The Structure and Stability Trends of Fluoro(methyl)plumbanes**

By *Martin Kaupp* and *Paul von R. Schleyer**

The dramatic differences in the stability of inorganic and organometallic Pb^{IV} compounds are best exemplified by comparing tetraalkyllead with lead tetrahalides: While Et_4Pb, for example, is a relatively stable compound with (still) considerable industrial use, $PbCl_4$ decomposes even at low temperatures.[1] On the other hand, Et_2Pb is unknown but $PbCl_2$ is perfectly stable. These remarkable differences between inorganic and organometallic compounds are of general importance in the chemistry of the heavy elements in groups 13 and 14 but do not yet seem to be fully understood.[2] We herein present ab initio pseudopotential calculations[3] on the structures of fluoro(methyl)plumbanes **1**–**3** which have the general formula $(CH_3)_nPbF_{4-n}$ ($n = 1-3$), as well as $(CH_3)_4Pb$ and PbF_4, and compare their stabilities with those of the corresponding divalent species $(CH_3)_2Pb$, CH_3PbF, and PbF_2.

$(CH_3)_3PbF$	$(CH_3)_2PbF_2$	CH_3PbF_3
1	**2**	**3**

The optimized geometries[3] of **1**–**3** are shown in Figure 1. The bond angles in all of these unsymmetrically substituted species deviate significantly from idealized tetrahedral values.[4] While the F-Pb-F angles are smaller than 109.5°, the C-Pb-C angles are considerably larger. This is most apparent in **2** with its C-Pb-C angle of approximately 135°. Similarly, the C_3Pb unit in **1** approaches planarity. These angle distortions have consequences for the polymeric arrangements found in the solid state: R_3PbX and R_2PbX_2 compounds (R is an alkyl or aryl group, X an electronegative substituent) usually form chain structures of types **4** and **5**, respectively.[1b] Note the almost planar PbR_3 arrangement in **4** (cf. **1**) and the *trans* orientation of the alkyl groups in **5** (cf. **2**). The calculated Pb–C and Pb–F bonds shorten when the number of fluorine substituents is increased,[5] consistent with the results of calculations on the fluoromethanes and -silanes.[6]

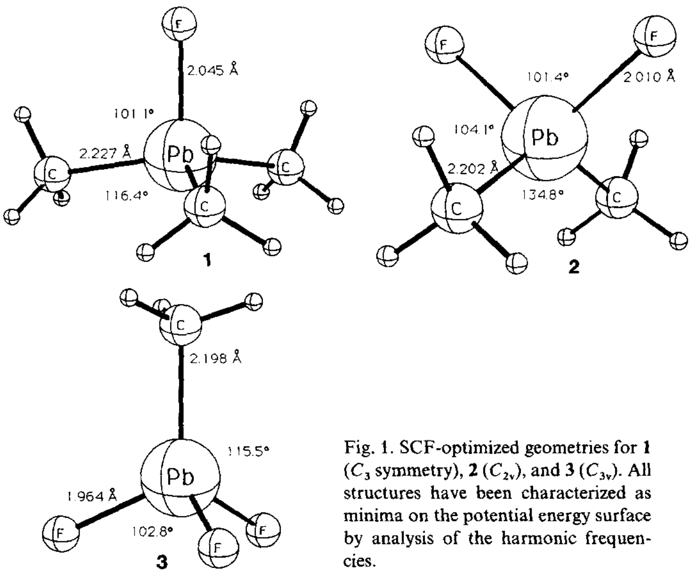
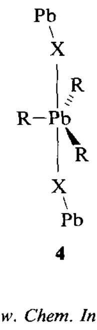


Fig. 1. SCF-optimized geometries for **1** (C_3 symmetry), **2** (C_{2v}), and **3** (C_{3v}). All structures have been characterized as minima on the potential energy surface by analysis of the harmonic frequencies.

Both the distorted bond angles and the contracted bond lengths may be rationalized by hybridization arguments with



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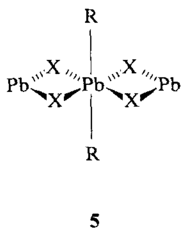

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nonorthogonal hybrid orbitals.[6a, 7] Figure 2 displays the partial atomic charges on lead, the p:s ratio n of the Pb-sp^n hybridization of the hybrid orbitals used for Pb–C and Pb–F bonding, and the p:s ratio of the average Pb hybridization (Weinhold et al.'s "natural population/hybridization analysis" (NPA)[8] was employed). With increasing fluorine substitution, the positive charge on lead increases, and to the contributions of the p orbitals to the Pb hybrid orbitals and the bonding decrease. The larger contributions of the s orbitals to the bonds lead to the observed bond length contraction. Since the hybrid orbitals directed towards the electronegative fluorine substituents generally exhibit roughly twice as much p character as the hybrids used for Pb–C bonding (Fig. 2), the observed deviations from 109.5° angles follow expectations based on Bent's rule.[9]

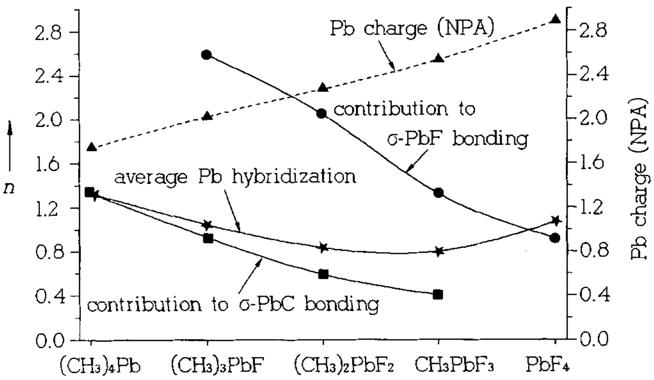

Fig. 2. p:s Ratio n of the Pb-sp^n hybridization (based on "natural population analysis" NPA[7]) and partial atomic charges on lead (NPA[7]) for the homologous series of fluoro(methyl)plumbanes (the average lead NPA hybridization and the p:s ratios of the contributions of the lead hybrid orbitals to the σ-bonding "natural localized MOs" (NLMOs)[7] are given). The differences between the average p:s ratio and the p:s ratio of the lead contributions to the σPb–F bonding NLMOs in PbF_4 are due to small hyperconjugative interactions.

The energies ΔE for the 1,1-elimination of F_2, methyl fluoride, or ethane from these Pb^{IV} compounds (to give Pb^{II} derivatives) are shown in Figure 3. In general, these reactions become less endothermic or more exothermic as the number of fluorine substituents increases. For example, elimination of CH_3F from $(CH_3)_3PbF$ (**1**) is *endothermic*, whereas loss of CH_3F is quite *exothermic* for CH_3PbF_3 (**3**). Obviously, the tetravalent lead compounds are destabilized in this sense by electronegative substituents. As a result, the disproportionation reaction $2\,(CH_3)_2Pb \rightarrow Pb(^3P) + (CH_3)_4Pb$ is exothermic, but the reaction $2\,PbF_2 \rightarrow Pb(^3P) + PbF_4$ is strongly endothermic.[10].

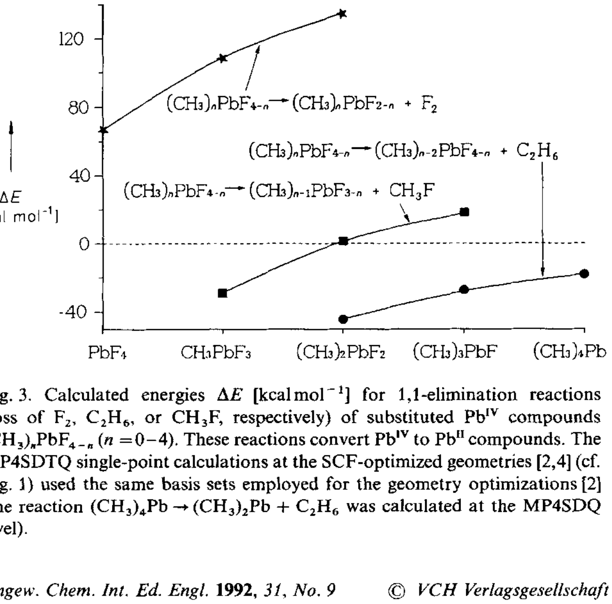

Fig. 3. Calculated energies ΔE [kcal mol^{-1}] for 1,1-elimination reactions (loss of F_2, C_2H_6, or CH_3F, respectively) of substituted Pb^{IV} compounds $(CH_3)_nPbF_{4-n}$ ($n = 0$–4). These reactions convert Pb^{IV} to Pb^{II} compounds. The MP4SDTQ single-point calculations at the SCF-optimized geometries [2,4] (cf. Fig. 1) used the same basis sets employed for the geometry optimizations [2] (the reaction $(CH_3)_4Pb \rightarrow (CH_3)_2Pb + C_2H_6$ was calculated at the MP4SDQ level).

This destabilization of Pb^{IV} compounds by electronegative substituents may also be explained by the hybridization. The increasing metal charge contracts the lead 6s orbitals more strongly than the 6p orbitals.[11] Thus, the already significant differences in the radial extension of s and p orbitals in compounds of heavy main-group elements[7] become even larger. Since efficient hybridization requires the size of the orbitals involved to be similar, electronegative substituents increase the hybridization defects[7] (cf. Fig. 2) which leads to less efficient covalent bonding. A possible gain in ionic bonding contributions in the polyhalo compounds most probably is compensated by the increased electrostatic repulsions between the substituents.

In contrast to these Pb^{IV} compounds, alkanes and silanes are stabilized by geminal fluorine substitution.[6] This was shown to be due to negative hyperconjugation $n(F) \rightarrow \sigma^*(AH, AF)$ (A = C, Si).[6a] Due to less favorable orbital overlap, these hyperconjugative interactions which lead to a delocalization of the electron density do not contribute significantly to the stabilization of multiply fluorosubstituted alkylplumbanes. Preliminary calculations on the corresponding parent compounds (H instead of alkyl) with both quasi-relativistic and nonrelativistic lead pseudopotentials indicate that relativistic effects also contribute to the trends discussed here. We will present more detailed analyses of a larger set of such group 14 derivatives in a the full paper.

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1, 420-54-2; **2**, 23890-85-9; **3**, 21986-71-0; $(CH_3)_2Pb$, 63588-56-7; CH_3PbF, 142947-24-8; PbF_2, 7783-46-2.

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[1] a) F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5. Ed., Wiley, New York, **1988**. b) P. G. Harrison in *Comprehensive Coordination Chemistry*, Vol. 3, (Ed.: G. Wilkinson), Pergamon, Oxford, **1987**, p. 183.

[2] Schwerdtfeger et al. have recently studied a) organothallium compounds (P. Schwerdtfeger, P. D. W. Boyd, G. A. Bowmaker, H. G. Mack, H. Oberhammer, *J. Am. Chem. Soc.* **1989**, *111*, 15) and b) a series of heavy-element hydrides and halides (P. Schwerdtfeger, G. A. Heath, M. Dolg, M. A. Bennett, *J. Am. Chem. Soc.*, in press.) by pseudopotential calculations.

[3] Full Hartree-Fock gradient geometry optimizations have been carried out with the Gaussian 90 program (Gaussian 90, Revision F, M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. J. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, L. R. Kahn, J. J. P. Stewart, S. Topiol, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1990**). Quasi-relativistic 4-valence-electron pseudopotentials for Pb and C, and a 7-valence-electron pseudopotential for F have been used with double-zeta valence basis sets augmented by d-polarization functions and, in the case of fluorine, by a diffuse sp set (W. Küchle, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1991**, *74*, 1245. W. Küchle, A. Bergner, M. Dolg, H. Stoll, H. Preuss, to be published. M. Dolg, Ph.D. Thesis, Universität Stuttgart, **1989**. *Gaussian Basis Set for Molecular Calculations* (Ed.: S. Huzinaga), Elsevier, New York, **1984**). M. Kaupp, P. von R. Schleyer, H. Stoll, H. Preuss. *J. Am. Chem. Soc.* **1991**, *113*, 6012). A [4s1p]/(2s1p) basis set was used for hydrogen (T. H. Dunning, H. Hay in *Methods of Electronic Structure Theory* (Modern Theoretical Chemistry, Vol. 3), (Ed.: H. F. Schaefer III), Plenum, New York, **1977**, p. 1). The main geometry parameters calculated for the divalent species are: RPb-C = 2.323 Å, ∢C-Pb-C = 93.0° (Me_2Pb); RPb-C = 2.300 Å, RPb-F = 2.062 Å, ∢C-Pb-F = 92.9° (MePbF); RPb-F = 2.027 Å, ∢F-Pb-F = 95.8° (PbF_2).

[4] See a) P. von R. Schleyer, *Abstract Orgn.* 352, Am. Chem. Soc. Meet. San Francisco, CA, April, **1992**, b) R. Boese, D. Bläser, N. Niederprüm, M.

Nüsse, W. Brett, P. von R. Schleyer, M. Bühl, N. J. R. van E. Hommes, *Angew. Chemie* **1992**, *104*, 356; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 314.

[5] Our calculated Pb–F separation in PbF_4 is 1.924 Å; the Pb-C bond length in $(CH_3)_4Pb$ is 2.248 Å (in good agreement with relativistic all-electron calculations and experiment, cf.: J. Almlöf, K. Faegri, Jr., *Theor. Chim. Acta* **1986**, *69*, 438).

[6] a) A. E. Reed, P. von R. Schleyer, *J. Am. Chem. Soc.* **1987**, *109*, 7362; b) D. A. Dixon, *J. Phys. Chem.* **1988**, *92*, 86.

[7] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272; W. Kutzelnigg, *Theochem* **1988**, *169*, 403.

[8] A. E. Reed, R. B. Weinstock, F. Weinhold. *J. Chem. Phys.* **1985**, *83*, 735.

[9] H. A. Bent, *Chem. Rev.* **1961**, *61*, 275.

[10] The MP4 energy for the first reaction is -18.3 kcal mol^{-1}, that for the second $+90.0$ kcal mol^{-1}, when corrected for zero-point vibrational energy and for atomic spin–orbit coupling of Pb(^{3}P) (cf. ref. [11b]). See ref. [2b] for QCISD(T) results on the lead hydrides and fluorides.

[11] a) For a given principal quantum number, orbitals with higher angular momentum quantum number generally are affected less strongly by an increase of the nuclear charge. This is obvious from the spin–orbit-averaged experimental s → p excitation energies (ref. [11b]) for Pb^{+1} (176 kcal mol^{-1}), Pb^{+2} (206 kcal mol^{-1}), and Pb^{+3} (258 kcal mol^{-1}). b) C. E. Moore, *Atomic Energy Levels*, Circular Nat. Bur. Standards 467, Washington, **1958**.