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 sp^2-hybridized carbon is attached to tin and a shorter carbon–tin bond is expected. Although X-ray and gas-phase 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 atoms[16] and elongated bonds.

Although steric protection of the low-valent tin center certainly plays an important role in its stability, a space-filling model of 1 (Figure 2) shows that the trifluoromethyl groups of the ligands form *intra*molecular 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 Å[6]). 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 ^{119}Sn 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.

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[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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[18] Zuckerman et al. already postulated fluorine–tin contacts in the closely related bis[2,6-bis(trifluoromethyl)phenyl]stannylene.[2] Escudié et al. found short phosphorus–fluorine contacts in a diphosphene bearing this ligand.[4] A good measure of the extent of these interactions is the ratio $r(\mathrm{M{-}F_{obsd}}):r$(van der Waals), which equals 0.73 in 1.

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

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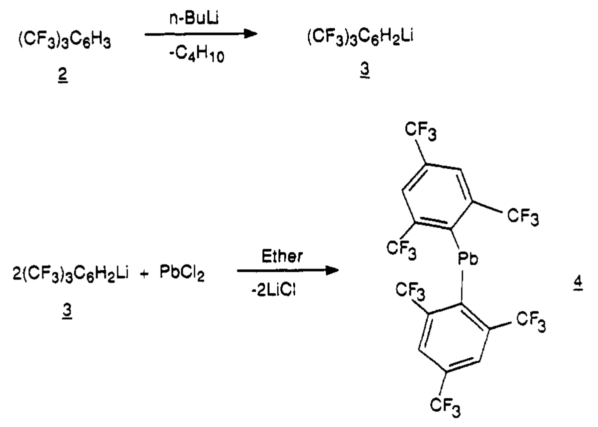
Summary: Reaction of $PbCl_2$ with 2,4,6-$(CF_3)_3C_6H_2Li$ results in the formation of the first stable diaryllead(II) compound, $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Pb$ (**4**). X-ray structural analysis shows that in the solid state **4** is a bent monomer. **4** reacts with 2,4,6-$(CF_3)_3C_6H_2SH$ (**5**) in hydrocarbon solutions to produce the solvent-free thiolate $[2,4,6\text{-}(CF_3)_3C_6H_2S]_2Pb$ (**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 1922[3] but is not reproducible.[4] A difficulty in obtaining these compounds is their tendency to disproportionate. For example, the reaction of $PbCl_2$ 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

Scheme I



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[1] See, for example: Elschenbroich, C.; Salzer, A. *Organometallchemie*; B. G. Teubner: Stuttgart, FRG, 1986; p 159.

[2] Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268.

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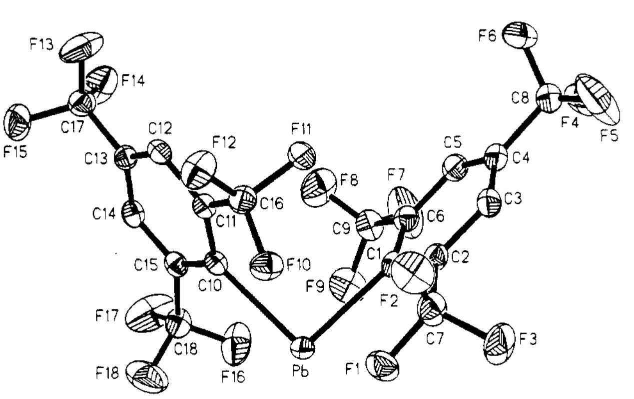
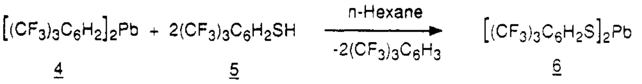


Figure 1. Molecular structure of 4 (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Pb–C1 = 2.361 (4), Pb–C(10) = 2.371 (4), C1–Pb–C10 = 94.5 (1).

Scheme II



$$[(CF_3)_3C_6H_2]_2Pb + 2(CF_3)_3C_6H_2SH \xrightarrow[-2(CF_3)_3C_6H_3]{\text{n-Hexane}} [(CF_3)_3C_6H_2S]_2Pb$$

4 5 6

toward air, moisture, and light.

We, and others, have recently exploited the 2,4,6-tris(trifluoromethyl)phenyl substituent[5-7] to stabilize a number of new main-group compounds, including the unusually stable diphosphene $[2,4,6\text{-}(CF_3)_3C_6H_2P]_2$[6] and $[2,4,6\text{-}(CF_3)_3C_6H_2OTl]_2$,[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 $2,4,6\text{-}(CF_3)_3C_6H_2Li$ (**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 $[2,4,6\text{-}(CF_3)_3C_6H_2]_2Pb$ (**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.

The single-crystal X-ray structural analysis[9] 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)°). In the gas phase smaller L–Pb–L angles are observed for $Pb[N(SiMe_3)_2]_2$ (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 $PbCl_2$. More interesting is the reaction of 2 equiv of $2,4,6\text{-}(CF_3)_3C_6H_2SH$ (**5**)[5] in pentane, which yields the solvent-free thiolate $[2,4,6\text{-}(CF_3)_3C_6H_2S]_2Pb$ (**6**) as a yellow analytically pure precipitate (Scheme II).[14]

Acknowledgment. We thank Professors H. W. Roesky and G. M. Sheldrick for helpful discussions and the Fonds der Chemischen Industrie for support of this work.

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.

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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*/*z* 769 (M^+, 39%), 751 ($M^+ - F$, 100). ^1H NMR (C_6D_6, 80 MHz): δ 8.14 ($^4J(Pb,H)$ = 13 Hz). ^{19}F NMR (C_6D_6, 75.39 MHz, $CFCl_3$ external): δ −59.4 (12 F, *o*-CF_3, $^4J(Pb,F)$ = 358 Hz), −63.1 (6 F, *p*-CF_3, $^6J(Pb,F)$ = 6 Hz). ^{13}C 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*-CF_3), 128.4 (m, C3), 123.6 (q, $^1J(C,F)$ = 272 Hz, *p*-CF_3). ^{207}Pb NMR (C_6D_6, 52.33 MHz): δ 4878 (m, $^4J(Pb,F)$ = 358 Hz, 11 of the 13 expected lines were observed).

[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, β = 97.93 (1)°, V = 2054.4 Å, Z = 4, d_{calcd} = 2.488 g/cm³, μ(Mo Kα) (graphite monochromator) = 8.44 mm⁻¹. The data were collected with use of $2\theta-\omega$ scans on a Stoe-Siemens AED diffractometer at −120 °C: 4055 measured reflections, 4017 unique reflections, and 3660 observed reflections with $F \geq 3\sigma(F)$; $2\theta_{max} = 52°$. Structure solution and refinement were performed with use of SHELXS86[10] 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, $w^{-1} = \sigma^2(F) + 0.0002F^2$, and maximum/minimum rest electron density +1.2/−1.1 Å^{-3}.

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[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 $C_{18}H_4F_{18}S_2Pb$: 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 ($2,4,6\text{-}(CF_3)_3C_6H_2SPb^+$, 32), 275 ($C_6H_2(CF_2)_2CF_3S$, 100). ^1H NMR (C_6D_6, 80 MHz): δ 7.97 (s, 4 H). ^{19}F NMR (C_6D_6, 75.39 MHz, $CFCl_3$ external): δ −59.9 (12 F, *o*-CF_3, $^5J(Pb,F)$ = 353 Hz), −62.6 (6 F, *p*-CF_3).