Cluster Compounds

DOI: 10.1002/anie.201307795

Unusual 14-Electron Fragments $[Pd(\eta^3\text{-}Bi_{3-x}Pb_x)]^{(x+1)-}$ as Pseudo Lead Atoms in *closo*-$[Pd@Pd_2Pb_{10}Bi_6]^{4-}$**

Rodica Ababei, Werner Massa, Klaus Harms, Xiulan Xie, Florian Weigend, and Stefanie Dehnen**

Dedicated to Professor Werner Uhl on the occasion of his 60th birthday

Contemporary research on Zintl ions pushes the boundaries of inorganic chemistry, materials science, and cluster physics. In particular, the area of main-group metal clusters embedding one to three d-block or f-block metal atoms, designated as intermetalloid clusters, has developed rapidly during the last decade.[1]

Anions such as onion-type $[As@Ni_{12}@As_{20}]^{3-}$[2] or its Sn/Cu analogue[3] are spectacular examples, besides complex deltahedra like *closo*-$[Ni_x@\{Bi_6Ni_6(CO)_8\}]^{4-}$,[4] or non-deltahedral clusters $[M@Ge_{10}]^{x-}$ (M = Fe, Co).[5] These are interesting not only for their architectures and complexity, but also as they point toward new aspects of cluster formation, bonding, as well as to dynamics in solution or in the gas phase. Oligo-/polymers of Zintl anions were also brought into focus,[1] as well as organic derivatives to reduce charges and add functionalities, as in neutral $[Ge_9\{Si(SiMe_3)_3\}_3\{SnPh_3\}]$.[6]

As Zintl anions usually act as precursors to intermetalloid clusters, the low solubility of many Zintl phases has been a limitation of the synthetic approach. Hence, most investigations were undertaken with fairly soluble polytetrelide or polypnictogenide anions $(E^{14}{}_9)^{4-}$,[1a,7] $(E^{15}{}_7)^{3-}$,[8] or $(Bi_2)^{2-}$,[9] which was only recently extended by reactions of tetrahedral $(E^{14}{}_4)^{4-}$ anions, albeit in liquid ammonia.[10] Heterometallic Group 14/15 or 13/15 anions proved advantageous in this regard, as they possess lower charges and consequently higher solubilities. Reactions with $(Sn_2Sb_2)^{2-}$,[11] $(Sn_2Bi_2)^{2-}$,[12] or $(InBi_3)^{2-}$[13] with various transition metal complexes yielded first ternary intermetalloid anions, such as $[Sn_2Sb_5(ZnPh)_2]^{3-}$,[11] $[Zn@Zn_5Sn_3Bi_3@Bi_5]^{4-}$,[14] $[Ni_2@Sn_7Bi_5]^{3-}$,[15] $[Ln@Sn_xBi_{14-x}]^{4-}$, and $[Ln@Sn_xBi_{13-x}]^{4-}$ (Ln = La, Ce, Eu),[16] $[Pd_3@Sn_8Bi_6]^{4-}$,[17] or $\{[La@In_2Bi_{11}]_2(\mu\text{-}Bi)_2\}^{6-}$.[18] We have recently shown that reactions of pseudo homoatomic $(Pb_2Bi_2)^{2-}$ with Ni^0 or Zn^{2+} lead to homologous results.[19] However, we noted that solubilities and yields improve dramatically on using the Pb/Bi anion, which prompted us to perform further studies with this precursor.

In contrast to the above observations, the reaction of $[K([2.2.2]crypt)]_2(Pb_2Bi_2)\cdot 2\,en$[19] with $[Pd(PPh_3)_4]$, as a source of Pd^0, in ethane-1,2-diamine (en) produced an unprecedented intermetalloid anion with several structural and electronic peculiarities.

$[K([2.2.2]crypt)]_4[Pd@Pd_2Pb_{10}Bi_6]\cdot 2\,en$ (**1**), comprising the heaviest intermetalloid cluster anion known to date, was obtained as extremely air-sensitive, black crystal plates (Scheme 1). We provide the crystal structure, ^{207}Pb NMR spectra, X-ray spectroscopic and mass spectrometric investigations, as well as quantum chemical studies on the stability and electronic structure of the anion.

$$[K([2.2.2]crypt)]_2(Pb_2Bi_2)\cdot en + [Pd(PPh_3)_4] \xrightarrow[\text{crystallization at 4°C}]{\text{en, filtration, layering by toluene,}} [K([2.2.2]crypt)]_4[Pd@Pd_2Pb_{10}Bi_6]\cdot 2\,en\ (\mathbf{1},\ 60\%)$$

Scheme 1. Synthesis and crystallization of compound **1**.

The K/Pd/Pb/Bi ratio (4:3:10:6) of **1** was confirmed by energy dispersive X-ray spectroscopy (EDX; Supporting Information, Table S3), and the composition of the anion was confirmed by detection of the mass peak by electrospray ionization mass spectrometry (ESI-MS) of single crystals of **1** dissolved in dimethylformamide (DMF; SI, Figure S3–S9); these also affirmed the anion to be stable in solution, and its potassium adduct $[K_1Pd_3Pb_{10}Bi_6]^-$ (*m*/*z* 3684.39; SI, Figure S4) to be transferrable into the gas phase.

At 4 °C, compound **1** crystallizes in the triclinic space group $P\bar{1}$,[20] as determined by single-crystal X-ray diffraction; the structure of the $[Pd@Pd_2Pb_{10}Bi_6]^{4-}$ anion is shown in Figure 1.

The molecular structure of the cluster, representing a Pd-centered $[Pd_2(Pb/Bi)_{10}]$ icosahedron with two main-group element triangles attached, has no symmetry, but three different pseudo symmetries can be considered (C_{2v}, C_S, or C_2), depending on the assignment of two Pb and four Bi atoms (Pb/Bi)9,10, and (Bi/Pb)3–6. However, as Pb and Bi atoms are not distinguishable by X-ray diffraction, the assignment of the

---

[*] Dr. R. Ababei, Prof. Dr. W. Massa, Dr. K. Harms, Dr. X. Xie, Prof. Dr. S. Dehnen
Fachbereich Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
E-mail: dehnen@chemie.uni-marburg.de
Homepage: http://www.uni-marburg.de/fb15/ag-dehnen
Priv.-Doz. Dr. F. Weigend
Institut für Nanotechnologie Karlsruher Institut für Technologie (KIT)
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen (Germany)
E-mail: florian.weigend@kit.edu

[**] This work was supported by the Deutsche Forschungsgemeinschaft (DFG) within the framework of GRK 1782. We thank Dr. U. Linne and J. Bamberger for ESI-MS measurements.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201307795.

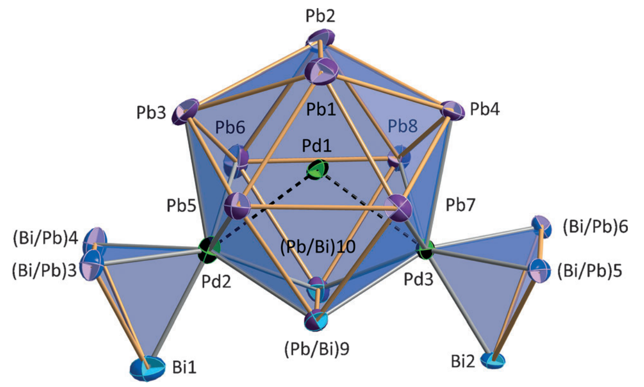

Figure 1. Structure of the anion in **1** (ellipsoids set at 50% probability), with Pb/Bi assignment according to DFT-based perturbation calculation. Selected bond lengths [Å] and angles [°]: Bi–(Bi/Pb) 2.965(2)–3.004(2), (Bi/Pb)–(Bi/Pb) or (Pb/Bi)–(Pb/Bi) 3.002(2)–3.036(2), Pb–Pb 3.118(2)–3.382(3), Pb–(Bi/Pb) 3.158(2)–3.208(2), Pd–Bi 2.744(3)–2.750(3), Pd–(Bi/Pb) 2.781(3)–2.963(3), Pd1–Pb 2.823(3)–3.035(3), Pd2,3–Pb 2.905(3)–2.938(3), Pd–Pd 2.754(4)–2.769(4); Pd2-Pd1-Pd3 106.4(1).

atoms to the atomic positions was done by means of quantum chemical calculation: The quantities known from the experiment (charge $q=-4$, Bi/Pb ratio of 6:10, atomic coordinates) were used for the optimum choice of the reference wavefunction that was subject to perturbational treatment,[21] which served to determine preferred sites for the lighter versus the heavier atom. A DFT calculation (density functional theory with BP86 functional[22] and dhf-TZVP bases,[23] compensation of the negative charge with the conductor-like screening model[24]) performed with the program system TURBOMOLE[25] with an average nuclear charge at each of the 16 Pb/Bi positions, $Z_{\mathrm{av}}=(10\,Z_{\mathrm{Pb}}+6\,Z_{\mathrm{Bi}})/16=82.375$, was performed for $q=-4$, yielding a stable closed-shell occupation (HOMO–LUMO gap of 1.2 eV). It was shown previously[21] that the first-order energy change upon change of the nuclear charge for each position can easily be calculated from the electrostatic potential at the respective position. As shown in Figure S11, this first-order estimation indicates that positions labeled in Figure 1 as Bi1 and Bi2 are clearly preferred by Bi atoms (ca. 90 kJ mol^{-1}), whereas positions Pb1–Pb8 are preferred by Pb atoms (Pb1 and Pb2 by ca. 95 kJ mol^{-1}, Pb3 and Pb4 by ca. 60 kJ mol^{-1}, Pb5–8 by ca. 30 kJ mol^{-1}). For the six positions (Bi/Pb)3–6 and (Pb/Bi)9,10, Bi atoms are preferred by ca. 30–50 kJ mol^{-1}. The immediate conclusion from these treatments would be a composition of eight Pb and eight Bi atoms for the system and thus a charge of −2, which was not realized in the crystal. For the actual charge of −4, ten Pb and six Bi atoms are thus required, four of which are predicted to reside at four of the six positions (Bi/Pb)3–6 and (Pb/Bi)9,10. Indeed, energies for compounds with any distribution of four Bi and two Pb atoms at these six positions are similar (after full DFT treatment including optimization of structure parameters).

The intuitively assigned distribution would comprise two (η^3-Bi$_3$)$^-$ units attached to a $(\mathrm{Pd_2Pb_{10}})^{2-}$ icosahedron (optimized in C_{2v} symmetry). However, two isomers were found, which are slightly more favorable in energy (ca. 20 kJ mol^{-1}). For both, positions labeled (Pb/Bi)9 and (Pb/Bi)10 are occupied by Bi atoms. For the first, (Bi/Pb)3 and (Bi/Pb)5 (or equally (Bi/Pb)4 and (Bi/Pb)6) are occupied by Pb atoms (C_s symmetry); for the second, (Bi/Pb)3 and (Bi/Pb)6 (or equally (Bi/Pb)4 and (Bi/Pb)5) are Pb atoms (C_2 symmetry). Comparison of calculated and measured distances indicates no preference of one of the three isomers. Mean values and standard deviations for all distances below 3.50 Å are similar, 5.2 ± 4.0 pm for C_{2v}, 5.4 ± 4.4 pm for C_s and 5.2 ± 5.2 pm for C_2. Smallest errors, 5.0 ± 3.9 pm, are found for the averaged atom distribution at the six positions in question (realized by pseudo atoms with $Z=82.666$). These numbers have to be related to comparably large scattering in measured data, for example, distances ranging from 2.870 to 2.969 Å for Pd2,3-(Pb/Bi)9,10 or distances ranging from 2.967 to 3.039 Å in the (η^3-Bi$_{3-x}$Pb$_x$) rings.

Most probable is thus the co-existence of all of these isomers that may be summarized as $\{\mathrm{Pd@Pb_{10-2\mathit{x}}Bi_{2\mathit{x}}}[\mathrm{Pd}(\eta^3\text{-}\mathrm{Bi_{3-\mathit{x}}Pb_{\mathit{x}}})]_2\}^{4-}$ ($x=0$, 1). Given that the situation in the solid state and solution dynamics are similar, which does not necessarily need to be the case, this is also in line with the findings of ESI mass spectra of the single crystals, for which apart from Bi$_3$ fragments (as released from the first isomer) also Bi$_2$Pb units (fragments of the other two isomers) are observed with similar abundances (SI, Figure S8; as confirmed previously,[19] the precursor itself, as a potential source of impurity, does not produce significant amounts of these fragments under ESI-MS conditions). Additionally, also a species with one (Bi$_3$)$^-$ and one (Bi$_2$Pb)$^{2-}$ ring (no symmetry) could exist, representing a hybrid of all of the situations. The observed ^{207}Pb chemical shifts also suggest a mixture of isomers.

The central $(\mathrm{Pd_2Pb_{10-2\mathit{x}}Bi_{2\mathit{x}}})^{2-}$ icosahedron that embeds a third Pd atom is similar to the topology of known $[\mathrm{M@E_{12}}]^{q-}$ anions (M/E/q = Ir/Sn/3;[26a] Ni/Pb/2,[26b] Pd/Pb/2,[26b] Pt/Pb/2[26b,c]), which were generated by the use of $(\mathrm{E_9})^{4-}$ (E = Sn, Pb) and represent homoatomic stannaspherene or plumbaspherene cages, according with Wade–Mingos[27] 26-electron *closo*-clusters. However, in **1**, the icosahedron itself is a pallada-plumbaspherene (or a pallada-bisma-plumbaspherene in case of the other isomers), thus heterometallic in nature, which has only been described so far for the Ni/Bi or Zn/Bi icosahedra in *closo*-$[\mathrm{Ni_{0.334}@\{Bi_6Ni_6(CO)_8\}}]^{4-}$[4] or in $[\mathrm{Zn_9Bi_{11}}]^{5-}$,[28a] as well as for the central, cationic $[\mathrm{Bi_{10}Au_2}]^{6+}$ heteroicosahedron in $[\mathrm{Bi_{10}Au_2}](\mathrm{SbBi_3Br_9})_2$.[28b] Naturally, with two of the icosahedral sites substituted by Pd atoms, the electron number is different from those of the plumbaspherenes, and thus requires electron donating ligands to achieve an isoelectronic situation.

The Pb–Pb distances (3.118(2)–3.382(3) Å) are in good agreement with the values found for other polyplumbide cages as in $[\mathrm{M@Pb_9(CO)_3}]^{4-}$ (M = Cr, Mo, W; Pb–Pb 3.03-3.41 Å),[29] $[\mathrm{Ni@Pb_{10}}]^{2-}$,[30a] $[\mathrm{Cu@Pb_9}]^{3-}$,[30b] or $[\mathrm{M@Pb_{12}}]^{2-}$ (M = Ni, Pd, Pt; Pb–Pb 3.02–3.23 Å).[26b,c] The Bi–Bi/Pb distances (2.965(2)–3.004(2) Å) are within those observed at other Bi-containing polyanions, such as Bi/Ni (2.954(1)–3.1204(6) Å)[4] or Zn/Bi (3.1072(8)–3.3121(9) Å)[28a] heteroatomic clusters, the quoted La/In/Bi cluster (2.9724(9)–3.3847(7) Å),[18] or the (Bi$_4$)$^{2-}$ ring (2.936(2)–2.967(2) Å),[31] and somewhat shorter than in Bi-containing polycations like $[M@Bi_{10}]^{q+}$ ($M/q = Pd/4$, $Au/5$; 3.082(2)–3.198(2) Å).[28b,32] Together with the interstitial atom, the three Pd atoms adopt an angular arrangement (Pd-Pd-Pd 106.4(1)°, Pd···Pd 2.754–2.769(4) Å). The distances compare well with values reported for $[Pd_2@Ge_{18}]^{4-}$ (2.831(1) Å),[33] or those within $[Pd_3@Sn_8Bi_6]^{4-}$ (2.756(2)–2.774(2) Å);[17] unlike in **1**, the Pd_3 unit of the latter formed an equilateral triangle and was completely embedded within the Sn/Bi cage. The only further example for an open arrangement of three Group 10 metals within an intermetalloid cluster is given in $[(Ni\text{-}Ni\text{-}Ni)@(Ge_9)_2]^{4-}$ with a straight alignment of three nickel atoms within and on the shared apex of two Ni-capped $(Ge_9)^{2-}$ cages.[34]

The most intriguing difference of the anion in **1** with all known homoatomic, heteroatomic, or intermetalloid Zintl anions is the presence of the triangular $(Bi_{3-x-}Pb_x)^{(x+1)-}$ unit, which, in agreement with the ESI-MS data, may be either $(Bi_3)^-$, thus the second monocyclic polybismutide anion beside the square $(Bi_4)^{2-}$, or $(Bi_2Pb)^{2-}$. In both cases, the cycle contains 16 valence electrons in the sum, thus two electrons more than a hypothetic "$(Bi_3)^+$", which would be isoelectronic with the two-electron Hückel-aromatic cyclopropenylium cation $(C_3H_3)^+$.[35,36] Thus, it should represent an η^3-four-electron ligand to contribute to a 14-electron fragment $[Pd(\eta^3\text{-}Bi_{3-x}Pb_x)^{(x+1)-}]$, which serves to accomplish the required electron number for a *closo*-cluster according to Wade–Mingos rules, as most simply explained on the isomer with two $(Bi_3)^-$ rings ($x = 0$): in the presence of two transition-metal atoms, the icosahedron should comprise a total of 70 valence electrons to match the number of $2n + 2 = 26$ skeleton electrons upon subtraction of *exo*-cluster electrons. Indeed, 10 Pb atoms plus 2 $[Pd(Bi_3)]^-$ fragments plus 1 interstitial Pd^0 atom plus 2 additional negative charges result in $10 \times 4 + 2 \times 14 + 0 + 2 = 70$ valence electrons. Identical numbers are obtained for the Pb/Bi-exchanged isomers ($x = 1$).

We investigated by quantum-chemical treatments (BP86/dhf-TZVP), whether regarding the isomer with Pb atoms at positions (Pb/Bi)9,10 (that is, $x = 0$) as "$[Pd@Pb_{12}]^{2-}$ with two Pb atoms replaced with $[Pd(\eta^3\text{-}Bi_3)]^-$ units" is justified, and whether an analogous description is possible for the isomer with Bi atoms at those positions. At first, structure parameters of this isomer were optimized, next, the $[Pd(\eta^3\text{-}Bi_3)]^-$ units were replaced with Pb atoms, and finally, atomic charges were calculated for the resulting three systems (for $[Pd@Pb_{12}]^{2-}$ and for $[Pd(\eta^3\text{-}Bi_3)]^-$ without further optimization of structure parameters). We employed the method by Bader[37] in a preliminary implementation in a local version of TURBOMOLE.[25]

In $[Pd@Pb_{12}]^{2-}$, the central Pd atom carries a comparably high charge of 0.61 e⁻, the two Pb atoms that replaced the two $[Pd(Bi_3)]^-$ units (labeled as Pb11 and Pb12) comprise a charge of 0.26 e⁻ each, Pb1 and Pb2 of 0.14 e⁻; charges for the other atoms are below 0.1 e⁻. For the $[Pd(Bi_3)]^-$ unit, 0.42 e⁻ is found at the Pd atom and ca. 0.2 e⁻ for each Bi atom. Replacement of a Pb atom with this unit without recalculation of density and charges corresponds to summarizing of the numbers of the last two columns in Table 1. This leads to a charge of −0.68 e⁻ for the respective Pd atoms. Validation of this description is evident by the similarity of these charges with that resulting from the density calculated for the entire system (first column in Table 1). The charges of the three Pd atoms are lower by ca. 0.1 e⁻, that of Pb1 and Pb2 higher by ca. 0.15 e⁻, and differences for the other atoms are 0.03 e⁻ or smaller; the accumulated changes in atomic charges amount to 0.77 e⁻. These small differences support the above description of the C_{2v}-symmetric anion in **1**.

Table 1: Atomic charges according to a Bader analysis based on the BP86/dhf-TZVP density for the cluster ion in **1** assigned as $\{Pd@Pb_{10}[Pd(\eta^3\text{-}Bi_3)]_2\}^{4-}$ ($x = 0$; structure parameters optimized within C_{2v} symmetry), for the modified ion $[Pd@Pb_{12}]^{2-}$ and for the $[Pd(\eta^3\text{-}Bi_3)]^-$ fragment.

Atoms	Atomic charges [e⁻]		
	$\{Pd@Pb_{10}[Pd(\eta^3\text{-}Bi_3)]_2\}^{4-}$	$[Pd@Pb_{12}]^{2-}$ [a]	$[Pd(\eta^3\text{-}Bi_3)]^-$ [a]
Pb1,2	−0.27	−0.14	–
Pb3–8	−0.09...0.10	−0.08...0.09	–
Pb9,10	−0.01	−0.04	–
Pd2,3/Pb11,12	−0.58	−0.26	−0.42
Pd1	−0.52	−0.61	–
Bi	−0.18...0.22	–	−0.19...0.20

[a] Without further structure optimization.

For the isomers with interchanged positions (Pb/Bi)9,10 and (Bi/Pb)3,5 (or (BiPb)3,6)), the respective description would be $\{Pd@Pb_8Bi_2[Pd(\eta^3\text{-}Bi_2Pb)]_2\}^{4-}$ ($x = 1$), with "two $[Pd(\eta^3\text{-}Bi_2Pb)]^{2-}$ units replacing two Pb atoms in $[Pd@Pb_{10}Bi_2]^{\pm 0}$". This would, however, mean a rather inhomogeneous assignment of negative charges, which is not expected for a polyanion consisting of elements with similar electronegativities. In fact, the analogous calculation of charge differences between fragments $[Pd(\eta^3\text{-}Bi_2Pb)]^{2-}$ plus $[Pd@Pb_{10}Bi_2]$ and the entire cluster $\{Pd@Pb_8Bi_2[Pd(\eta^3\text{-}Bi_2Pb)]_2\}^{4-}$ (both isomers, C_s and C_2) yields accumulated values of ca. 3.1 e⁻, indicating an equilibration of charges in the "real" cluster and thus a significant deviation from this simple model.

Whereas in the reported bimetallic $[Pd@Pb_{10}]^{2-}$ plumbaspherene the Pb atoms are all equivalent on the NMR timescale, the distinct differences of the Pb atoms in **1** is reflected by ^{207}Pb NMR spectroscopy investigations of solution of single crystals in DMF at −5 °C (SI, Figure S10). One observes four peaks, one of which accords with the precursor signal (−3870 ppm), indicating that the sample included microcrystalline or powdery precursor, which tends to precipitate along with the products.[14–17] The three product peaks are very broad, most likely representing an overlay of several signals of Pb atoms with similar electronic situations.

To correlate the order of the experimentally observed ^{207}Pb chemical shifts, as well as the number and broadness of the signals, with the anionic structure, the electrostatic

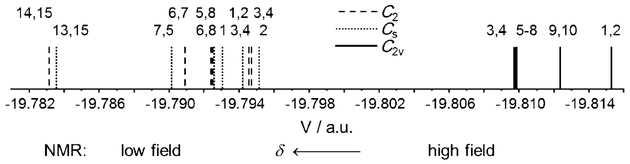

Figure 2. Electrostatic potential at the (possible) Pb nuclei *i* ($i=1$–15), without the contribution from the respective nucleus *i*, in the three discussed isomers of $\{Pd@Pb_{10-2x}Bi_{2x}[Pd(\eta^3\text{-}Bi_{3-x}Pb_x)]_2\}^{4-}$.

potential at each atomic position *i* was calculated (without the contribution of the nuclear charge at *i*) for each of the three isomers (Figure 2).

Both chemical shifts and electrostatic potential values at the nuclei are sensitive to the chemical environment in a similar manner and thus the latter may serve at least for a qualitative picture for the interpretation of the measured ^{207}Pb NMR spectra. There are two explanations possible in principle: 1) only the C_{2v}-symmetric isomer is observed, with three groups of signals being distant from each other by approximately equal values; however, in this case, one would not be in the position to explain the observed broadness of all three peaks; 2) the co-existence of the three isomers is observed, with the three signal groups representing the three "packages" of electrostatic potential values shown in Figure 2; here, the relative position of the signal groups are not exactly equidistant, but still well-separated, with each of them covering a considerable range in agreement with the broad signals, even according with the peak with the smallest width arising in lowest field, the broadest appearing in moderate low field, and a somewhat less broad high-field signal (SI, Figure S10). These findings once more support the second interpretation of a co-existence of the isomers as the most probable.

We conclude that the employment of a pseudo-homoatomic precursor anion $(Pb_2Bi_2)^{2-}$ instead of homoatomic $(Pb_9)^{4-}$ significantly affects the product formation in reactions with $[Pd(PPh_3)_4]$: a trimetallic cluster anion with 19 atoms is formed with a unique 14-electron $[Pd(\eta^3\text{-}Bi_{3-x}Pb_x)^{(x+1)-}]$ unit ($x=0$, 1) that formally replaces two Pb atoms of the Pd-centred plumbaspherene obtained upon use of $(Pb_9)^{4-}$. Although the intuitively suggested replacement of the Pb atoms with $[Pd(\eta^3\text{-}Bi_3)]^-$ is supported by only small differences in atomic charges as compared to the $[Pd@Pb_{12}]^{2-}$ anion, a combination of comprehensive experimental and quantum chemical studies show that a co-existence of several isomers with Pb/Bi exchange on six atomic positions is most likely.

Experimental Section

Synthesis: All manipulations were performed under an argon atmosphere (standard Schlenk or glovebox techniques) using dry and freshly destilled solvents stored under Ar. [2.2.2]crypt (Cryptofix, Merck) was dried in vacuum for 13 h. Tetrakis(triphenylphosphine)-palladium(0) (99%, Aldrich) was used as received. For details of the synthesis and analyses of **1**, see the Supporting Information.

Single-crystal X-ray diffraction: Data collection was performed at 100 K on a D8 Quest area detector system (Bruker AXS) using Mo Kα radiation. A numerical absorption correction based on measured crystal faces has been applied. The structure was solved by direct methods and refined with SHELX software.[38] For details see the Supporting Information. CCDC 951743 (**1**) contains 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.

Quantum chemical methods: DFT treatments were carried out with the program system TURBOMOLE[25] using the BP86 functional[22] with dhf-ECPs[39] and dhf-TZVP basis sets[23] as well as respective auxiliary basis sets;[40] spin–orbit effects are treated self-consistently within the DFT procedure.[41] The COSMO solvation model[24] was applied with default parameters. Atomic charges were calculated according to Bader's mothod,[37] with a preliminary implementation in our local version of TURBOMOLE, mainly following the technique proposed by Rodriguez et al.[42]

Received: September 4, 2013

Keywords: ^{207}Pb NMR spectroscopy · intermetalloid clusters · isolobal analogy · perturbational treatment · X-ray diffraction

[1] a) J. D. Corbett, *Angew. Chem.* **2000**, *112*, 682; *Angew. Chem. Int. Ed.* **2000**, *39*, 670; b) T. F. Fässler, S. D. Hoffmann, *Angew. Chem.* **2004**, *116*, 6400; *Angew. Chem. Int. Ed.* **2004**, *43*, 6242; c) S. C. Sevov, J. M. Goicoechea, *Organometallics* **2006**, *25*, 5678; d) S. Scharfe, F. Kraus, S. Stegmaier, T. F. Fässler, *Angew. Chem.* **2011**, *123*, 3712; *Angew. Chem. Int. Ed.* **2011**, *50*, 3630; e) T. F. Fässler, *Zintl Ions, Principles and Recent Developments*, Springer, Berlin, **2011**, p. 91.

[2] M. J. Moses, J. C. Fettinger, B. W. Eichhorn, *Science* **2003**, *300*, 778.

[3] S. Stegmaier, T. F. Fässler, *J. Am. Chem. Soc.* **2011**, *133*, 19758.

[4] J. M. Goicoechea, M. W. Hull, S. C. Sevov, *J. Am. Chem. Soc.* **2007**, *129*, 7885.

[5] a) B. Zhou, M. S. Denning, L. D. Kays, J. M. Goicoechea, *J. Am. Chem. Soc.* **2009**, *131*, 2802; b) J.-Q. Wang, S. Stegmaier, T. F. Fässler, *Angew. Chem.* **2009**, *121*, 2032; *Angew. Chem. Int. Ed.* **2009**, *48*, 1998.

[6] F. Li, A. Munos-Castro, S. C. Sevov, *Angew. Chem.* **2012**, *124*, 8709; *Angew. Chem. Int. Ed.* **2012**, *51*, 8581.

[7] T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347.

[8] H.-G. von Schnering, W. Hönle, *Chem. Rev.* **1988**, *88*, 243.

[9] L. Xu, S. Bobev, J. El-Bahraoui, S. C. Sevov, *J. Am. Chem. Soc.* **2000**, *122*, 1838.

[10] a) M. Waibel, F. Kraus, S. Scharfe, B. Wahl, T. F. Fässler, *Angew. Chem.* **2010**, *122*, 6761; *Angew. Chem. Int. Ed.* **2010**, *49*, 6611; b) M. Waibel, T. Henneberger, L.-A. Jantke, T. F. Fässler, *Chem. Commun.* **2012**, *48*, 8676; c) S. Stegmaier, M. Waibel, A. Henze, L.-A. Jantke, A. J. Karttunen, T. F. Fässler, *J. Am. Chem. Soc.* **2012**, *134*, 14450.

[11] F. Lips, I. Schellenberg, R. Pöttgen, S. Dehnen, *Chem. Eur. J.* **2009**, *15*, 12968.

[12] a) S. C. Critchlow, J. D. Corbett, *Inorg. Chem.* **1982**, *21*, 3286; b) F. Lips, M. Raupach, W. Massa, S. Dehnen, *Z. Anorg. Allg. Chem.* **2011**, *637*, 859; c) U. Friedrich, M. Neumeier, C. Koch, N. Korber, *Chem. Commun.* **2012**, *48*, 10544.

[13] L. Xu, S. C. Sevov, *Inorg. Chem.* **2000**, *39*, 5383.

[14] F. Lips, S. Dehnen, *Angew. Chem.* **2009**, *121*, 6557; *Angew. Chem. Int. Ed.* **2009**, *48*, 6435.

[15] F. Lips, S. Dehnen, *Angew. Chem.* **2011**, *123*, 986; *Angew. Chem. Int. Ed.* **2011**, *50*, 955.

[16] a) F. Lips, R. Clérac, S. Dehnen, *Angew. Chem.* **2011**, *123*, 991; *Angew. Chem. Int. Ed.* **2011**, *50*, 960; b) F. Lips, M. Hołyńska, R. Clérac, U. Linne, I. Schellenberg, R. Pöttgen, F. Weigend, S. Dehnen, *J. Am. Chem. Soc.* **2012**, *134*, 1181.

[17] F. Lips, R. Clérac, S. Dehnen, *J. Am. Chem. Soc.* **2011**, *133*, 14168.

[18] B. Weinert, F. Weigend, S. Dehnen, *Chem. Eur. J.* **2012**, *18*, 13589.

[19] R. Ababei, J. Heine, M. Hołyńska, G. Thiele, B. Weinert, X. Xie, F. Weigend, S. Dehnen, *Chem. Commun.* **2012**, *48*, 11295.

[20] Crystallization at room temperature yields another polymorph (monoclinic, $P2_1/n$) containing the same anion; as it is a reflection twin in (100) with heavy rotational disorder of the pseudospherical counterion complexes, the quality of the results is lower than that of the other polymorph presented herein.

[21] a) F. Weigend, C. Schrodt, R. Ahlrichs, *J. Chem. Phys.* **2004**, *121*, 10380; b) F. Weigend, C. Schrodt, *Chem. Eur. J.* **2005**, *11*, 3559.

[22] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[23] F. Weigend, A. Baldes, *J. Chem. Phys.* **2010**, *133*, 174102.

[24] A. Klamt, G. J. Schürmann, *Chem. Soc. Perkin Trans. 1* **1993**, *5*, 799.

[25] TURBOMOLE V6.4 2012, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.

[26] a) J.-Q. Wang, S. Stegmaier, B. Wahl, T. F. Fässler, *Chem. Eur. J.* **2010**, *16*, 1793; b) E. N. Esenturk, J. Fettinger, B. Eichhorn, *J. Am. Chem. Soc.* **2006**, *128*, 9178; c) E. N. Esenturk, J. Fettinger, Y.-F. Lam, B. Eichhorn, *Angew. Chem.* **2004**, *116*, 2184; *Angew. Chem. Int. Ed.* **2004**, *43*, 2132.

[27] a) K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1; b) D. M. P. Mingos, *Nature Phys. Sci.* **1972**, *236*, 99; c) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311.

[28] a) J. M. Goicoechea, S. C. Sevov, *Angew. Chem.* **2006**, *118*, 5271; *Angew. Chem. Int. Ed.* **2006**, *45*, 5147; b) B. Wahl, L. Kloo, M. Ruck, *Angew. Chem.* **2008**, *120*, 3996; *Angew. Chem. Int. Ed.* **2008**, *47*, 3932.

[29] a) L. Yong, S. D. Hoffman, T. F. Fässler, *Eur. J. Inorg. Chem.* **2005**, 3663; b) J. Campbell, H. P. A. Mercier, H. Franke, D. P. Santry, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.* **2002**, *41*, 86; c) B. W. Eichhorn, R. C. Haushalter, *J. Chem. Soc. Chem. Commun.* **1990**, 937.

[30] a) E. N. Esenturk, J. Fettinger, B. Eichhorn, *Chem. Commun.* **2005**, 247; b) S. Scharfe, T. F. Fässler, S. Stegmaier, S. D. Hoffmann, K. Ruhland, *Chem. Eur. J.* **2008**, *14*, 4479.

[31] a) N. Kuznetsov, T. F. Fässler, *Z. Anorg. Chem.* **2002**, *628*, 2537; b) A. Cisar, J. D. Corbett, *Inorg. Chem.* **1977**, *16*, 2482.

[32] a) M. Ruck, V. Dubenskyy, T. Söhnel, *Angew. Chem.* **2003**, *115*, 3086; *Angew. Chem. Int. Ed.* **2003**, *42*, 2978; b) V. Dubenskyy, M. Ruck, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2458; c) B. Wahl, M. Erbe, A. Gerisch, L. Kloo, M. Ruck, *Z. Anorg. Chem.* **2009**, *635*, 743.

[33] J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2005**, *127*, 7676.

[34] J. M. Goicoechea, S. C. Sevov, *Angew. Chem.* **2005**, *117*, 4094; *Angew. Chem. Int. Ed.* **2005**, *44*, 4026.

[35] The tendency of $[\mathrm{Bi}_x]^q$ to form isoelectronic aggregates is known from the 40-electron $[\mathrm{Bi}_9]^{5+}$ cation,[36] or the 18-electron, ozone-like $[\mathrm{Bi}_3]^{3-}$ within the heteroatomic *closo*-clusters $[\mathrm{Bi}_3\mathrm{M}_2(\mathrm{CO})_6]^{3-}$ (M = Cr, Mo).[4]

[36] a) R. M. Friedman, J. D. Corbett, *Inorg. Chem.* **1973**, *12*, 1134; b) H. von Benda, A. Simon, W. Bauhofer, *Z. Anorg. Allg. Chem.* **1978**, *438*, 53; c) M. Ruck, *Z. Anorg. Allg. Chem.* **1998**, *624*, 521.

[37] R. F. W. Bader, *Acc. Chem. Res.* **1985**, *18*, 9.

[38] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

[39] a) B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563; b) K. A. Peterson, D. Figgen, M. Dolg, H. Stoll, *J. Chem. Phys.* **2007**, *126*, 124101.

[40] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[41] a) M. K. Armbruster, F. Weigend, C. van Wüllen, W. Klopper, *Phys. Chem. Chem. Phys.* **2008**, *10*, 1748; b) A. Baldes, F. Weigend, *Mol. Phys.* **2013**, DOI: 10.1080/00268976.2013.802037.

[42] J. Rodriguez, A. Köster, P. W. Ayers, A. Santo-Valle, A. Vela, G. Merino, *J. Comput. Chem.* **2008**, *29*, 1082.