

μ -Benzene in a Heterobimetallic Fluoroalkoxide: CH \cdots FC Hydrogen Bonding?

Daniel J. Teff, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University,
Bloomington, Indiana 47405-4001Received May 23, 1997[Ⓢ]

The syntheses of Lewis base-free [Pb(HFIP)₂] (HFIP = OCH(CF₃)₂) and [Li(HFIP)] are described. [Pb(OR)₂] (OR = OⁱPr or HFIP) reacts with [LiOR] to give [PbLi(OR)₃]_n, which sublimates intact at a temperature lower than the sublimation temperatures of its constituent alkoxides. By multinuclear solution NMR spectroscopy, evidence for more than one [PbLi(OR)₃] oligomer is found. The HFIP heterobimetallic species crystallizes from benzene as a dimer (i.e., *n* = 2) with 1 equiv of C₆H₆ in its lattice, while the nonfluorinated analog does not. The numerous CH \cdots FC distances observed by a crystallographic study approach the sum of the van der Waals radii of H and F. Crystallographic data (*P* $\bar{1}$ at -172 °C) for [Pb₂Li₂(HFIP)₆(C₆H₆)]: *a* = 10.020(4) Å, *b* = 12.367(5) Å, *c* = 9.784(4) Å, α = 106.03(2)°, β = 107.72(2)°, and γ = 105.36(2)° with *Z* = 1.

Introduction

While a few homoleptic, homometallic fluoroalkoxides have been reported, heterometallic fluoroalkoxide species are less common. This may be due, in part, to the decreased basicity of the alkoxide oxygen which is therefore less likely to adopt a bridging role. We are interested in how the properties of Pb(OR)₂ and Pb_xZr_y(OR)_{2x+4y} are affected when the nature of the OR group is changed. After using principles of steric bulk to influence the oligomerization, metal ratio, and volatility in this system, we now turn to the use of fluorinated ligands to probe their effect on the formation of homo- and heterometallic alkoxides of Pb.

A number of homometallic fluorinated alkoxide species have appeared in the literature in the last few years, and the properties of fluorinated alkoxide species are just starting to yield information about the ligands themselves. It is believed that increasing the fluorine content of a ligand will decrease intermolecular interactions and thus increase the volatility of a species. This has been found to be true in some cases, but has not proven to be universally true.¹ We have reported that the volatility of [Na(OR_f)] increases with increasing fluorine content, while the volatility of [Zr(OR_f)₄] is virtually unchanged with increasing fluorine content. A recent report² of the syntheses of [M(OR_f)₂(L)] (M = Ge, Sn, Pb) shows that using a combination of fluoroalkoxide ligands and a Lewis base can successfully limit oligomerization.

Finally, the fluorinated alkoxide is often chosen for its ability to sterically protect a metal center and reduce intermolecular interactions. Due to the low polarizability of fluorine, it has fewer attractive interactions yet, with the aid of crystallography, interactions with acidic protons are now being reported. The H \cdots F interactions most often reported range from 2 to 3 Å, and when they become smaller than the sum of the van der Waals radii of H and F (2.5–2.7 Å), they cannot be ignored. We report here some H \cdots F interactions which approach this distance and find that, instead of decreasing the intermolecular interactions (which was our original goal), such interactions with lattice benzene increase intermolecular interactions. The covalent fluorine reported here is a weak hydrogen bond acceptor,

especially in relation to the weakest of hydrogen bond donors: an sp² C–H in an otherwise unactivated hydrocarbon. It is thus clear that the traditional van der Waals radius sum criterion (which may be based on compounds which already contain such an H/F attraction) must be applied with caution. A discussion of the pitfalls of rigidly using cutoff criteria is available.³

Experimental Section

All manipulations were carried out under a dry nitrogen or argon atmosphere using oven-dried glassware. Solvents were freshly distilled under argon from appropriate drying agents and stored under nitrogen. HOCH(CF₃)₂ was purchased from Aldrich and stored over activated molecular sieves. Li[N(SiMe₃)₂]·Et₂O,⁴ Pb[N(SiMe₃)₂]₂,⁵ and [Pb(Oⁱ-Pr)₂]⁶ were prepared according to literature methods. Pb[N(SiMe₃)₂]₂ was distilled prior to use and used in its solid form. ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on a 300 MHz Varian Gemini 2000 spectrometer at 300, 75.6, and 282 MHz, respectively. ⁷Li and ²⁰⁷Pb NMR spectra were recorded on a Varian UNITY Inova 400 MHz spectrometer at 156 and 84 MHz. Spectra of fluorinated species were recorded in C₆F₅CF₃/TMS or C₆F₅CF₃/C₆D₅CD₃ with ¹H and ¹³C NMR spectra referenced to internal TMS or C₆D₅CD₃, respectively. All other samples were run in deuterated C₆D₆ or C₆D₅CD₃. These ¹H spectra were referenced to the protio impurity resonance of the deuterated solvent (7.15 ppm for C₆D₆ and 2.09 ppm for the upfield resonance of C₆D₅CD₃), and ¹³C spectra were referenced to the resonance of the deuterated solvent (128.0 ppm for C₆D₆ and 20.4 ppm for the upfield resonance of C₆D₅CD₃). ¹⁹F spectra were referenced to the methyl-bound C₆F₅CF₃ fluorines (-58.06 ppm).⁷ ⁷Li spectra were referenced to an external sample of LiClO₄ in D₂O (4 M, 0.0 ppm),⁸ and ²⁰⁷Pb spectra were referenced to an external sample of neat PbEt₄ (73.3 ppm).⁹ All spectra were recorded with positive shifts to higher frequencies. Molecular weight measurements were done in a Childs-type apparatus¹⁰ (using Signer principles¹¹) at 25 °C with a benzophenone standard.

(3) Steiner, T. *J. Chem. Soc., Chem. Commun.* **1997**, 727.(4) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.(5) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.(6) Goel, S. C.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 4640.(7) The ¹⁹F NMR chemical shift of the methyl-bound fluorines of neat C₆F₅CF₃ was measured in-house and found at -58.06 ppm relative to neat CFC₃ (δ = 0 ppm).(8) Popov, A. I. *Pure Appl. Chem.* **1975**, *41*, 275.(9) Kennedy, J. D.; McFarlane, W.; Payne, G. S. *J. Chem. Soc., Dalton Trans.* **1977**, 2332.(10) Childs, C. E. *Anal. Chem.* **1954**, *26*, 1963.(11) Signer, R. *Justus Liebigs Ann. Chem.* **1930**, *478*, 246.[Ⓢ] Abstract published in *Advance ACS Abstracts*, September 1, 1997.(1) Samuels, J. A.; Foltling, K.; Huffman, J. C.; Caulton, K. G. *Chem. Mater.* **1995**, *7*, 929.(2) Suh, S.; Hoffman, D. M. *Inorg. Chem.* **1996**, *35*, 6164.

Benzophenone was purchased from Aldrich and sublimed under dynamic vacuum before use. Elemental analyses were performed in-house on a Perkin Elmer 2400 Series II CHNS/O analyzer. Thermogravimetric analyses (TGA) were recorded on a TA Instruments 951 thermogravimetric analyzer at ambient pressure in a He-filled glovebox. All measurements were run at 5 °C/min from ambient temperature to 700 °C with a 40 mL/min He purge of the sample chamber.

Synthesis of [Li(OⁱPr)]. Li[N(SiMe₃)₂]·Et₂O (5.00 g, 20.7 mmol) was dissolved in 40 mL of Et₂O, and a slight excess of neat HOⁱPr (1.66 mL, 27.6 mmol) was added dropwise to give a clear, colorless solution. After 10 min of stirring, the solvent was removed *in vacuo* and 1.18 g (87% yield) of colorless, solid material was sublimed at 140 °C and 10⁻² Torr to a cold finger apparatus. ¹H NMR (C₆D₆, 25 °C): δ 4.09 (septet), 1.32 (d). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 63.2 (s), 29.9 (s). ⁷Li NMR (C₆D₆, 25 °C): δ 0.73 (s). MS (EI, 15 eV): *m/z*⁺ Li₂(OⁱPr)⁺ (100), Li₃(OⁱPr)₂⁺ (14), Li₄(OⁱPr)₃⁺ (83), Li₅(OⁱPr)₄⁺ (10), Li₆(OⁱPr)₅⁺ (72), Li₇(OⁱPr)₆⁺ (18), Li₈(OⁱPr)₇⁺ (19), Li₉(OⁱPr)₈⁺ (7). Anal. Calcd for C₃H₇OLi: C, 54.57; H, 10.69. Found: C, 54.30; H, 10.13.

Synthesis of [PbLi(OⁱPr)₃]. [Pb(OⁱPr)₂] (2.08 g, 6.39 mmol) was suspended in 20 mL of Et₂O, and a solution of [Li(OⁱPr)] (0.422 g, 6.39 mmol) was added to the suspension via cannula transfer. After 10 min of stirring, a clear, colorless solution remained. The solvent was removed *in vacuo*, and the remaining solid was sublimed at 80 °C and 10⁻² Torr to a cold finger apparatus. A nonoptimized yield of 1.39 g (56% yield) of slightly sticky, colorless solid was recovered. ¹H NMR (C₆D₅CD₃, 90 °C): δ 5.13 (septet), 1.26 (d); (C₆D₅CD₃, 50 °C) δ 5.16 (br), 1.27 (d); (C₆D₅CD₃, 25 °C) δ 5.20 (br septet, 90%), 4.94 (v br, 10%), 1.28 (d, 100%); (C₆D₅CD₃, -40 °C): δ 5.22 (septet, 90%), 4.90 (br, 10%), 1.32 (d, 100%). ¹³C{¹H} NMR (C₆D₆, 25 °C): δ 64.5 (s), 29.9 (s). ⁷Li NMR (C₆D₆, 25 °C): δ 1.31 (s, 90%), 1.14 (s, 10%). ²⁰⁷Pb NMR (C₆D₆, 25 °C): δ 1652 (s, 88%), 1565 (s, 12%). Anal. Calcd for C₉H₂₁O₃PbLi: C, 27.62; H, 5.41. Found: C, 27.97; H, 5.13.

Synthesis of [Li(HFIP)]. Li[N(SiMe₃)₂]·Et₂O (1.06 g, 4.39 mmol) was dissolved in 20 mL of Et₂O, and to this solution was added neat HOCH(CF₃)₂ (0.47 mL, 4.5 mmol) dropwise to give a clear solution. After 10 min of stirring at 25 °C, the solvent was removed *in vacuo*. The remaining product was transferred to a sublimation apparatus, and 0.726 g (48% yield) of sticky solid was recovered from a cold finger apparatus. ¹H NMR (C₆F₅CF₃/C₆D₅CD₃, 25 °C): δ 4.30 (br septet, ³J_{H-F} = 5.7 Hz); (-45 °C) δ 4.27 (vbr septet, ³J_{H-F} = 3.7 Hz). ¹⁹F NMR (C₆F₅CF₃/C₆D₅CD₃, 25 °C): δ -80.1 (doublet, ³J_{H-F} = 5.9 Hz); (-45 °C) δ -80.4 (doublet, ³J_{H-F} = 3.4 Hz). ¹³C{¹H} NMR (C₆F₅-CF₃/C₆D₅CD₃, 25 °C): δ 74.2 (septet, ²J_{C-F} = 23.4 Hz, OCH(CF₃)₂), 125.8 (quartet, ¹J_{C-F} = 213, OCH(CF₃)₂). ⁷Li NMR (C₆F₅CF₃, 25 °C): δ 0.09 (s). MS (EI, 15 eV): *m/z*⁺ Li₂(HFIP)⁺ (100), Li₄(HFIP)₃⁺ (100), Li₆(HFIP)₅⁺ (47). Anal. Calcd for C₃HF₆OLi: C, 20.71; H, 0.58. Found: C, 20.51; H, 0.51.

Synthesis of [Pb(HFIP)₂]_n. Pb[N(SiMe₃)₂]₂ (3.05 g, 5.78 mmol) was dissolved in 25 mL of Et₂O, and neat HOCH(CF₃)₂ (1.30 mL, 12.3 mmol) was added dropwise, giving a clear, colorless solution. Stirring at 25 °C for 10 min and removal of the solvent *in vacuo* gave a sticky, white powder. Vacuum sublimation at 85 °C gave 2.87 g (92% yield) of a *crystalline, waxy* solid. ¹H NMR (C₆F₅CF₃/C₆D₅-CD₃, 95 °C): δ 5.45 (br septet, ³J_{H-F} = 6.0 Hz); (25 °C) δ 5.51 (v br); (-10 °C) δ 5.52 (br), 4.93 (br); (-40 °C) δ 5.51 (br), 4.90 (br); (-45 °C) δ 5.51 (br), 4.89 (br). ¹⁹F NMR (C₆F₅CF₃/C₆D₅CD₃, 25 °C): δ -77.4 (v br); (-10 °C) δ -77.6 (br); (-40 °C) δ -77.3 (br), -77.7 (br, d satellites, ⁴J_{Pb-F} = 78 Hz); (-45 °C) δ -77.3 (v br), -77.7 (v br). ¹³C{¹H} NMR (C₆F₅CF₃/C₆D₅CD₃, 25 °C): δ 72.8 (d septets, ²J_{C-F} = 23.7 Hz, OCH(CF₃)₂), 126.2 (quartet, ¹J_{C-F} = 214 Hz, OCH(CF₃)₂). ²⁰⁷Pb{¹⁹F} NMR (C₆F₅CF₃, -30 °C): δ -1038 (br s). MS (EI, 15 eV): *m/z*⁺ Pb₂(HFIP)₃⁺ (45), Pb(HFIP)⁺ (44). Anal. Calcd for C₆H₂F₁₂O₂Pb: C, 13.31; H, 0.37. Found: C, 13.35; H, 0.33. Degree of oligomerization measured (C₆F₆, 25 °C): 2.71.

Synthesis of [PbLi(HFIP)₃]. Li(HFIP) (0.367 g, 2.12 mmol) was dissolved in 20 mL of Et₂O and added dropwise to a solution of Pb(HFIP)₂ (1.14 g, 2.11 mmol) in 15 mL of Et₂O. The clear solution was stirred for 1 h, and the solvent was removed *in vacuo*. The resulting white solid was sublimed *in vacuo* at 85 °C to give 1.34 g (89% yield) of product. ¹H NMR (C₆F₅CF₃, 25 °C): δ 5.90 (br, d

Table 1. Crystallographic Data for Pb₂Li₂[OCH(CF₃)₂]₆(C₆H₆)

formula	C ₂₄ H ₁₂ O ₆ F ₃₆ Li ₂ Pb ₂	fw	1508.58 g·mol ⁻¹
<i>a</i>	10.020(4) Å	space group	<i>P</i> 1̄
<i>b</i>	12.367(5) Å	<i>T</i>	-172 °C
<i>c</i>	9.784(4) Å	<i>λ</i>	0.710 69 Å ^a
<i>α</i>	106.03(2)°	<i>ρ</i> _{calc}	2.441 g cm ⁻³
<i>β</i>	107.72(2)°	<i>μ</i>	84.5 cm ⁻¹
<i>γ</i>	105.36(2)°	<i>R</i> (<i>F</i> _o) ^b	0.0661
<i>V</i>	1026.20 Å ³	<i>R</i> _w (<i>F</i> _o) ^c	0.0615
<i>Z</i>	1		

^a Graphite monochromator. ^b *R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^c *R*_w = [Σw(|*F*_o| - |*F*_c||)²/Σw|*F*_o|²]^{1/2} where *w* = 1/σ²(*F*_o).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Pb₂Li₂(HFIP)₆(C₆H₆)

Pb(1)-O(2)	2.291(11)	O(12)-Li(35)	1.949(26)
Pb(1)-O(12)	2.279(14)	O(22)-Li(35)	2.007(25)
Pb(1)-O(22)	2.268(14)(26)		
O(2)-Pb(1)-O(12)	74.78(26)	Pb(1)-O(12)-Li(35)	106.8(7)
O(2)-Pb(1)-O(22)	74.2(4)	C(13)-O(12)-Li(35)	116.1(9)
O(12)-Pb(1)-O(22)	88.3(4)	Pb(1)-O(22)-C(23)	128.1(6)
Pb(1)-O(2)-C(3)	127.8(7)	Pb(1)-O(22)-Li(35)	108.5(9)
Pb(1)-O(12)-C(13)	130.9(6)	C(23)-O(22)-Li(35)	117.0(10)
		O(12)-Li(35)-O(22) ^f	173.9(15)

satellites, ³J_{H-Pb} = 60.6 Hz, 36 H); (C₆F₅CF₃, -90 °C) δ 6.20 (br, 12 H), 5.90 (br, 24 H). ¹⁹F NMR (C₆F₅CF₃, 25 °C): δ -77.5 (d, ³J_{H-F} = 3.2 Hz, d satellites, ⁴J_{Pb-F} = 289 Hz, 36 F); (C₆F₅CF₃, -90 °C) δ -77.2 (br, 12 F), -77.5 (br, 12 F), -78.7 (br, 12 F). ¹³C{¹H} NMR (C₆F₅-CF₃, 25 °C): δ 73.0 (d septets, ²J_{C-F} = 36.6 Hz, OCH(CF₃)₂), 125.9 (quartet, ¹J_{C-F} = 287 Hz, OCH(CF₃)₂). ⁷Li NMR (C₆F₅CF₃, 25 °C): δ 0.91 (s, 90), 0.15 (s, 10). ²⁰⁷Pb NMR (C₆F₅CF₃, 25 °C): δ 708 (19 lines of q, ⁴J_{Pb-F} = 291 Hz, ³J_{Pb-H} = 61 Hz); {¹H} δ intensity (calc; obs) 727 (1.2%; 0.9%), 723 (3.3%; 3.2%), 720 (7.1%; 7.7%), 716 (12.1%; 12.0%), 713 (16.7%; 16.8%), 709 (18.5%; 19.0%), 706 (16.7%; 16.8%), 703 (12.1%; 12.0%), 6.99 (7.1%; 7.7%), 696 (3.3%; 3.2%), 656 (1.2%; 0.9%); ¹²{¹⁹F} δ 710 (q, ³J_{Pb-H} = 56 Hz). MS (EI, 15 eV): *m/z*⁺ PbLi(HFIP)₂⁺ (100), Pb₂Li₂(HFIP)₅⁺ (31). Anal. Calcd for C₉H₃F₁₈O₃PbLi: C, 15.11; H, 0.42. Found: C, 15.05; H, 0.42. Degree of oligomerization measured (C₆F₆, 25 °C): 1.63.

Alternatively, Pb₂Li₂(HFIP)₆(C₆H₆) crystals can be grown by slow diffusion of C₆H₆ into a solution of [PbLi(HFIP)₃] in C₆F₅CF₃. Anal. Calcd for C₂₄H₁₂F₃₆O₆Pb₂Li₂: C, 19.11; H, 0.80. Found: C, 19.06; H, 0.82.

X-ray Structure Determination of Pb₂Li₂(HFIP)₆(C₆H₆). A small crystal was affixed to the end of a glass fiber and transferred to the goniostat, where it was cooled to -172 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space was used to determine that the crystal possessed no symmetry or systematic absences, corresponding to one of the triclinic space groups. Subsequent solution and refinement confirmed the centrosymmetric choice (Table 1). The data were collected (6° < 2θ < 45°) using a standard ω-2θ technique with fixed backgrounds at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged. The structure was readily solved using direct methods (MULTAN78) and Fourier techniques. Hydrogen atoms were placed in fixed calculated positions for the final cycles of refinement. A final difference Fourier was featureless; the largest peaks (ca. 1.9 e⁴Å³) were near the Pb position. The results of the study are shown in Table 2 and as Supporting Information.

Results

[Li(OⁱPr)]_n. The reaction of Li[N(SiMe₃)₂] with HOⁱPr in Et₂O at room temperature gives [Li(OⁱPr)], a colorless powder, which sublimates at 140 °C and 10⁻² Torr. Since this is surely

(12) In the spectra exhibiting Pb-F coupling, only 11 of the 19 expected lines (from lead coupling to 18 fluorines on three alkoxide groups) are observable due to signal-to-noise limitations. Intensities of the lines are consistent with calculated values.

oligomeric, this "salt" is highly soluble in many hydrocarbon solvents such as Et₂O and C₆H₆. Only one chemical environment is detected by ¹H, ¹³C, and ⁷Li NMR at 25 °C, consistent with a symmetric oligomer or fluxional species in solution. Its mass spectrum shows high abundances of [Li₂(OⁱPr)]⁺ (100%), [Li₄(OⁱPr)₃]⁺ (83%), and [Li₆(OⁱPr)₅]⁺ (72%), with [Li₃(OⁱPr)₂]⁺ (14%), [Li₅(OⁱPr)₄]⁺ (10%), [Li₇(OⁱPr)₆]⁺ (18%), [Li₈(OⁱPr)₇]⁺ (19%), and [Li₉(OⁱPr)₈]⁺ (7%) detected in smaller quantities.

[PbLi(OⁱPr)₃]. The Lewis acid–base reaction of [Li(OⁱPr)]_n with a suspension of [Pb(OⁱPr)₂]_n (n is large) in Et₂O at room temperature causes the depolymerization of [Pb(OⁱPr)₂]_n to give [PbLi(OⁱPr)₃]. The resulting product is soluble in common hydrocarbon solvents and sublimates at 80 °C and 10⁻² Torr as a colorless, powdery solid. Only one chemical environment is detected by ¹³C NMR at 25 °C, but a second species is detected by ¹H, ⁷Li, and ²⁰⁷Pb NMR. At 25 °C, the ¹H NMR spectrum shows a sharp septet and a second broad line in the methine region integrating to approximately 9:1. The methyl region has only a sharp doublet. Cooling the sample to -40 °C gives sharper lines of the same intensity, but the lower-intensity methine peak is not resolved into a multiplet. The methyl region remains as a sharp doublet. On warming the sample to 50 °C, the two peaks in the methine region coalesce to a broad line near the weighted average of the two lines at 25 °C. By 90 °C, this broad line sharpens to a single septet shifted slightly upfield. In each of its ⁷Li and ²⁰⁷Pb NMR spectra, two singlets are observed in a ratio of approximately 9:1. There are thus two different oligomers of PbLi(OⁱPr)₃ present in toluene solution.

[Li(HFIP)]. Synthesis of [Li(HFIP)] is effected by reaction of Li[N(SiMe₃)₂] with HOCH(CF₃)₂ in Et₂O at room temperature. The resulting solid is somewhat waxy, but less so than its Pb analog. It is very soluble in Et₂O, THF, C₆F₆, and C₆F₅CF₃ and can be sublimed at 70 °C and 10⁻² Torr as a slightly waxy solid. Only one chemical environment is detected by ¹H, ¹³C, ¹⁹F, and ⁷Li NMR at 25 °C, consistent with either a symmetric oligomer or fluxional species in solution. Its mass spectrum includes high abundances of [Li₂(HFIP)]⁺ (100%) and [Li₄(HFIP)₃]⁺ (100%), with [Li₆(HFIP)₅]⁺ (47%) being the highest detected oligomer in the gas phase. Alkoxide oxygen bridges between metals are suspected to be the major factor for oligomerization; Li–F coupling was not detected by either ⁷Li or ¹⁹F NMR, and thus coupling information either is lost in a fluxional process or is nonexistent.

[Pb(HFIP)₂]. The reaction between Pb[N(SiMe₃)₂]₂ and HOCH(CF₃)₂ gives [Pb(HFIP)₂], which is a waxy, colorless solid which is very soluble in Et₂O, THF, C₆F₆, and C₆F₅CF₃. This compound shows a septet for its methine proton at 90 °C in 1:1 d₈-toluene/f₈-toluene (for solubility and lock), but this is broad at 25 °C and is resolved into two lines of unequal intensity at -10 °C; these sharpen by -40 °C into multiplets of intensity ~2.5:1. These are clearly not due to inequivalent nuclei within one molecule because flash freezing to -60 °C followed by recording a ¹H NMR spectrum at -45 °C reverses the intensities. Thus, these are two equilibrating species (whose equilibrium can be perturbed below -45 °C). The ¹⁹F NMR spectrum is wholly consistent with these conclusions; one broad line at 25 °C begins to decoalesce at -10 °C and is fully decoalesced at -40 °C. The (unequal) intensities at -40 °C can be reversed by flash freezing to -60 °C and then recording the ¹⁹F NMR spectrum again at -45 °C. Of special interest are the ²⁰⁷Pb satellites (⁴J_{Pb–F} = 78 Hz) on only the upfield resonance at -40 °C. From these observations, we conclude that [Pb(HFIP)₂] exists as two equilibrating forms, probably dimer and trimer (compare Pb₃(OⁱBu)₆).⁶ The lack of detectable coupling of the fluorine of one form to lead is attributed to

residual dissociative fluxionality (e.g., dimer ⇌ 2 monomers), or intramolecular fluxionality which averages J_{Pb–F} to a small value. Certainly these collective observations indicate two species to be present in nonpolar solvents and are consistent with the isopiestic molecular weight measurement which is not an integral multiple of the empirical formula weight. In the gas phase, the EI mass spectrum shows [Pb₂(HFIP)₃]⁺ (m/z = 915, 45%) and [Pb(HFIP)]⁺ (m/z = 374, 44%). Although [Pb(HFIP)₂] sublimates (85 °C and 10⁻² Torr) to deposit crystalline material, crystals could not be isolated due to its waxy character. An irreversible phase transition at low temperature (about -78 °C) further frustrates crystal structure determination.

[PbLi(HFIP)₃]. The simple Lewis acid–base reaction of [Li(HFIP)] with [Pb(HFIP)₂] in Et₂O at room temperature gives [PbLi(HFIP)₃]. The resulting powdery, white solid is not waxy as are its constituent precursors and forms crystals containing lattice benzene when a warm saturated benzene solution is slowly cooled to room temperature. Its solubility in toluene or benzene is poor, even at elevated temperatures, but it is quite soluble in Et₂O, THF, C₆F₆, and C₆F₅CF₃. High-quality crystals containing lattice benzene can also be grown by slow diffusion of C₆H₆ into a solution of [PbLi(HFIP)₃] in C₆F₅CF₃. Sublimation at 85 °C and 10⁻² Torr leaves a powdery, noncrystalline deposit on a cold finger apparatus. It is thus believed that molecular ordering in the solid state (i.e., crystallization) is not easily achieved in the absence of lattice benzene. A single chemical environment is observed in its ¹H, ¹³C, ¹⁹F, and ²⁰⁷Pb NMR spectra at room temperature. Doublet satellites (⁴J_{Pb–F} = 289 Hz) in correct abundance (~20%) are found in its ¹⁹F spectrum due to coupling to Pb, leading to the conclusion that there is significant coupling to only a single Pb center. Its 25 °C ²⁰⁷Pb NMR spectrum shows 11 (of 19 expected)¹² lines which arise from Pb coupling to 18 fluorines. Each of these lines is split into a quartet due to Pb coupling to three hydrogens on three OR_f groups. At -90 °C, its ¹H NMR spectrum shows two chemical environments which integrate to a 1:2 ratio. This integral is consistent with the solid-state structure, where a mirror plane and a center of inversion result in two HFIP chemical environments of ratio 1:2. Further, its ¹⁹F NMR spectrum at -90 °C consists of three equal intensity peaks which represent the three chemical environments expected due to diastereotopic CF₃ groups of the μ₂-HFIP groups which lie to either side of (but not bisected by) the mirror plane of the molecule. While all information above suggests that there is only one species in solution, a second species is detected in its ⁷Li NMR spectrum; its spectrum, like that of the nonfluorinated analog, consists of two singlets in a ratio of approximately 9:1. It is likely that the second species is not detected by ²⁰⁷Pb NMR because of broadness and multiplicity of the line and/or inadequate signal-to-noise. Except for the presence of C₆H₆ in the NMR spectra of [Pb₂Li₂(HFIP)₆(C₆H₆)], all other lines were identical to those in the spectra of [PbLi(HFIP)₃]. Molecular weight measurements indicate that [PbLi(HFIP)₃] is nearly dimeric in solution (degree of aggregation = 1.63 in C₆F₆ at 25 °C), and in the gas phase, [Pb₂Li₂(HFIP)₅]⁺ (m/z = 1263, 31%) and [PbLi(HFIP)₂]⁺ (m/z = 548, 100%) were both detected in high abundance in the EI mass spectrum.

Thermogravimetric Analyses. [Li(OⁱPr)] vs [Li(HFIP)]. As determined by TGA, the sublimation onset for [Li(OⁱPr)] (Figure 1) occurs at 153 °C (Table 3). In the case of [Li(HFIP)], sublimation onset was observed at 58 °C, which is 95 °C lower than that of the nonfluorinated species. The fluorinated species, possibly due to greater steric bulk of the ligand, may achieve lower nuclearity upon volatilization to give a lower sublimation temperature.

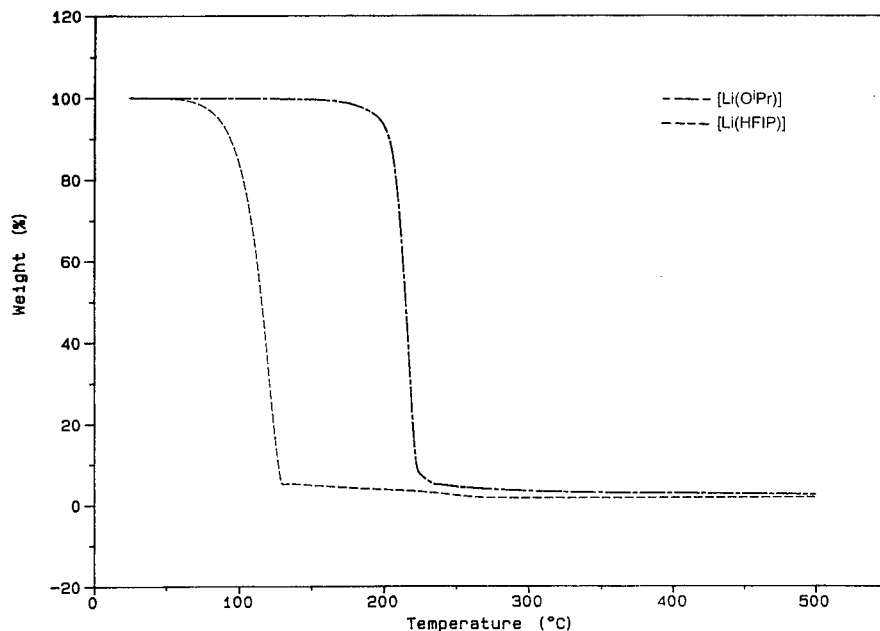


Figure 1. Thermogravimetry of [Li(OⁱPr)] vs [Li(HFIP)].

Table 3

compd	onset T , °C	T at max. rate of loss, °C	T , after max. loss, °C	residual at 450 °C, %
[Li(O ⁱ Pr)]	153	216	238	3
[Li(HFIP)]	58	119	134	2
[Pb(O ⁱ Pr) ₂]	118	210	220	16
[Pb(HFIP) ₂]	88	154	167	1
[PbLi(O ⁱ Pr) ₃]	93	166	197	4
[PbLi(HFIP) ₃]	84	154	170	2

[Pb(OⁱPr)₂] vs [Pb(HFIP)₂]. The TGA profile for [Pb(OⁱPr)₂] shows the sublimation onset temperature at 118 °C (Figure 2). The profile shows the remaining amount of material to be approximately 16% at 450 °C. If complete decomposition on the TGA pan were to occur to leave PbO or Pb metal, either 69% or 64% of the total mass would remain, respectively. Because the mass remaining is less than that calculated for either decomposition product, this indicates that sublimation and decomposition both contribute to the mass loss. In contrast, the sublimation onset temperature of [Pb(HFIP)₂] is at 88 °C and only 1% of the beginning mass remained at 450 °C. Comparison of the final percentages of material present in both runs suggests that decomposition occurred only in the case of the OⁱPr species.

[PbLi(OⁱPr)₃] vs [PbLi(HFIP)₃]. Sublimation of [Li(OⁱPr)] and [Pb(OⁱPr)₂] is initiated at 153 and 118 °C, respectively. These homometallic compounds have a *higher* sublimation temperature than the 1:1 heterometallic compound formed from these two species. The sublimation onset temperature of [PbLi(OⁱPr)₃] is 93 °C (Figure 3). However, the HFIP analog begins to sublime at 84 °C, showing a slight improvement of volatility in the fluoro analog. Though marked improvements in volatility upon the use of fluorinated ligands were seen in the cases of the homometallic species, the difference between the sublimation temperatures of the two heterometallic species is only 9 °C, possibly owing to low nuclearity compared to the homometallic species.

[Pb₂Li₂(HFIP)₆(C₆H₆)] vs [Pb₂Li₂(HFIP)₆]. The [PbLi(HFIP)₃]₂ compound with lattice benzene is observed (Figure 4) to lose benzene at 43 °C (Table 4), and by about 94 °C, the onset temperature for sublimation, approximately 5% of the mass is lost (loss of all benzene would yield a 5.2% mass loss). Other than the initial loss of benzene and an apparently higher

sublimation onset, the thermogram almost exactly mirrors the thermogram of pure [Pb₂Li₂(HFIP)₆]. Thus, the contained benzene is merely lost during attempted sublimation and does not play a role in altering sublimation temperature.

Solid-State Structure of [Pb₂Li₂(HFIP)₆(C₆H₆)]. Single, well-formed crystals grown by slowly cooling a 60 °C benzene solution to room temperature gave diffraction intensities which led to the structure of Pb₂Li₂(HFIP)₆(C₆H₆) shown in Figure 5 (see also Table 2). This molecular species, structurally similar to Sn₂Li₂(OⁱBu)₆,¹³ can be viewed as two Pb(HFIP)₂ units bridged by a four-membered Li₂(μ_3 -HFIP)₂ ring. A molecular inversion center lies at the center of this ring relating unprimed to primed atoms. The Li₂(μ -OR)₂ unit, compared to that of Sn₂-Li₂(OⁱBu)₆, is nearly a perfect square with μ_3 -O-Li- μ_3 -O' and Li- μ_3 -O-Li' angles (85.0(11)° and 95.0(10)° versus 76.3-(3)° and 103.7(3)°, respectively) within 5° of 90°. Alkoxide groups of this ring bridging to lead are μ_3 , and the Pb- μ -OR-Li bridges are μ_2 . The M- μ_3 -O distances (Pb(1)-O(2) = 2.291(11) Å; Li(35)-O(2) = 2.27(3), Li(35)'-O(2) = 2.30-(3) Å) are understandably longer than the M- μ_2 -O distances (Pb(1)-O(12) = 2.279(14), Pb(1)-O(22) = 2.268(14) Å; Li-(35')-O(12) = 1.95(3), Li(35)-O(22) = 2.007(25) Å). While the Pb- μ -O and Li- μ_3 -O bonds in Pb₂Li₂(HFIP)₆(C₆H₆) are ~0.2 Å longer compared to the respective Sn- μ -O and Li- μ_3 -O bonds in Sn₂Li₂(OⁱBu)₆, the Li- μ_2 -O bonds in Pb₂Li₂(HFIP)₆(C₆H₆) are within 0.03–0.08 Å of those in Sn₂Li₂(OⁱBu)₆. The O-Pb-O angles around lead, O(2)-Pb(1)-O(12) = 74.78(26), O(2)-Pb(1)-O(22) = 74.2(4)°, O(12)-Pb(1)-O(22) = 88.3(4)°, are acute compared to the O-Sn-O angles in Sn₂Li₂(OⁱBu)₆ (79.7(1)°, 80.1(1)°, 97.6(1)°). This decrease is as expected for moving down a group in the periodic table. The Li atom has a pseudo trigonal bipyramidal geometry with O(22) and O(12)' in the axial positions (O(22)-Li(35)-O(12)' = 173.9(18)°) and O(2) and O(2)' in equatorial positions (O(2)-Li(35)-O(2)' = 85.0(11)°).

While the structures of Pb₂Li₂(HFIP)₆(C₆H₆) and Sn₂Li₂(OⁱBu)₆ vary little when considering the M^{II}₂M^I₂(OR)₆ framework, a greater difference is seen in the crystal packing modes of these two. The packing motif of Sn₂Li₂(OⁱBu)₆ forms hexagonally close-packed layers whereas Pb in Pb₂Li₂(HFIP)₆(C₆H₆) appears

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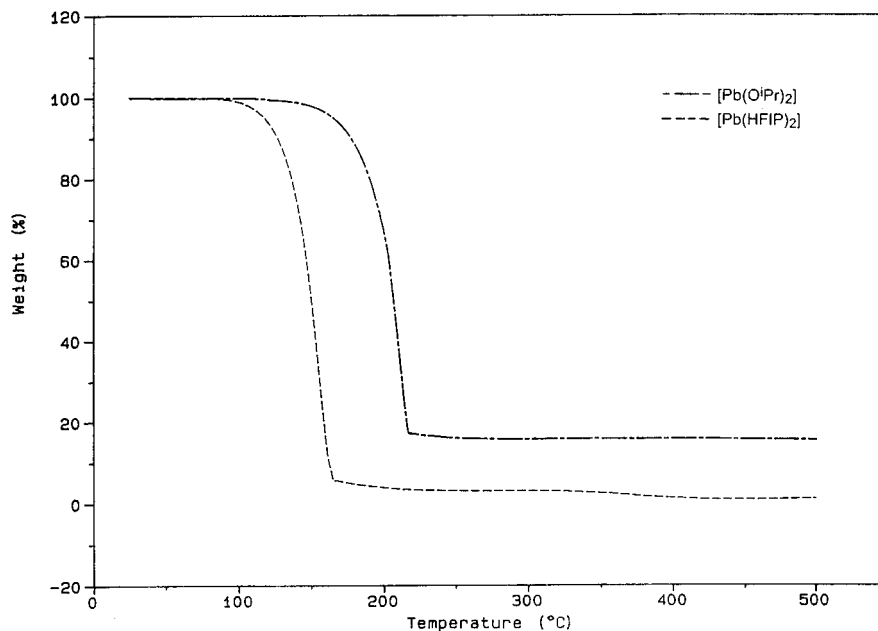


Figure 2. Thermogravimetry of [Pb(OⁱPr)₂] vs [Pb(HFIP)₂].

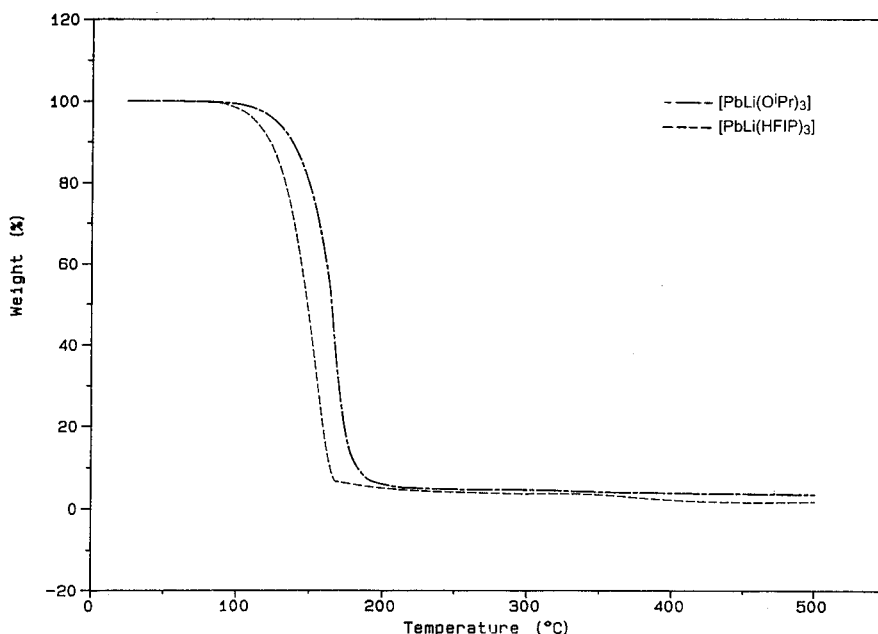


Figure 3. Thermogravimetry of [PbLi(OⁱPr)₃] vs [PbLi(HFIP)₃].

to have face-on interactions with benzene rings which “cap” each end of a Pb₂Li₂(HFIP)₆ unit. This mode continues along one dimension (Figure 6) with alternating metal alkoxide and benzene units to form a linear polymer. With such an intimate fit between these two independent molecules in the solid state, one would assume that a primary interaction between a metal and benzene would exist. One apparent possibility of an interaction is benzene acting as a π -donor to lead. Arene donors to soft, electron-rich metal complexes are well-documented in the literature.^{14,15} One arene complex of lead is (η^6 -C₆H₆)Pb(AICl₄)₂·C₆H₆,¹⁵ which has an average Pb–C_{bound} distance of 3.11 Å. In Pb₂Li₂(HFIP)₆(C₆H₆), the average distance is 3.59 Å, which is quite long by comparison. This distance may possibly be explained by the fact that each benzene is equidistant

from two lead atoms. Also to be considered is the small variance in the Pb–C distances of Pb₂Li₂(HFIP)₆(C₆H₆). These distances, which are from 3.574(15) to 3.601(15) Å, place the benzene ring carbons nearly equidistant from lead with a variance of only 0.027 Å. The reported Pb–C₆H₆ center distance for (η^6 -C₆H₆)Pb(AICl₄)₂·C₆H₆ is 2.77 Å and is much shorter in comparison to that of Pb₂Li₂(HFIP)₆(C₆H₆) (3.31 Å). The benzene which is found between two “fluorine-coated” metal alkoxides might simply be considered an “insulator” which reduces the intermolecular fluorine–fluorine repulsive¹⁶ interactions, thereby lowering the crystal lattice energy.

Also to be considered in this system is the possibility of H···F interactions (hydrogen bonds). The electronegative F atom interacts with electropositive atoms such as alkali metals,^{1,17} and acidic^{17,18} or even carbon-bound hydrogens. Interactions between C–H···F have been reported to range anywhere from

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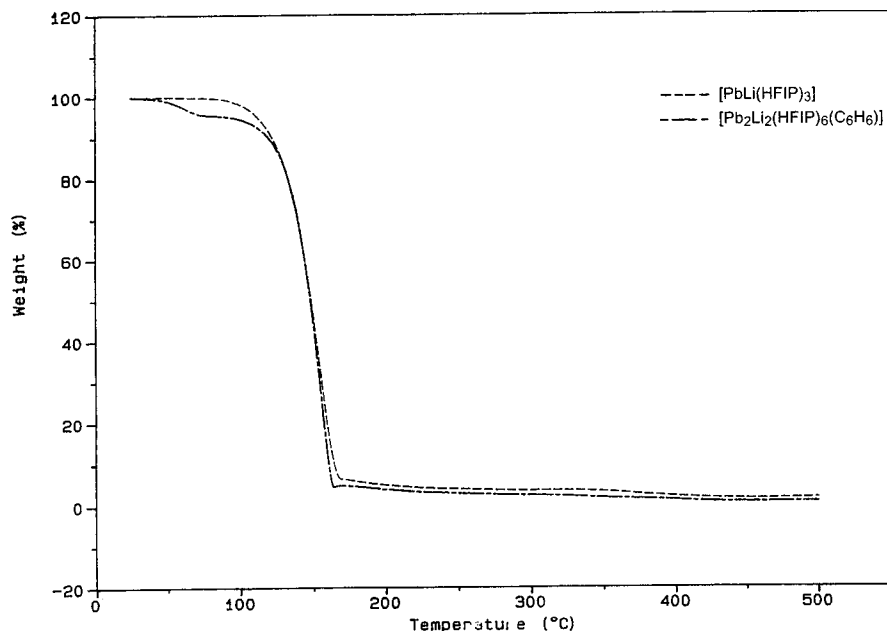


Figure 4. Thermogravimetry of $[\text{Pb}_2\text{Li}_2(\text{HFIP})_6]$ vs $[\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)]$ showing that the only differing feature is loss of C_6H_6 from the latter.

Table 4

compd	T at first onset, $^\circ\text{C}$	percent lost	T at second onset	T at max. rate of loss, $^\circ\text{C}$	T , after max. loss, $^\circ\text{C}$	residual at 450 $^\circ\text{C}$, %
$[\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)]$	43	5	94	154	166	1

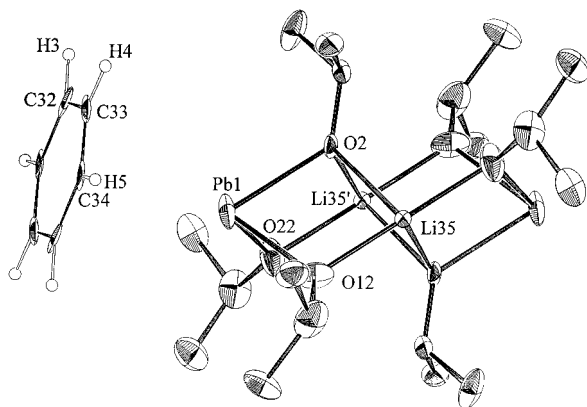


Figure 5. ORTEP representation of $[\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)]$ with selective labeling. A center of symmetry in the center of the benzene relates labeled atoms to their unlabeled counterparts. Within the alkoxide, a second center of symmetry at the center of the $\text{Li}_2(\mu_3\text{-HFIP})_2$ ring relates labeled atoms to their respective counterparts (here represented by $\text{Li}(35)$ relating to $\text{Li}(35)'$). Alkoxide fluorines and hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

2.1^{19a,b} to 3.1^{19c} Å, where the sum of the van der Waals radii of H and F is 2.5–2.7 Å.²⁰ However, a recent insightful and provocative review^{21a} concludes that “covalently-bonded F hardly ever acts as a H-bond acceptor and then only in exceptional molecular and crystal environments.” Observation

of the linear polymer of $\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)$ down a column (i.e., the linear axis) (Figure 7) shows alignment of the 6-fold axis of benzene with the approximate 3-fold axis of the $\text{Pb}(\text{HFIP})_3$ unit. Instead of having a staggered conformation where benzene hydrogens would lie between protruding CF_3 fluorines, the hydrogens and fluorines eclipse. These $\text{H}\cdots\text{F}$ distances range from 2.71 to 3.051 Å and are longer than the sum of the van der Waals radii. Fluorine atoms are also aligned along the periphery of the column toward the benzene hydrogens of adjacent columns (Figure 8). In total, four columns of alkoxides have CF_3 groups aligned toward a single benzene *in addition to* those within the column. The intercolumnar $\text{H}\cdots\text{F}$ distances range from 2.595 to 2.820 Å. These aligned fluorines are nearly coplanar with the benzene and lie within 0.51 Å of the benzene C_6 plane. They are thus more linear than those within a column; near linearity is a characteristic of traditional hydrogen bonding.^{21b} The intra- and intercolumnar $\text{H}\cdots\text{F}$ close contacts are numerous (total of 24 per benzene or 3–5 per hydrogen) compared to the one or, occasionally, two $\text{H}\cdots\text{F}$ interactions most often reported in the literature to be hydrogen bonds. If $\text{H}\cdots\text{F}$ attractions are electrostatic in origin, a great number of $\text{F}(\delta^-)$ interactions with a single $\text{H}(\delta^+)$ seems plausible. Since bifurcated hydrogen bonds are already established to be longer than 1:1 hydrogen bond pairings, the fact that the distances found here are at the van der Waals sum demands that they not be ignored. An alternative rationale of these “contacts” involves the symmetry match that is observed. The mutual geometries of the benzene and the three HFIP groups (within a column) are complimentary and stack like hexagonal plates. Etter has reported an example of benzene encapsulated by six 3.0 Å $\text{C}-\text{H}\cdots\text{O}$ distances, each longer than the van der Waals sum (2.4 Å), but described as “favorable for hydrogen-bond formation.”²²

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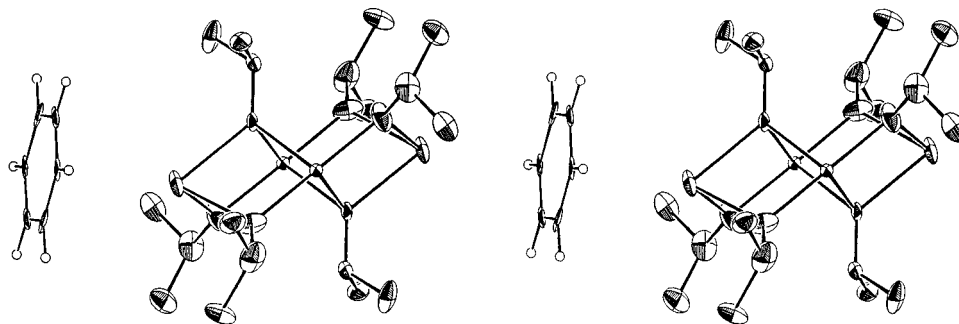


Figure 6. ORTEP representation of two $\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)$ units, showing the linear polymer structural arrangement with alternating benzene and alkoxide units. Alkoxide fluorines and hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

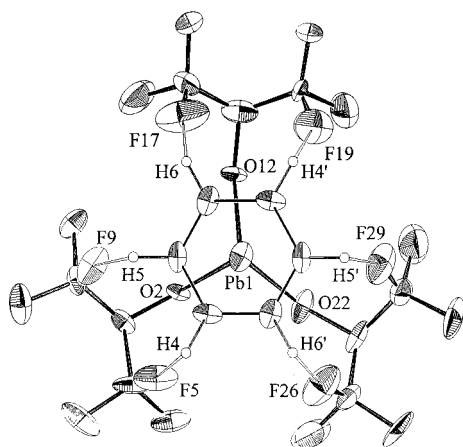


Figure 7. Selectively labeled ORTEP representation of only the $(\text{C}_6\text{H}_6)\text{Pb}(\text{HFIP})_3$ fragment of $[\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)]$, looking down the linear polymer axis. Shown here is the alignment of benzene hydrogens with alkoxide fluorines. Open lines drawn from hydrogen to fluorine are not intended to indicate a bonding interaction but are used to represent the closest $\text{H}\cdots\text{F}$ distances. Alkoxide hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

Discussion

[Li(OⁱPr)]. The reaction of $\text{Li}[\text{N}(\text{SiMe}_3)_2]$ with HO^iPr at room temperature to form $[\text{Li}(\text{O}^i\text{Pr})]$ is an alternate synthesis to alcoholysis of lithium metal. This method avoids carbonate and hydroxide contaminants which might arise from synthesis using impure lithium metal. The $[\text{Li}(\text{O}^i\text{Pr})]$ solid is powdery and sublimates at 140°C and 10^{-2} Torr. At ambient pressure, its TGA profile shows a relatively high (153°C) onset temperature for sublimation, possibly due to the presence of high-nuclearity oligomers (i.e., $n \leq 9$) in the gas phase as detected by mass spectrometry.

[PbLi(OⁱPr)₃]. The formation of $[\text{PbLi}(\text{O}^i\text{Pr})_3]$ is achieved by reaction of its two constituent homometallic alkoxides. During this reaction, $[\text{Pb}(\text{O}^i\text{Pr})_2]$ is depolymerized by the added $[\text{Li}(\text{O}^i\text{Pr})]$. This product sublimates at a much lower temperature than its constituents and thus likely has low nuclearity (i.e., $n = 1, 2$) in the gas phase. By TGA at ambient pressure, the sublimation onset is 93°C , which is 25°C lower than the lowest onset temperature of its constituents. Much like $[\text{Sn}_2\text{Li}_2(\text{O}^i\text{Bu})_6]$,¹³ this species is highly fluxional in solution at 25°C and shows NMR spectra too simple to be consistent with a static dimer, even at -90°C . A possible fluxional mechanism involves simple “rotation” of the alkoxides with respect to the Li centers (Scheme 1). This would involve the switching of the alkoxide oxygens between μ_2 and μ_3 bridging roles. A fluxional process involving two species is evident by variable-temperature ^1H NMR. At -40°C , two peaks in the methine region are sharper relative to their 25°C spectrum. When the sample is warmed above room temperature, the two peaks

coalesce to one broad peak (at 50°C) and eventually sharpen to a single septet (at 90°C). Throughout the temperature variation, the methyl region has only a single, sharp doublet. This most likely is due to accidental degeneracy of the two peaks due to a small difference in chemical shift, even on changing temperature. The second species is detected at about 10% abundance in both its ^7Li and ^{207}Pb NMR spectra. Observance of two species in solution at the same abundance by ^7Li and ^{207}Pb NMR suggests that there are two oligomers present (i.e., two species containing both Pb and Li). On the basis of solution molecular weight measurements of its fluorinated analog and other similarities, it is likely that the two species present are a monomer and dimer and are in equilibrium. A monomer–dimer equilibrium would give a second route by which the observed dimer would have apparent fluxionality to become a deceptively simple singlet. Disassembly of the dimer into two monomers (Scheme 2) would make all of the alkoxide environments equivalent. Reassembly would essentially scramble the environments. It is also possible that both pathways (i.e., Schemes 1 and 2) operate simultaneously.

[Li(HFIP)]. Formation of heteronuclear, homometallic HFIP species of Pb or Li is accomplished by a Bronsted acid–base reaction under mild conditions. The $[\text{Li}(\text{HFIP})]$ species, unlike its powdery-solid O^iPr counterpart, is waxy and has a sublimation temperature around 70°C . Analysis by TGA shows an onset temperature for sublimation of 58°C . This sublimation temperature is much lower (by 95°C) than that of its nonfluorinated counterpart (Figure 1). Several alkali fluoroalkoxides^{1,17} have shown the tendency to have an interaction of the metal center with fluorines on the alkoxide groups. This should increase the nuclearity of the metal alkoxide and, as a result, increase the sublimation temperature. In the $[\text{Li}(\text{OR})]$ case, no Li–F interactions have been detected (NMR evidence) and the sublimation temperature is decreased by use of fluorinated ligands. Further, the mass spectrum shows fragments which are consistent with “hexamer” and lower masses. In the case of the nonfluorinated species, oligomers as large as a “nonamer” were detected. For this reason, the nonfluorinated species, achieving aggregates of higher nuclearity, is predicted to have a higher sublimation temperature. By NMR, “implied” fluxionality (due to its very simple NMR spectra) was not significantly slowed even upon lowering the temperature to -45°C (the freezing point of a 1:1 d_8 -toluene/ f_8 -toluene mixture). The single peak in its ^7Li NMR shows no coupling to fluorine. It is possible that coupling is present but is averaged, due to fluxionality, to a small value.

[Pb(HFIP)₂]. By ^1H NMR studies, $[\text{Pb}(\text{HFIP})_2]$ shows evidence of having more than one oligomer present in solution; a single, broad peak at room temperature decoalesces to two lines by -40°C whose intensities reverse upon flash freezing and warming to -45°C . Further evidence suggesting more than one oligomer present includes isopiestic and mass spectral

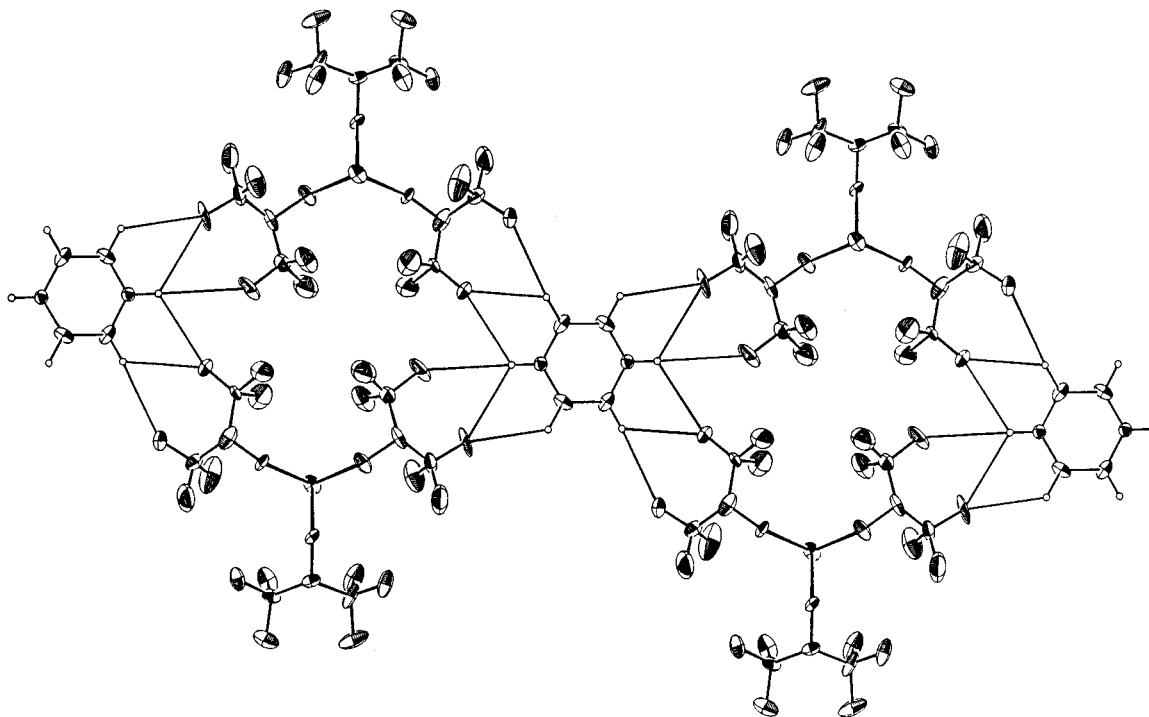
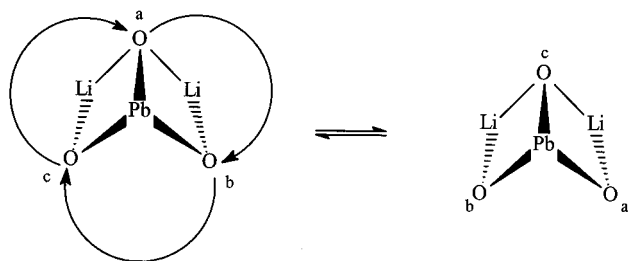
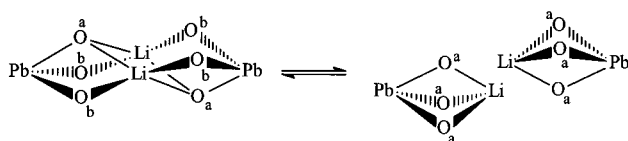


Figure 8. ORTEP representation of the $\text{Pb}(\text{HFIP})_3$ fragments and benzene units of $[\text{Pb}_2\text{Li}_2(\text{HFIP})_6(\text{C}_6\text{H}_6)]$ looking down the linear polymer axis. Each $\text{Pb}(\text{HFIP})_3$ fragment and benzene represents a linear polymer column, and thus seven columns are shown. Depicted here is the intracolumnar alignment of fluorines with the benzene rings. Open lines from hydrogens to fluorines show closest $\text{H}\cdots\text{F}$ distances. Alkoxide hydrogens are omitted for clarity. Thermal ellipsoids are drawn at 40% probability.

Scheme 1



Scheme 2



analyses. Similar reports about the observation of more than one oligomer being present in solution have been made for $[\text{Pb}(\text{O}^t\text{Bu})_2]_n$ ($n = 2, 3$). It has been reported that, at lower temperatures (i.e., cryoscopy in benzene), higher oligomers are observed,^{6,23} whereas at higher temperatures (i.e., ebullioscopy in benzene), lower oligomers are encountered.^{23,24} The evidence for this phenomenon includes molecular weight^{6,24} measurements and NMR studies.²³ This behavior suggests an equilibrium which is shifted by temperature (eq 1). Variable-temperature ^1H and ^{19}F NMR studies of $[\text{Pb}(\text{HFIP})_2]$ show that two species are present and the equilibrium is significantly perturbed at lower temperatures.



The fluorinated analog of $[\text{Pb}(\text{O}^i\text{Pr})_2]$ shows a marked improvement in solubility in donor solvents; the very sparingly

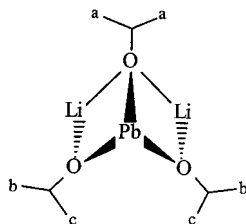
soluble polymer $[\text{Pb}(\text{O}^i\text{Pr})_2]$ ⁶ is not readily dissolved in donor or fluorinated solvents, while $[\text{Pb}(\text{HFIP})_2]$ is. Upon changing the ligand from O^iPr to HFIP, the molecular weight is lowered to a value between dimeric and trimeric (degree of aggregation = 2.71 in C_6F_6 at 25 °C). This is the result of fewer intermolecular interactions imposed by fluorine content of the ligand. The intermolecular fluorine-fluorine repulsion also lowers the sublimation temperature, even though ligand mass is increased by nearly three times. While $[\text{Pb}(\text{O}^i\text{Pr})_2]$ sublimates at 120 °C and 10^{-2} Torr, $[\text{Pb}(\text{HFIP})_2]$ sublimates at 85 °C and 10^{-2} Torr (Figure 2). Analysis by TGA at ambient pressure also indicates that the nonfluorinated polymer is less volatile and tends to partially decompose upon attempted sublimation. Decomposition can apparently be avoided by sublimation under reduced pressure.⁶

$[\text{PbLi}(\text{HFIP})_3]$. The ^{19}F NMR spectrum of the compound $[\text{PbLi}(\text{HFIP})_3]$ shows coupling to Pb resulting in doublet satellites. These satellites are at about 20% abundance (i.e., 10% for each satellite peak) and are consistent with significant coupling to only one Pb center. Were there averaged coupling to two equivalent lead centers ($I = 1/2$ at 22% abundance), the line pattern would be 1.2%:17.2%:63.1%:17.2%:1.2%. Thus, the doublet satellites would appear to be about 34% abundant while the outer lines could be easily lost in the base line of a spectrum. By ^{19}F NMR at 25 °C, the coupling observed is consistent with three alkoxides retaining connectivity to one Pb center; 11 lines (of 19 expected),¹² from coupling to 18 fluorines, each split into quartets, from coupling to three hydrogens, were found. Coupling found from three alkoxides to only one Pb suggests an intramolecular fluxional mechanism which involves exchange of μ_2 - and μ_3 -bridging roles without loss of connectivity to the metal. This could occur by simple rotation of the alkoxide "triangle" with respect to the Li centers as seen in Scheme 1, allowing exchange of alkoxide bridging roles while

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Scheme 3



retaining connectivity with only one Pb center. That is, Pb/O bonds persist through the rearrangement.

The ^1H NMR spectrum of $[\text{PbLi}(\text{HFIP})_3]$ at $-90\text{ }^\circ\text{C}$ shows two lines which integrate to 1:2. This integration pattern is consistent with that which is expected for the solid-state structure; the alkoxides arranged about a mirror plane and inversion center result in two chemical environments (“a” and “b”) which are of ratio 2:4 (at left in Scheme 2). While the protons in this static structure have only two environments, the fluorines should have three environments considering that the CF_3 groups lying to either side of the mirror plane are diastereotopic (Scheme 3). Three equal-intensity environments (“a”, “b”, and “c”) are both predicted and observed. Although the lines observed in the $-90\text{ }^\circ\text{C}$ ^{19}F NMR spectrum are not sharp multiplets, fluxionality on the NMR time scale is slowed significantly to give an NMR spectrum wholly consistent with its static solid-state structure.

Conclusions

Both $[\text{Pb}(\text{O}^i\text{Pr})_2]$ and $[\text{Li}(\text{O}^i\text{Pr})]$ can be synthesized using simple Bronsted acid–base techniques, and when they are reacted together they form the heterometallic complex $[\text{PbLi}$

$(\text{O}^i\text{Pr})_3]$. The sublimation temperature of $[\text{PbLi}(\text{O}^i\text{Pr})_3]$ is lower than those of its constituent alkoxides, which is a situation which permits the heterometallic species to sublime, in preference to decomposition into its constituent binary alkoxides.²⁵ The species $[\text{Pb}(\text{HFIP})_2]$ and $[\text{Li}(\text{HFIP})]$ are waxy, homoleptic fluoroalkoxide compounds whose volatilities are much improved over those of their nonfluorinated counterparts. When these are reacted together in Et_2O solvent, they form the powdery solid, heterometallic fluoroalkoxide, $[\text{PbLi}(\text{HFIP})_3]$, which crystallizes from benzene with 1 equiv of benzene in its lattice. There appears to be an interaction between the lattice benzene and the fluoroalkoxide, where fluorines are found within what may be considered fluorine–hydrogen bonding distances. This interaction, however, is believed to be weak, and orientation of molecules within the crystal is certainly the result of many small contributions from varied factors, including shape compatibility.²⁶

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Supporting Information Available: Full crystallographic details for $\text{Pb}_2\text{Li}_2[\text{OCH}(\text{CF}_3)_2]_6(\text{C}_6\text{H}_6)$ including tables of crystallographic data, fractional coordinates and isotropic thermal parameters, and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

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 (26) For a discussion of other weak hydrogen bonds in crystals (i.e., $\text{CH}\cdots\text{O}$), see: Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290.