Lead-Centered Radical

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Stable Mononuclear Lead(III) Compound: A Lead-Centered Radical[**]

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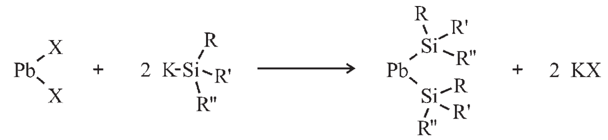
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 65th birthday

Stable compounds with unpaired electrons are predominantly found within the realm of the transition metals. Stable or at least persistent[1] molecular radicals of main-group elements are still rare. Most of the known examples are either formed by certain combinations of electron-rich atoms of high electronegativity, such as oxygen, nitrogen, or fluorine, or stabilized by bulky substituents or extensive delocalization of the unpaired electron. Radicals of the heavier elements of Groups 13–15 were not structurally characterized until 1993, even though persistent species such as $E[Y(SiMe_3)_2]_3$ ($E = Ge, Sn, Y = N, CH$) and $E[CH(SiMe_3)_2]_2$ ($E = P, As$) were synthesized before 1980 in the pioneering work of Lappert and co-workers.[2] Stable mononuclear radicals centered at Si, Ge, and Sn were synthesized by oxidation of corresponding alkali-metal salts and structurally characterized by Sekiguchi and co-workers only very recently.[3] All efforts at synthesizing stable mononuclear radicals of Tl, Pb, and Bi have so far failed. The radical cluster anion Pb_9^{3-} could be isolated in salts.[4] Its relative stability against disproportionation or oligomerization results from delocalization of the unpaired electron over the whole cluster skeleton as well as from intermolecular coulomb repulsion.

Herein we report the synthesis and structural characterization of the first stable molecular mononuclear lead(III) compound $PbEbt_3$ (**1**; $Ebt = Si(SiMe_3)_2Et$). It was obtained during experiments to find a general synthetic route to homoleptic silyl-substituted plumbylenes $Pb(SiRR'R'')_2$.[5] We at first tried metathesis reactions of hydrocarbon-soluble Pb^{II} salts and alkali-metal silanides according to Scheme 1. This reaction was used in the synthesis of the first known example of this class of compounds: dihypersilylplumbylene ($PbHyp_2$; $Hyp = Si(SiMe_3)_3$).[6] Although plumbylenes with more sterically demanding groups than hypersilyl could be obtained via this route, reactions of silanides with less sterically demanding groups ($R = R' = SiMe_3$; $R'' = Me, Et, iPr, CH_2Ph$) in most cases led to complicated product mixtures along with elementary lead.[7]



R, R', R'' = hydrocarbyl, triorganosilyl etc.
$X = N(SiMe_3)_2, OC_6H_3tBu_2$-2,6

Scheme 1. Metathesis reactions for the synthesis of silyl-substituted plumbylenes.

Three crystalline products could be obtained in larger quantities from the reaction of KEbt (**2**) with $Pb[N(SiMe_3)_2]_2$ in *n*-pentane ($R = Et$; $R' = R'' = SiMe_3$). $KN(SiMe_3)_2$, the expected side-product according to Scheme 1, precipitated from *n*-pentane. After addition of diethyl ether to the residual solution, orange-yellow crystals formed, which were identified as the corresponding potassium tris(silyl)plumbanide $(Et_2O)_2KPbEbt_3$ (**3**; Figure 1), most probably formed through addition of potassium silanide **2** to the initially produced plumbylene **4** (Scheme 2). Upon further concentration of the solution at −60°C, green-brown needle-shaped crystals appeared. ^1H NMR spectra of this substance exhibited three very intense and very broad resonances of an evidently paramagnetic species (intensity ratio: ca. 18:2:3) as well as weak signals of diamagnetic contaminants.

The crystal structure analysis of the green-brown crystals revealed the plumbyl radical **1** (Figure 2),[8] which was most probably formed by oxidation of the primarily produced plumbanide **3** by $Pb[N(SiMe_3)_2]_2$. This supposition is in agreement with the analogous syntheses of related Si, Ge, and Sn radicals reported by Sekiguchi and co-workers,[3] and was corroborated experimentally by changing the initial stoichiometry from 2:1 to 3:1. In this case, **3** was isolated and oxidized in a subsequent step to give **1**. Higher yields of **1**

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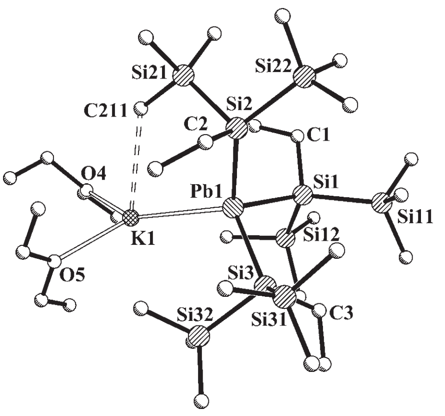
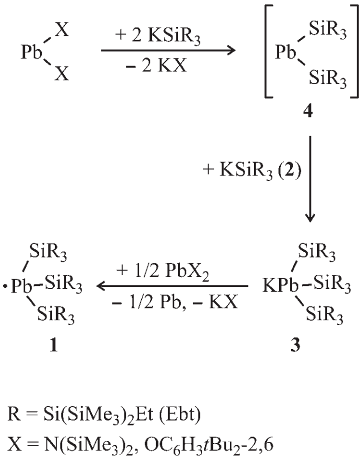


Figure 1. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: K1–Pb1 3.593(2), Pb1–Si1 2.709(2), Pb1–Si2 2.713(2), Pb1–Si3 2.723(2), K1–O4 2.579(9), K1–O5 2.715(7); K1···C211 3.491(10), Si1-Pb1-Si2 103.53(6), Si1-Pb1-Si3 100.16(7), Si2-Pb1-Si3 109.50(6), K1-Pb1-Si1 110.18(6), K1-Pb1-Si2 113.94(6), K1-Pb1-Si3 117.72(6).



Scheme 2. Proposed reaction path for the formation of plumbyl radical **1**.

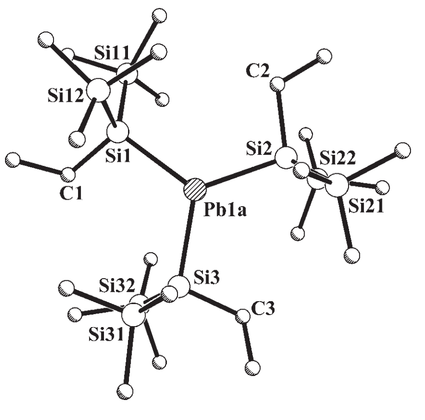


Figure 2. Molecular structure of **1**. Only one of the three unique molecules is displayed. Selected bond lengths [Å] and angles [°]: Pb1a–Si1 2.630(3), Pb1a–Si2 2.635(3), Pb1a–Si3 2.669(3); Si1-Pb1a-Si2 121.37(10), Si1-Pb1a-Si3 116.84(11), Si2-Pb1a-Si3 115.18(11).

and **3** were obtained by replacing $Pb[N(SiMe_3)_2]_2$ with $Pb(OC_6H_3tBu_2\text{-}2,6)_2$, as $KOC_6H_3tBu_2\text{-}2,6$, unlike $KN(SiMe_3)_2$, is almost insoluble in the employed solvents and thus can be removed completely by crystallization.

A second signal appeared in the EPR spectra (Figure 3a) of solutions of the isolated crystals in *n*-hexane at room temperature which might indicate the presence of minor amounts (10–15%) of a further radical species (**1'**).[9,17] Both EPR signals are very broad (ca. 60 Gauss) and show large *g* values, but no fine structure or satellites are observed. The EPR data of frozen solutions of **1** reveal axial symmetry, as is expected for PbR_3 radicals (Figure 3b). The observed isotropic *g* value of 2.106 and the extent of anisotropy ($g_\perp = 2.246$, $g_\parallel = 1.899$) as a result of large spin–orbit coupling at the lead atom are similar to those found for related (transient) lead(III) alkyls and aryls,[10] but are much larger than those of organic radicals and analogous derivatives of the lighter homologues Si, Ge, and Sn.[1,3] The signal width and the absence of fine structure are not caused only by the large anisotropy, as even the markedly sharper signals (15 Gauss) in the frozen solutions show no fine structure. The many unresolved hyperfine interactions with the 69 hydrogen atoms of the Ebt substituents as well as fast relaxation due to spin–orbit coupling contribute to the observed line width. The apparent absence of ^{207}Pb satellites could point to an

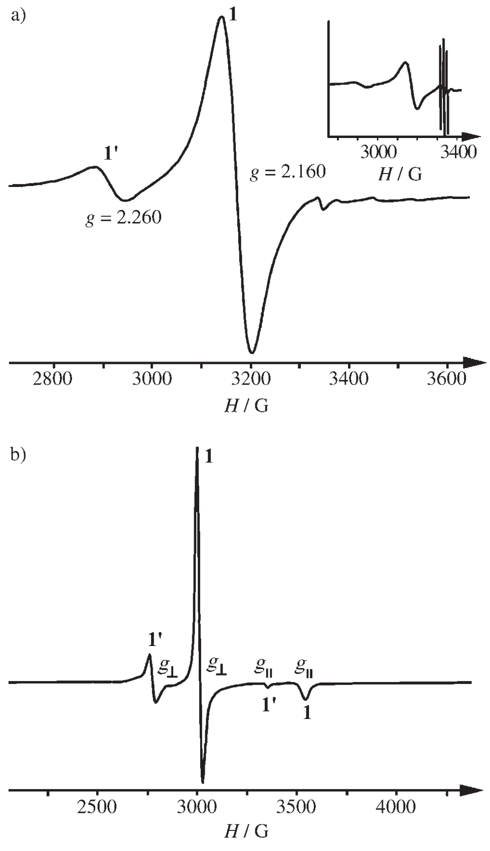


Figure 3. EPR spectra of **1** and **1'**: a) in *n*-hexane at 298 K; the inset shows the resonances relative to TEMPO ($g = 2.0059$); b) in glassy *n*-hexane at 150 K. TEMPO = 2,2,6,6-tetramethyl-1-piperidinoxyl.

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extremely large hyperfine coupling constant $a(^{207}Pb) > 8000$ Gauss and thus outside the range of the employed spectrometer. However, the $a(^{207}Pb)$ value for $PbMe_3$ was reported to be only about 1850 Gauss.[10] Further experiments are in progress to clarify this point.[17]

Whereas the known (transient) PbR_3 radicals are thought to exhibit pyramidal structures, the sterically overcrowded **1** is almost planar (Σ(Si-Pb-Si) = 355° (av))[11] (Figure 2). The unpaired electron is thus expected to be located in an orbital with high p character (and possible partial delocalization into σ^*(Si–Si) orbitals), and the Pb–Si bonds should in turn show significant contributions of the relativistically contracted 6s Pb orbital. The mean Pb–Si bond length of 264 pm[11] is indeed markedly shorter than those of bis(silyl)plumbylenes (270–278 pm) or the tris(silyl)plumbanide **3** (Figure 1).[5,6,8] Structural data and population analysis[12] for both these compounds indicate that lead makes only minor use of its 6s orbital in bonding to the substituents. Consequently, long Pb–Si bonds are observed for **3** (av 271 pm), and, despite the steric demand of the ethylbis(trimethylsilyl)silyl groups, the average Si-Pb-Si bond angle is only 104°.

Crystals of **1** can be stored indefinitely below −20 °C, and frozen solutions in C_6D_6 show no observable changes over several months. At room temperature, solutions of **1** decompose completely within a few days ($t_{1/2}(C_6D_6, 25\,°C) = 8.5$ h). The compound decomposes through a first-order reaction with respect to **1** to form elementary lead and the Pb^{IV} compound Ebt_4Pb (**5**). The derived activation energy of 99(6) kJ mol^{-1} is consistent with Pb–Si bond fission as the rate-determining step.[13]

The formation of plumbanides from plumbylenes is not restricted to the ethylbis(trimethylsilyl)silyl derivatives. Dihypersilylplumbylene ($PbHyp_2$; Hyp = $Si(SiMe_3)_3$) as well as the homologous stannylene $SnHyp_2$ also react similarly. After treatment of $PbHyp_2$ with KHyp in diethyl ether, potassium trihypersilylplumbanide can be isolated as the crystalline etherate $(Et_2O)_2KPbHyp_3$.[7] In contrast to **3**, $(Et_2O)_2KPbHyp_3$ in solution is in equilibrium with its components, KHyp and $PbHyp_2$. The homologous tin compound $KSnHyp_3$, however, does not dissociate to a detectable extent into KHyp and $SnHyp_2$. Both $SnHyp_3^-$ and $PbHyp_3^-$ can again be oxidized to yield the corresponding Hyp_3E radicals (E = Sn, Pb).[14] Whereas Hyp_3Sn is far more stable than **1** and could also be structurally characterized, Hyp_3Pb decomposes very quickly in solution, even at low temperatures, and could not be isolated thus far.

Future work will concentrate on further characterization of the radicals already prepared as well as on the synthesis of further tetrel(III) species, as well as on their spectroscopy and reactivity. A particular focus is on the development of alternative routes to the key intermediates, the symmetrically and unsymmetrically substituted tetrelanides ME[SiRR′R″] (M = metal; E = Sn, Pb; R = hydrocarbyl, triorganosilyl).

Experimental Section

All manipulations were performed by using Schlenk techniques under a dry argon atmosphere. Silanide **2** was prepared according to a literature method.[15] The EPR spectra were recorded with a BRUKER EMX 10/12 spectrometer at 9.38 GHz on 10^{-2} M solutions.

3: A suspension of $Pb(OC_6H_3\text{-}tBu_2\text{-}2,6)_2$ (6.03 g, 9.78 mmol) in diethyl ether (100 mL) was added with stirring over 3 h to a cooled (−60 °C) solution of **2** (7.12 g, 29.3 mmol) in diethyl ether (100 mL). The mixture changed color from brown to red-orange. The mixture was stirred at −30 °C for 45 min and filtered at −70 °C. Upon concentration of the solution at −50 °C to a volume of approximately 10 mL and addition of *n*-pentane (20 mL), **3** crystallized at −60 °C as yellow-orange needles. Yield 68 % (6.65 g, 6.62 mmol). ^1H NMR (400.13 MHz, [D_6]benzene, 25 °C): $\delta = 0.48$ [s, $Si(CH_3)_3$], 1.00 [t, Et_2O], 1.35 [t, $SiCH_2CH_3$, $J = 7.0$ Hz], 1.44 [m, $SiCH_2CH_3$], 3.16 ppm [q, Et_2O]; $^{13}C\{^1H\}$ NMR (100.62 MHz, [D_6]benzene, 25 °C): $\delta = 4.0$ [$Si(CH_3)_3$, $^1J_{Si,C} = 41.09$ Hz], 11.2 [$SiCH_2CH_3$], 15.4 [Et_2O], 17.8 [$SiCH_2CH_3$], 65.8 ppm [Et_2O]; $^{29}Si\{^1H\}$ NMR (79.49 MHz, [D_6]benzene , 25 °C): $\delta = -78.2$ [PbSi, $^1J_{Pb,Si} = 1378.4$ Hz], −9.6 ppm [SiMe$_3$, $^2J_{Pb,Si} = 20.4$, $^1J_{Si,C} = 41.0$ Hz]; $^{207}Pb\{^1H\}$ NMR (84.91 MHz, [D6]benzene, 25 °C): $\delta = -1119.8$ ppm.

1: A suspension of $Pb(OC_6H_3\text{-}tBu_2\text{-}2,6)_2$ (0.63 g, 1.02 mmol) in *n*-pentane (20 mL) was added with stirring to a cooled (−60 °C) suspension of **3** (2.06 g, 2.05 mmol) in *n*-pentane (20 mL). The green reaction mixture was stirred for 45 min at −60 °C, then for 10 min at room temperature, and finally filtered at −70 °C. The filtrate was concentrated at −60 °C to a volume of 10 mL, filtered again at −80 °C, and evaporated to dryness at −50 °C. The residue was dissolved in diethyl ether (5 mL) and concentrated to a volume of 0.5 mL. Green-brown needles of **1** grew at −60 °C. Yield 57 % (0.95 g, 1.16 mmol). UV/Vis (diethyl ether): $\lambda_{max}(\varepsilon) = 571$ nm (535,6 M^{-1} cm^{-1}). MS (IE, 70 eV): m/z (%): 817 (4.1) [M^+], 614 (8.3) [$M^+ - SiEt(SiMe_3)_2$], 85 (100), 73 (44.6) [$SiMe_3$].

5: In a typical experiment a solution of **1** in Et_2O or benzene was stored in the dark at room temperature for four days. The color slowly changed from green-brown to greenish yellow, and lead precipitated. After the solution was filtered and evaporated to dryness, the oily green residue was crystallized from Et_2O at −60 °C to yield yellow needles of **5**. Yield 86–91 %. ^1H NMR (400.13 MHz, [D_6]benzene, 25 °C): $\delta = 0.43$ [s, $Si(CH_3)_3$], 1.20 [t, $SiCH_2CH_3$, $J = 7.8$ Hz], 1.46 ppm [m, $SiCH_2CH_3$]; $^{13}C\{^1H\}$ NMR (100.62 MHz, [D_6]benzene , 25 °C): $\delta = 4.7$ [$Si(CH_3)_3$, $^3J_{Pb,C} = 7.7$, $^1J_{Si,C} = 43.7$ Hz], 14.1 [$SiCH_2CH_3$, $^2J_{Pb,C} = 38.7$ Hz], 15.6 ppm [$SiCH_2CH_3$, $^3J_{Pb,C} = 45.3$ Hz]. $^{29}Si\{^1H\}$ NMR (79.49 MHz, [D_6]benzene, 25 °C): $\delta = -42.0$ [PbSi, $^1J_{Si,Si} = 52.6$, $^1J_{Pb,Si} = 254.8$ Hz], −7.5 ppm [SiMe$_3$, $^2J_{Pb,Si} = 8.5$, $^1J_{Si,C} = 43.8$, $^1J_{Si,Si} = 52.3$ Hz]; $^{207}Pb\{^1H\}$ NMR (84.91 MHz, [D_6]benzene, 25 °C): $\delta = -543.3$ ppm. Structural parameters from the X-ray analysis are available in the Supporting Information.

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Keywords: EPR spectroscopy · lead · radicals · structure elucidation · X-ray diffraction

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[1] The differentiation made between the terms “persistent” and “stable” is somewhat arbitrary. Radicals are termed “stable” if they could be isolated and stored indefinitely as pure compounds. For recent review articles, see: P. P. Power, *Chem. Rev.* **2003**, *103*, 789; V. Y. Lee, A. Sekiguchi, *Eur. J. Inorg. Chem.* **2005**, 1209.

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[8] Crystal data for **1** and **3**: Data collection on a Bruker-SMART AXS diffractometer, $\lambda(\text{Mo}_{K\alpha})$ (0.71073 Å) at $T = 193$ K; structure solution by direct methods, refinement against F^2-values (SHELXTL package[16]). **1**: $C_{24}H_{69}PbSi_9$, $M = 817.79$, triclinic, space group $P\bar{1}$, $a = 9.9521(8)$, $b = 20.1737(12)$, $c = 33.873(2)$ Å, $\alpha = 78.620(4)$, $\beta = 84.955(4)$, $\gamma = 86.354(5)°$, $V = 6633.8(8)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.228\ \text{g cm}^{-3}$, $\mu = 40.71\ \text{cm}^{-1}$, $F(000) = 2526$, 109482 reflections collected, 32937 unique ($R_{int} = 0.1467$), 10287 with $I > 2\sigma(I)$. Empirical absorption correction with MULABS ($t_{min}/t_{max} = 0.0998/0.4545$). Three unique molecules were found. Two well separated maxima were located in the Fourier maps for all lead atoms. Site occupation factors for each pair of related split positions could be freely refined. Anisotropic displacement parameters were used for all atoms except hydrogen and carbon atoms of one disordered ethyl group per unique molecule; hydrogen atom were treated with riding models. Final residuals: R_1 ($I > 2\sigma(I)$) = 0.0617, wR_2 (all data) = 0.1347, *GOF* 0.851. **3**$\cdot(Et_2O)_{0.5}$: $C_{34}H_{94}KO_{2.5}PbSi_9$, $M = 1042.19$, monoclinic, space group $I2/a$, $a = 41.483(3)$, $b = 20.1316(12)$, $c = 15.1980(9)$ Å, $\beta = 84.955(4)°$, $V = 12047.7(13)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.149\ \text{g cm}^{-3}$, $\mu = 30.72\ \text{cm}^{-1}$, $F(000) = 4360$, 79683 reflections collected, 14995 unique ($R_{int} = 0.1454$), 7640 with $I > 2\sigma(I)$. Empirical absorption correction with MULABS ($t_{min}/t_{max} = 0.1584/0.6078$). The cocrystallised solvent (Et_2O) was disordered and treated with a split model. Anisotropic displacement parameters were used for all atoms except hydrogen; hydrogen atoms were treated with riding models. Final residuals: R_1 ($I > 2\sigma(I)$) = 0.0579, wR_2 (all data) = 0.1422, *GOF* 0.915. CCDC-616678 (**1**), -616679 (**3**) 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.

[9] The EPR data of **1′** correspond to a Pb-centered, axially symmetric radical with $g_\perp = 2.436$, $g_\| = 2.015$.

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[11] The given values are averages of the three unique molecules.

[12] Population analyses on model systems are supplied in the Supporting Information.

[13] The solution EPR spectrum (Figure 3a) comprises a very weak signal with a *g* value of approximately 2.006. According to the observed hyperfine coupling pattern it may be assigned to the Ebt radical formed through initial fission of the Pb–Si bond.

[14] The *g* values (and signal widths) of $SnHyp_3$ and $PbHyp_3$ were determined in Et_2O at room temperature to be 2.039 (11 Gauss) and 2.095 (51 Gauss), respectively. Hyperfine coupling to $^{117/119}$Sn of 596 Gauss (av) is observed for $SnHyp_3$.

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[17] Additional EPR measurements provide strong evidence that radical **1** is not contaminated by a second species **1′** but that the additional low-field feature in the EPR spectra in solution is instead part of the hyperfine coupling pattern ($a(^{207}\text{Pb}) \approx 520$ Gauss) of the ^{207}Pb isotopomer. The associated signals in the high-field region are extremely broadened and hardly detectable because of a very anisotropic rotation. Further details will be presented elsewhere.

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