



Dismutation of Tricyanoboryllead Compounds: The Homoleptic Tetrakis(tricyanoboryl)plumbate Tetraanion

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Dedicated to Professor Holger Braunschweig on the occasion of his 60th birthday

Abstract: A series of unprecedentedly air-stable (tricyanoboryl)plumbate anions was obtained by the reaction of the boron-centered nucleophile $\text{B}(\text{CN})_3^{2-}$ with triorganylead halides. Salts of the anions $[\text{R}_3\text{PbB}(\text{CN})_3]^-$ ($\text{R}=\text{Ph}, \text{Et}$) were isolated and found to be stable in air at room temperature. In the case of Me_3PbHal ($\text{Hal}=\text{Cl}, \text{Br}$), a mixture of the anions $[\text{Me}_{4-n}\text{Pb}\{\text{B}(\text{CN})_3\}_n]^{n-}$ ($n=1, 2$) was obtained. The $[\text{Et}_3\text{PbB}(\text{CN})_3]^-$ ion undergoes stepwise dismutation in aqueous solution to yield the plumbate anions $[\text{Et}_{4-n}\text{Pb}\{\text{B}(\text{CN})_3\}_n]^{n-}$ ($n=1-4$) and PbEt_4 as by-product. The reaction rate increases with decreasing pH value of the aqueous solution or by bubbling O_2 through the reaction mixture. Adjustment of the conditions allowed the selective formation and isolation of salts of all anions of the series $[\text{Et}_{4-n}\text{Pb}\{\text{B}(\text{CN})_3\}_n]^{n-}$ ($n=2-4$) including the homoleptic tetraanion $[\text{Pb}\{\text{B}(\text{CN})_3\}_4]^{4-}$.

Introduction

Compounds with B–C bonds are valuable reagents in synthetic chemistry and building blocks in materials science.^[1] Triethylborane was the first example for an organic molecule with a B–C bond that was described as early as 1860.^[2] Since then, a wealth of different synthetic methods towards compounds with B–C bonds have been

developed,^[1] e.g. hydroboration.^[3] In contrast to boron-carbon compounds, their higher homologues with boron-tetrele bonds have been less studied. More than 100 years after BEt_3 , first examples for molecules with a B–Si bond, borazines with silyl groups at boron, were reported.^[4] Only one year later, in 1961, salts of the $[\text{Ph}_3\text{SiBPh}_3]^-$ ion were described together with salts of the germanium homologue $[\text{Ph}_3\text{GeBPh}_3]^-$.^[5] The latter anion was the first compound with a Ge–B bond. The Sn–B bond was exemplified in 1964 by a series of triethylstannylboranes.^[6] Since then, further structurally diverse boron-tin derivatives have been reported, which include the anion $[\text{MePhNB}(\text{SnMe}_3)_3]^-$.^[7] Si–B compounds have attracted considerable interest as reagents in organic chemistry^[8] and molecules with Sn–B bonds have been used in borylation reactions.^[9]

In contrast to their lighter homologues, compounds with an electron-precise Pb–B bond remain rare, which reflects the low stability/high reactivity of these compounds, in general. In 1976, the diazaborolidine derivative $\text{Me}_3\text{PbB}(\text{NMeCH}_2)_2$ (**Ia**, Figure 1) was the first example for this class of compounds. Compound **Ia** was found to decompose rapidly at room temperature.^[10] A similar behavior was reported for $\text{Ph}_3\text{PbB}(\text{N}i\text{PrCH}_2)_2$ (**Ib**),^[11] whereas no data on the thermal stability of the related benzodiazaborolidine $\text{Ph}_3\text{PbB}\{o\text{-(N}i\text{Pr)}_2\text{C}_6\text{H}_4\}$ (**Ic**, Figure 1) have been reported.^[12] So far, the $[\text{Me}_3\text{PbBH}_3]^-$ ion (**II**), which decomposes even at low temperatures, is the sole charged boron-lead species with an electron-precise B–Pb bond.^[13] Both compounds **III**^[14] and **IV**^[15] were obtained from boron-based anions (Figure 1). **III** was formed from a borolyl anion and Me_3PbCl via a radical mechanism. In contrast, **IV** was presumably formed from Ph_3PbCl and a cyanoboryl anion via nucleophilic substitution. The syntheses of **III** and **IV** are without precedence since **Ia**, **Ib**, **Ic**, and **II** were formed by the reaction of LiPbR_3 ($\text{R}=\text{Me}, \text{Ph}$) with an electrophilic boron species. So far, **III** and **IV** are the only $\text{Pb}^{\text{IV}}\text{--B}$ species that were structurally characterized.^[14,15] The bis(boryl) lead(II) derivative $\text{Pb}\{\text{B}(\text{NDippCH}_2)_2\}_2$ (**V**, Figure 1) was obtained from an anionic boron-centered nucleophile. Probably, the unprecedented stability of **V** is due to the sterically demanding boryl substituents.^[16] In addition to **V**, a plumbylene adduct with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ ^[17] is a further rare example for a $\text{Pb}^{\text{II}}\text{--B}$ species.^[18] In addition to the aforementioned $\text{Pb}^{\text{II/IV}}$ compounds with an electron-precise Pb–B bond, boron clusters with $\text{Pb}_{\text{cluster}}$ atoms have

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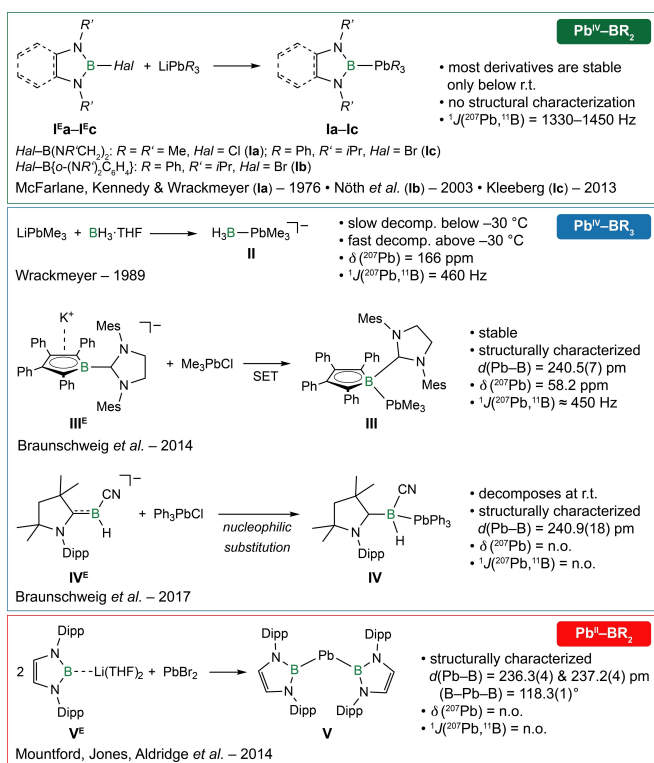


Figure 1. Synthesis of compounds with electron-precise Pb–B bonds.

been reported,^[19] and the coordination of boratabenzenes to Pb^{II} was described.^[20]

Cyanoboron compounds often exhibit high chemical, electrochemical, and thermal stabilities,^[21] and cyanoborates have been tested in many materials applications.^[21,22] Especially, chemical and electrochemical very robust room-temperature ionic liquids (ILs) have been developed^[23,24] and used as electrolyte components for electrochemical devices.^[22,25] Despite tetracoordinate borate anions, other cyanoboron species often reveal unprecedented stabilities. Important examples are boron(I) species,^[26] which are stabilized by one or more CN groups,^[15,27–31] e.g. the monoanion **IV^E** (Figure 1)^[15,31] and the tricyanoborate dianion $\text{B}(\text{CN})_3^{2-}$.^[28–30] The $\text{B}(\text{CN})_3^{2-}$ dianion reacts as boron-centered nucleophile^[29,32] and provides access to other cyanoborates, for example $[\text{EtB}(\text{CN})_3]^-$ and $[\text{B}_2(\text{CN})_6]^{2-}$.^[33,34] In contrast to reactions with non-metal electrophiles, reactions of $\text{B}(\text{CN})_3^{2-}$ with metal precursors are with the exception of the formation of mercury(II) complexes, e.g. $[\text{Hg}[\text{B}(\text{CN})_3]_2]^{2-}$,^[35] unknown.

In this contribution we report on the synthesis of tricyanoborylplumbate anions including the homoleptic $[\text{Pb}\{\text{B}(\text{CN})_3\}_4]^{4-}$ ion from triorganylead halides and $\text{K}_2\text{B}(\text{CN})_3$ ^[28–30] as initial starting materials. The borylplumbates are indefinitely stable in the solid state and solution, they can be handled in air, and some are even stable in water. Especially noteworthy is the dismutation of alkyl(tricyanoboryl)plumbate anions in water and hydrochloric acid to give bis-, tris-, and

tetrakis(tricyanoboryl)plumbate anions and PbEt_4 , which is without precedence in metal boryl chemistry.^[36]

Results and Discussion

The reaction of $\text{K}_2\text{B}(\text{CN})_3$ ^[30] with Ph_3PbBr and Et_3PbCl gave the corresponding tricyanoboryl complexes $[\text{Ph}_3\text{PbB}(\text{CN})_3]^-$ (**1^{Ph}**) and $[\text{Et}_3\text{PbB}(\text{CN})_3]^-$ (**1^{Et}**) (Figure 2). **K1^{Et}** was isolated from the reaction mixture on gram scale (> 4 g) in a yield as high as 80%. The $[\text{Ph}_3\text{PbB}(\text{CN})_3]^-$ ion (**1^{Ph}**) was precipitated as $[\text{PPh}_4]^+$ salt from an aqueous solution in a yield of 15%. The comparably low yield of $[\text{PPh}_4]^+\text{1^{Ph}}$ is due to the formation of $\text{K}_2[\text{B}_2(\text{CN})_6]$ ^[33] that was identified by ¹¹B NMR spectroscopy as side product. Both salts are thermally very robust with decomposition temperatures of 182 and 177 °C for $[\text{PPh}_4]^+\text{1^{Ph}}$ and **K1^{Et}**, respectively (DSC onset). This thermal stability is in stark contrast to the very low stability of the $[\text{Me}_3\text{PbBH}_3]^-$ ion (**II**, Figure 1).^[13]

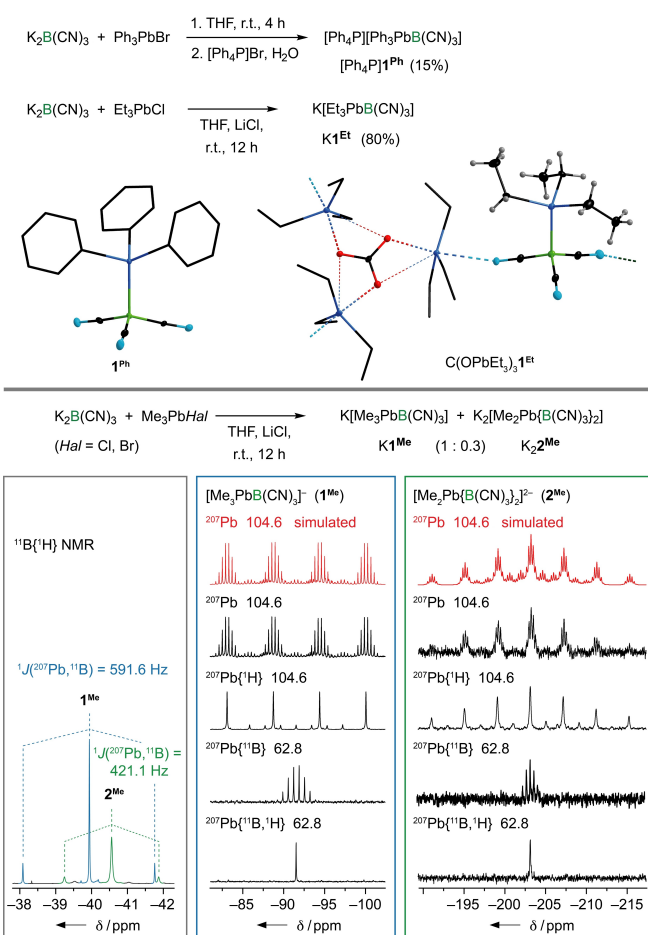


Figure 2. Syntheses of $[\text{Ph}_4\text{P}]\text{1^{Ph}}$ and **K1^{Et}**, crystal structures of **1^{Ph}** ($[\text{Ph}_4\text{P}]^+$ salt) and $[\text{C}(\text{OPbEt}_3)_3\text{1^{Et}}]^+$ (top; ellipsoids are drawn at the 25% probability level except for the H atoms that are either depicted with arbitrary radii or omitted for clarity, C atoms of the phenyl groups of **1^{Ph}** and the Et groups of the $\text{C}(\text{OPbEt}_3)_3^+$ ion are shown as wire-and-stick models),^[37] formation of **K1^{Me}** and **K2^{2Me}**, and ¹¹B and ²⁰⁷Pb NMR spectra of **1^{Me}** and **2^{Me}** (bottom).

[PPh₄]**1^{Ph}** did not decompose in air, which allowed the growth of crystals from acetone/dichloromethane without any decomposition. Crystallization of **K1^{Et}** from acetone in air afforded crystals of C(OPbEt₃)₃**1^{Et}** (Figure 2). Obviously, the **1^{Et}** anion undergoes slow decomposition in air, which explains the presence of the so far unknown C(OPbEt₃)₃⁺ cation, which is a carbonate anion with a PbEt₃⁺ cation bonded to each O atom. The carbonate anion is a result of CO₂ uptake from air. The lead atoms of these PbEt₃ units are coordinated to one N atom of a plumbate anion, which completes the trigonal bipyramidal coordination sphere at lead. In summary, the structure of C(OPbEt₃)₃**1^{Et}** may be interpreted as a two-dimensional coordination polymer composed of carbonate and **1^{Et}** anions interconnected by PbEt₃⁺ counter cations. The Pb–B distances of 234.1(13)/235.1(12) and 231(3) pm for **1^{Ph}** and **1^{Et}** are shorter than *d*(Pb–B) of **III** and **IV** (Figure 1). This points towards stronger Pb–B bonds in **1^{Ph}** and **1^{Et}**, which is in line with the unprecedentedly high stabilities of salts of both tricyanoborylplumbate anions.

Surprisingly, the reaction of K₂B(CN)₃ with trimethyllead halides did not result in [Me₃PbB(CN)₃][−] (**1^{Me}**) as sole B–Pb species (Figure 2). In the ¹¹B{¹H} NMR spectrum a second signal with ²⁰⁷Pb satellites (¹*J*(²⁰⁷Pb,¹¹B) = 421.1 Hz) close to the signal of **1^{Me}** was observed (Figure 2). In the ²⁰⁷Pb NMR spectra two signals were identified that correspond to the ¹¹B NMR signals of **1^{Me}** and the second B–Pb derivative. A detailed analysis of the ²⁰⁷Pb NMR signals using ¹¹B and ¹H decoupling allowed the assignment of the signals of **1^{Me}** and revealed the unknown derivative to be the [Me₂Pb{B(CN)₃}₂]^{2−} dianion (**2^{Me}**). So, the ²⁰⁷Pb NMR signal shows the coupling to two ¹¹B nuclei (septet) and to six protons (septet). In addition, the satellites of the mixed ¹⁰B/¹¹B isotopologue of **2^{Me}**, which has a relative ratio of 32 %, were assigned (Figure 2).

The tetraethylammonium salt [NEt₄]**1^{Et}** was synthesized from **K1^{Et}** and [NEt₄]Cl in water in a yield of 54 %. The isolated salt contained 6 % of [NEt₄]₂[Et₂Pb{B(CN)₃}₂]^{2−} ([NEt₄]₂**2^{Et}**). The assignment of the NMR signals of **2^{Et}** is based on the coupling scheme in the ²⁰⁷Pb NMR spectrum (septet with an intensity distribution of 1:2:3:4:3:2:1, ²*J*(²⁰⁷Pb,¹¹B) = 383.1 Hz, Figure 3) and a comparison to the NMR spectroscopic data of **2^{Me}** (Figure 2). Since dianion **2^{Et}** was not present in the starting compound, its formation must have occurred during metathesis in aqueous solution. The conversion of **1^{Et}** into **2^{Et}** was monitored in oxygen-free water by NMR spectroscopy and it was complete after 24 hours (Figure S9 in the Supporting Information). PbEt₄ had formed as oily by-product that separated as droplets from the aqueous phase. It was extracted with pentane and characterized by NMR spectroscopy (*δ*(²⁰⁷Pb) = 75.0 ppm).^[38,39] The dismutation did not take place in other solvents, e.g. in ethanol. Even in a mixture of equal amounts of water/ethanol the dismutation was very slow. The dismutation of [Et₃PbB(CN)₃][−] (**1^{Et}**) in water to give [Et₂Pb{B(CN)₃}₂]^{2−} (**2^{Et}**) was found to be faster in the presence of oxygen. The reaction was practically complete after 80 minutes (Figure S10 in the Supporting Information), whereas full conversion required ca. 1 day in the absence of oxygen.

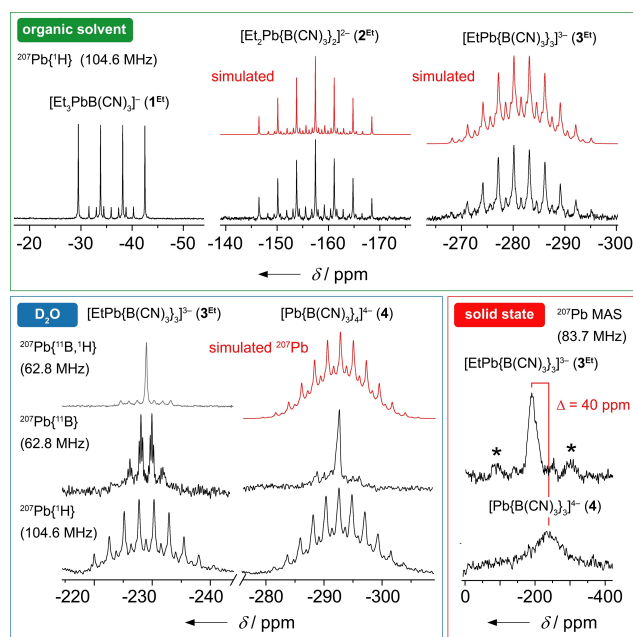


Figure 3. ²⁰⁷Pb{¹H} NMR spectra of **1^{Et}**, **2^{Et}** (CD₃CN), and **3^{Et}** ([D₂]DMF) (top); ²⁰⁷Pb{¹¹B,¹H}, ²⁰⁷Pb{¹¹B}, and ²⁰⁷Pb{¹H} NMR spectra of **3^{Et}** (H₂O*) and ²⁰⁷Pb{¹¹B} and ²⁰⁷Pb NMR spectra of **4** (H₂O*) (bottom, left), and ²⁰⁷Pb CP/MAS NMR spectra of [Me₂DABCO]₃(**3^{Et}**)₂·4 KI and [Me₂DABCO]₂·4·2 KI (bottom, right).

An even enhanced conversion was achieved by bubbling elemental O₂ through an aqueous solution of **K1^{Et}**. A solution of **K1^{Et}** was treated with O₂ for 5 minutes and subsequently the borate anions were precipitated as [Fe(bpy)₃]²⁺ salts (bpy = 2,2-bipyridine). The mixture of [Fe(bpy)₃]²⁺ salts contained **2^{Et}** (54 %), **1^{Et}** (13 %), [B(OH)(CN)₃][−][40] (9 %), [BH(CN)₃][−][24] (2 %), and unknown borate anions (22 %). So, although the reaction rate for the dismutation was strongly increased in the presence of O₂, the dismutation was accompanied by side reactions, which did not occur when oxygen was excluded. Recrystallization of the product mixture afforded single-crystals of [Fe(bpy)₃]**2^{Et}** (Figure 4) and [Fe(bpy)₃][B(OH)(CN)₃]₂ (Figure S17 in the Supporting Information).

Dianion **2^{Et}** was selectively synthesized in water in the presence of air and precipitated as tetraethylammonium salt in a yield of 32 % (Figure 4). [NEt₄]₂**2^{Et}** was stored without decomposition for more than one year. The thermal degradation of [NEt₄]₂**2^{Et}** starts at temperatures above 140 °C (DSC onset).

Surprisingly, the dismutation did not stop with the formation of the bis(tricyanoboryl)plumbate dianion [Et₂Pb{B(CN)₃}₂]^{2−} (**2^{Et}**) but slowly proceeded to yield the tris(tricyanoboryl)plumbate trianion [EtPb{B(CN)₃}₃]^{3−} (**3^{Et}**) with further PbEt₄ as by-product. The conversion was not complete even after 15 days in oxygen-free water (Figure S9 in the Supporting Information). However, we found that dismutation of **1^{Et}** and **2^{Et}** is strongly accelerated under acidic conditions. The reaction seems to be solely dependent on the pH but not on the acid because hydrochloric acid and (H₃O)[BF(CN)₃]^[41] resulted in the same increase of the

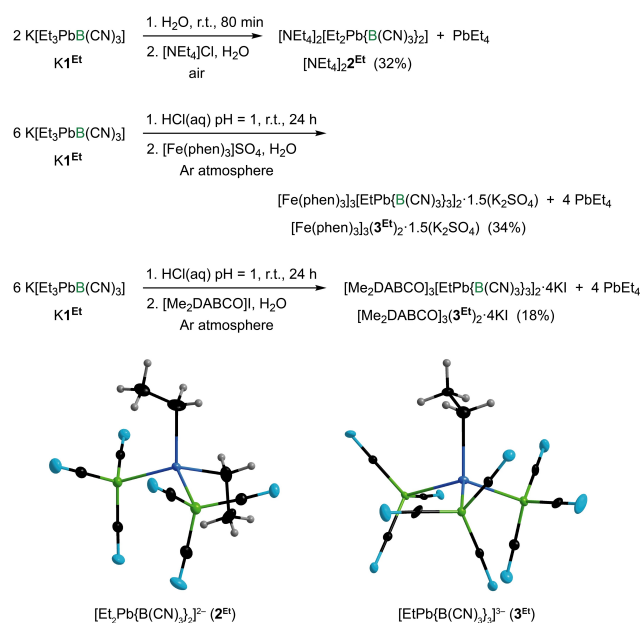


Figure 4. Synthesis of $[\text{NEt}_4]_2\mathbf{2}^{\text{Et}}$, $[\text{Fe}(\text{phen})_3]_3(\mathbf{3}^{\text{Et}})_2 \cdot 1.5(\text{K}_2\text{SO}_4)$, and $[\text{Me}_2\text{DABCO}]_3(\mathbf{3}^{\text{Et}})_2 \cdot 4\text{KI}$ (top) and crystal structures of $\mathbf{2}^{\text{Et}}$ ($[\text{Fe}(\text{bpy})_3]_2\mathbf{2}^{\text{Et}}$) and $\mathbf{3}^{\text{Et}}$ $[\text{Me}_2\text{DABCO}]_3(\mathbf{3}^{\text{Et}})_2 \cdot n\text{H}_2\text{O}$, ellipsoids are drawn at the 35 % probability level, bottom).^[37]

reaction rates. A faster reaction between PbPh_4 and $\text{Pb}(\text{O}_2\text{CCH}_3)_4$ to yield $\text{Ph}_2\text{Pb}(\text{O}_2\text{CCH}_3)_2$ in the presence of acetic acid was reported, earlier.^[42] In contrast, basic conditions (pH 10, KOH) did not alter the reaction rate compared to neutral water. At pH 3, the conversion of $\mathbf{1}^{\text{Et}}$ into $\mathbf{2}^{\text{Et}}$ took ca. 2–3 hours. At pH 1, $\mathbf{2}^{\text{Et}}$ was the sole tricyanoborylplumbate anion that was present in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum immediately after the start of the reaction (Figure S11 and S12, Tables S2 and S3 in the Supporting Information). At pH 1, the signal of dianion $\mathbf{2}^{\text{Et}}$ almost completely vanished within 1 day and trianion $\mathbf{3}^{\text{Et}}$ had formed together with some decomposition products (Table S3 and Figure S12 in the Supporting Information). Longer reaction times resulted in a decrease of the NMR signal of $\mathbf{3}^{\text{Et}}$ and an increase of the signal of decomposition products, mostly $[\text{B}(\text{OH})(\text{CN})_3]^-$.^[40]

The tris(tricyanoboryl)plumbate trianion $[\text{EtPb}(\text{B}(\text{CN})_3)_3]^{3-}$ ($\mathbf{3}^{\text{Et}}$) was isolated as $[\text{Fe}(\text{phen})_3]_3(\mathbf{3}^{\text{Et}})_2 \cdot 1.5(\text{K}_2\text{SO}_4)$ (phen = 1,10-phenanthroline) by precipitation from the reaction mixture by the addition of $[\text{Fe}(\text{phen})_3]\text{SO}_4$ in a yield of 34 %. The $[\text{Me}_2\text{DABCO}]^{2+}$ salt of $\mathbf{3}^{\text{Et}}$ ($\text{Me}_2\text{DABCO} = N,N'$ -dimethyl-1,4-diazabicyclo[2.2.2]octane) was obtained with KI as co-precipitate from an aqueous solution of $\text{K}_3\mathbf{3}^{\text{Et}}$ and $[\text{Me}_2\text{DABCO}]\text{I}_2$ in a yield of 18 %. In addition, a few crystals of $[\text{Me}_2\text{DABCO}]_3(\mathbf{3}^{\text{Et}})_2 \cdot n\text{H}_2\text{O}$ ($n \approx 6$) were obtained and a single-crystal X-ray diffraction (SC-XRD) study proved the formation of $\mathbf{3}^{\text{Et}}$ (Figure 4). Furthermore, $\mathbf{3}^{\text{Et}}$ was characterized by multinuclear NMR spectroscopy in solution and the solid state. In Figure 3 the ^{207}Pb NMR spectra of $\mathbf{3}^{\text{Et}}$ in solution, in $[\text{D}_7]\text{DMF}$ and D_2O , and in the solid state are depicted. In the solution spectra, the $^{207}\text{Pb}\{^1\text{H}\}$ signal of the major isotopologue $[\text{EtPb}\{^{11}\text{B}(\text{CN})_3\}_3]^{3-}$ is split into a decet

due to the coupling to three equivalent ^{11}B nuclei. The $^{207}\text{Pb}\{^{11}\text{B}\}$ signal shows the coupling to a single ethyl group; it is split into a quartet of triplets (Figure 3). Similar to the $^{207}\text{Pb}\{^1\text{H}\}$ NMR signals of $\mathbf{1}^{\text{Et}}$ and $\mathbf{2}^{\text{Et}}$, the signal of $\mathbf{3}^{\text{Et}}$ shows additional lines that correspond to the ^{10}B -containing isotopologues. The ^{207}Pb chemical shift of $\mathbf{3}^{\text{Et}}$ strongly depends on the environment as obvious from the spectra depicted in Figure 3 that were recorded on samples in D_2O or $[\text{D}_7]\text{DMF}$, or in the solid state. Strong shifts in $\delta(^{207}\text{Pb})$ are well documented and rationalized by the interaction of the Pb atom with solvent molecules.^[38,43,44] $[\text{Me}_2\text{DABCO}]_3(\mathbf{3}^{\text{Et}})_2 \cdot 4\text{KI}$ and $[\text{Fe}(\text{phen})_3]_3(\mathbf{3}^{\text{Et}})_2 \cdot 1.5(\text{K}_2\text{SO}_4)$ were handled in air, they showed no decomposition upon storage in the solid state for more than one year, and they were found to be thermally very robust with decomposition temperatures of 194 and 197 °C, respectively (DSC onset).

The removal of all volatiles from a reaction mixture that contained $[\text{EtPb}(\text{B}(\text{CN})_3)_3]^{3-}$ ($\mathbf{3}^{\text{Et}}$) as only tricyanoborylplumbate anion led to a mixture of $\mathbf{3}^{\text{Et}}$ and the homoleptic tetrakis(tricyanoboryl)plumbate tetraanion $[\text{Pb}(\text{B}(\text{CN})_3)_4]^{4-}$ ($\mathbf{4}$) (Figure 5). The mixture was taken-up into aqueous HCl at pH 1 and subsequently all volatiles were removed under vacuum. This procedure was repeated two times. The progress of the dismutation was monitored by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy (Figure 5). The formation of $\mathbf{4}$ was unambiguously proven by NMR spectroscopy. So, the $^{207}\text{Pb}\{^{11}\text{B}\}$ NMR signal reveals no coupling and the $^{207}\text{Pb}\{^1\text{H}\}$ NMR signal shows the coupling to four ^{11}B nuclei. It is split into a tridecet, of which the two outer lines are not resolved due to their very low intensity. Furthermore, the anions $\mathbf{1}^{\text{Et}}$, $\mathbf{2}^{\text{Et}}$, $\mathbf{3}^{\text{Et}}$, and $\mathbf{4}$ show an (i) increase in $\delta(^{11}\text{B})$, (ii) a decrease in $\delta(^{207}\text{Pb})$, and (iii) a decrease in $^1J(^{207}\text{Pb},^{11}\text{B})$ with increasing number of $\text{B}(\text{CN})_3$ groups.

Despite the signals of $\mathbf{3}^{\text{Et}}$, $\mathbf{4}$, and $[\text{B}(\text{OH})(\text{CN})_3]^-$, additional signals were observed in the region of -27.5 to -31.5 ppm and similar signals have been observed during dismutation to yield $\mathbf{2}^{\text{Et}}$ and $\mathbf{3}^{\text{Et}}$, as well (Figure S12 and S14 in the Supporting Information). All these signals reveal the coupling to two ^{207}Pb nuclei. Presumably, the larger coupling constant of 300–500 Hz corresponds to $^1J(^{207}\text{Pb},^{11}\text{B})$ and the smaller coupling constant of ca. 10 Hz is due to geminal or vicinal couplings. $^2J(^{207}\text{Pb},^{11}\text{B})$ would fit to a diplumbane and $^3J(^{207}\text{Pb},^{11}\text{B})$ to a plumboxane or a related oxygen-bridged species, as exemplified in Figure 5.^[43] A strong dependence of $\delta(^{207}\text{Pb})$ on the pH of the reaction mixture was observed for these signals, which indicates a plumboxane-like species. As obvious from the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra in Figure 5, the intensity of these signals decreases during the reaction and so far, it was not possible to isolate one of them. A thorough analysis of the relative intensities of all signals present in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectra did not provide final evidence whether these intermediate B–Pb species led to the final formation of an anion of the series $[\text{Et}_{4-n}\text{Pb}(\text{B}(\text{CN})_3)_n]^{n-}$ or to decomposition, i.e. $[\text{B}(\text{OH})(\text{CN})_3]^-$.

Species with interconnected Pb atoms, similar to the plumboxane-like structure depicted in Figure 5 or larger Pb^{IV} clusters with oxygen bridges, may be key intermediates in the ligand exchange reactions leading to $\mathbf{2}^{\text{Et}}$, $\mathbf{3}^{\text{Et}}$, $\mathbf{4}$, and PbEt_4 . So, the formation of mono- or diprotonated

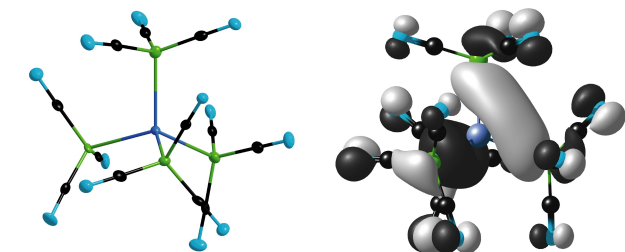
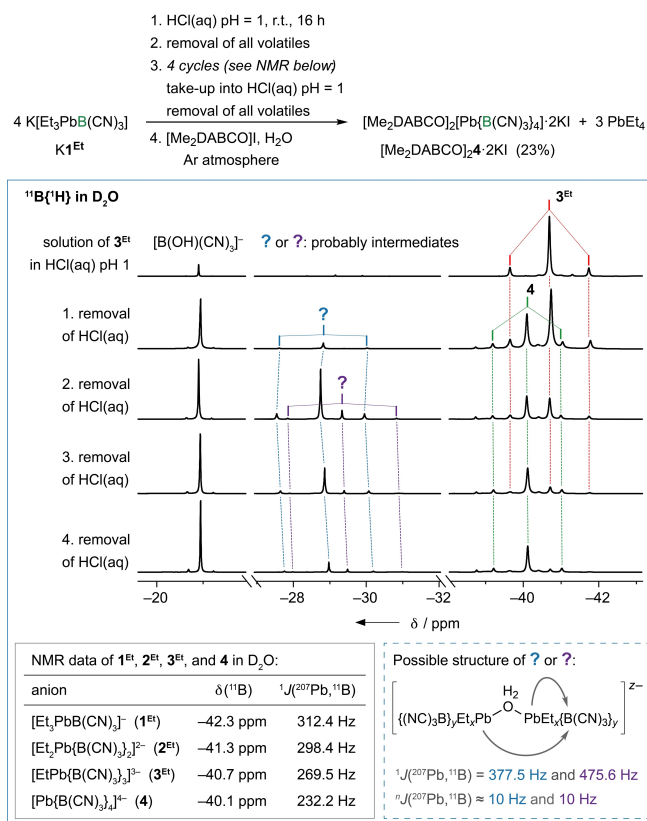


Figure 5. Synthesis of [Me₂DABCO]₂·4·2KI (top), ¹¹B{¹H} NMR spectra of a reaction mixture of K1^{Et} to result in 3^{Et} (16 h in HCl(aq), top spectrum) followed by removal of all volatiles under vacuum and successive addition of HCl(aq) and removal of all volatiles under reduced pressure (middle), crystal structure of 4 ([Me₂DABCO]₂·4·5 DMSO, ellipsoids are drawn at the 35% probability level),^[37] and one of the triply degenerate HOMOs of 4 (B3LYP/6-311++G(d,p)/SDD/COSMO(H₂O), bottom).

Pb–O–Pb units could explain the necessity of water for the exchange reactions. This would also rationalize the pH-dependence of the reaction rates. The increase of the reaction rate in the presence of O₂ is not as obvious. Eventually, Pb–O–O–Pb species are involved if elemental oxygen is available that enable a faster exchange of tricyanoboryl and ethyl groups between the two Pb centers.

The addition of [Me₂DABCO]₂ to an aqueous solution of the crude product mixture of 4 resulted in [Me₂DABCO]₂·4 with 2 equivalents of KI as co-precipitate. The solid is stable up to 209 °C (DSC onset). It is almost insoluble in any solvent. So, the salt was characterized by solid-state NMR spectroscopy, elemental analysis, and vibra-

tional spectroscopy. The ²⁰⁷Pb MAS signal reveals a strong shift towards a higher resonance frequency compared to the signal in D₂O. This shift is even more pronounced than for 3^{Et} (Figure 3). [Me₂DABCO]₂·4·2KI is marginally soluble in hot DMSO. Cooling a saturated hot dimethyl sulfoxide solution (100 °C) afforded a few single crystals of [Me₂DABCO]₂·4·5 DMSO that were characterized by SC-XRD (Figure 5). The structure shows the tetrahedral surrounding at lead. The geometry of 4 is close to T symmetry, which agrees to DFT calculations that predict T symmetry for the minimum structure. The four B(CN)₃ groups are rotated off the staggered orientation to minimize steric repulsion, which prevents the higher T_d symmetry. The Pb–B distance of 239.0(14) pm of 4 is the longest in the series of plumbate anions [Et_{4-n}Pb{B(CN)₃}_n]ⁿ⁻ (n=1–4; Table S11 in the Supporting Information). The Pb–B distance increases with increasing number of B(CN)₃ groups at lead. However, the experimental trend is not significant, but it is well reproduced by calculated values. DFT calculations predict an analogous increase of the Pb–C distances along the series PbEt₄, 1^{Et}, 2^{Et}, and 3^{Et}. The B–C and C≡N distances remain basically unchanged within the series. Similarly, ν(CN) does not strongly change either (Table S11 in the Supporting Information).

The dismutation starting with [Et₃PbB(CN)₃]⁻ (1^{Et}) in water is unprecedented and the selective accessibility of 2^{Et}, 3^{Et}, and 4 is unexpected, as well. Redistributions of tetraalkyl and aryllead(IV) compounds typically occur in the presence of Lewis acid catalysts and require high temperatures and result in complex mixtures of organyl lead(IV) compounds.^[45–47] Most likely, the separation of PbEt₄ from the reaction mixture is the driving force for the dismutations yielding the tricyanoborylplumbate anions. Each further step of the dismutation requires longer reaction times or harsher conditions. So, the synthesis of 4 requires the removal of the by-product PbEt₄ in vacuum. The calculated enthalpies and Gibbs free energies for the stepwise dismutations predict (i) the reactions to be slightly endothermic and endergonic and (ii) that the reactions become more endothermic and endergonic with increasing number of B(CN)₃ groups (see the Supporting Information for more details). Thus, the theoretical data support the hypothesis that the separation of PbEt₄ is necessary for the dismutations and they are in line with the stepwise formation of the tricyanoborylplumbate anions.

The methyl derivatives [Me₃PbB(CN)₃]⁻ (1^{Me}) and [Me₂Pb{B(CN)₃}₂]²⁻ (2^{Me}) showed dismutations similar to those found for the related ethyl-substituted tricyanoborylplumbate anions (Figure S15 and S16 in the Supporting Information). However, larger amounts of decomposition products had formed. This is an indication for a lower stability of the methyl derivatives compared to the respective ethyl plumbates. A lower stability of methyl compared to ethyllead(IV) compounds, is well documented in the literature.^[46] In addition, the dismutations were not as selective as those of the related ethyl derivatives. For example, the NMR studies imply an equilibrium of 2^{Me} and [MePb{B(CN)₃}₃]³⁻ (3^{Me}). Thus, we were not able to isolate salts of the anions [Me_{4-n}Pb{B(CN)₃}_n]ⁿ⁻ (n=1–3, 1^{Me}, 2^{Me},

3^{Me}) as pure compound. In contrast to the ethyl and methyl derivatives, the phenyl-substituted plumbate anion $[\text{Ph}_3\text{PbB}(\text{CN})_3]^-$ (1^{Ph}) did not show any dismutation, at all.

The $[\text{Ph}_3\text{PbB}(\text{CN})_3]^-$ anion (1^{Ph}) is irreversibly oxidized at a potential of 0.60 V in acetonitrile (Figure 6). The formal replacement of phenyl against ethyl groups leads to a significantly lower electrochemical stability ($E_{\text{ox}}=0.22$ V). The stepwise exchange of ethyl against tricyanoboryl groups results in lower oxidation potentials of 0.10 V for 2^{Et} and -0.07 V for 3^{Et} . The cyclic voltammogram of 3^{Et} was measured in DMF since $[\text{Me}_2\text{DABCO}]_3(3^{\text{Et}})_2$ is not soluble in acetonitrile (Figure 6). Due to the insolubility of $[\text{Me}_2\text{DABCO}]_2\mathbf{4}$ in all common solvents, it was not possible to obtain a CV. The trend in E_{ox} parallels the HOMO energies that increase in the order 1^{Ph} , 1^{Et} , 2^{Et} , and 3^{Et} (Table S8 in the Supporting Information). The HOMOs of the $\text{B}(\text{CN})_3$ -substituted plumbate anions are similar to those of PbEt_4 (Figure S22 in the Supporting Information), which is evident especially from an inspection of the threefold degenerate HOMO of the tetrahedral $[\text{Pb}\{\text{B}(\text{CN})_3\}_4]^{4-}$ tetraanion ($\mathbf{4}$) in Figure 5. The HOMO also shows the distribution of the electron density across the whole tetraanion including the CN groups. Especially the electron withdrawing cyano groups stabilize the tricyanoboryl group, which in turn is the key to the stability of the $\text{Pb}-\text{B}$ bonds in $\mathbf{4}$ as well as in the mixed phenyl- and ethyl(tricyanoboryl)plumbate anions 1^{Ph} , 1^{Et} , 2^{Et} , and 3^{Et} .

It is well known that tetraalkyllead compounds undergo reductive elimination in solution upon UV radiation.^[46–48] The tricyanoborylplumbate anions show an analogous reductive elimination of $[\text{B}_2(\text{CN})_6]^{2-}$ and $[\text{EtB}(\text{CN})_3]^-$, as well (Figure 7). According to results of DFT calculations, the reductive eliminations to yield plumbylenes PbR_2 ($R = \text{Et}$, $\text{B}(\text{CN})_3^-$) are exergonic and exothermic (Table S10 in the Supporting Information). Dialkylplumbylenes are well

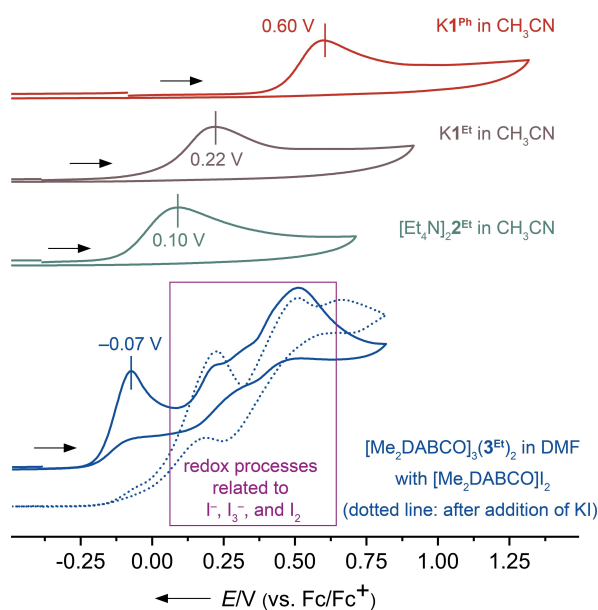


Figure 6. Cyclic voltammograms of $\text{K}1^{\text{Ph}}$, $\text{K}1^{\text{Et}}$, $[\text{Et}_4\text{N}]_2\mathbf{2}^{\text{Et}}$, and $[\text{Me}_2\text{DABCO}]_3(3^{\text{Et}})_2$.

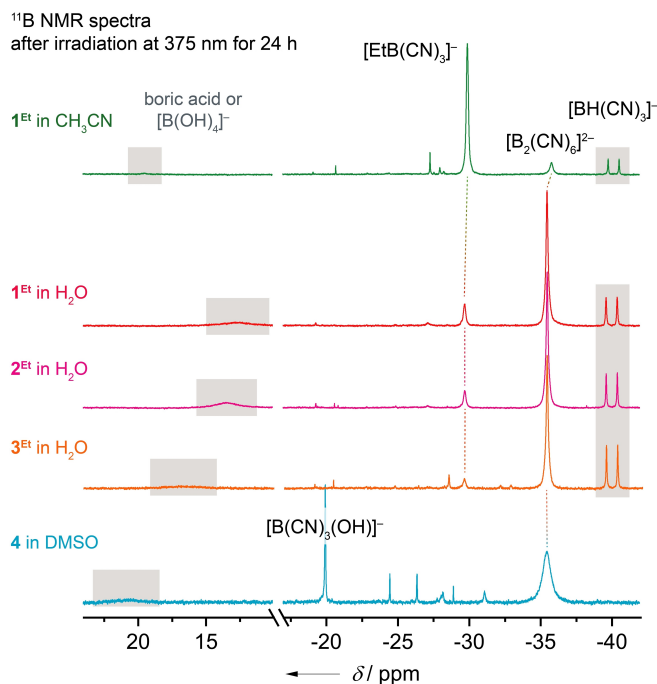


Figure 7. ^{11}B NMR spectra of the reaction products of 1^{Et} , 2^{Et} , 3^{Et} , and $\mathbf{4}$ after irradiation of solutions in CH_3CN , water, and DMSO at 375 nm for 24 hours. Water was added to the reaction mixtures of 1^{Et} in CH_3CN and $\mathbf{4}$ in DMSO to ensure dissolution of all boron species. The dark-grey side product, most likely metallic lead, was separated before the NMR spectroscopic studies.

known to be unstable, they can decompose via reductive elimination or disproportionation. So, the possible decomposition intermediates PbEt_2 , $[\text{EtPbB}(\text{CN})_3]^-$, and $[\text{Pb}\{\text{B}(\text{CN})_3\}_2]^{2-}$ should undergo further decomposition to yield $[\text{B}_2(\text{CN})_6]^{2-}$, $[\text{EtB}(\text{CN})_3]^-$, and elemental Pb as final products. The attempted synthesis of the plumbylene dianion $[\text{Pb}\{\text{B}(\text{CN})_3\}_2]^{2-}$ using PbCl_2 and $\text{K}_2\text{B}(\text{CN})_3^{2-}$ failed, and $[\text{B}_2(\text{CN})_6]^{2-}$ was obtained. This observation supports the assumption that $[\text{Pb}\{\text{B}(\text{CN})_3\}_2]^{2-}$ is not stable in contrast to the structurally characterized bis(boryl)plumbylene \mathbf{V} in Figure 1. The presence of metallic lead is evident from the greyish material that is formed during UV irradiation. The product distribution depends on the solvent used. So, UV irradiation of 1^{Et} in wet acetonitrile predominantly gave $[\text{EtB}(\text{CN})_3]^-$ whereas in water $[\text{B}_2(\text{CN})_6]^{2-}$ was the main product.

Similarly, 2^{Et} and 3^{Et} resulted in water in mixtures with $[\text{B}_2(\text{CN})_6]^{2-}$ as major boron-containing species. So, most likely fast dismutation to result in plumbate anions with more than one $\text{B}(\text{CN})_3$ group followed by reductive elimination seems to take place in water.

Conclusion

Unprecedented borylplumbate anions were obtained and found to be surprisingly thermally, chemically, and electrochemically stable. The dismutations of the mixed ethyl(tricyanoboryl)plumbate anions $[\text{Et}_{4-n}\text{Pb}\{\text{B}(\text{CN})_3\}_n]^{n-}$

($n=1-3$, n^{Et}) that finally result in the homoleptic tetrakis(tricyanoboryl)plumbate anion $[Pb\{B(CN)_3\}_4]^{4-}$ (**4**) in hydrochloric acid at pH 1 is novel in many ways. Analogous dismutation reactions of organyllead(IV) compounds have not been reported, transborylations of the $B(CN)_3$ group are without precedence, and equivalent dismutations of boryl substituents leading to boryl complexes with multiple boryl groups at a single metal center are unknown, as well. The present contribution highlights the stabilizing effect of the tricyanoboryl group and shows its potential for the synthesis of unprecedented organometallic boron-containing molecules.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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