Inorganic Chemistr Article

Persistent Radicals of Trivalent Tin and Lead

Marco Becker,[†] Christoph Förster,[†] Christian Franzen,[†] Johannes Hartrath,[†] Enzio Kirsten,[†] Jörn Knuth,[†] Karl W. Klinkhammer,^{*,†} Ajay Sharma,[‡] and Dariush Hinderberger^{*,‡}

Institut für Anorganische and Analytische Chemie, Johannes Gutenberg-Universität Mainz, Duesbergweg 10–14, 55128 Mainz, Germany, and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

Received June 28, 2008

In this report we present synthetic, crystallographic, and new electron paramagnetic resonance (EPR) spectroscopic work that shows that the synthetic route leading to the recently reported, first persistent plumbyl radical •PbEbt₃ (Ebt = ethylbis(trimethylsilyl)silyl), that is, the oxidation of the related PbEbt₃-anion, was easily extended to the synthesis of other persistent molecular mononuclear radicals of lead and tin. At first, various novel solvates of homoleptic potassium metallates KSnHyp₃ (4a), KPbHyp₃ (3a), KSnEbt₃ (4b), KPblbt₃ (3c), and KSnlbt₃ (4c) (Hyp = tris(trimethylsilyl)silyl, lbt = isopropylbis(trimethylsilyl)silyl), as well as some heteroleptic metallates, such as [Li(OEt₂)₂][SnⁿBuHyp₂] (3d), [Li(OEt₂)₂][PbⁿBuHyp₂] (4d), [Li(thf)₄][PbPhHyp₂] (3e), and [K(thf)₇][PbHyp₂{N(SiMe₃)₂}] (3f), were synthesized and crystallographically characterized. Through oxidation by tin(II) and lead(II) bis(trimethylsilyl)amides or the related 2,6-di-tert-butylphenoxides, they had been oxidized to yield in most cases the corresponding radicals. Five novel persistent homoleptically substituted radicals, that is, •SnHyp₃ (2a), •PbHyp₃ (1a), •SnEbt₃ (2b), •SnIbt₃ (2c), and •Pblbt₃ (1c), had been characterized by EPR spectroscopy. The stannyl radicals 2a and 2c as well as the plumbyl radical 1c were isolated as intensely colored crystalline compounds and had been characterized by X-ray diffraction. Persistent heteroleptically substituted radicals such as •PbHyp2Ph (1e) or •PbHyp₂Et (1g) had also been generated, and some selected EPR data are given for comparison. The plumbyl radicals •PbR₃ exhibit a clean monomolecular decay leading to the release of a temperature-dependent stationary concentration of branched silyl radicals. They may thus serve as tunable sources of these reactive species that may be utilized as reagents for mild radical silvlations and/or as initiators for radical polymerizations. We present EPR-spectroscopic investigations for the new tin- and lead-containing compounds giving detailed insights into their electronic and geometric structure in solution, as well as structural studies on the crystalline state of the radicals, some of their anionic precursors, and some side-products.

Introduction

Recently, we reported the synthesis of the first stable plumbyl radical •PbEbt₃ (**1b**, Ebt = ethylbis(trimethylsilyl)-silyl).¹ It had been obtained through oxidation of the silyl-substituted potassium plumbanide KPbEbt₃ (**3b**) by molecular lead(II) salts. Analogous reactions had been utilized shortly before by Sekiguchi et al. in the synthesis of the homologous series •E(SitBu₂Me)₃ of silyl (E = Si), germyl (E = Ge),

and stannyl (E = Sn) radicals.² However, persistent or stable mononuclear radicals of all heavier tetrels³ but the heaviest congener lead have been known for more than 30 years.⁴ Starting with the pioneering work of Lappert and co-workers

^{*} To whom correspondence should be addressed. E-mail: hinderberger@ mpip-mainz.mpg.de (D.H.), klink@uni-mainz.de (K.W.K.).

[†] Johannes Gutenberg-Universität Mainz.

^{*} Max-Planck-Institut für Polymerforschung.

 ^{(1) (}a) Förster, C.; Klinkhammer, K. W.; Tumanskii, B.; Krüger, H.-J.; Kelm, H. Angew. Chem. 2007, 119, 1174–1177. (b) Angew. Chem., Int. Ed. 2007, 46, 1156–1159.

^{(2) (}a) Sekiguchi, A.; Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Ichinohe, M. J. Am. Chem. Soc. 2002, 124, 9865. (b) Sekiguchi, A.; Fukawa, T.; Lee, V. Ya.; Nakamoto, M. J. Am. Chem. Soc. 2003, 125, 9250. (c) Chrostowska, A.; Dargelos, A.; Graciaa, A.; Baylère, P.; Lee, V. Ya.; Nakamoto, M.; Sekiguchi, A. Organometallics 2008, 27, 2915. (d) For a recent review, see Inoue, S.; Ichinohe, M.; Sekiguchi, A. Organometallics 2008, 27, 1358.

⁽³⁾ The term "tetrels" had been suggested by the IUPAC as common name for the elements of group 14. To avoid terms such as "anions of the elements of group 14", it will be used together with derived denominations for derivatives such as tetryls (ER₃), tetrelanes (ER₄), or tetrelanides (MER₃) throughout this article.

⁽⁴⁾ For recent reviews, see (a) Power, P. P. Chem. Rev. 2003, 103, 789.
(b) Lee, V. Y.; Sekiguchi, A. Eur. J. Inorg. Chem. 2005, 1209.

who synthesized radicals such as $\bullet E[N(SiMe_3)_2]_3$ or $\bullet E[CH-(SiMe_3)_2]_3$,⁵ such radicals have been the subject of several papers in the last three decades. In the 1990s a revival of radical chemistry of group 14 had been observed. Several oligonuclear radicals with varying degree of delocalization of the unpaired electron had been prepared since then.⁶

Our early electron paramagnetic resonance (EPR) measurements on the mononuclear plumbyl radical 1b in solution revealed strong, broad, and structureless resonances for 1b at a g value markedly larger than for all related radicals of the lighter congeners in group 14.1 A second signal was present at even higher g-values. It was at first attributed to a second, lead-centered radical species. The expected satellite pattern according to hyperfine-coupling within the isotopomer ²⁰⁷PbEbt₃ could not readily be found, however. Therefore, we at first proposed a very large hyperfine-coupling constant for this isotopomer lying outside the range of the employed spectrometer. In this report we present a detailed analysis of new EPR data of 1b which reveals that the second signal does not derive from a further radical species but is part of the low-field manifold of the ²⁰⁷Pb hyperfine splitting pattern. Additionally, we present synthetic and analytic work that shows that the synthetic route mentioned above, that is, the oxidation of appropriate tetrel anions, may easily be extended to the synthesis of further related persistent homoleptic molecular radicals of lead and tin: •PbHyp₃ (1a), •PbIbt₃ (1c), •SnHyp₃ (2a), •SnEbt₃ (2b), and •SnIbt₃ (2c) (Hyp = $Si(SiMe_3)_3$, Ibt = isopropylbis(trimethylsilyl)silyl), and by slight modifications may also give access to related heteroleptic species such as SnHyp₂Ph and PbHyp₂Ph. We furthermore present detailed continuous wave EPR (CW EPR) and low-temperature, echo-detected EPR data on the four selected persistent molecular tetryl radicals 1a, 1b, 2a, and 2c, (see Figure 1) which allow the characterization of the structure and dynamics of these molecules in fluid and frozen solution.

Experimental Section

Syntheses. Preparation of Compounds. Reactions were performed under an argon atmosphere using standard Schlenk lines, and the resulting air-sensitive compounds were manipulated under nitrogen atmosphere within a drybox. Syntheses of the potassium salts KHyp, KEbt, and KIbt, as well as those of the molecular Sn(II) and Pb(II) precursors Sn[N(SiMe_3)_2]_2, Pb[N(SiMe_3)_2]_2, SnHyp₂ (**5**), and PbHyp₂ (**6**), were carried out as reported previously.^{7–10} Diethyl ether and pentane were distilled from LiAlH₄. Toluene and tetrahydrofuran were distilled from Na/benzophenone. All solvents



Figure 1. Molecular structures of the four persistent or stable lead- and tin based radicals that were characterized in detail using EPR spectroscopy.

were stored under Ar over 3 Å molecular sieves. All other reagents not mentioned in the following were synthesized by procedures according to the literature or purchased and used without further purification.

Sn(OC₆H₃'Bu₂-2,6)₂ and Pb(OC₆H₃'Bu₂-2,6)₂.¹¹ To a 350 mL *n***-pentane solution of Sn[N(SiMe₃)₂]₂ (16.66 g, 37.9 mmol) or Pb[N(SiMe₃)₂]₂ (20.01 g, 37.9 mmol) was added 2,6-di-***tert***-butylphenol (15.64 g, 75.8 mmol), and the resulting yellow (Sn) or orange (Pb) suspension was stirred overnight. The solid was separated by filtration through a sintered glass filter (G4), washed three times with 20 mL of toluene and subsequently dried in dynamic vacuum. The products are obtained as bright yellow or orange powder in yields of 92 and 94%, respectively and are only sparingly soluble in organic solvents.**

Sn(**OC**₆**H**₃^t**Bu**₂**-2**,6)₂. Anal. Calcd for $C_{28}H_{42}O_2Sn: C, 63.53; H, 8.00$. Found: C, 63.64; H, 8.12. ¹H NMR (C₆D₆): δ 7.48 (d, 4H), 6.74 (t, 2H), 1.62 (s, 18H).

Pb(OC₆H₃'Bu₂-2,6)₂. Anal. Calcd for $C_{28}H_{42}O_2Pb$: C, 54.43; H, 6.85. Found: C, 54.56; H, 6.96. ¹H NMR (C₆D₆): δ 7.36 (d, 4H), 6.90 (t, 2H), 1.58 (s, 18H).

[Li(thf)₄][PhHyp₂Pb] (3e). To a stirred yellow 10 mL di-*n*butylether solution of phenyllithium (1.91 mmol) at 0 °C was added quickly a green 6 mL solution of 6 (1.34 g, 1.91 mmol) in diethyl

- (7) Harris, D. H.; Lappert, M. F. J. Chem. Soc., Chem. Commun. 1974, 895.
- (8) Marschner, C. Eur. J. Inorg. Chem. 1998, 221.
- (9) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. Organometallics 2002, 21, 1023.
- (10) Klinkhammer, K. W.; Schwarz, W. Angew. Chem., Int. Ed. 1995, 34, 1334.
- (11) Sn(OC₆H₃'Bu₂-2,6) ₂ was synthesized before in moderate yield by reaction of SnI₄ and KOC₆H₃'Bu₂-2,6 (detailed procedure not given) and had been characterized crystallographically: Barnhart, D. M.; Clark, D. L.; Watkin, J. G. *Acta Cryst. C* **1994**, *50*, 702. Related tetrel aryloxides with an additional 4-Me substituent had also been described before. However, the better solubility of the corresponding alkali metal aryloxides in organic solvents, make them less suitable as oxidizers in the synthesis of tetryl radicals. For preparation and properties see: Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2086. Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2088.

⁽⁵⁾ See, for example, (a) Davidson, P. J.; Hudson, A.; Lappert, M. F.; Lednor, P. W. J. Chem. Soc., Chem. Commun. 1973, 829. (b) Cotton, J. D.; Cundy, C. S.; Harris, D. H.; Hudson, A.; Lappert, M. F.; Lednor, P. W. J. Chem. Soc., Chem. Commun. 1974, 651. (c) Lappert, M. F.; Lednor, P. W. Adv. Organomet. Chem. 1976, 14, 345. (d) Hudson, A.; Lappert, M. F.; Lednor, P. W. J. Chem. Soc., Dalton Trans. 1976, 2369.

⁽⁶⁾ See, for example, (a) Olmstead, M. M.; Pu, L.; Simons, R. S.; Power, P. P. *Chem. Commun.* **1997**, 1595. (b) Olmstead, M. M.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 11705. (c) Pu, L.; Haubrich, S. T.; Power, P. P. *J. Organomet. Chem.* **1999**, *582*, 100.

Persistent Radicals of Trivalent Tin and Lead

ether (prepared at -60 °C). The resulting orange solution was evaporated to dryness, and the obtained solid was redissolved in 2 mL of tetrahydrofuran. After storing at -60 °C for 18 h crystalline yellow plumbanide **3e** was isolated in 88% yield. ¹H NMR (C₆D₆): δ 8.75 (d, 2H), 7.12 (t, 2H), 7.01 (t, 1H), 0.50 (d, 4H); ¹³C NMR (C₆D₆): 123.3, 127.8, 147.5, 5.8; ²⁹Si NMR (C₆D₆): -122.9 (*Si*Si₃), -4.8 (*Si*Me₃).

Li(thf)₂SnHyp₂ⁿBu (4d) and Li(thf)₂PbHyp₂ⁿBu (3d). A 0.5 mL portion of a 2.0 M solution of *n*-butyllithium in *n*-hexane was added at -60 °C to 10 mL of diethyl ether. Under intense stirring, a precooled 5 mL dark brown (respectively blue) solution of 5 in *n*-pentane (0.71 g, 1 mmol) (respectively **6** (0.65 g, 1 mmol) was quickly added to this mixture, and an immediate color change to yellow (respectively orange) was observed. After evaporating to dryness the resulting solid was recrystallized from *n*-pentane. The lithium stannanide 4d (respectively plumbanide 3d) was obtained as a pale yellow (respectively orange) crystalline material in 65% (respectively 86%) yield. 4d: ¹H NMR (C₆D₆): δ 3.26 (q, 8H, OCH2CH3), 1.81 (m, 2H), 1.62 (m, 2H), 1.56 (m, 2H), 1.12 (t, 3H, CH₃ (*ⁿ*Bu)), 0.92 (t, 12H, OCH₂CH₃), 0.51 (s, 54H, Hyp); ¹³C NMR (C₆D₆): 65.2 (Et₂O), 39.0, 30.1, 14.5 (Et₂O), 14.1, 5.9 (Hyp); ²⁹Si NMR (C₆D₆): -142.1 (SiSi₃), -7.2 (SiMe₃ [¹J_{SiC} 42.1 Hz]); ¹¹⁹Sn-NMR (C₆D₆): -345 [¹J_{LiSn} 534 Hz]; ⁷Li NMR (C₆D₆): 0.54. 3d: ¹H NMR (C₆D₆): δ 3.22 (q, 8H, OCH₂CH₃), 2.22 (m, 2H), 2.05 (m, 2H), 1.60 (m, 2H), 1.15 (t, 3H), 0.94 (t, 12H, OCH₂CH₃), 0.55 (s, 54H, Hyp); ¹³C NMR (C₆D₆): 65.1 (Et₂O), 40.2, 32.4, 14.9 (Et₂O), 13.9, 6.9 (*Hyp*); ²⁹Si NMR (C₆D₆): -142.6 (SiSi₃), -5.4(SiMe₃ [¹J_{SiC} 42.1 Hz]);⁷Li NMR (C₆D₆): 1.36.

General Procedure for the Generation of Heteroleptic Stannyl and Plumbyl Radicals •EHyp₂R. A solution of 2 mmol of the stannylene 5 or the plumbylene 6 in 10 mL of *n*-pentane, respectively, was added to about 15 mL solution of 1.1 equiv of the appropriate hydrocarbyllithium at -80 °C. This had been freshly prepared by mixing the commercial available alkane or ether solution (approximately 1–2 mol/L) with 10 mL of precooled tetrahydrofuran. Under intense stirring, the solution was allowed to warm to room temperature and kept at 20 °C for 1 h. After filtering out the precipitate, the resulting solution was treated with 0.55 equiv of solid Pb[OC₆H₃tBu₂-2,6]₂, giving a deeply colored solution of the desired radical, which could be identified by its EPR signals. ¹H NMR spectra recorded on this solution generally show the presence of varying amounts of diamagnetic byproducts.

General Procedure for the Synthesis of the Homoleptic Tetrelanides KE[SiR(SiMe₃)₂]₃ 3b, 3c, 4b, and 4c. An equimolar mixture of the appropriate silane SiR(SiMe₃)₃ (20 mmol) and KO'Bu (20 mmol) was dissolved in 100 mL of tetrahydrofuran and stirred for 12 h. The resulting yellow or orange solution was evaporated to dryness and heated in dynamic vacuum to 30-40 °C for 1d. The residue was then dissolved in diethyl ether, cooled to -60 °C, and a suspension of E(OAr*)2 (6.67 mmol) in 100 mL of diethyl ether was added slowly during 3 h. The yellow to red reaction mixture was stirred for an hour at -30 °C and afterward filtered at -50 °C. The volume of the filtrate was reduced to about 10 mL at -50 °C, and 20 mL of *n*-pentane was added. After 2 d at -60 °C the tetrelanide had precipitated as a yellow to red crystalline material (67-85% overall yield). Additional amounts of the tetrelanide may be obtained from the mother liquor by repeated concentration and cooling.

3b: K(OEt₂)₂Pb[SiEt(SiMe₃)₂]₃: 72% yield; ¹H NMR (C₆D₆): δ 3.16 (q, 8H, OCH₂CH₃), 1.44 (m, 6H), 1.35 (t, 9H), 1.00 (t, 12H, OCH₂CH₃), 0.48 (s, 18H, *SiMe*₃); ¹³C NMR (C₆D₆): 65.8 (OCH₂CH₃), 17.8 (PbCH₂CH₃), 15.4 (OCH₂CH₃), 11.2 (PbCH₂-

CH₃), 4.0 (SiMe₃ [¹ J_{SiC} 41.1 Hz]); ²⁹Si NMR (C₆D₆): -78.2 (SiSi₃ [¹ J_{PbSi} 1378 Hz]), -9.6 (SiMe₃ [² J_{PbSi} 20.4 Hz]); ²⁰⁷Pb-NMR (C₆D₆): -1119.8.

3c: K(OEt₂)₂Pb[Si²Pr(SiMe₃)₂]₃: 67% yield; ¹H NMR (C₆D₆): δ 3.14 (q, 8H, OCH₂CH₃), 1.48 (d, 18H), 1.04 (sept, 3H), 1.01 (t, 12H, OCH₂CH₃), 0.51 (s, 18H, *SiMe*₃); ²⁹Si NMR (C₆D₆): -79.3 (*Si*Si₃ [¹J_{PbSi} 1378 Hz]), -9.3 (*Si*Me₃).

4b: K(OEt₂)₃Sn[SiEt(SiMe₃)₂]₃: 85% yield; ¹H NMR (C₆D₆): δ 3.14 (q, 12H, OCH₂CH₃), 1.22 (q, 6H), 1.03 (t, 9H), 1.02 (t, 18H, OCH₂CH₃), 0.41 (s, 18H, *SiMe*₃); ²⁹Si NMR (C₆D₆): -76.1 (*Si*Si₃ [¹J_{PbSi} 1378 Hz]), -11.0 (*Si*Me₃); ¹¹⁹Sn-NMR (C₆D₆): -702.6.

4c: K(OEt₂)₂Sn[Si²Pr(SiMe₃)₂]₃: 79% yield; ¹H NMR (C₆D₆): δ 3.16 (q, 8H, OCH₂CH₃), 1.44 (d, 18H), 1.67 (sept, 3H), 1.01 (t, 12H, OCH₂CH₃), 0.50 (s, 18H, *SiMe*₃); ¹³C NMR (C₆D₆): 65.8 (OCH₂CH₃), 25.6 (PbCH₂CH₃), 15.4 (OCH₂CH₃), 4.7 (SiMe₃); ²⁹Si NMR (C₆D₆): -63.5 (*Si*Si₃), -10.7 (*Si*Me₃).

(OEt₂)₂KPbHyp₃ (3a') and [K(thf)₆][PbHyp₃] (3a''). Solventfree KHyp (1.43 g, 5 mmol) was suspended in 10 mL of *n*-pentane and cooled to -60 °C. Then 10 mL of diethyl ether was added. A cooled (-60 °C) 15 mL *n*-pentane solution of **6** (3.56 g, 5 mmol) was slowly added to the KHyp suspension, and a color change to red-violet as well as precipitation of a violet solid was observed. The reaction mixture was stirred for 2 h, and the cold solution evaporated to dryness. The obtained solid was recrystallized from *n*-pentane. **3a'** was isolated as red-violet platelets in 89% yield. Recrystallization from tetrahydrofuran or direct synthesis in this solvent yielded the thf-solvate **3a''** as violet rod-shaped crystals in 86% yield.

3a': ¹H NMR (C₆D₆): δ 3.21 (q, 8H, OCH₂CH₃), 1.05 (t, 12H, OCH₂CH₃), 0.57 (s, 18H, *SiMe*₃); ¹³C NMR (C₆D₆): 65.9 (OCH₂-CH₃), 14.2 (OCH₂CH₃), 4.6 (SiMe₃); ²⁹Si NMR (C₆D₆): -129.9 (*Si*Si₃), -9.5 (*Si*Me₃).

[K(thf)₆][SnHyp₃] (4a") and [K(thf)₄(C₆H₆)₂][K(SnHyp₃)₂] (4a""). To a 20 mL diethyl ether solution of KHyp (0.315 g, 1.1 mmol) was slowly added a 10 mL diethyl ether solution of 5 (0.713 g, 1.1 mmol) at -60 °C. The brown solution was stirred for 2 h at -60 °C and further 15 min at room temperature. After concentration in vacuum to a volume of 5 mL, tetrahydrofurane (2 mL) was added. Storing at -60 °C for 2 d afforded needle-shaped orange crystals of 4a" in 65% yield.

Thorough drying of 4a'' for 12 h at 30 °C and subsequent recrystallization from a saturated benzene solution (25°/6 °C) finally gave orange platelets of the potassiate 4a'''.

4a": ¹H NMR (C₆D₆): δ 0.55 (s, 81H, *SiMe*₃); ¹³C NMR (C₆D₆): 7.2 (SiMe₃); ²⁹Si NMR (C₆D₆): -134.1 (*SiS*₁₃), -7.2 (*SiMe*₃).

4^{""}: ¹H NMR (C₆D₆): δ 0.53 (s, 81H, *SiMe*₃); ¹³C NMR (C₆D₆): 6.9 (SiMe₃); ²⁹Si -NMR (C₆D₆): -132.3 (*Si*Si₃), -7.5 (*Si*Me₃).

[K(thf)₇][PbHyp₂{N(SiMe₃)₂}] (3f). Twelve milliliters of a solution of KN(SiMe₃)₂ (0.31 g, 1.54 mmol) in a 5:1 mixture of tetrahydrofuran and diethyl ether was added to a green 5 mL diethyl ether solution of **6** (1.10 g, 1.54 mmol) at -60 °C, resulting in an immediate color change to red-brown. After 2 h the solution was warmed to room temperature and stirred for an additional 15 min. After solvent reduction to 5 mL and storing at -60 °C for 2 d, **3f** had been obtained as red platelets (85% yield), which, however, proved not suitable for X-ray analysis. A suitable red single crystalline block was finally obtained by recrystallization from toluene.¹H NMR (C₆D₆): δ 3.52 (m, thf), 1.40 (m, thf), 0.41 (s, Hyp), 0.17 (s, N(SiMe₃)₂); ¹³C NMR (C₆D₆): 68.3 (thf), 25.8 (thf),

8.3 (Hyp), 7.2 (N(SiMe₃)₂); ²⁹Si NMR (C₆D₆): -31.6 (SiSi₃), -20.1 (NSi₂), 7.9 (SiSi₃). UV-vis (*n*-pentane): 238 (sh, 3.09×10^4), 303 (sh, 1.36×10^4), 341 (sh, 5.96×10^3), 455 (1.61×10^3).

•SnHyp₃ (2a). 2a was either synthesized by oxidation of pure stannanide 4a or preferably in a one-pot fashion without isolating 4a prior to oxidation. The latter procedure started from a 10 mL diethyl ether solution of solvated KHyp (K(thf)_{0.8}Hyp, 1.53 g, 4.44 mmol). A suspension of $Sn(OC_6H_3^TBu_2-2,6)_2$ (0.87 g, 1.64 mmol) in 10 mL of diethyl ether was added to the KHyp solution in four portions during 2 h at -60 °C. The resulting orange-red mixture was warmed to -30 °C and stirred for another 30 min. Then again 10 mL of a suspension of $Sn(OC_6H_3'Bu_2-2,6)_2$ (0.42 g, 0.80 mmol) in diethyl ether was added in four portions at -60 °C during 1 h. The resulting dark brown mixture was warmed to -30 °C and stirred for 45 min. After subsequent cooling to -60 °C it was filtered and the filtrate was concentrated at -50 °C in a dynamic vacuum to 10 mL. From this solution very pure 2a was isolated by crystallization at -60 °C for 2 d in 49% yield (0.7 g 0.81 mmol). UV-vis (*n*-pentane): $343 (1.46 \times 10^3)$, 457 (sh, 100).

Generation of •PbHyp₃ (1a). Five milliliters of an *n*-pentane solution of Pb[N(SiMe₃)₂]₂ (0.46 g, 0.88 mmol) was added to a 20 mL tetrahydrofuran solution of $(OEt_2)_2$ KPbHyp₃ (**3a'**) (2 g, 1.76 mmol) at -60 °C and stirred for 2 h. After filtration at -60 °C the mixture was concentrated to 5 mL in a dynamic vacuum at -20 °C. By storing at -60 °C for 1 week most of the formed PbHyp₂ (**6**) was isolated as the blue-green thf-solvate Hyp₂Pb•thf (**6a**) and plumbanide **3f**. EPR experiments on the dark green mother liquor prove the presence of significant amounts of **1a**. By NMR, further **6**, the octasilane Hyp₂, and small amounts of KN(SiMe₃)₂ could be detected as diamagnetic contaminations.

•SnEbt₃ (2b), •SnIbt₃ (2c), and •PbIbt₃ (1c). Solid Sn(OC₆H₃·Bu₂-2,6)₂ (2.65 g, 5 mmol) or Pb(OC₆H₃·Bu₂-2,6)₂ (3.08 g, 5 mmol) was added to a 50 mL diethyl ether solution of stannanide **4b** (10 mmol), stannanide **4c** (10 mmol), or plumbanide **3c** (10 mmol) at -60 °C, respectively. The reaction mixture was stirred at -60 °C for 1 h and at -30 °C for 30 min. The resulting brown-red (**2b** and **2c**) or brown-green suspensions (**1c**) were filtered at -30 °C, and the filtrates were concentrated to 5 mL in a dynamic vacuum. After storing at -60 °C for 2 weeks (**2c**) or 2 days (**1c**), the respective radicals **2c** and **1c** could be isolated as large orange-yellow or small green platelets in 65% and 43% yield, while •Sn₃Ebt (**2b**) did not crystallize, but was isolated as an orange-yellow oil (approximately 70% yield). Very small black crystals of the *hexaprisma*-hexastannane **7** were embedded within the crystals of **2c**.

X-ray Crystallographic Study. All crystals were covered with inert oil at -50 °C and mounted to a nylon loop using an X-TEMP 2 system.¹² They were then transferred to the diffractometer under permanent cooling. X-ray diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). Data were collected at -80 or -100 °C with a frame width of 0.5° either in ω or in ϕ . The diffraction frames were integrated using the SAINT package and most were corrected for absorption with MULABS.^{13,14} The structures were solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.¹⁵

Scheme 1. General Synthetic Routes Leading to Alkali Metal Tetrelanides^a



 $Y = SiR_3$, alkyl, aryl, NR_2 M = Li, Na, K

^{*a*} (a) *homoleptic* silyl-substituted tetrelanides KER₃ (E = Sn, Pb; R = Hyp, Ebt, Ibt), i.e. the series **3a-c** and **4a-c**. $EX_2 = E[N(SiMe_3)_2]_2$ or preferably $E(OC_6H_3$ -Bu-2,6)_2 in aprotic coordinating solvents; (b) *heteroleptic* tetrelanides: dihypersilyltetrelandiyls EHyp₂ are synthesized and isolated first and then in a subsequent step are reacted with alkali metal hydrocarbyls or other alkali metal salts MY.

CCDC 692387–692399 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystal parameters and basic information related to data collection and structure refinement are, however, summarized in Tables S1–S3 in the Supporting Information.

In all of the listed compounds but hexastannane **7**, all nonhydrogen atoms were refined anisotropically while the positions of all hydrogen atoms were generated with appropriate geometric constraints and allowed to ride on their respective parent carbon atoms with fixed isotropic thermal parameters. Compound **7** had been obtained as very small crystals only ($V < 10^{-3}$ mm³). Because of weak reflection data only the tin and silicon atoms could be refined anisotropically while the carbon atoms were refined with isotropic thermal parameters.

EPR Spectroscopy. CW EPR spectra in fluid (T = 293 K) solution at X-band (~9.4 GHz) were measured either on a Bruker ELEXSYS 580 spectrometer with a rectangular cavity (4103TM, Q-values typically 3000) and an Oxford open flow cryostat cooling system or a Magnettech MiniScope MS200 benchtop CW EPR spectrometer with a variable-temperature cooling/heating finger. The tin and lead substances were dissolved in 1:1 mixtures of n-pentane and *n*-heptane and subsequently transferred into EPR sample tubes (quartz glass, 4 mm outer diameter tubes for the ELEXSYS 580 spectrometer, 3 mm outer diameter for the MiniScope MS200). Echo-detected, field-swept EPR spectra were recorded with a primary echo sequence $(\pi/2)$ - τ - (π) - τ -echo while sweeping the magnetic field using the same Bruker ELEXSYS 580 spectrometer with a dielectric resonator (MD4EN, overcoupled to Q-values of typically 100). The temperature was set to 20 K by cooling with liquid helium using an Oxford cryostat and cooling system.

The samples were prepared as concentrated solutions (concentrations typically >10 mM) and the sample volume was always large enough to fill the complete resonator volume in the probehead (>300 μ L).

⁽¹²⁾ Kottke, T.; Stalke, D. J. Appl. Crystallogr. 1993, 26, 615-619.

⁽¹³⁾ SMART Data Collection and SAINT-Plus Data Processing Software for the SMART System (various versions); Bruker Analytical X-Ray Instruments, Inc.: Madison, WI, 2000.

⁽¹⁴⁾ Blessing, B. Acta Crystallogr. 1995, A51, 33.

^{(15) (}a) Sheldrick, G. M. SHELXTL, Version 5.1; Bruker AXS: Madison, WI, 1998. (b) Sheldrick, G. M. SHELXL-97; University of Göttingen: Göttingen, Germany, 1997.



3c



Figure 2. Molecular structures of the alkali metal tetrelanides 3a, 3c, 3d, 4b, and 4d forming contact-ion pairs. Selected bond lengths and angles are given in [Å, deg]. (Et₂O)₂KPbHyp₃ (**3a**'): K1-O1 2.596(6), K1-O2a 2.683(9), Pb1-K1 3.694(2), Pb1-Si1 2.851(2), Pb1-Si2 2.809(2), Pb1-Si3 2.837(2), Si1-Pb1-Si2 106.02(7), Si1-Pb1-Si3 109.34(7), Si2-Pb1-Si3 107.98(7), Si1-Pb1-K1 113.55(6), Si2-Pb1-K1 116.37(6), Si3-Pb1-K1 103.35(6). (Et₂O)₂KPbIbt₃ (**3c**): K1–O2 2.60(2), K1–O1 2.77(2), Pb1–K1 3.607(4), Pb1–Si1 2.705(5), Pb1–Si2 2.722(5), Pb1–Si3 2.726(6), Si1–Pb1–Si2 105.4(2), Si1-Pb1-Si3 105.8(2), Si2-Pb1-Si3 107.9(2), Si1-Pb1-K1 110.42(15), Si2-Pb1-K1 114.04(15), Si3-Pb1-K1 112.8(2). (Et₂O)₂LiPbnBuHyp₂ (3d): Li1-O1 1.906(11), Li1-O2a 1.874(15), Pb1-Li1 2.954(10), Pb1-C1 2.323(5), Pb1-Si1 2.726(2), Pb1-Si2 2.741(2), Si1-Pb1-Si2 113.18(5), C1-Pb1-Si1 2.741(2), Si1-Pb1-Si2 2.741(2), Si1-Si2 2.741(2), Si1-Si2 2.741(2), Si1-Si2 2.741(2), Si1-Si2 2.741(2), Si1-Si2 2.741(2), Si1-Si2 2.741(2), Si1 93.15(15), C1-Pb1-Si2 96.02(15), C1-Pb1-Li1 120.6(3), Si1-Pb1-Li1 115.4(2), Si2-Pb1-Li1 115.3(2). (Et₂O)₃KSnEbt₃ (4b): K1-O4 2.768(3), K1-O5 2.808(3), K1-O6 2.701(4), Sn1-K1 3.7234(9), Sn1-Si1 2.6738(8), Sn1-Si2 2.6442(8), Sn1-Si3 2.6735(9), Si2-Sn1-Si3 105.67(3), Si2-Sn1-Si1 104.82(3), Si3-Sn1-Si1 100.87(3), Si2-Sn1-K1 121.74(2), Si3-Sn1-K1 113.55(2), Si1-Sn1-K1 107.90(2). (Et₂O)₂LiSnnBuHyp₂ (4d): Li1-O1 1.909(5), Li1-O2a 1.895(11), Sn1-Li1 3.020(5), Sn1-C1 2.233(3), Sn1-Si1 2.6544(7), Sn1-Si2 2.6668(7), Si1-Sn1-Si2 114.29(2), C1-Sn1-Si1 94.15(8), C1-Sn1-Si2 97.68(9), C1-Sn1-Li1 119.88(12), Si1-Sn1-Li1 113.23(11), Si2-Sn1-Li1 115.19(10).

Data Analysis. All spectral simulations were performed with home-written programs in MATLAB (The MathWorks, Inc.) employing the EasySpin toolbox for EPR spectroscopy.¹⁶ Simulations of CW EPR spectra in fluid solution were performed using a model, which is based on the slow-motion theory and a program developed by Schneider and Freed as implemented in EasySpin. These simulations can account for the effect of intermediate or slow rotational diffusion of the radical on the EPR spectra.¹⁷ Lowtemperature, powder-type EPR spectra were simulated by directly computing the resonance fields and transition probabilities over a triangular orientational powder grid, again as implemented in EasySpin.

The corresponding magnetic parameters (g- and hyperfine (A-) tensor elements) found from the simulations of all tin- and leadcentered radicals are given in Table 4.

Results and Discussion

The homoleptic silvl-substituted tetrelanides KE(SiR₃)₃ (E = Sn {3a-c}, Pb {4a-c}; R = Hyp, Ebt, Ibt) are obtained in good to excellent yields by the reaction of 3 equiv of the proper bulky alkali metal silanides with soluble lead(II) or tin(II) salts such as E[N(SiMe₃)₂]₂ or preferably E(OC₆H₃-^tBu-2,6)₂¹¹ in aprotic coordinating solvents (Scheme 1a). For E = Pb, the oxidation of the potassium silanide is observed as a side reaction, giving elementary lead and metal-free silanes. The latter become the predominant products if inorganic lead salts such as PbCl₂ are used as starting material.

In the absence of coordinating solvents or if the anion of the alkali metal silanide reaches a certain size, the equilibrium (2) in Scheme 1 (top) is markedly shifted to the left side. If very large silanide anions are introduced, plumbanides cannot be isolated any more. We have found that (from THF solution) the critical size which still allows for the isolation of solvated homoleptic potassium plumbanides is reached

⁽¹⁶⁾ Stoll, S.; Schweiger, A. J. Magn. Reson. 2006, 178, 42-55; see http:// www.easyspin.org.

⁽¹⁷⁾ Schneider, D. J.; Freed, J. H. In Biological Magnetic Resonance Vol.8: Spin Labeling - Theory and Applications; Berliner, L. J., Reuben, L. J., Eds.; Plenum Press: New York, 1989.

Becker et al.

Scheme 2. Generation of the Persistent or Stable Lead- and Tin-Based Radicals by Oxidation of the Alkali Metal Salts (Scheme 1) with Appropriate Oxidants (See Text for Details)^a





Scheme 3. Formation and Decay of the Hypersilyl-Based Lead Radical

 $Ox = E[N(SiMe_3)_2]_2, E(OAr^*)_2, HOAr^*; Ar^* = 2,6^{-t}Bu_2C_6H_3$

^{*a*} Oxidation is achieved by molecular tin(II) or lead(II) salts such as $E[N(SiMe_3)_2]_2$ and $E(OAr^*)_2$ or the phenol Ar^*OH ($Ar^* = C_6H_3$ -'Bu₂-2,6); (a) *homoleptic* tetryl radicals; (b) *heteroleptic* tetryl radicals.

for the hypersilyl anion Si(SiMe₃)₃⁻ (Hyp⁻). While the respective stannanide KSnHyp₃ (**4a**), probably because of the stronger Sn–Si bonds, does not dissociate to SnHyp₂ and KHyp to a notable extent, solutions of the plumbanide KPbHyp₃ (**3a**) exhibit broad ¹H- and ¹³C NMR resonances with chemical shifts markedly depending on the concentration, and in the solid-state structure of the solvate (Et₂O)₂-KPbHyp₃ (**3a**', Figure 2) very long Pb–Si bonds are observed. Replacing one of the nine methyl groups of the hypersilyl substituent for a *tert*-butyl group completely prevents the formation of the respective plumbanide. Instead, unreacted Pb[Si(Si'BuMe₂)(SiMe₃)₂] and K[Si(Si'BuMe₂)-(SiMe₃)₂] are detected as the predominant species in solution by ¹H-, ¹³C-, and ²⁹Si NMR experiments.¹⁸

Heteroleptic tetrelanides are also available if bis(silyl)tetrelandiyls are synthesized and isolated first and are then in a subsequent step reacted with alkali metal hydrocarbyls or other alkali metal salts (Scheme 1b). Following this route, we were able to isolate several unsymmetrically substituted tetrelanides bearing two hypersilyl groups and an alkyl, aryl, or amido substituent. The synthesis is obviously restricted to systems where the respective bis(silyl)tetrelandiyl possesses a sufficient kinetic stability to allow for its isolation. Dihypersilyltetrelandiyls, $SnHyp_2$ (5; as the dimer 5₂) and $PbHyp_2(6)$,¹⁰ are such species of sufficient stability and can therefore be used for the synthesis of a range of heteroleptic hypersilyl-substituted tetrelanides such as 3d, 3e, 3f, and 4d. However, heteroleptic derivatives comprising less demanding groups such as ethylbis(trimethylsilyl)silyl (Ebt) are hitherto unknown, because tetrelandiyls such as Ebt₂E are not accessible under the conditions used for the preparation of the hypersilyl derivatives 5 and 6.

The next step to tetryl radicals would be the oxidation of the alkali metal salts with appropriate oxidants (Scheme 2). We found that molecular tin(II) or lead(II) salts such as $E[N(SiMe_3)_2]_2$ or $E(OC_6H_3$ -'Bu₂-2,6)₂ can be used. Since the alkali metal salts of 2,6-di-*tert*-butylphenol exhibit very low solubility in weakly polar solvents and may thus be easily separated from the much better soluble tetrelanides, $E(OC_6H_3-$ ¹Bu₂-2,6)₂ for most cases is the better choice.¹¹ For plumbanides even the 2,6-di-*tert*-butylphenol itself was found to be a suitable oxidant, though here protolysis of E–Si bonds has been detected as a side-reaction.¹⁹

The yields of homoleptic tetryl radicals (series 1 and 2) obtained by oxidation of the homoleptic tetrelanides (series 3 and 4) are good in most cases but far from quantitative (according to NMR spectra of the reaction mixtures). Several diamagnetic compounds, most of them still unidentified, can be detected as side-products by NMR spectroscopy and sometimes prevent the isolation of the tetryl radical. Trihypersilylplumbyl •PbHyp₃ (1a) is only formed in a maximum yield of about 20% since most of the introduced plumbylene **6** was recovered as the thf-adduct Hyp₂Pb•thf (**6a**, Figure 6) and the heteroleptic plumbanide 3f. As mentioned above and depicted in Scheme 3, the introduced potassium trihypersilylplumbanide (3a) is most probably present in an equilibrium mixture with KHyp and 6. Therefore, not only 3a is oxidized to the desired plumbyl radical 1a, but also (or preferably) KHyp is oxidized to yield the octasilane Hyp₂. By detracting KHyp from the equilibrium, 6 is formed and precipitates as thf-adduct 6a in the presence of tetrahydrofuran at lower temperatures or as plumbanide 3f by reaction with KN(SiMe₃)₂ which in turn has been formed as sideproduct from the metathesis of Pb[N(SiMe₃)₃]₂ with KHyp. Further PbHyp₂ (6) may result from thermal decomposition of •PbHyp₃ (1a). EPR measurements on 1a solutions indicate a high stationary concentration of the hypersilyl radical in solution which is in accordance with the presumed dissociation of **1a** into **6** and Hyp radicals.

Nevertheless, two plumbyl radicals, that is, **1b** and **1c**, are isolated as almost pure compounds by recrystallization from pentane or ether/*n*-pentane mixtures as green-brown crystalline solids. Crystalline stannyl (as well as silyl and germyl) radicals had already been reported very recently for slightly different substitution patterns by Sekiguchi et al.^{2b} Here, further species could be generated (Table 4) of which

⁽¹⁸⁾ Förster, C.; Klinkhammer, K. W., to be published.

⁽¹⁹⁾ At this moment we do not know whether the oxidation of 3b by 2,6di-*tert*-butylphenol proceeds via single-electron transfer or via the intermediate formation of the plumbane HPbEbt₃ and a subsequent thermal induced Pb-H bond fission.

⁽²⁰⁾ Klinkhammer, K. W. Chem. Eur. J. 1997, 3, 1418.



Figure 3. Structures of the anions of the alkali metal plumbanides **3e** and **3f**. The counter cations have been omitted for clarity. Selected bond lengths and angles are given in [Å, deg]. [Li(thf)₄][PbPhHyp₂] (**3e**): cation: Li–O (av.) anion: Pb1–Si1 2.7664(14), Pb1–Si2 274.81(12), Pb1–C31 2.324(4), Si1–Pb1–Si2 111.5(9), Si1–Pb1–C11 103.8(2), Si2–Pb1–C11 104.6(2). [K(thf)₇]{Pb[N(SiMe_3)_2]Hyp_2} (**3f**): cation: K–O1 2.861(12), K–O2 2.769(10), K1–O3 2.732(10), K1–O4 2.755(12), K1–O5 2.753(13), K1–O6 2.846(12), K1–O7 2.755(12); anion: Pb1–Si1 2.872(3), Pb1–Si2 2.819(3), Pb1–N1 2.377(8), Si1–Pb1–Si2 111.5(9), Si1–Pb1–N1 103.8(2), Si2–Pb1–N1 104.6(2).



Figure 4. Structure of the ate-complex $[K(thf)_4(benzene)_2][K(SnHyp_3)_2]$ (4a^{*m*}) in the crystal. Selected bond lengths and angles are given in [Å, deg]. Cation: K2–O (av.) 2.67, K2–C013 3.215(3); anion: K1–Sn1 3.7202(1), K1–Sn1–Si1 110.85 (1), K1–Sn1–Si2 110.15(1), K1–Sn1–Si3 110.04(1), Sn1–Si1 2.7222(4), Sn1–Si2 2.7301(4), Sn1–Si3 2.7283(4).

•SnHyp₃ (**2a**) and •SnIbt₃ (**2c**) are isolated in high yields as brown and orange-yellow crystalline materials, respectively. The plumbyl radical •PbHyp₃ (**1a**) is formed as side-product only but could be characterized unambiguously by EPR experiments. •SnEbt₃ (**2b**) had also been synthesized but refused to crystallize from the obtained orange-yellow oily mixture and could therefore not be separated from diamagnetic contaminations. A notable side-product from the synthesis of **2c** is the hexastannaprismane Sn₆Ibt₆ (**7**, Figure 6). It was found in small amounts as very small black crystals embedded into the large orange-yellow specimens of radical **5** and could be identified by X-ray diffraction. Whether it is formed along the synthesis of **2c** or through its decomposition remains an open question.

Some heteroleptic tetryl radicals $RHyp_2E^{\bullet}$ could also been generated via the oxidation of heteroleptic alkali metal salts such as $RHyp_2ELi$ (E = Sn, Pb; R = Ph, alkyl). Though to date no crystalline compound could be isolated, several species such as $PhHyp_2Pb^{\bullet}$ (1e) and $EtHyp_2Pb^{\bullet}$ (1g) had been identified unambiguously by their unique EPR-spectroscopic

Table 1. Structural Parameters for Selected Solvated HomolepticSilylsubstituted Alkali Metal Tetrelanides $[Cat][E(SiR_3)_3]$ and thePotassiate 4a'''

_						
Е	Cat		R	$M-E^a$	E-Si ^a	Si-E-Si
Sn	Na(toluene)	$(4a^*)^{20}$	Нур	3.07	2.70	109.2-110.5
Sn	$K(C_6H_6)_2(thf)_4$	(4a''')	Нур	3.72^{b}	2.73	107.9-109.1
Sn	K(OEt ₂) ₃	(4b)	Ebt	3.72	2.66	101.0-105.7
Sn	Li(thf) ₂	23	Si'Bu ₂ Me	2.83	2.66	109.5-119.3
Sn	Li(toluene)	23	Si'Bu ₂ Me	2.77	2.66	108.2-119.6
Sn	Li(thf) ₃	24	SiMe ₃	2.87	2.57	98.4-98.9
Sn	Na(15-cr-5)	25	SiMe ₃	3.08	2.59	98.8-99.4
Pb	K(OEt ₂) ₂	(3a ')	Нур	3.69	2.83	106.0-109.3
Pb	K(OEt ₂) ₂	$(3b)^1$	Ebt	3.59	2.72	100.2-109.5
Pb	$K(OEt_2)_2$	(3c)	Ibt	3.61	2.72	105.8-107.9

^{*a*} Mean values. ^{*b*} In the anion.

data (Table 4). A detailed description of their synthesis, their geometric and electronic structure and their analytical data will be topic of a subsequent paper.

Molecular Structures. Figures 2–4 show the molecular structures of some novel homoleptic and heteroleptic alkali metal tetrelanides in the solid-state. They have been prepared in either of the two ways described above, (i) by reacting a

Table 2. Structural Parameters for Heteroleptic Silylsubstituted Alkali

 Metal Tetrelanides [Cat][EHyp₂Y]

Е		Cat	Y	М-Е	E-Si ^a	E-X	Si-E- Si	Si-E- X ^a
Sn	(4d)	Li(Et ₂ O) ₂	<i>n</i> Bu	3.02	2.65	2.23	114.3	95.9
Sn	20	Cs^{b-13}	CH ₂ Ph	4.19	2.68	2.24	110.2	96.4
Pb	(3d)	Li(OEt ₂) ₂	<i>n</i> Bu	2.95	2.73	2.32	113.2	94.5
Pb	(3e)	Li(OEt ₂) ₂	Ph	с	2.75	2.32	112.6	95.6
Pb	(3f)	K(thf)7	N(SiMe ₃) ₂	С	2.85	2.38	111.5	104.1

^{*a*} Mean values. ^{*b*} Mixed stannanide/amide showing intramolecular coordination by benzyl groups. ^{*c*} Solvent-separated ions.

hydrocarbon-soluble tin or lead salt with 3 equiv of the potassium salt of a branched silane or (ii) by reacting **5** or **6** with an equimolar amounts of an alkali metal salt MY of hypersilane, of a hydrocarbon, or of an amine ($Y = SiR_3$; hydrocarbyl, NR₂). Most of the characterized species, for which selected structural data are given in Tables 1 and 2, have been isolated from diethyl ether or other coordinating solvents as contact-ion-pairs with an M–E bond linking the solvated cation with the stannanide or plumbanide anion (Figure 2).

For trihypersilvl substituted derivatives MEHyp₃ 3a and 4b such structural motifs are also found. The solvates (toluene)NaSnHyp₃ (**4a**^{*})²⁰ and **3a**•2Et₂O (**3a**', Figure 2) gave reasonable structural data, whereas the related salt $4a \cdot 3Et_2O$ (4a') is severely disordered and no reliable structural parameters could be derived. Solvent separated ionpairs are present in [Li(thf)₄][PbPhHyp₂] (3d) and [K(thf)₇]- $[PbHyp_2{N(SiMe_3)_2}]$ (**3f**, Figure 3) as well as in the salts 3a•6THF (3a") and 4a•6THF (4a"). While 3d and 3f have been fully characterized, the two isomorphous THF-solvates 3a" and 4a" show severe disorder or twinning in the crystalline state, and only a rough structural picture could be derived so far, showing that both salts consist of isolated K(thf)₆-cations and pyramidal EHyp₃-anions. However, when the crystals of 4a" are exposed to dynamic vacuum for several hours and subsequently crystallized from benzene, very large orange crystals of a well ordered phase are isolated with the composition $(thf)_2(benzene)KSnHyp_3$ (4a'''). An X-ray diffraction experiment reveals an unexpected structure: 4a crystallizes as a unique potassium potassiate (Figure 4). It comprises two novel structural motifs: a [K(thf)₄- $(\text{benzene})_2]^+$ cation in which the two benzene molecules are coordinating, in a unprecedented fashion, through a C-H bond and the first structurally characterized potassiate anion, [Hyp₃Sn-K-SnHyp₃]⁻ with linearly two-coordinate potassium. However, a closer look at the C_i -symmetric anion reveals the presence of six intramolecular agostic Me····K bonding interactions leading to K-C distances of 3.40-3.49 Å. An analogous treatment of the plumbanide 3a did not lead to an analogous bis(plumbyl)potassiate but to an almost quantitative decomposition and the formation of KHyp, elementary lead, and the octasilane Hyp₂.

All M–E bonds are expected to be predominantly ionic, within the neutral contact-ion pairs of 3a' or $4a^*$ as well as within the potassiate anion of 4a'''. The M–E bond length depends on the size of the alkali metal ion M and the tetryl ion E, the coordination number of M, and the steric demand of the whole anion. Common structural features for all

tetrelanide ions are pyramidal EY₃-skeletons, relatively long E–Si bonds and small Si–E–Si or Si–E–Y angles (Tables 1 and 2). Similar structural data had been determined for tetrelanide fragments EY₃ of other alkali metal derivatives of stannanes and plumbanes before and are generally attributed to the presence of a lone-pair with predominant s-character at E and E–Si or E–Y bonds with a predominant p-character of the contributing orbital at the central E-atom.^{21–25}

Figure 5 displays the molecular structures of the novel structurally characterized homoleptic stannyl and plumbyl radicals 1c, 2a, and 2c. From etheral solutions trihypersilylstannyl (2a) crystallizes together with half an equivalent of ether. In the crystal two unique molecules are present. Both exhibit a well ordered structure with an approximate (noncrystallographic) C₃-symmetry. The Si-Sn-Si angles range from 116.9-119.8°; the sum of angles of 354.2° shows that the molecules are nearly but not perfectly planar. For the related stannyl radical •Sn(SiMe'Bu₂)₃ as well as for its Si- and Ge-analogues Sekiguchi reported a fully planar structure within the error of the experiment (Table 3). The Sn-Si bonds (2.648 Å) in the stannyl radical 2a are significantly shorter than those in the respective distannene Sn_2Hyp_4 (**5**₂) (2.672 Å),¹⁰ the sodium trihypersilylstannanide $4a^*$ (2.70 Å),²⁰ and the potassium potassiate 4a''' (2.726 Å). As one would expect, this finding may indicate a larger contribution of Sn 5s orbitals to the Sn-Si bonds in the radicals 2a and 2c than in the distance $(5)_2$ or than the stannanide anions of 4a and 4a*. While •SnIbt₃ (2c) with 2.625 Å (av.) has Sn-Si bond lengths similar to those found in the radical \cdot Sn(SiMe'Bu₂)₃ (2.618 Å),² the Sn–Si bonds in 2a are slightly elongated owing to the greater bulkiness of the hypersilyl substituent as compared to the Me'Bu₂Si group. The structural data of **2c** are unfortunately biased by disorder such that the Si-Sn-Si bond angles are less well defined. The mean value for the major orientation is 118.0°. A remarkable difference between the solid-state structure of radical 2c and the structures of the other tin and lead radicals is its significant deviation from C_3 -symmetry (which is not reflected in the EPR spectra of the frozen solutions, however). While in all other stannyl radicals the substituents are positioned paddle-wheel-like, in 2c two Ibt-substituents are oriented in such a way that their less sterically demanding parts, the ⁱPr-groups, face each other, thus allowing for a small Si2-Sn1-Si3 angle of 106.7°: As a consequence, two Ibt-groups approach each other via their bulkiest parts, leading to an Si1-Sn1-Si3 angle of 131.5°.

The related novel plumbyl radical \bullet PbIbt₃ (1c) is also paddle-wheel-shaped and expectedly exhibits somewhat longer Pb-Si bonds (2.68 Å) than the less sterically hindered

- (24) Cardin, C. J.; Cardin, D. J.; Clegg, W.; Coles, S. J.; Constantine, S. P.; Rowe, J. R.; Teat, S. J. J. Organomet. Chem. **1999**, 573, 96.
- (25) Fischer, R.; Baumgartner, J.; Marschner, C.; Uhlig, F. Inorg. Chim. Acta 2005, 358, 3174.

⁽²¹⁾ Reed, D.; Stalke, D.; Wright, D. S. Angew. Chem., Int. Ed. Engl. 1991, 30, 1459.

⁽²²⁾ Armstrong, D. R.; Davidson, M. G.; Moncrieff, D.; Stalke, D.; Wright, D. S. Chem. Commun. 1992, 1413.

⁽²³⁾ Fukawa, T.; Nakamoto, M.; Lee, V. Ya.; Sekiguchi, A. Organometallics 2004, 23, 2376.

Persistent Radicals of Trivalent Tin and Lead



Figure 5. Molecular structures of some of the radicals in the crystal. Selected bond lengths and angles are given in [Å, deg]. •SnHyp₃ **2a**: Sn1–Si1 2.6523(12), Sn–Si2 2.6355(13), 2.6486(13), Si1–Sn1–Si2 116.93(4), Si1–Sn1–Si3 119.80(4), Si2–Sn1–Si3 117.51(4). •SnIbt₃ **2c**: Sn1a–Si2a 2.607(9), Sn1a–Si1a 2.618(10), Sn1a–Si3a 2.621(7), Si2a–Sn1a–Si1a 131.5(3), Si2a–Sn1a–Si3a 106.7(3), Si1a–Sn1a–Si3a 115.7(3). •PbIbt₃ **1c**: Pb1–Si1a 2.678(5), Pb1–Si2 2.679(2), Pb1–Si3a 2.676(2), Si1a–Pb1–Si2 117.34(12), Si1a–Pb1-Si3a 115.9(2), Si2–Pb1–Si3a 117.1(2).



Figure 6. Molecular structures of the THF-adduct **6a** and hexastannaprismane **7** in the crystal. Selected bond lengths and angles are given in [Å, deg]. Hyp₂Pb•THF (**6a**): Pb1–O1 2.531(5), Pb–Si1 2.743(2), Pb–Si2 2.7318(15), Si1–Pb1–Si2 112.89(5), Si1–Pb1–O1 93.32(12), Si2–Pb1–O1 96.30(13). Sn₆Ibt₆ (**7**): All methyl groups (two on each carbon and three on each silicon) as well as all remaining hydrogen atoms had been omitted for clarity. Sn1–Sn4 2.827(10), Sn1–Sn6 2.851(10), Sn1–Sn3 2.866(9), Sn2–Sn3 2.811(10), Sn2–Sn4 2.853(9), Sn2–Sn5 2.850(7), Sn3–Si3 2.584(10), Sn3–Sn6 2.839(7), Sn4–Sn5 2.849(10), Sn5–Sn6 2.821(10), Sn1–Si1 2.566(10), Sn2–Si2 2.582(9), Sn4–Si4 2.586(9), Sn5–Si5 2.577(10), Sn6–Si6 2.594(9).

Table 3. Selected Structural Parameters for Silylsubstituted Tetryl Radicals ER_3 (E = Sn, Pb)

	2 (
Е	R	E-Si ^a	Si-E-Si	$\Sigma(Si-E-Si)$	
Sn	Нур	2.64	116.9-119.8	354	4a
Sn	Ibt	2.62	106.7-131.3	354	4c
Sn	tBu ₂ Me	2.63	119.7-120.2	360	2b
Pb	Ebt	2.64	115.2-121.4	353	3b
Pb	Ibt	2.68	115.9-117.1	350	3c
	1				

^a Mean values.

•PbEbt₃ (**1b**, 2.65 Å).¹ In these plumbyl radicals a trend similar to that in the stannyl radicals is observed: the Pb–Si bonds are significantly shorter than for silylsubstituted plumbandiyls such as **6** (2.702 Å) and Pb[Si(SiMe₃)₂(Si'Pr₃)]₂ (2.745 Å) or the related plumbanide **3a'** (2.715 Å). Unfortunately, the structural parameters are again biased by disorder. However, the derived sums of the Si–Pb–Si angles of 350° and 355° for the two refined orientations are very

similar to the respective value for \cdot PbEbt₃ **1b** (353°) and again prove a non-planar structure for this plumbyl radical.

Two side-products occurring during the synthesis of the tetryl radicals **1a** and **2c** could also be structurally characterized and are depicted in Figure 6. The right-hand side of Figure 6 displays the molecular structure of the hexastannaprismane **7** derived from diffraction data on very small black crystals that were embedded into larger orange crystals of the stannyl radical **2c**. While the Sn₆Si₆-scaffold is very similar compared to the related hexastannaprismane, ('Bu₃Si)₆-Sn₆ that was structurally characterized by Wiberg some years ago,²⁶ the Sn–Sn and Si–Si bonds in **7** as compared to ('Bu₃Si)₆Sn₆ are shorter by 7 and 13 pm, respectively, because of the less bulky substituents.

Figure 6 (left) shows the molecular structure of the tetrahydrofuran-adduct **6a**, which is formed alongside the

Table 4. EPR Data of Selected Mononuclear Tetryl Radicals ER3

	Е	R	g _{iso} (293 K)	a _{iso} (293 K)/mT	g	A/mT
1a ^a	Pb	Нур	2.089	(²⁰⁷ Pb): 84.3	[2.237, 2.213, 1.893]	(²⁰⁷ Pb): [42.0, 44.0, 175]
$\mathbf{1b}^{a}$	Pb	SiEt(SiMe ₃) ₂	2.105	(²⁰⁷ Pb): 50.6	[2.246, 2.245, 1.888]	(²⁰⁷ Pb): [13.9, 15.3, 144.2]
$1c^a$	Pb	Si ⁱ Pr(SiMe ₃) ₂	2.097	(²⁰⁷ Pb): 79.1		
$1g^a$	Pb	Hyp (2x), Et	2.055	(²⁰⁷ Pb): 125.8	[2.226, 2.079, 1.890]	(²⁰⁷ Pb): [104.0, 142.0, 147.0]
1e	Pb	Hyp (2x), Ph	2.043	(²⁰⁷ Pb): 124.3	[2.255, 1.998, 1.894]	
24	Pb	Me	2.039 (77K)		[2.106, 2.097, 1.914]	(²⁰⁷ Pb): [115, 115, 324]
$2a^a$	Sn	Нур	2.042	$(^{117}Sn): 59.8$	[2.074, 2.074, 1.991]	(^{117}Sn) : [36.3, 36.3, 107.8]
$2\mathbf{h}^a$	Sn	SiiPr(SiMea)	2.055	$(^{117}Sn): 02.4$ $(^{117}Sn): 30.1$		(**511): [58.0, 58.0, 112.5]
20	511	5111(5htte3)2	2.055	$(^{119}\text{Sn}): 41.6$		
$2c^a$	Sn	SiEt(SiMe ₃) ₂	2.053	(¹¹⁷ Sn): 37.7	[2.080, 2.079, 1.985]	(¹¹⁷ Sn): [18.8, 20.9, 90.2]
				(^{119}Sn) : 39.8		(^{119}Sn) : [20.9, 24.0, 94.4]
24	Sn	Me	2.016 (77K)		[2.030, 2.024, 1.995]	(^{11/} Sn): [133.2, 119.2, 206.7]
-	G		2 000	(1170) 1 (0.0		(^{119}Sn) : [141.5, 126.2, 215.7]
5a	Sn	$CH(S_1Me_3)_2$	2.009	(^{117}Sn) : 169.8 (^{119}Sn) : 177.6	[2.016, 2.016, 1.994]	
32	Sn	Tar^b	2 001	(117Sn): 177.0		
52	511	1 ai	2.001	$(^{119}Sn): 182.7$		
33	Sn	Н		3800	[2.024, 2.024, 2.015]	
5d	Sn	N(SiMe ₃) ₂	1.991	(¹¹⁷ Sn): 317.6		
		())2		(¹¹⁹ Sn): 342.6		
2b	Sn	SitBu ₂ Me	2.048	(^{117/119} Sn): 32.9		
2a	Ge	SitBu ₂ Me	2.023	$(^{73}\text{Ge}): 2.0$		
32	Ge	Tar ^b	2.005	(⁷³ Ge): 8.5		
2a	Si	SitBu ₂ Me	2.006	(²⁹ Si): 5.8		

^{*a*} The isotropic values g_{iso} and a_{iso} from simulations of the solution CW EPR spectra at 293 K; *g*- and *A*-tensors from simulations of frozen solution spectra. Margins of error are $\Delta g = \pm 0.0002$; $\Delta A = \pm 0.1$ mT. ^{*b*} Tar = C₆HⁱBu-2-Me₃-4,5,6.

preparation of **1a** and may be independently prepared as bluegreen crystals in quantitative yields by addition of tetrahydrofuran to a solution of **6** in *n*-pentane and subsequent crystallization at -60 °C. As expected, **6a** possesses a pronounced pyramidal Si₂PbO-scaffold (sum of angles around Pb: 302.5°). The length of the Pb–O dative bond (2.53 Å) is somewhat longer than in the thf-adduct of the more polar lead thiolate Pb{S[C₆H₂(CF₃)₃-2,4,6]₂ (2.50 Å)²⁷ but significantly shorter than in the extremely sterically overcrowded thf-adduct of the molybdylplumbylene Pb[Mo(η -C₅Me₅)(CO)₃]₂ (2.75 Å).²⁸

EPR Spectroscopy. Figure 7 displays CW EPR spectra of the four compounds **1a**, **1b**, **2a**, and **2c** at room temperature (293K), while Figure 8 depicts the echo-detected, field-swept EPR spectra at low temperature (20K). Overlaid in red we also present spectral simulations including the hyperfine pattern expected from the magnetically active isotopes ²⁰⁷Pb (I = 1/2, natural abundance of 22.1%) and ¹¹⁷Sn (I = 1/2, natural abundance of 7.5%) as well as ¹¹⁹Sn (I = 1/2, natural abundance of 8.6%).

Room-Temperature CW EPR Spectra. When measuring solutions of the four compounds in alkanes at room temperature (293 K), the usually orientation-dependent (i.e., anisotropic, tensorial) magnetic interactions of the electron spin with the magnetic field (the electron-Zeeman interaction) and the interaction of the electron spin with magnetic nuclear spins (the hyperfine (hf) interaction) are averaged to their isotropic, scalar values g_{iso} and a_{iso} .²⁹ While the spectra of the stannyl radicals **2a** and **2c** are shown in panels a and b

of Figure 7, spectra of the plumbyl radicals 1a and 1b are presented in panels c and d of Figure 7, respectively. All spectra in Figure 7 show the same general pattern and possess a strong main signal from the radical centered at nonmagnetic Pb- and Sn-isotopes, as well as peak patterns that reflect hyperfine splitting from the magnetically active isotopes. The hyperfine coupling constants that were extracted from the spectral simulations are summarized in Table 4. In general, the isotropic g-values g_{iso} can be seen as the fingerprint for the individual radical species, and the isotropic hf coupling constants a_{iso} characterize the interaction between the electron spin and the nuclear spin of the magnetically active nuclei.²⁹ In the case of the Sn-based radicals, we find for **2a** $g_{iso} =$ 2.042 and an $a_{iso}(^{117}Sn) = 59.8 \text{ mT}, a_{iso}(^{119}Sn) = 62.4 \text{ mT}$ while 2c shows significantly higher g- and lower a-values: $g_{\rm iso} = 2.053, a_{\rm iso}(^{117}{\rm Sn}) = 37.7 \text{ mT}, a_{\rm iso}(^{119}{\rm Sn}) = 39.8 \text{ mT}.$ As it is expected, the ratio of the hf coupling constants for the two isotopomers reflects the ratio of the respective gyromagnetic ratios $\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn})$. Because of the larger hf coupling of 2a, in this case even the characteristic splitting pattern for the two isotopomers can be distinguished, while for **2c** the hf lines still overlap.

The lead-based radicals show *g*-values that deviate stronger from the free electron *g*-value. For **1a** we find $g_{iso} = 2.089$ and $a_{iso}(^{207}\text{Pb}) = 84.3 \text{ mT}$, while **1b**, as is the case for the respective stannyl radical, shows a higher *g*- and a lower *a*-value: $g_{iso} = 2.105$, $a_{iso}(^{207}\text{Pb}) = 50.6 \text{ mT}$. When exchanging the central Sn^{III} (fifth period in the periodic table of elements) with the heavier congener Pb^{III} (sixth period), the larger contribution of the spin-orbit coupling is responsible for an even greater deviation of the plumbyl radicals' *g*-values from the free electron *g*-value $g_e = 2.0023$.

⁽²⁶⁾ Wiberg, N.; Lerner, H.-W.; Nöth, H.; Ponikwar, W. Angew. Chem., Int. Ed. 1999, 38, 1103.

⁽²⁷⁾ Labahn, D.; Brooker, S.; Sheldrick, G. M.; Roesky, H. W. Z. Anorg. Allg. Chem. 1992, 610, 163.

⁽²⁸⁾ Hitchcock, P. B.; Lappert, M. F.; Michalczyk, M. J. J. Chem. Soc., Dalton Trans. 1987, 2635.

⁽²⁹⁾ Atherton, N. M. Principles of Electron Spin Resonance; Ellis Horwood: New York, 1993.

Persistent Radicals of Trivalent Tin and Lead



Figure 7. CW EPR spectra of the radicals depicted in Figure 1 in mixtures of *n*-pentane and *n*-hexane at 273 K. All experimental spectra (black) are overlaid with spectral simulations (red). (a) \cdot SnHyp₃ (2a), the inset shows the full spectrum; the enlarged part shows the detailed hyperfine splitting pattern; (b) \cdot SnIbt₃ (2c), the inset shows the full spectrum; the enlarged part shows the detailed hyperfine splitting pattern; (c) \cdot PbHyp₃ (1a), (d) \cdot PbEbt₃ (1b); the respective lines marked with an asterisk are from a stationary concentration of a silyl-based radical, which for 1a is displayed in detail in (e).



Figure 8. Echo-detected, field swept EPR spectra of the radicals depicted in Figure 1 in mixtures of *n*-pentane and *n*-heptane at 20 K. All experimental spectra (black) are overlaid with spectral simulations (red). The approximate *g*-tensor element positions are marked with arrows, and the largest hf coupling tensor element A_{zz} is marked by dashed lines. (a) **2a**; (b) **2c**; (c) **1a**; (d) **1b**; the asterisk marks features from an unknown impurity or paramagnetic side product.

Note that two heteroleptic plumbyl radicals **1e** and **1g** for which we report g- and A-values in this work (spectra not shown; for the values see Table 4) also have markedly smaller g-values and significantly larger a_{iso} -values as compared to the homoleptic Pb-based radicals.

One interesting feature in Figure 7 is the asymmetric broadening of the hyperfine lines, which in the case of the two plumbyl radicals (see Figure 7c,d) even leads to such a strong broadening that the high-field line is not distinguishable from the background signal any more. Note that the difficulties in observing the high-field line manifolds of plumbyl radicals have led to some confusion about the purity of the materials in the initial report on these materials.¹ This effect can be understood when considering the modulation of the anisotropic electron Zeeman and hf interactions by the rotational motion. It can be accounted for by using a slow motion model for spectral simulations that is based on solving the stochastic Liouville equation (simulations shown in Figure 7).^{16,29} We find that a characteristic rotational correlation time of $\tau_{\rm c} \approx 1.3 {\, \cdot \,} 10^{-10}~{\rm s}$ can nicely reproduce the hf splitting and intensity pattern for the two lead-based

radicals, while we find significantly faster rotation with $\tau_c \approx 6.3 \times 10^{-11}$ s for the two tin-based radicals (all measured in the same solvent mixture). This apparent slowdown in the rotational motion when the central atom Sn is replaced with the larger and much heavier Pb can be attributed to the overall increased mass of the plumbyl radical molecules.

Note that in the spectra of 1a and 2a, and to a lesser degree also in the spectra of 1b and 2c, additional narrow lines corresponding to significant amounts of a radical species with a g-value of 2.0058 rather close to the value of a free electron and a characteristic hyperfine splitting pattern are observed (marked with asterisks in Figure 7. This five-line pattern is shown in Figure 7e and can be described as one intense central line and two pairs of hyperfine lines. We assign this specific EPR pattern to a silicon-based decay product of our stannyl and plumbyl radicals, the hypersilyl ligand radical •Si(SiMe₃)₃ (or •SiⁱPr(SiMe₃)₂, and •SiEt(SiMe₃)₂ in the case of •SnIbt₃ and •PbEbt₃, respectively). The strong central line stems from the electron spins located on the almost 96% of Si nuclei that are not magnetic and therefore do not lead to a hyperfine splitting. The g-value of 2.0058 and the observed hyperfine-splittings of 6.25 mT and 0.86 mT (due to the 4.2% ²⁹Si nuclei) are in reasonable agreement to the values of branched silyl radicals found in literature.^{4,30}

As can be expected, the difference of the splitting patterns between the hypersilyl ligand radical and the ligand radicals derived from •Elbt₃ and •EEbt₃ lies mainly in the intensityratios of the ²⁹Si hyperfine lines. The splittings (i.e., position of the lines) are virtually identical. From the ratio of the isotropic hyperfine splitting constants it is obvious that in the hypersilyl ligand radical the electron spin is mainly located on the one Si-atom with the largest hyperfine splitting ($\rho_s \sim 0.841$) but is delocalized to a certain degree onto the three Si atoms of the trimethylsilyl groups ($\rho_s \sim 0.053$ for each).

We can quantify the concentration of the hypersilyl radical decay product in solutions of PbHyp₃ by measuring the double integral of the CW EPR spectral excerpt that contains the Si-based radical signal. The double integral is a direct measure of the number of electron spins. We find that the concentration of the Si-based radical remains constant within the precision of the experiment for several hours at room temperature (or elevated temperatures) while the decay of the Pb-based radical is apparent. This leads to the conclusion that the concentration of the hypersilyl radical is a stationary intermediate in the decomposition reaction of •PbHyp₃. The fact that a stationary concentration of the hypersilyl radical builds up in a highly reproducible manner opens up new possibilities for use of the radical as a clean silylating agent. Note that despite the highly intense central silyl-radical line, the overall contribution to the concentration of electron spins (i.e., the double integral) was never more than 1.5%.

Low-Temperature EPR Spectra. In frozen solution the anisotropies of the *g*- and hf (*A*-) tensors of the radicals are not averaged out any more and now dominate the spectra. The echo-detected EPR spectra of the four radicals at 20 K along with powder-averaged EPR spectral simulations are presented in Figure 8. The *g*- and *A*-tensor elements are summarized in Table 4. All spectra consist of one main spectral component that is typical for a radical with an approximately axial *g*-tensor ($g_{xx} \approx g_{yy} \neq g_{zz}$) and less intense pattern spreading out to lower and higher magnetic field values that stem from the hyperfine coupling to the magnetic nuclei in the respective isotopomers. In Figure 8 we also indicate the approximate position of the g_{xx}/g_{yy} and g_{zz} tensor elements in the isotopomers that have no magnetically active Sn and Pb nuclei.

Our simulations clearly show that also the hf tensor for homoleptic radicals is nearly axial $(A_{xx} \approx A_{yy} \neq A_{zz})$ with $A_{zz} \gg A_{xx}/A_{yy}$, and in Figure 8 the splitting from the A_{zz} tensor element is marked by dashed lines. For both cases, tin and lead, the hypersilyl compounds display the significantly larger hyperfine coupling $(a_{iso} \text{ as well as all the})$ A-tensor elements) when compared with the radicals having unsymmetrically substituted ligands (2c and 1b, respectively). In addition, the heteroleptic lead-based radicals 1g and 1d clearly have an orthorhombic low-temperature EPR-spectrum (see Table 4, data not shown, $g_{xx} \neq g_{yy} \neq g_{zz}$) and $(A_{xx} \neq A_{yy})$ $\neq A_{zz}$ with g-values smaller than those of the homoleptic radicals and hyperfine values significantly larger than those of the homoleptic radicals. There are only few reports in the literature on EPR investigations of simple mononuclear triorganylstannyl and triorganylplumbyl radicals such as •PbMe₃, •SnMe₃, or •Sn*i*Bu₃.³¹ Two general trends can nonetheless be easily recognized going from hydrogen via organyl to silyl substitution (Table 4): (i) g-values increase and (ii) hyperfine-coupling constants markedly decrease. It becomes obvious that those trends have to be attributed mainly to differences in electronic properties of the substituents and only to a lesser extent to different steric demands of the substituents (vide infra).

Electronic and Geometric Structure and the Dynamics of the Radicals. The information gained from the EPR spectra in both, fluid solution at room temperature and in frozen solution at 20 K, together with structural data from X-ray diffraction give unique insight into these new compounds. Conclusions can be drawn not only about the electronic structure but also about the geometric structure and the dynamic properties of the persistent or stable heavy main group element radicals. Some of the generated radicals, which we have extensively characterized by EPR measurements, could also be obtained as suitable crystals for X-ray diffraction, others were obtained as microcrystalline powders

^{(30) (}a) Bennett, S. W.; Eaborn, C.; Hudson, A.; Jackson, R. A.; Root, K. D. J. J. Chem. Soc. A 1970, 348–351. (b) Azinovic, D.; Bravo-Zhivotovskii, D.; Bendikov, M.; Apeloig, Y.; Tumanskii, B.; Veprek, S. Chem. Phys. Lett. 2003, 374, 257–263.

 ^{(31) (}a) Bennett, J. E.; Howard, J. A. Chem. Phys. Lett. 1972, 15, 322–324. (b) Booth, R. J.; Fieldhouse, S. A.; Symons, M. C. R. J. Chem. Soc., Dalton Trans. 1976, 1506–1515.

⁽³²⁾ Della Bona, M. A.; Cassani, M. C.; Keates, J. M.; Lawless, G. A.; Lappert, M. F.; Stürmann, M.; Weidenbruch, M. J. Chem. Soc., Dalton Trans. 1998, 1187.

⁽³³⁾ Morehouse, R. L.; Christiansen, J. J.; Gordy, W. J. Chem. Phys. 1966, 45, 1751.



Figure 9. Scheme of the proposed axial *g*-or *A*-tensor frame (right-hand side) and main contribution to the SOMO bearing the unpaired electron (left-hand side).

or as viscous oils only (vide supra). As mentioned before, the structural data derived for crystalline species are unfortunately frequently biased by disordering in the solid state. Nevertheless, the diffraction data revealed that all silvl substituted tetryl radicals exhibit a nearly but not fully planar structure, which is also consistent with the nearly axial gand A-tensors found for the radicals and is schematically displayed in Figure 9. Surprisingly, among the tin-based radicals the most pronounced pyramidalization is found for trihypersilyltin (2a) although the hypersilyl group is the bulkiest substituent used and should therefore lead to less pyramidalization. Unfortunately, because of its lower stability we were not able to get crystals for its lead analogue 1a. The EPR data (in particular the larger isotropic hf coupling constants) for both 1a and 2a indicate a higher degree of pyramidalization than for the other plumbyl and stannyl radicals.

As pointed out by Sekiguchi et al. crowding is not the only reason for the almost planar structures of silyl substituted group 14 radicals. Hyperconjugation, that is, delocalization of spin density into the antibonding $\sigma^*(Si-Si)$ -orbitals, also has to be taken into account. Detailed quantum-chemical analyses are lacking, however, and are on the agenda in our groups. A further typical structural feature of all tetryl radicals ER₃ is the comparably short E–Si bond found in the solid-state (vide supra) being markedly shorter than that determined for the related tetrelandiyls ER₂ and close to those observed in stressfree tetrelanes ER₄. This can be explained by assuming a significantly higher contribution of the contracted 6s orbital of lead in bonding to the silyl substituents than in the related plumbandiyls, in which this orbital predominantly contributes to the lone-pair.

The EPR measurements can add further information about the geometric structure of the radicals. As displayed in Figure 9, a fully planar group 14 radical should have a 5p (tin) or 6p (lead) singly occupied molecular orbital (SOMO) bearing the unpaired electron and the overall hybridization should be sp^2 , that is, the three ligands should be bound via such sp² hybrid orbitals. In this ideal sp²-hybridization case, except for minor spin polarization effects (polarization of the electrons in the closed shells),²² the isotropic hf coupling should be zero (or have only small values), since the main contribution to a_{iso} comes from unpaired spin density in s-(σ -)type orbitals and the unpaired electron resides in a p_zorbital. Two factors lead to a significant a_{iso} in fluid solution for our tin and lead tetryl radicals: (i) an intrinsic pyramidalization, probably as an effect of the different ligands, and (ii) the structure is dynamic and even a perfectly planar molecule will oscillate along the molecular z-direction such that a dynamic pyramidalization takes place. The static pyramidalization can be approximated when inspecting the *A*-tensor elements. All four investigated tetryl radicals have an *A*-tensor with an A_{zz} -value that is much larger than the respective *x*-and *y*-values A_{xx} and A_{yy} , which are (almost) equal, that is, the tensor is axial as depicted in Figure 9. The hypersilyl compounds **1a** and **2a** do not only have a larger a_{iso} but also the *A*-tensor elements along all three directions are larger than in the respective other radical (e.g., for the plumbyl radicals: **1a**, [42.0 44.0 175] mT vs **1b**, [13.9 15.3 144.2] mT). This is fully consistent with a larger pyramidal deviation from planarity in the case of the hypersilyl tetryl radicals also in frozen solution.

The most pronounced pyramidalization can be found for the Pb-based heteroleptic radicals 1e and 1g, which is due to the size difference for the individual ligands (two hypersilyl ligand and one ethyl or phenyl ligand, respectively). This is expected and leads to a much stronger s-type character for the orbital bearing the unpaired electron, which in turn leads to a much larger isotropic contribution to the hyperfine coupling (see Table 4). Also note that the *g*-values for 1e and 1g are much closer to the *g*-value reported for PbMe₃.

At room temperature and if light is excluded, the stannyl radicals 2a-2c show only a very slow decomposition. Although small amounts of branched silyl radicals are always detected in solution, their decay rates could not be determined so far; half-life times of at least several weeks at room temperature can, however, be estimated. All plumbyl radicals synthesized show half-life times of a few hours at room temperature. While in the case of trihypersilyl plumbyl 1a the corresponding plumbandiyl $\mathbf{6}$ and the octasilane Hyp₂ are detected as main products, the less hindered 1b cleanly decomposes within a few days giving elementary lead and PbEbt₄. No intermediate and almost no side-products are found. Most probably, the corresponding plumbandiyl PbEbt₂ is the first intermediate, since the rate-determining step is first order in 1b and the activation barrier had been measured to be about 100 KJ mol⁻¹.¹ This would be fully in accordance with a Pb-Si bond fission as the first and rate-determining step. The generated Ebt radical which could be detected by EPR to be present in a stationary concentration may then quickly react with remaining 1b to produce the plumbane PbEbt₄. The facts that hardly any side-products are observed and that the rate for the formation of PbEbt₄ is equal to the rate of the decomposition of 1b within the experimental errors leads to the conclusion that the plumbandiyl PbEbt₂ is not stable under these conditions, but disproportionates very quickly to give further amount of elementary Pb and PbEbt₄. Oligonuclear plumbanes or diplumbenes are very probable intermediates and trapping experiments are in our hands.

Conclusions and Outlook

We were able to synthesize a series of homoleptic and heteroleptic alkali metal stannanides and plumbanides, and via subsequent oxidation got access to further persistent mononuclear tin and lead radicals, respectively, showing either a homoleptic or a heteroleptic substitution pattern. While the homoleptic tetryl radicals 1b, 1c, 2a, and 2c could be isolated as crystalline compounds, others such as the homoleptic 1a and 2b or the heteroleptic species 1e and 1g could only be characterized by EPR experiments. EPRspectroscopic studies enable us to draw conclusions about the electronic and geometric structure as well as the dynamics of these novel, molecular persistent tin and lead tetryl radicals, even for those cases where the radical is not stable or clean enough to be isolated as a pure compound. As indicated in the X-ray diffraction results on some of the radicals, the structures are best described as almost planar with varying small pyramidal distortion (flexible pyramidal). Interestingly, we find that the bulkiest ligand, hypersilyl, shows the largest deviation from planarity for both cases, stannyl and plumbyl radicals. This may possibly be due either to differences in ligand-ligand interactions among the C_3 symmetric hypersilyl groups compared with Ebt and Ibt groups having approximate C_s symmetry or to a different extent of hyperconjugation with the lone-pair on E. For a more detailed discussion of the radical structure, more sophisticated pulse EPR methods are necessary. Currently, we study the electronic structure of the radicals by measuring the hyperfine coupling to the ligand protons and silicon nuclei by means of pulse electron-nuclear double resonance (ENDOR) and methods based on electron spin echo envelope modulation (ESEEM, HYSCORE). These methods give detailed information about small hyperfine couplings between ligands and nuclei and should help in elucidating not only the spin density distribution from the central main group element onto the ligand but also the fine details of distortion from planarity.

The clean decay of the •PbHyp₃ (**1a**) and •PbEbt₃ (**1b**) radicals in particular is of interest since its first step seems to deliver a stationary concentration of a well defined branched silyl radical, which may be useful in synthetic approaches as a clean silylating agent. Efforts toward the preparation of polymer-supported silyl substituted tetrelanides and respective tetryl radicals and thus precluding a contamination by soluble tin or lead containing side products are currently underway.

Acknowledgment. The authors thank Christian Bauer for technical support, Bernd Mathiasch for NMR measurements, and Hans Wolfgang Spiess for continuing support. This work is dedicated to the memory of Professor Nils Wiberg.

Supporting Information Available: Tables with crystal and structure refinement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC801198P