Cluster Compounds

Molecular Lead Clusters—From Unexpected Discovery to Rational Synthesis

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In memory of Peter Böttcher

Anionic cluster compounds of lead have been known for more than one century.[1] The first species, $NaPb_4$ and KPb_2, were obtained as early as 1891 by Joannis from the reaction of alkali metals with lead in liquid ammonia.[2] Extensive exploration of this chemistry was done by Kraus, Zintl, and others during the first decades of the 20th century.[3] Addition of cryptands finally allowed for the isolation of macrocrystalline material and the structural characterization of several species, such as $[Pb_5]^{2-}$, $[Pb_9]^{4-}$, and $[Pb_9]^{3-}$.[4] The structures observed may all be understood using Wade's electron-counting rules. Molecular lead clusters bearing hydrocarbon or related substituents are unknown to date. There are some reports, however, about transition-metal carbonyl complexes of anionic lead clusters.[5] Only for the lighter congeners germanium and tin, are organic- or organoelement-substituted species available.[6] For most of these compounds the synthesis was not by derivatization of anionic clusters, but proceeded through cluster formation from smaller units.[7] Wade's rules are usually, but not generally obeyed for such compounds or for the related clusters of the neighboring elements of Group 13.[8]

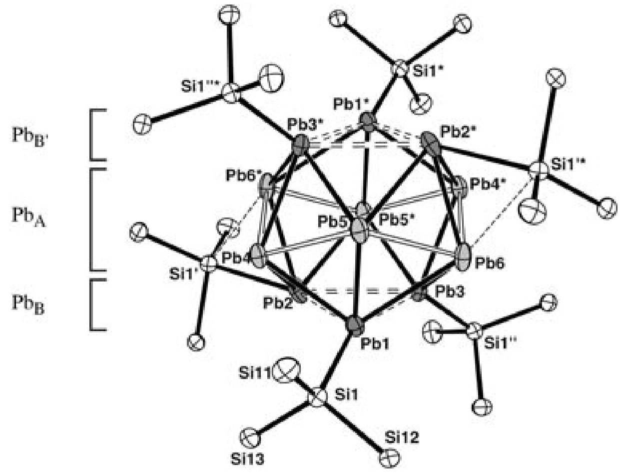

Figure 1. Structure of **1** (C and H atoms omitted for clarity). Selected bond lengths [pm]: Pb1-Pb2 336.83(10), Pb1-Pb3 332.39(9), Pb1-Pb4 311.33(13), Pb1-Pb5 310.7(5), Pb1-Pb6 334.81(12), Pb2-Pb3 338.87(11), Pb2-Pb4 319.99(10), Pb2-Pb5* 321.6(2), Pb2-Pb6* 305.61(13), Pb3-Pb6 323.21(12), Pb3-Pb4* 310.21(12), Pb3-Pb5* 311.4(9), Pb4-Pb5 326.9(6), Pb4-Pb6* 324.49(10), Pb5-Pb6 322.9(9), Pb1-Si1 269.5(2), Pb2-Si1′ 308.5(2), Pb3-Si1″ 263.7(2), Pb6-Si1′ 328.3(2).

We have investigated the reaction of dihypersilylplumbylene $[\{(Me_3Si)_3Si\}_2Pb]$ ($[Hyp_2Pb]$) with phosphine in inert solvents, such as toluene or *n*-pentane. As main product the heterocubane $[(HypPPb)_4]$ (Hyp = hypersilyl, $Si(SiMe_3)_3$) was isolated.[9] At short reaction times and low temperature several intermediates could be detected by NMR spectroscopy. In attempts to isolate one of these species, the initial reaction mixture was stored at −60 °C for several days. Indeed a few dark brown well formed crystals were found in a matrix of unconsumed blue Hyp_2Pb. To our surprise, the structure analysis revealed that the compound contains no phosphorous, but is the molecular lead cluster $[Pb_{12}Hyp_6]$ (**1**).[10] Despite of disordering of the lead core about the crystallographic threefold axis, it can be shown that the model in Figure 1 is the only one having sensible Pb–Pb separations that is consistent with the diffraction data. The hypersilyl groups are well ordered, however, and clearly determine the arrangement of the molecules within the crystal. The enveloped twelve lead atoms constitute a distorted icosahedron. Six atoms (Pb_A) bear no substituent and form a puckered ring with chair conformation (the belt). Each of the remaining six atoms (Pb_B,$Pb_{B'}$) bears a hypersilyl group. Together they form two three-membered rings above and below the central Pb_6 belt. The Pb–Pb separations between neighboring lead atoms range from 305.6(1) to 339.0(1) pm. The largest distances are found between the lead atoms of type Pb_B (av. 336.1 pm), shorter ones between the lead atoms of the belt (Pb_A) (av. 324.8 pm), and the shortest between Pb_A and Pb_B (av. 316.5 pm). Although there is some overlap between these ranges, the description of the polyhedron as an icosahedron with two opposite open faces would be in line with Wade's rules, since with 30 electrons for the Pb_{12} skeleton a *arachno*-type cluster is expected. A further structural detail of compound **1** is noteworthy. Whereas four hypersilyl groups are bonded in the expected terminal fashion, the other two substituents each bridge two lead atoms. As a consequence the bridged edge (Pb2–Pb6*) is the shortest within the cluster.

Unfortunately, compound **1** can only be obtained in traces and no spectroscopic data may be provided to date. The question arises how this cluster is formed in the reaction of $PbHyp_2$ and PH_3 and if there are alternative routes giving access to larger quantities.

NMR spectroscopy data of the reaction mixture as well as the composition of the isolated intermediates, such as the cyclic dimer $[\{Hyp(H)PPbHyp\}_2]$ and of the main products [Eq. (1)] indicate that after the initial addition step, ligand

$$[PbHyp_2] + PH_3 \rightarrow [(HypPPb)_4] + Hyp_2 + HypH + HypPH_2 + Pb + \mathbf{1}(\text{traces}) + \ldots \quad (1)$$

exchange between the lead and phosphorus centers occurs, which leads to the adduct $[Hyp(H)Pb \leftarrow PH_2Hyp]$. After elimination of HypH and/or H_2 this adduct may either give the Pb–P heterocycles or on dissociation may yield $HypPH_2$ and the elusive hydridoplumbylene [Pb(H)Hyp]. Recently a

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related hydridoplumbylene with an extremely bulky *meta*-terphenyl substituent was postulated by Power et al. as the key intermediate in the formation of the first diplumbyne.[11] In contrast to this particular kinetically stabilized diplumbyne, we expect that the analogous but less-shielded [Pb_2Hyp_2], which would form from dimerization and hydrogen loss of [Pb(H)Hyp], would not be stable under ambient conditions, but owing to its bis(plumbylene) nature would undergo addition and insertion reactions, thus possibly resulting in the formation of stable or less stable lead cluster compounds.

To support our assumption we looked for a rational synthesis of [Pb(H)Hyp]. At first we investigated the reaction of the [$PbHyp_2$] with several hydride sources, such as B_2H_6, $[BH_4]^-$ and $[AlH_4]^-$ under various conditions, but only found the formation of lead and HypH (with B_2H_6) or the reversible formation of adducts (with $NaBH_4$ and $LiAlH_4$). Finally we succeeded by treating [$PbHyp_2$] with the triphenylphosphine adduct of copper hydride [Eq. (2); L = PPh_3].[12] During the reaction at −20 °C almost no lead precipitated, and from the resulting dark brown solution appreciable amounts of dark brown crystals were isolated. The structural analysis reveals that indeed a lead cluster had been formed, not the expected [$Pb_{12}Hyp_6$] (**1**), however, but the novel cluster [$Pb_{10}Hyp_6$] (**2**).

$$[\mathrm{PbHyp_2}] + [\mathrm{CuH}\cdot \mathrm{L}]_6 \rightarrow \\ \mathbf{2} + [\mathrm{HypCuL_2}] + [\mathrm{Hyp_3H_6Cu_9L_2}] + \mathrm{HypH} + \ldots \qquad (2)$$

The NMR spectroscopic data from the crude reaction mixture shows that ligand exchange has taken place, since the main products, beside cluster compound **2** are HypH and the new hypersilyl copper(I) derivatives [$HypCu(PPh_3)_2$] and [$Hyp_3H_6Cu_9(PPh_3)_2$]. Small amounts of further products are present, however, which give rise to lowfield shifted ^{1}H NMR signals (δ = 0.6–0.8 ppm) as does compound **2** (δ = 0.64 ppm). We therefore assume that a mixture of several cluster compounds is produced, from which only the predominant and less-soluble species crystallizes easily. The best structural parameters were derived from specimens with cocrystallized benzene.[10] The whole molecule has crystallographic C_s symmetry and the Pb_{10} core approximately C_{3v} symmetry (Figure 2). The Pb_{10} polyhedron is best derived from a Pb_{12} icosahedron by replacing one trigonal face by a single lead atom. This picture would match the prediction made by Wade's rules which only hold for cluster compound **2** if it is formally composed from a [Hyp_6Pb_9]*hypho*-type cluster dianion (26 skeletal electrons) and a Pb^{2+} countercation (Figure 3). The Pb–Pb separations within the *hypho*-Pb_9 fragment (Pb1 to Pb6) of **2** differ only slightly (312.36(4)–320.99(5) pm) and are all within the same range found for compound **1** and lead cluster anions, whereas the three bonds to the capping atom Pb7 are significantly shorter (299.80(4)–300.58(6) pm) indicating higher bond orders, that is, less delocalized bonds. In contrast to **1**, all six hypersilyl groups are located at the puckered six-membered ring (Pb_A), whereas the capping Pb_3 triangle (Pb_B) only consists of "naked" Pb atoms. The hypersilyl groups are all bonded in a terminal fashion. The three Pb–Si bonds to the silicon atoms (Si4, Si4′, Si6) that lie more or less in the plane the unsubstituted lead triangle (Pb1, Pb2, and Pb2′), perhaps for steric reasons, are significantly longer (276.4(2)–277.8(4) pm) than the remaining ones (268.8(2)–270.0(3) pm).

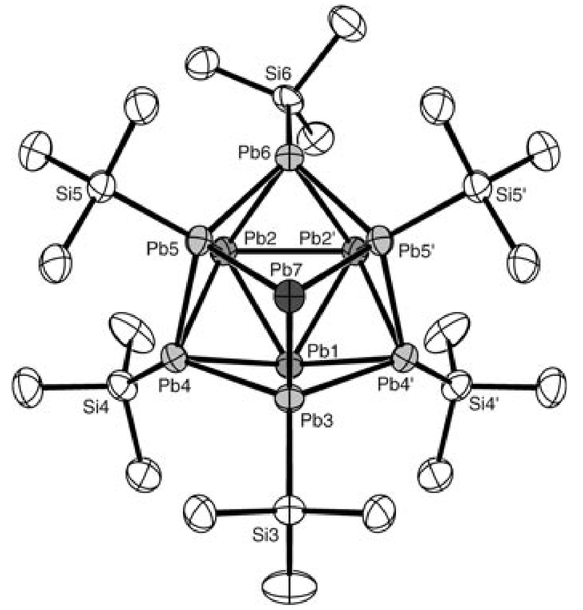

Figure 2. Structure of **2** (C and H atoms omitted for clarity). Selected bond lengths [pm] and angles [°]: Pb1-Pb2 320.11(5), Pb2-Pb2′ 320.99(5), Pb1-Pb3 314.00(6), Pb1-Pb4 320.45(4), Pb2-Pb4 319.39(4), Pb2-Pb5 312.36(4), Pb2-Pb6 319.44(5), Pb3-Pb4 314.98(3), Pb3-Pb7 300.58(6), Pb4-Pb5 315.38(4), Pb5-Pb6 316.05(4), Pb5-Pb7 299.80(4), Pb3-Si3 270.0(3), Pb4-Si4 276.4(2), Pb5-Si5 268.8(2), Pb-Si6 277.8(4); Pb3-Pb7-Pb5 86.94(1), Pb5-Pb7-Pb5′ 86.46(1).

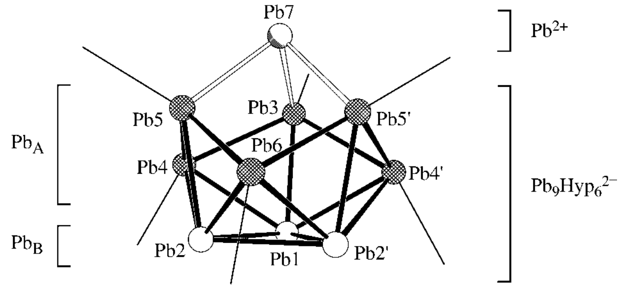

Figure 3. The $Pb_{10}Si_6$ skeleton of **2** illustrating the applicability of Wade's rules.

The ^{1}H NMR spectrum of **2** in [D_8]toluene at room temperature has only one signal at δ = 0.59 ppm for all the hypersilyl groups indicating a dynamic behavior of the $Pb_{10}Si_6$ core. On cooling, the resonance signal splits into two signals of equal intensity ($\delta\nu$ = 18 Hz; T_c = 243–248 K) giving an approximate activation barrier of 50 kJ mol^{-} for the scrambling process. By ESI mass spectroscopy of compound **2** the molecular ion [$Pb_{10}Hyp_6$] was not found, instead the ion $[Pb_{10}Hyp_5]^+$ could be detected as particle of highest mass (*m*/*z* 3311). The UV/Vis spectra of **2** show strong absorptions across the whole visible spectral range with only two weakly pronounced maxima at 656 and 770 nm (both: ε = 49000).

At ambient temperature and if light is excluded, solid **2** is indefinitely stable under argon. In solution at room temperature **2** quickly decomposes, yielding elementary lead and initially nearly equal amounts of the octasilane Hyp-Hyp and the plumbylene [PbHyp$_2$].[13] Since the reaction rate is first order in **2**, the initial formation of "naked" lead clusters can be postulated. To get more information on this species we are currently studing the decomposition of **2** in inert polymer matrices.

Experimental Section

1: In a typical experiment LiPH$_2$·0.86 DME (1.0 g, 8.53 mmol) was treated with 2,6-di-*tert*-butylphenol (1.76 g, 8.53 mmol) at −70 °C in DME (25 mL). The solution was warmed slowly to room temperature, and the produced gaseous PH$_3$ fed into a Schlenk tube containing a dark blue solution of [PbHyp$_2$] (1.60 g, 0.89 mmol) in *n*-pentane (25 mL) at −60 °C. After warming it to −30 °C for 30 min the solution turned deep red and dark red solid material precipitated. The solution was decanted to another Schlenk tube and concentrated to about 3 mL. After storage of the solution at −60 °C for two weeks several dark brown rod-shaped crystals of **1** were found among large amounts of dark blue crystals of unconsumed [PbHyp$_2$].

2: A solution of [PbHyp$_2$] (3.01 g, 4.28 mmol) in toluene (20 mL) was added to a suspension of [{HCuPPh$_3$}$_6$] (1.40 g, 4.28 mmol) in toluene (30 mL) at −25 °C under intense stirring. After 25 min the reaction mixture was warmed to room temperature and stirred for another 20 min. The suspension turned from deep violet to brown. After the filtration and washing with toluene the filtrate was concentrated to 9 mL and cooled to −60 °C for 24 h. Dark brown rhombus-shaped crystals of **2** are obtained (0.73 g, 0.20 mmol, 47.0 %). ^{1}H NMR (400.13 MHz, [D$_6$]benzene, 25 °C): $\delta = 0.63$ ppm; ^{13}C NMR (100.62 MHz, [D$_6$]benzene, 25 °C): $\delta = 9.1$ ppm. MS (ESI; Et$_2$O/MeCN (4:1)): *m/z* (%): 3311 (100, M^+-Hyp), 2816 (8, [Pb$_{10}$Hyp$_3$]$^+$), 2113 (25, [Pb$_9$Hyp]$^+$), 2099 (43, [Pb$_9$Hyp−H−CH$_3$]$^+$, 717 (51, [Hyp$_2$MePb]$^+$).

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[1] Reviews: a) J. D. Corbett, *Struct. Bonding (Berlin)* **1997**, *87*, 157; b) T. F. Fässler in *Metal Clusters in Chemistry* (Eds.: P. Braunstein, L. A. Oro, P. R. Raithby), Wiley-VCH, Weinheim, **1998**, 1610–1642.

[2] C. R. Joannis, *C. R. Hebd. Seances Acad. Sci.* **1891**, *113*, 795; C. R. Joannis, *C. R. Hebd. Seances Acad. Sci.* **1892**, *114*, 587.

[3] See for example: C. A. Kraus, *J. Am. Chem. Soc.* **1907**, *29*, 1571; E. Zintl, J. Goubeau, W. Z. Dullenkopf, *Z. Phys. Chem. Abt. B* **1932**, *16*, 183.

[4] First reports: D. Kummer, L. Diehl, *Angew. Chem.* **1970**, *82*, 881; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 895; P. A. Edwards, J. D. Corbett, *Inorg. Chem.* **1976**, *15*, 903.

[5] See for example: B. W. Eichhorn, R. C. Haushalter, *J. Chem. Soc. Chem. Commun.* **1990**, 937.

[6] For a recent review see: A. Schnepf, *Angew. Chem.* **2004**, *116*, 680; *Angew. Chem. Int. Ed.* **2004**, *43*, 664.

[7] Very recently Sevov and Ugrinov reported some examples of nucleophilic addition reactions to anionic germanium clusters resulting in organoelement substituted cluster anions: A. Ugrinov, S. C. Sevov, *Chem. Eur. J.* **2004**, *10*, 3727 and literature cited herein.

[8] See: A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 4344; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532.

[9] S. L. Yao, Y. Xiong, K. W. Klinkhammer, unpublished results.

[10] Structural Analyses: Bruker AXS CCD SMART, Mo$_{K\alpha}$($\lambda = 0.71073$ Å); computer programs: SHELXS-97, PLATON, Siemens diffractometer software. Crystal data for **1** (Pb$_{12}$Si$_{24}$C$_{54}$H$_{162}$·C$_5$H$_{12}$): crystal size: 0.6 × 0.5 × 0.3 mm^3, rhombohedral (hex. setting), space group $R\bar{3}$, $a = 16.1051(3)$, $c = 41.6827(10)$ Å, $V = 9363.0(3)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.152$ g cm^{-3}, $F(000) = 5544$, μ(Mo$_{K\alpha}$) = 16.374 mm^{-3}, $T = 173$ K, 23 469 reflections, 5159 unique ($R_{int} = 0.1139$), structure solution by direct methods, refinement on F^2($2\theta_{max} = 56.6°$), 3637 unique (2σ), 192 parameters, 13 restraints, R_1 ($I > 2\sigma$) = 0.0452, wR_2 (all data) = 0.1137, GOF = 1.009, $\rho(e)$(min/max) = −0.930/1.630 e Å^{-3} (near Pb); absorption correction with MULABS ($T_{min}/T_{max} = 0.01649/0.05882$). Although the Pb$_{12}$ core is disordered about the threefold axis, only one model can be derived having meaningful Pb−Pb separations. All non-hydrogen atoms were refined anisotropically, H atoms riding with fixed thermal parameters. Crystal data for **2** (Pb$_{10}$Si$_{24}$C$_{54}$H$_{162}$·(C$_6$H$_6$)$_3$): crystal size: 0.3 × 0.3 × 0.2 mm^3, monoclinic, space group $P2_1/m$, $a = 15.6703(3)$, $b = 25.1007(5)$, $c = 18.6999(4)$ Å, $V = 6685.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.884$ g cm^{-3}, $F(000) = 3536$, μ(Mo$_{K\alpha}$) = 12.786 mm^{-3}, $T = 193$ K, 36 258 reflections, 9966 unique ($R_{int} = 0.0610$), structure solution by direct methods, refinement on F^2($2\theta_{max} = 50.2°$), 7175 unique (2σ), 224 parameters, 609 restraints, R_1 ($I > 2\sigma$) = 0.0275, wR_2 (all data) = 0.0523, GOF = 0.906, $\rho(e)$(min/max) = −1.138/0.884 e Å^{-3} (near Pb); absorption correction by equivalent reflections with MULABS ($T_{min}/T_{max} = 0.01320/0.04077$). All non-hydrogen atoms could be refined anisotropically, H atoms riding with fixed thermal parameters. CCDC-247552 (**1**) and CCDC-247553 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[11] L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524.

[12] An analogous ligand exchange between [Hyp$_2$Pb] and aryl copper complexes has been successfully used in the synthesis of other heteroleptic plumbylenes: J. Klett, K. W. Klinkhammer, M. Niemeyer, *Chem. Eur. J.* **1999**, *5*, 2531.

[13] [PbHyp$_2$] decomposes within several hours also giving lead and Hyp-Hyp as the only products. Both decomposition reactions—of **2** and of [PbHyp$_2$]—are first order in starting material. The half-life periods were determined by ^{1}H NMR spectroscopic monitoring to be 4 (**2**) and 47 h ([PbHyp$_2$]).