900 Hz) with $\delta_{Pb} \approx 2470$ (from external $PbMe_4$ in toluene).

Reactions of 1 and 2 with $(C_6F_5)_2$, 2,4-$C_6H_3(NO_2)_2F$ and C_6F_6

With a 3.33 x 10^{-2} M concentration of the various substrates, S, in $CHCl_3$ or $CDCl_3/CHCl_3$ (1/2 v/v) at 294±3 K, the results summarized in Table 1 were obtained for reactions with $[Pb(EPh)_3]^-$.

TABLE 1

Reactions of $[Pb(EPh)_3]^-$ with Various Substrates, S

S	S/ 1 or 2	E	Time (h)	Comments
DFBP	3/1	S	24	Essentially complete reaction (by ^{19}F NMR); DFBP:4-C_6F_5.C_6F_4(SPh):4,4'-(C_6F_4{SPh})$_2$ = 0.7:1:0.6.
	3/2	S	24	Close-to-complete reaction (by ^{19}F NMR); 4,4'-(C_6F_4{SPh})$_2$:4-C_6F_5.C_6F_4(SPh) = 7:1
	3/3	S	24	Major product (by ^{19}F NMR) remains 4,4'-(C_6F_4{SPh})$_2$.
	3/1	Se	24	Very little reaction (by ^{19}F NMR); DFBP:4-C_6F_5.C_6F_4(SePh) = 7:1
	3/2	Se	24	Incomplete reaction (by ^{19}F NMR); DFBP:4-C_6F_5.C_6F_4(SePh):4,4'-(C_6F_4{SePh})$_2$ = 3.3:1:0.07.
	3/2	Se	168	Incomplete reaction (by ^{19}F NMR); DFBP:4-C_6F_5.C_6F_4(SePh):4,4'-(C_6F_4{SePh})$_2$ = 1.1:1:0.2. Ph_2Se_2 evident by TLC and ^{77}Se NMR.
	1/2	Se	168	Incomplete reaction (by ^{19}F NMR); DFBP:4-C_6F_5.C_6F_4(SePh):4,4'-(C_6F_4{SePh})$_2$ = 0.5:1:0.6. Ph_2Se_2 evident (TLC, ^{77}Se NMR)
FDNB	3/1 or 1/2	S	24	Complete reaction to $C_6H_3(NO_2)_2$(SPh) (by TLC).
	3/1	Se	24	Incomplete reaction to $C_6H_3(NO_2)_2$(SePh), with some formation of Ph_2Se_2 (by TLC).
HFB	1/2	S	168	Incomplete reaction (by ^{19}F NMR); HFB:4-$C_6F_4(SPh)_2$ = 1:0.18.
	1/2	Se	168	No reaction (by ^{19}F NMR).

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

A white precipitate of, presumably, PbF_2, is particularly apparent when DFBP/1 mixtures react. In addition $[AsPh_4]F$ can be isolated from such mixtures after equilibration.

DISCUSSION

The ^{207}Pb NMR signal found in $Pb(SPh)_2$/DMF mixtures is in the general region expected for a $Pb^{II}S_3$ kernel. For comparison, at 294 K δ_{Pb} = 2881 ($\Delta\nu_{\frac{1}{2}}$ ≈ 30 Hz) for a solution containing 0.1 mol of 1 per litre of DMF. (Under the same conditions, δ_{Pb} = 3244 ($\Delta\nu_{\frac{1}{2}}$ ≈ 160 Hz) for 2.) The data for 1 are close to values found for $[Pb(SPh)_3]^-$ in other solvents [4,5]. Also, δ_{Pb} ≈ 2457 for $[Pb(SP\{c\text{-}C_6H_{11}\}_3)_3]^{2+}$ in SO_2 at 203 K [6]. Thus the spectrum of $Pb(SPh)_2$ in DMF points to an ionization of the type shown in eqn.1. The large linewidth

$$(2n + 3)\ Pb(SPh)_2 + x\ DMF \rightleftharpoons [Pb(DMF)_x]^{2+} + 2\ [(PhS)_2Pb\{-S-\overset{Ph}{\underset{}{}}-Pb\overset{SPh}{\underset{}{}}\}_nSPh]^- \quad (1)$$

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 $[Pb_{n+1}(SPh)_{2n+3}]^-$ with n > 0 [4,5]. Therefore we suggest that $[Pb(SPh)_3]^-$ is the important anion and SPh^--carrier in $Pb(SPh)_2$/DMF. In support of this assertion, 1 causes substitution of DFBP, FDNB and HFB in $CHCl_3$ or $CDCl_3/CHCl_3$ as described above, though the reaction with HFB is incomplete even after one week at room temperature. The results with DFBP up to DFBP/1 = 3/2, and with FDNB/1 = 1/1 show that $[Pb(SPh)_3]^-$ acts as a source of three SPh^-, as expected. As a result of the reactions, 1 is converted into PbF_2 and $[AsPh_4]F$.

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 $[Pb(SePh)_3]^-$ to Ph_2Se_2 was found, particularly at long reaction times. Previously, exhaustive substitution of HFB with NaSPh was shown to give $4\text{-}C_6F_2(SPh)_4$ while that with NaSePh gave $4\text{-}C_6F_4(SePh)_2$ and copious amounts of Ph_2Se_2 [3].

The compounds $4,4'\text{-}(C_6F_4\{SPh\})_2$ (3), $2,4\text{-}C_6H_3(NO_2)_2(EPh)$ (E = S or Se) and $4\text{-}C_6F_4(SPh)_2$ are known [1,3,7,8]. Neither $4\text{-}C_6F_5.C_6F_4(EPh)$ (E = S or Se) nor $4,4'\text{-}(C_6F_4\{SePh\})_2$ have been reported previously. The absence of significant concentrations of $C_6F_5(SPh)$ in 1:HFB mixtures or of further substitution in 1:3 mixtures is consistent with earlier work using other sources of SPh^- [1,3].

The ^{19}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}F NMR, e.g. Ref 11, relative intensities and the overall pattern of the changes that occur on substitution. In the series $C_{12}F_{10-x}(EPh)_x$, the deshielding of ^{19}F that occurs on ortho substitution varies with E in the order Se > S and is very similar in magnitude to values found for $C_6F_{6-x}(EPh)_x$ [3,12].

Overall, the properties of 1 as a source of the SPh^- nucleophile provide strong presumptive evidence for the importance of $[Pb(SPh)_3]^-$ as the source of SPh^- in $Pb(SPh)_2$/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 $Pb(SPh)_2$ [13] and 1 and 2 [5].

TABLE 2

^{19}F NMR chemical shifts of decafluorobiphenyl and some EPh-substituted derivatives in $CDCl_3$ at 294 K

Compound	δ_F[a,b]					
	F_4	$F_{3,5}$	$F_{2,6}$	$F_{2',6'}$	$F_{3',5'}$	$F_{4'}$
$C_{12}F_{10}$[c]	-150.2	-160.8	-137.9			
4-C_6F_5.C_6F_4(SPh)		-132.2	-137.5[d]	-137.7[d]	-160.8	-150.3
4-C_6F_5.C_6F_4(SePh)[e]		-126.7	-137.5[d]	-137.5[d]	-160.8	-150.5
4,4'-(C_6F_4(SPh))$_2$[f]		-132.3	-137.4			
4,4'-(C_6F_4(SePh))$_2$[g]		-126.9	-137.3			

[a]Estimated error ±0.1 ppm or less.

[b]At 282.2 MHz, resonances are symmetrical multiplets except as noted.

[c]Lit: δ_F = -138($F_{2,6}$), -161($F_{3,5}$), -150(F_4) [9]; -137.5($F_{2,6}$), -161.4($F_{3,5}$), -150.3(F_4) [10] (both with conversion to current convention).

[d]Distorted multiplet indicating non-zero inter-ring F–F coupling.

[e]^{77}Se NMR: δ_{Se} = 293.2±0.1 (triplet, $J(^{77}Se–^{19}F)$ = 11±2 Hz).

[f]Lit[1]: δ_F = -130.0, -135.3 (with conversion to current convention), unassigned.

[g]^{77}Se NMR: δ_{Se} = 292.0±0.1 (triplet, $J(^{77}Se–^{19}F)$ = 12±1 Hz).

Spectroscopy

Carbon-13, ^{19}F and ^{77}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 $CDCl_3$, external $PhCF_3$ in $CDCl_3$ and external Ph_2Se_2 in $CDCl_3$, respectively. For ^{19}F and ^{77}Se, chemical shifts were converted to the more normal $CFCl_3$ and Me_2Se references using δ_F(external $CFCl_3$ in $CDCl_3$) = δ_F(external $PhCF_3$in $CDCl_3$) - 63.23 and δ_{Se}(external pure Me_2Se) = δ_{Se}(external Ph_2Se_2 in $CDCl_3$) - 461.0. Lead-207 NMR spectra of DMF solutions of $Pb(SPh)_2$, 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 $Pb(NO_3)_2$(aq) primary reference. Conversion to external $PbMe_4$ in toluene as reference was made using δ_{Pb}(external $PbMe_4$ in toluene) = δ_{Pb}(external 0.1 M $Pb(NO_3)_2$(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}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 x 10^{-4} mol of the organic substrate and the appropriate amount of the lead salt in 3 mL of $CDCl_3/CHCl_3$ (1/2 v/v) as solvent. These mixtures were stirred at room temperature (294±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 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 $CHCl_3$ as solvent.

Several reactions of DFBP with 1 were monitored continuously by ^{19}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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