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Preliminary communication

Synthesis and spectroscopic properties of tetrakis(trifluoromethyl)plumbane, $(CF_3)_4Pb$

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Abstract

Tetrakis(trifluoromethyl)plumbane, $(CF_3)_4Pb$, has been prepared by aryl/CF_3 exchange from tetraarylplumbanes, PbR_4 (R = phenyl, *p*-tolyl), and $(CF_3)_4Sn$. Separation from the excess of $(CF_3)_4Sn$ was achieved by the selective complexation of the much more strongly Lewis-acidic $(CF_3)_4Sn$ with 1,10-phenanthroline. The $(CF_3)_4Pb$ was fully characterised by means of vibrational, mass, and multinuclear NMR spectroscopy.

Tetrakis(trifluoromethyl)plumbane, $(CF_3)_4Pb$, was first prepared in small quantities by the reaction of $PbCl_2$ with CF_3 radicals generated from a hexafluoroethane plasma source [1]. Preparative scale methods that utilise CF_3 reagents, such as those employed in the preparation of $(CF_3)_4Ge$ [2] or $(CF_3)_4Sn$ [3,4], are not known. Recently we reported that $(CF_3)_4Sn$ may be used for the synthesis of mixed alkyl(trifluoromethyl)plumbanes, $(CF_3)_nPbR_{4-n}$, starting from PbR_4 ($R = CH_3$, C_2H_5; $n = 1$–3) [5]. The ability of the methyl or ethyl group to replace the CF_3 group, however, decreases with increase in the number of CF_3 groups already attached to lead. Rather high reaction temperatures and long reaction times are thus required, and this results in extensive decomposition of both reactants and product. No formation of $(CF_3)_4Pb$ was observed in these reactions.

We have now found that tetraarylplumbanes such as tetraphenyl- or tetrakis(*p*-tolyl)plumbane undergo exchange with $(CF_3)_4Sn$ under mild conditions, and the tris(trifluoromethyl)plumbanes $(CF_3)_3PbPh$ and $(CF_3)_3Pb(p\text{-tolyl})$ are formed in high yields [6]. At elevated temperatures and with a large excess of $(CF_3)_4Sn$, the remaining aryl group is replaced and $(CF_3)_4Pb$ is obtained, in yields of up to 60%, according to eq. 1.

$$PbR_4 + 4(CF_3)_4Sn \xrightarrow{80^\circ C} (CF_3)_4Pb + 4(CF_3)_3SnR \qquad (1)$$

(R = phenyl, *p*-tolyl)

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Table 1

Infrared and Raman spectral data for $(CF_3)_4Pb$ [a]

IR (gas)	Ra (liq.)	Symmetry [b]	Assignment
2303 vw			$2 \times 1156 = 2312$
2268 vw			$1156 + 1110 = 2266$
2215 vw			$2 \times 1110 = 2220$
2195 vw			$1156 + 1034 = 2190$
2136 vw			$2 \times 1070 = 2140$
1242 w			$721 + 521 = 1242$
1156 vvs	1165 vvw, sh	f_2	ν_s CF_3
	1153 m, p	a_1	
1110 m		f_1	
1070 vvs	1058 m	f_2	$\nu_{as}CF_3$
1034 m	1038 w	e	
721 m	721 s, p	f_2/a_1	δ_s CF_3
	521 w	$e+f_2$	δ_{as} CF_3
242 m, sh			$193 + 48 = 241$
229 s	230 w, sh	f_2	ν_{as} PbC_4
	214 m	$e+f_2$	ρ CF_3
	193 vs, p	a_1	ν_s PbC_4
	48 m	$e+f_2$	δ PbC_4

[a] In cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, b = broad, p = polarised. [b] See text.

The volatility of $(CF_3)_4Pb$ and $(CF_3)_4Sn$ allows their separation from the less-volatile $(CF_3)_3SnR$ by fractional condensation but the separation of the resulting $(CF_3)_4Sn/(CF_3)_4Pb$ mixture requires chemical methods. In general, the Lewis acidity of trifluoromethyltin derivatives is much higher than that of the corresponding lead compounds [6]. Upon addition of a non-volatile donor such as 1,10-phenanthroline, $(CF_3)_4Sn$ is selectively complexed to give a stable, non-volatile 1:1 complex [7]. The identity of $(CF_3)_4Pb$ is fully confirmed by its spectroscopic data. Assignment of the vibrational frequencies, given in Table 1, is straightforward in the light of those for $(CF_3)_4Sn$ [8] and $(CF_3)_4Ge$ [9]. The observation of the symmetry-forbidden e and f_1 components of $\nu_{as}(CF_3)$ in the IR spectrum hints at a slight deviation from ideal tetrahedral symmetry. Their assignment is confirmed by the overtone spectrum around 2200 cm^{-1}; that is, in contrast to the unobserved overtone of the e mode, 2×1034 cm^{-1} ($a_1 + e$), the f_1 overtone (2×1110 cm^{-1}, $a_1 + e + f_2$) at 2115 cm^{-1} contains an IR allowed f_2 component. Furthermore, the e mode appears as a very weak depolarised band in the Raman spectrum. The Pb–C stretch modes are clearly discernable around 200 cm^{-1} in the Raman (ν_s) and IR (ν_{as}) spectrum, respectively. As in the case of $(CF_3)_4Ge$ [9] and $(CF_3)_4Sn$ [8], splitting of the two $\rho(CF_3)$ modes is expected to be small, and in fact is not resolved for $(CF_3)_4Pb$; the high-energy shoulder of the IR band at 229 cm^{-1} is therefore assigned to a combination tone.

Another possibility for the synthesis of $(CF_3)_4Pb$ involves the bromination of $(CF_3)_3PbPh$ followed by trifluoromethylation with donor-stabilised $(CF_3)_2Cd$:

$$(CF_3)_3PbPh + Br_2 \longrightarrow (CF_3)_3PbBr + PhBr \qquad (2)$$

$$(CF_3)_3PbBr + (CF_3)_2Cd \longrightarrow (CF_3)_4Pb + CF_3CdBr \qquad (3)$$

Details of the preparation and properties of tris(trifluoromethyl)halo- and tris(trifluoromethyl)aryl-plumbanes will be reported separately [6].

Experimental

$(CF_3)_4Sn$ (0.8 g, 2.0 mmol) was condensed *in vacuo* onto 0.2 g (0.35 mmol) of Pb(*p*-tolyl)$_4$. After heating at 80°C for 30 min, the $(CF_3)_4Pb$ and excess of $(CF_3)_4Sn$ were removed on a vacuum line and trapped at -95°C. The relative amounts of $(CF_3)_4Pb$ and $(CF_3)_4Sn$ were determined by ^{19}F NMR spectroscopy. A quantity of 1,10-phenanthroline equimolar to that of $(CF_3)_4Sn$ was added. $(CF_3)_4Pb$ was separated from the precipitated non-volatile tin complex in 57% yield as a colourless liquid with a melting point of -35°C. NMR: ^{19}F: $\delta(CF_3)$ -30.9 ppm, ^2J(PbF) 819.2 Hz, ^1J(CF) 382.4 Hz, ^4J(FF) 4.3 Hz; ^{13}C: $\delta(CF_3)$ 153.3 ppm, ^1J(PbC) 1017.1 Hz, ^3J(CF) 9.7 Hz; ^{207}Pb: δ -562.2 ppm. MS (EI 70 eV; $m_{Pb} = 208$): m/e 465 $[(CF_3)_3PbCF_2]^+ < 1$; 415 $[(CF_3)_3Pb]^+$ 90; 346 $[(CF_3)_2Pb]^+$ 31; 277 $[(CF_3)Pb]^+$ 90; 227 $[PbF]^+$ 91; 208 $[Pb]^+$ 100%.

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