ingly, the C-Sn-C angles lie within a quite narrow range, while the carbon-tin bonds are elongated by 0.08 Å when the substituent is changed from methyl to 2,4,6-tris(trifluoromethyl)phenyl. Note that in the latter ligand an sp²-hybridized carbon is attached to tin and a shorter carbon-tin bond is expected. Although X-ray and gasphase electron diffraction parameters have to be compared carefully,¹⁵ the data above indicate that possible electrostatic ligand-ligand repulsions lead to an elongation of bonds rather than a widening of angles. Additionally, reduced electron density on the tin-bonded carbon atoms by the electron-withdrawing trifluoromethyl groups will result in increasing repulsive interactions between the electropositive tin atom and the adjacent carbon atoms¹⁶ and elongated bonds.

Although steric protection of the low-valent tin center certainly plays an important role in its stability, a spacefilling model of 1 (Figure 2) shows that the trifluoromethyl groups of the ligands form intramolecular fluorine-tin contacts, leaving one side of the molecule sterically unprotected. The averaged fluorine-tin bond length F7-Sn/F10-Sn is 2.67 Å; the F2-Sn/F16-Sn bond distance is longer (2.82 Å) but still considerably shorter than the sum of the van der Waals radii (F, 1.47 Å; Sn, 2.17 Å⁶). The shortest *inter* molecular fluorine-tin distance is 3.51 Å and will not significantly contribute to the stability of 1. The position of the trifluoromethyl groups is not defined by steric congestions but by maximizing fluorine-tin interactions without interligand repulsions.

The stabilizing influence of the 2,4,6-tris(trifluoromethyl)phenyl ligand is only partly due to steric shielding. Despite the electron-withdrawing character of the trifluoromethyl group through the σ -bond framework and negative hyperconjugation,¹⁷ the *electron-donating* ability via the lone pairs at the fluorine atoms is clearly established and is probably the most important factor preventing oligo- or polymerization of 1.¹⁸ Obviously, these intramolecular contacts are observed in solution as well and might be responsible for the surprising high-field shift of the ¹¹⁹Sn NMR signal.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond distances and angles (3 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, and Reactivity of the First Stable Diaryllead(II) Compound

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Summary: Reaction of PbCl₂ with 2,4,6-(CF₃)₃C₆H₂Li results in the formation of the first stable diaryllead(II) compound, $[2,4,6-(CF_3)_3C_6H_2]_2Pb$ (4). X-ray structural analysis shows that in the solid state 4 is a bent monomer. 4 reacts with 2,4,6-(CF₃)₃C₆H₂SH (5) in hydrocarbon solutions to produce the solvent-free thiolate [2,4,6-(C- $F_{3}_{3}C_{6}H_{2}S]_{2}Pb$ (6).

Lead(II) compounds with σ -aryl substituents are unknown,¹ and the only authentic lead(II) alkyl is $[(Me_3Si)_2CH]_2Pb$ (1), which was obtained in minimal yield (3%) by Lappert et al. in 1976.² The synthesis of diphenyllead(II) was reported in 1922³ but is not reproducible.⁴ A difficulty in obtaining these compounds is their

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tendency to disproportionate. For example, the reaction of PbCl₂ with aryllithium or aryl Grignard reagents leads to organolead(IV) compounds and elemental lead.⁴ Further complications result from the reactivity of these complexes as indicated by the extreme sensitivity of 1

⁽¹⁵⁾ The molecular structures of $[(Me_3Si)_2N]_2Sn$ determined by X-ray and GED methods differ by 8.7° in the N-Sn-N angle (104.7 vs 96°, respectively).

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Figure 1. Molecular structure of 4 (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Pb-C1 = 2.361 (4), Pb-C(10) = 2.371 (4), C1-Pb-C10 = 94.5 (1).



toward air, moisture, and light.

We, and others, have recently exploited the 2,4,6-tris-(trifluoromethyl)phenyl substituent⁵⁻⁷ to stabilize a number of new main-group compounds, including the unusually stable diphosphene $[2,4,6-(CF_3)_3C_6H_2P]_2^6$ and $[2,4,6-(C-1)_3C_6H_2P]_2^6$ $F_3)_3C_6H_2OTI]_2$,^{7a} in which the thallium atom is two-coordinate. In this communication we report the use of this substituent to form the first fully characterized lead(II) diaryl.

Slow addition of $2,4,6-(CF_3)_3C_6H_2Li$ (3) to a suspension of $PbCl_2$ in ether results in a clear yellow solution, with no indication of the formation of metallic lead (Scheme I).⁸ Evaporation of the volatile components, followed by recrystallization of the solid residue from *n*-hexane, produced large yellow crystals of $[2,4,6-(CF_3)_3C_6H_2]_2Pb$ (4). 4 is thermally stable to its melting point (58 °C). In the solid state it is not light sensitive (this is not true for solutions, which slowly decompose when exposed to light). In contrast to 1, 4 is not thermochromic and its yellow color is retained between -196 °C and its melting point. The EI mass spectrum shows a molecular peak at m/z 769 with 39% relative intensity.

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(8) (a) Preparation of 3: 128 mL of an n-butyllithium solution (1.54 N in hexane) was added to 54.5 g (0.2 mol) of 2 in 160 mL of ether at a rate that maintained a gentle reflux. The metalation reaction was complete after stirring at room temperature for 24 h. (b) Preparation of 4: The solution of 3 resulting from (a) was added dropwise to a suspension of 27.8 g (0.1 mol) of $PbCl_2$ in 50 mL of ether. After a further 48 h the solvent was removed, the residue extracted with 400 mL of *n*-hexane, and the solution filtered through a thin Celite pad. Concentration to ca. 80 mL and cooling to -20 °C yielded 25.7 g (33%) of 4 as large yellow crystals, mp 58 °C. Anal. Calcd for $C_{18}H_4F_{18}Pb$: C, 28.1; H, 0.5. Found: C, 28.2; H, 0.7. IR (KBr/Nujol; ν , cm⁻¹): 1619 (s), 1573 (m), 1457 (vs), 1377 (s), 1283 (vs, br), 1196 (vs, br), 1103 (vs, br), 911 (s), 684 (s). EI-MS: m/2 769 (M⁺, 39%), 751 (M⁺ - F, 100). ¹H NMR ($C_{6}D_6$, 80 MHz): δ 8.14 (⁴J(Pb,H) = 13 Hz). ¹⁹F NMR (C_6D_6 , 75.39 MHz, CFCl₃ external): δ -59.4 (12 F, o-CF₃, ⁴J(Pb,F) = 358 Hz), -63.1 (6 F, p-CF₃, ⁶J(Pb,F) = 6 Hz). ¹³C NMR (C_6D_6 , 62.91 MHz): δ 258.5 (t, ¹J(Pb,C) = 1360 Hz, C1), 139.3 (q, ²J(C,F) = 30 Hz, C2), 130.7 (q, ²J(C,F) = 34 Hz, C4), 130.5 (q, ¹J(C,F) = 274 Hz, o-CF₃), 128.4 (m, C3), 123.6 (q, ¹J(C,F) = 272 Hz, p-CF₃). ²⁰⁷Pb NMR (C_6D_6 , 52.33 MHz): δ 4878 (m, ⁴J(Pb,F) = 358 Hz, 11 of the 13 expected lines were observed). solvent was removed, the residue extracted with 400 mL of n-hexane, and

The single-crystal X-ray structural analysis⁹ reveals that 4 is monomeric in the solid state (Figure 1). The shortest intermolecular Pb-Pb separation is 7.316 Å; Pb-Pb bonding can be ruled out.^{2,4} Four intramolecular Pb-F contacts may be contributing to the unusual stability of 4 (Pb-F1 = 2.785 Å; Pb-F9 = 2.793 Å; Pb-F10 = 2.839 Å; Pb-F16 = 2.966 Å). These Pb-F interactions are relatively weak, as can be seen by comparison with PbF_2 (Pb-F = 2.033 Å).¹¹ The only other example of a structurally characterized two-coordinate lead(II) compound with monodentate ligands is $Pb[N(SiMe_3)_2]_2$, which has been studied by both X-ray and electron diffraction.¹² As expected, both structures are bent. In the solid phase, the angle at lead (L-Pb-L) is smaller in 4 (94.5 (1)°) than in the silylamide $(103.6 (7)^\circ)$. In the gas phase smaller L-Pb-L angles are observed for Pb[N(SiMe₃)₂]₂ (91 (2)°) and PbF_2 (97 (2)°).^{11,12} Similar variations in the L-M-L angle are observed in two-coordinate germanium(II) and tin (II) compounds.13

4 is readily soluble in nonpolar solvents, and further reactions can be carried out in hydrocarbon solutions. Thus, addition of Cl_2 gas to a hexane solution of 4 causes quantitative production of PbCl₂. More interesting is the reaction of 2 equiv of 2,4,6-(CF_3)₃ C_6H_2SH (5)⁵ in pentane, which yields the solvent-free thiolate $[2,4,6-(CF_3)_3C_6H_2 S_{2}Pb$ (6) as a yellow analytically pure precipitate (Scheme II).14

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Supplementary Material Available: Tables of crystal data, data collection, solution and refinement parameters, atomic coordinates, bond distances and angles, anisotropic displacement coefficients, and hydrogen atom coordinates (6 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(9) Crystal data for 4: $C_{18}H_4F_{18}Pb$, $M_r = 769.5$, monoclinic, space group $P2_1/c$, a = 11.837 (1) Å, b = 11.993 (1) Å, c = 14.611 (2) Å, $\beta = 97.93$ (1)°, V = 2054.4 Å, Z = 4, $d_{calcd} = 2.488$ g/cm³, μ (Mo K α) (graphite monochromator) = 8.44 mm⁻¹. The data were collected with use of $20-\omega$ scans on a Stoe-Siemens AED diffractometer at -120 °C: 4055 measured reflections, 4017 unique reflections, and 3660 observed reflections with $F \ge 3\sigma(F)$; $2\theta_{max} = 52^{\circ}$. Structure solution and refinement were performed with use of SHELXSS¹⁰ and SHELXTL, semiempirical absorption and extinction corrections applied, all non-hydrogen atoms refined anisotropically, and hydrogen atoms inserted at calculated positions. Refinement of 335 parameters converged with R = 0.0286, $R_w = 0.0333$, w^{-1} = $\sigma^2(F)$ + 0.0002 F^2 , and maximum/minimum rest electron density +1.2/-1.1 Å⁻³.

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(d) Fjeldberg, T.; Hitchcock, P. B.; Lappert, M. F.; Smith, S. J.; Thorne, A. J. Chem. Soc., Chem. Commun. 1985, 939. (14) Preparation of 6: 5.88 g (18.8 mmol) of 5 was added to a stirred pentane solution (100 mL) of 4 (7.20 g, 9.4 mmol). After 2 h the lemon yellow precipitate was filtered off and dried under vacuum: yield 5.84 g (75%); decomposition at ca. 168 °C. Anal. Calcd for $C_{18}H_{4}F_{18}S_{2}Pb$: C, 25.9; H, 0.5. Found: C, 25.7; H, 0.7. IR (KBr/Nujol ν , cm⁻¹): 1625 (s), 1281 (s), 1268 (m), 1191 (s), 1152 (s), 1108 (s), 1039 (m), 916 (s), 723 (s), 685 (s). EI-MS: m/z 834 (M⁺, 7%), 521 (2,4,6-(CF₃)₃C₆H₂SPb⁺, 32), 275 (C₆H₂(CF₂)₂CF₃S, 100). ¹H NMR (C₆D₆, 80 MH2): δ 7.97 (s, 4 H). ¹⁹F NMR (C₆D₆, 75.39 MHz, CFCl₃ external): δ -59.9 (12 F, o-CF₃, ⁵J(Pb,F) = 353 Hz), -62.6 (6 F, p-CF₃). = 353 Hz), $-62.6 (6 \text{ F}, p-CF_3)$.

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