Inorg. Chem. **2006**, *45*, 409–414

Inorganic Chemistry
Article

Synthesis and Characterization of Novel Oxo-Centered Phosphanylzincates of Potassium and Cesium with a Central Zn$_6$O$_2$P$_4$ Double-Heterocubane Cage

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Received September 6, 2005

The hydrolysis reaction of K$_2$(MeZn)$_2$(PSi*t*Bu$_3$)$_2$ in THF/toluene solution yields the [(MeZn)$_4$Zn$_2$(μ_3-PSi*t*Bu$_3$)$_4$(μ_4-O)$_2$]$^{4-}$ anions independent of the applied stoichiometry. If the applied molar ratio resembles the composition of the anion, [(thf)K]$_2$[(η^6-toluene)K]$_2$[(MeZn)$_4$Zn$_2$(μ_3-PSi*t*Bu$_3$)$_4$(μ_4-O)$_2$] (**1**) crystallizes from a mixture of THF and toluene. In the case with less water, a phosphanediylzincate moiety is bonded to this anion, and [Zn(PSi*t*Bu$_3$)$_2$K$_4$(thf)$_6$]$_2$[(MeZn)$_4$Zn$_2$(μ_3-PSi*t*Bu$_3$)$_4$(μ_4-O)$_2$] (**2**) crystallizes. However, again the major product is **1**. The same anion is also observed with larger and softer cations, and [(thf)$_3$Cs$_2$]$_2$[(MeZn)$_4$Zn$_2$(μ_3-PSi*t*Bu$_3$)$_4$(μ_4-O)$_2$] (**3**) is obtained if the cesium zincate is used in this reaction. In all of these compounds, the anion is a slightly distorted Zn$_6$O$_2$P$_4$ double-heterocubane cage with a central Zn$_2$O$_2$ ring having Zn–O bond lengths of approximately 207 pm.

Introduction

Oxide-containing zinc compounds attracted the interest of many research groups because of their application in many fields. For example, oxygen-centered zinc cages can serve as support for organometallic frameworks[1] and as porous materials for hydrogen storage;[2] investigations regarding these cages as catalysts for CO$_2$ activation are in progress as well.[3] The common structural feature of all of these oxides is an oxygen-centered Zn$_4$ tetrahedron that was first described by Corbett and Hoskins 35 years ago.[4] Thereafter, many reports of Zn$_4$O fragments with the same structural moiety and a general formula of Zn$_4$(μ_4-O)L$_6$ have been published.[1−3,5] These fragments can be interconnected via vertexes giving Zn$_7$(μ_4-O)$_2$ stoichiometries[6] or via edges giving Zn$_6$(μ_4-O)$_2$ cages.[7] In molecules with a Zn$_4$(μ_4-O) cage, the edges are

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(1) (a) Saalfrank, R. W.; Reimann, U.; Göritz, M.; Hampel, F.; Scheurer, A.; Heinemann, F. W.; Büschel, M.; Daub, J.; Schünemann, V.; Trautwein, A. X. *Chem.*—*Eur. J.* **2002**, *8*, 3614−3619. (b) Chae, H. K.; Kim, J.; Friedrichs, O. D.; O'Keeffe, M.; Yagfi, O. M. *Angew. Chem.* **2003**, *115*, 4037−4039; *Angew. Chem., Int. Ed.* **2003**, *42*, 3907−3909. (c) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y. B.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523−527. (d) Lee, E. Y.; Jang, S. Y.; Suh, M. P. *J. Am. Chem. Soc.* **2005**, *127*, 6374−6381.

(2) (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127−1130. (b) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. *J. Am. Chem. Soc.* **2004**, *126*, 5666−5667. (c) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Brockrath, B. C.; Lin, W. *Angew. Chem.* **2005**, *117*, 74−77; *Angew. Chem., Int. Ed.* **2005**, *44*, 72−75.

(3) (a) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C. *Inorg. Chem.* **2002**, *41*, 973−980. (b) McCowan, C. S.; Caudle, M. T. *J. Chem. Soc., Dalton Trans.* **2005**, 238−246.

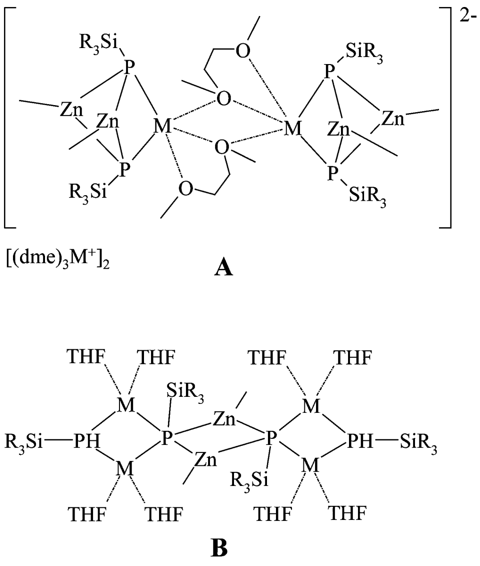
(4) Corbett, M.; Hoskins, B. F. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 261−264.

(5) (a) Masaki, M.; Matsunami, S.; Kimura, T.; Oshima, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 502−506. (b) Nicholas, P. P. *J. Org. Chem.* **1979**, *44*, 2126−2130. (c) Lee, C. F.; Chin, K. F.; Peng, S. M.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 467−470. (d) Harrison, W. T. A.; Phillips, M. L. F.; Chavez, A. V.; Nenoff, T. M. *J. Mater. Chem.* **1999**, *9*, 3087−3092. (e) Memzer, S.; Phillips, J. R.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2000**, 3269−3273. (f) McCowan, C. S.; Groy, T. L.; Caudle, M. T. *Inorg. Chem.* **2002**, *41*, 1120−1127. (g) Dell'Amico, D. B.; Calderazzo, F.; Farnocchi, S.; Labella, L.; Marchetti, F. *Inorg. Chem. Commun.* **2002**, *5*, 848−852. (h) Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F. *Inorg. Chim. Acta* **2003**, *350*, 661−664. (i) Shu, M.; Walz, R.; Wu, B.; Seebacher, J.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2003**, 2502−2511. (j) Zheng, S.-L.; Zhang, J.-P.; Chen, X.-M.; Huang, Z.-L.; Lin, Z.-Y.; Wong, W.-T. *Chem.*—*Eur. J.* **2003**, *9*, 3888−3896.

(6) Waheed, A.; Jones, R. A.; McCarty, J.; Yang, X. *J. Chem. Soc., Dalton Trans.* **2004**, 3840−3841.

10.1021/ic0515195 CCC: $33.50

Scheme 1



bridged by ligands; a deficit of ligands and steric requirements lead to the aggregation of this structural element. The L ligands in $Zn_4(\mu_4\text{-}O)L_6$ are often multidentate anions such as, for example, carboxylates. The arrangement of the six L ligands and the four zinc atoms in $Zn_4(\mu_4\text{-}O)L_6$ resembles an adamantane-like structure.

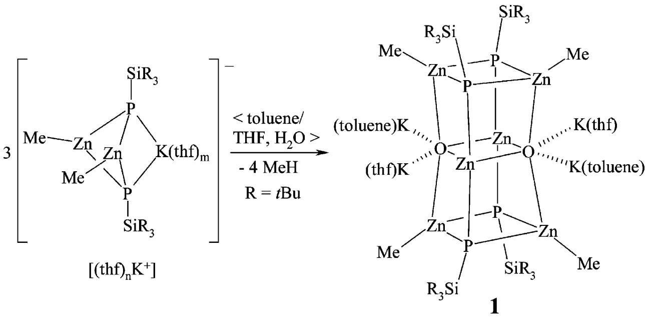
The synthesis of these oxygen-centered zinc tetrahedrons succeeds by reaction of the corresponding zinc compounds with water or even NaOH. A different reactivity has been observed for zincates. In heterobimetallic zincates such as $[M_2Zn_2\{N(SiMe_3)_2\}_4(O_2)_x(O)_{1-x}]$ (M/x = Na/0, K/1) with $M_2Zn_2N_4$ cycles, the oxide is surrounded planarily by the metal atoms, which justifies looking at these molecules as “inverse crown ethers”.[8] An oxygen atom in an octahedral environment has been observed for $Li_4Zn_2(\mu_6\text{-}O)L_6$ with L being N,N′-diphenylbenzamidinate; however, on the basis of the bond lengths, the authors suggest as an interpretation a linear Li_2O unit that is encapsulated by an organometallic framework.[9] Dialkylzinc, in the absence of a second metal, inserts oxygen from dry air into the Zn−C bond under the formation of alkoxides $[R_6Zn_7(OMe)_8]$ or alkylperoxides $[R_4Et_2Zn_4(OOEt)_2]$.[10]

The metalation of alkylzinc trialkylsilylphosphanides with alkali metals yielded the complexes **A** and **B** with central Zn_2P_2 cycles (Scheme 1; M = Na, K; R = *t*Bu) depending on the stoichiometry; the alkali metals bind to the phosphanediide ligands[11] thus giving tetracoordinate phosphorus atoms. In these two zincates, the Zn_2P_2 ring shows its structural flexibility because in **A** a bent cycle is realized, whereas in **B** a centrosymmetric cycle is formed.

During the synthesis and isolation of the zincates **A** and **B**, and in the course of the investigations regarding their reactivity, the extreme sensitivity toward moisture was striking. Therefore, hydrolysis reactions were investigated in order to study the possibility of building organometallic frameworks that incorporate oxide anions.

Results and Discussion

Synthesis. The complexes **A** and **B** with M = K reacted with moisture, according to eq 1, to form the potassium oxophosphanediylzincate $[(thf)K]_2[(\eta^6\text{-toluene})K]_2[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]$ (**1**) with a chemical ^{31}P NMR shift of $\delta = -248$. Furthermore, the other hydrolysis product, $H_2PSi\textit{t}Bu_3$ ($\delta = -264.3$),[12] has also been detected in this solution.



With the knowledge of the structure of **1**, we mixed the components potassium, dimethylzinc, and tri(*tert*-butyl)silylphosphane in a THF/toluene solution in a molar ratio of 2:3:2. This solution was then exposed to air for a few minutes by opening the Schlenk tube (or, alternatively, by exchange of the argon atmosphere by air), and was stirred at room temperature for several days. After we reduced the volume and cooled the solution to 4 °C, colorless crystals of **1** precipitated; the coordination spheres of potassium were saturated by THF and toluene molecules. Nevertheless, the coordination numbers of the potassium cations were very small because of the steric shielding by the demanding tri(*tert*-butyl)silyl groups.

A lower content of water yielded a few crystals of the complex $[Zn(PSi\textit{t}Bu_3)_2K_4(thf)_6]_2[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]$ (**2**) (Scheme 2) along with tri(*tert*-butyl)silylphosphane and **1**. The central cage is the same as in **1**; however, additional bis(potassium-phosphanediyl)zinc moieties coordinate to this central cage. The coordination number of the inner potassium atoms is also very small because of steric shielding by the bulky tri(*tert*-butyl)silyl substituents. Therefore, the reaction was repeated; however, methylzinc tri(*tert*-butyl)silylphosphanide was metalated by the softer cesium metal. After exposure to air for a few minutes, $[(thf)_3Cs_2]_2[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]$ (**3**) (Scheme 2) was isolated after a similar workup procedure. The central fragment is identical to those of **1** and **2**. The larger alkali metal is

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(7) Malik, M. A.; O’Brien, P.; Motevalli, M.; Jones, A. C. *Inorg. Chem.* **1997**, *36*, 5076−5081.

(8) Forbes, G. C.; Kennedy, A. R.; Mulvey, R. E.; Rowlings, R. B.; Clegg, W.; Liddle, S. T.; Wilson, C. C. *Chem. Commun.* **2000**, 1759−1760.

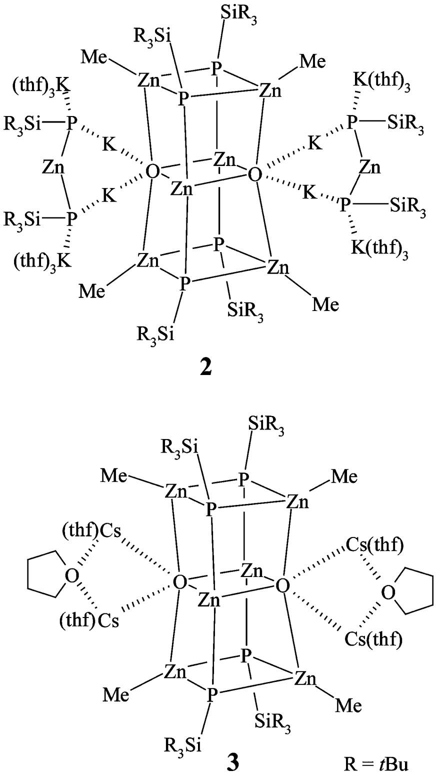
(9) Bond, A. D.; Linton, D. J.; Schooler, P.; Wheatley, A. E. H. *J. Chem. Soc., Dalton Trans.* **2001**, 3173−3178.

(10) Lewinski, J.; Marciniak, W.; Lipkowski, J.; Justyniak, I. *J. Am. Chem. Soc.* **2003**, *125*, 12698−12699.

(11) Sapelza, G.; Mayer, P.; Westerhausen, M. *Z. Anorg. Allg. Chem.* **2005**, in press.

(12) (a) Wiberg, N.; Schuster, H. *Chem. Ber.* **1991**, *124*, 93−95. (b) Wiberg, N.; Wörner, A.; Lerner, H.-W.; Karaghiosoff, K.; Fenske, D.; Baum, G.; Dransfeld, A.; Schleyer, P. v. R. *Eur. J. Inorg. Chem.* **1998**, 833−841.

Scheme 2



2

3 R = *t*Bu

bonded to the oxide and to a THF ligand. Another THF molecule coordinates to two cesium cations.

The addition of water or the exposure of the reaction solutions to pure water vapor leads to complete decomposition, and an unintelligible variety of as-of-yet unknown hydrolysis products has been observed by ^{31}P NMR spectroscopy dominated by major $H_2PSi\textit{t}Bu_3$. Therefore, exposure of the reaction solutions to air gives the highest yields; however, because of difficulties in predicting the stoichiometry, it is necessary to follow up the reaction with ^{31}P NMR spectroscopy.

Molecular Structures. The molecular structures of **1**, **2**, and **3** and their numbering schemes are represented in Figures 1−3. The inner $Zn_6O_2P_4$ cage consists of a double-heterocubane cage with a central Zn_2O_2 ring and external Zn_2P_2 cycles. The deviations from the cuboid geometry are rather small and mainly the consequence of the different radii of oxygen and phosphorus. The outer tetracoordinate phosphorus atoms are bound to the extremely bulky tri(*tert*-butyl)silyl groups, whereas the outer zinc atoms carry methyl substituents. Whereas the inner zinc atoms are tetracoordinate, the oxygen atoms are coordinated to the two additional alkali metal atoms K (**1** and **2**) and Cs (**3**). Therefore, the oxide anions present the center of a distorted M_2Zn_4 octahedron with the electropositive metals in a cis arrangement.

The outer zinc atoms are bound to alkyl groups, which reduces their charge in comparison to that of the inner zinc atoms. Therefore, the electrostatic attraction of the anions to the inner zinc atoms leads to a shortening of the bonds to the neighboring phosphorus and oxygen atoms. Selected structural parameters are summarized in Table 1. The Zn2−O1 distance is approximately 10 pm shorter than the Zn1−O1 and Zn3−O1 bond distances. A comparable observation accounts for the Zn−P bonds. These structural data give a double-heterocubane that is laced in at the Zn_2O_2 plane. As a consequence, the Zn1−O1−Zn3 as well as P1−Zn2−P2 angles deviate from linearity by nearly 10°.

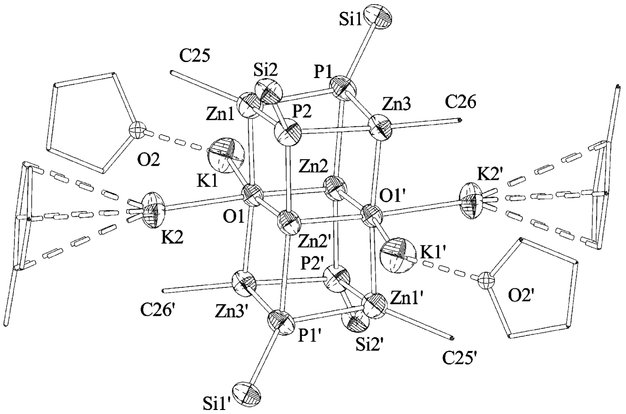


Figure 1. Molecular structure and numbering scheme of $[(thf)K]_2[(\eta^6\text{-toluene})K]_2[(MeZn)_4Zn_2(\mu_3\text{-PSi}\textit{t}Bu_3)_4(\mu_4\text{-O})_2]$ (**1**). The ellipsoids represent a probability at the level of 50%; the carbon atoms are drawn with arbitrary small radii. The H atoms and silicon-bonded *tert*-butyl groups are neglected for clarity reasons. Selected bond lengths (pm): K1−O1 264.0(3), K1−O2 257.7(6), K2−O1 260.9(3), K2−C27 (*i*-C) 350.6(7), K2−C28 (*o*-C) 335.2(8), K2−C29 (*m*-C) 320.2(8), K2−C30 (*p*-C) 318.3(9), K2−C31 (*m*-C) 332.6(9), K2−C32 (*o*-C) 347.3(8).

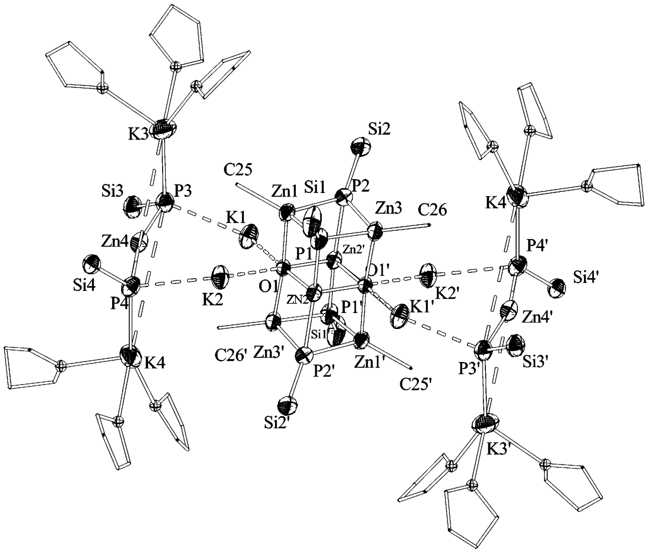


Figure 2. Molecular structure and numbering scheme of $[Zn(PSi\textit{t}Bu_3)_2K_4(thf)_6]_2[(MeZn)_4Zn_2(\mu_3\text{-PSi}\textit{t}Bu_3)_4(\mu_4\text{-O})_2]$ (**2**). The ellipsoids represent a probability at the level of 50%; the carbon atoms are drawn with arbitrary small radii. The H atoms and silicon-bonded *tert*-butyl groups are neglected for clarity reasons. Selected bond lengths (pm): K1−O1 266.9(4), K2−O1 268.3(4), K1−P3 321.4(2), K2−P4 327.1(3), K3−P3 318.7(3), K4−P4 321.8(3).

The octahedral environment of atom O1 shows distortions due to the larger distances to the alkali metal cations and due to the deviation of the M1−O1−Zn2′ and M1−O1−Zn2 angles (M = K, Cs) from linearity. The latter fact results from the bulky tri(*tert*-butyl)silyl groups, which open only a small coordination site at O1. These alkali metals are squeezed into this aliphatic environment and realize rather small coordination numbers. In **1**, two potassium atoms

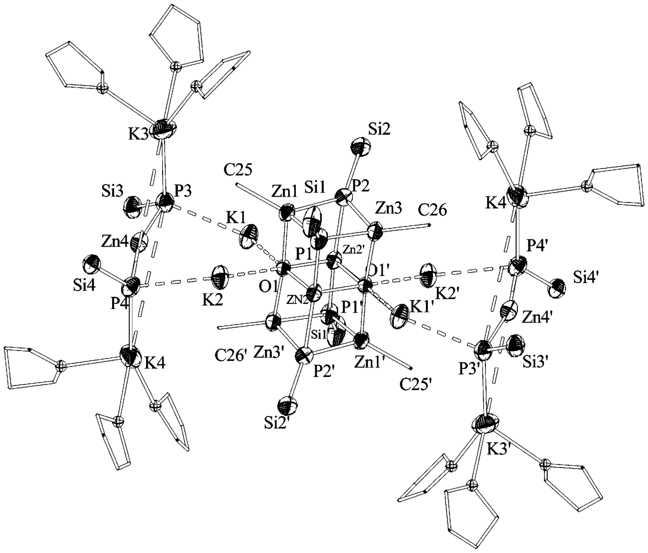


Figure 3. Molecular structure and numbering scheme of $[(thf)_3Cs_2]_2$-$[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]$ (**3**). The ellipsoids represent a probability at the level of 50%; the carbon atoms are drawn with arbitrary small radii. The H atoms and silicon-bonded *tert*-butyl groups are omitted for clarity reasons. Selected bond lengths (pm): Cs1−O1 294.8(3), Cs1−O2 328.5-(6), Cs1−O4 303.5(6), Cs2−O1 292.1(3), Cs2−O2 331.8(6), Cs2−O3 309.8(6).

Table 1. Selected Bond Lengths (pm) and the Coordination Sphere of the Oxygen Atom of the $[(MeZn)_4Zn_2(\mu_4\text{-}O)_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4]^{4-}$ Anion in **1**, **2**, and **3** with M = K (**1** and **2**), Cs (**3**)

	1	2	3
O1−Zn1	216.4(3)	214.6(4)	213.1(4)
O1−Zn2	206.2(3)	209.2(4)	207.0(4)
O1−Zn3′	216.2(3)	214.6(4)	211.8(4)
O1−Zn2′	208.6(3)	208.4(4)	208.1(4)
Zn1−P1	247.0(2)	245.8(2)	246.7(3)
Zn1−P2	243.4(2)	246.2(2)	247.5(3)
Zn1−C25	203.4(8)	202.9(7)	203.4(6)
Zn2−P1	233.3(2)	232.5(1)	233.6(2)
Zn2−P2′	233.4(2)	233.2(1)	233.6(3)
Zn3−P2	244.3(1)	245.8(2)	245.8(3)
Zn3−P1	248.4(2)	245.4(2)	244.5(3)
Zn3−C26	203.2(7)	203.2(7)	202.7(8)
P1−Si1	221.7(2)	219.4(3)	220.8(3)
P2−Si2	221.7(3)	220.0(3)	221.1(3)
Zn1−O1−Zn2	93.7(1)	91.8(1)	92.9(1)
Zn1−O1−Zn2′	93.1(1)	92.4(1)	92.5(1)
Zn1−O1−Zn3′	172.9(2)	173.8(2)	173.4(2)
Zn2−O1−Zn2′	87.4(1)	87.1(1)	88.2(1)
Zn2−O1−Zn3′	91.3(1)	91.9(2)	91.8(1)
Zn3′-O1−Zn2′	92.2(1)	92.8(1)	92.3(1)
M1-O1−Zn2′	168.9(1)	175.2(1)	176.4(2)
M2-O1−Zn2	174.7(1)	176.5(1)	178.0(2)

coordinate to THF molecules, and the others bind to toluene in a η^6-fashion. The arene−metal coordination is quite common for soft cations, and has been investigated in detail by NMR spectroscopy; Zhu et al. could show that Ag^+, Cs^+, and K^+ coordinate to benzene, whereas the hard Na^+ and Li^+ cations form only weak adducts with benzene in an aqueous alkali metal chloride or silver nitrate solution.[13] In **1**, the coordination gap between the extremely bulky tri(*tert*-butyl)silyl groups and the bulkiness of THF and toluene determine which solvent molecule binds to the potassium cation. The shape of the coordination gap at K2 is also responsible for the tilted coordination and the variation of the $K2-C_{toluene}$ distances between 318 and 351 pm.

Special attention must be given to the outer fragments of **2**. These moieties can be formulated as $Zn[P(Si\textit{t}Bu_3)K(thf)_3]_2$, and can be regarded as a bis[tris(tetrahydrofuran)potassium] bis(trialkylsilylphosphanediylzincate). Because of the small coordination number of 2 for Zn4, a very short average Zn4−P bond of 221.2 pm is observed. The deviation of the P3−Zn4−P4 angle of 163.38(8)° from linearity is a common feature for such structural fragments, and has been observed earlier.[14−16]

In **3**, each cesium atom binds to a THF molecule, whereas another THF ligand shows a rather scarce coordination behavior and bridges two alkali metal atoms. Therefore, the Cs−O bond lengths differ depending on the charge and the binding modus: The Cs(*n*)−O1 distances show an average value of 293.5 pm; the bond lengths to the terminally bound THF molecules lie at 306 pm, whereas the distances between cesium and the bridging THF molecule lie at 330 pm. The latter is a characteristic value for a $Cs_2(\mu\text{-thf})$ moiety, and has already been reported for $(\mu\text{-thf})Cs_2[\mu\text{-}P(H)C_6H_2\text{-}2,4,6\text{-}\textit{t}Bu_3]_2$ with comparable values.[17] Even though this structural unit of a THF molecule in a bridging position between two cesium atoms is rather unique, it has also been published for $[(thf)(\mu\text{-thf})_2Cs_2\{Me_2SiN(H)Si(Me)_2N\}_2]_\infty$,[18] $(\mu\text{-thf})Cs_2\{Si(SiMe_3)_3\}_2$,[19] and $[(\mu\text{-thf})Cs_2\{Ph(Me_3SiN)P\}_2]_\infty$[20] with similar Cs−O bond lengths.

Conclusions

The anion $[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]^{4-}$ is the only oxide-containing product that has been observed and isolated during protolysis reactions of alkali metal phosphanediylzincates. An oxide deficit leads to zincate moieties that are bonded at the periphery of the alkali metals. An excess of water leads to decomposition and numerous as-of-yet unknown and partly insoluble compounds. Because of the large coordination number at the oxygen atoms and the shielding of the alkali metals by the demanding trialkylsilyl substituents, the formation of organometallic frameworks or nets is prevented. Only small solvent molecules such as THF and toluene can bind to these alkali metals; an interconnection of two of these $[(MeZn)_4Zn_2(\mu_3\text{-}PSi\textit{t}Bu_3)_4(\mu_4\text{-}O)_2]^{4-}$ anions seems to be impossible. These complexes also show

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(13) Zhu, D.; Herbert, B. E.; Schlautman, M. A.; Carraway, E. R. *J. Environ. Qual.* **2004**, *33*, 276−284. For the importance of K−arene interactions in chemistry, biochemistry, and biology, see for example: (a) Gokel, G. W.; Barbour, L. J.; De Wall, S. L.; Meadows, E. S. *Coord. Chem. Rev.* **2001**, *222*, 127−154. (b) Ferdani, R.; Hu, J.; Leevy, W. M.; Pajewska, J.; Pajewski, R.; Villalobos, V.; Barbour, L. J.; Gokel, G. W. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 7−12. (c) Gokel, G. W.; Barbour, L. J.; Ferdani, R.; Hu, J. *Acc. Chem. Res.* **2002**, *35*, 878−888. (d) Gokel, G. W. *Chem. Commun.* **2003**, 2847−2852.

(14) Westerhausen, M.; Sapelza, G.; Zabel, M.; Pfitzner, A. *Z. Naturforsch.* **2004**, *59b*, 1548−1550.

(15) Westerhausen, M.; Bollwein, T.; Warchhold, M.; Nöth, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1141−1145.

(16) Westerhausen, M.; Sapelza, G.; Mayer, P. *Angew. Chem.* **2005**, *117*, 6391−6393; *Angew. Chem., Int. Ed.* **2005**, *44*, 6234−6237.

(17) Rabe, G. W.; Heise, H.; Yap, G. P. A.; Liable-Sands, L. M.; Guzei, I. A.; Rheingold, A. *Inorg. Chem.* **1998**, *37*, 4235−4245.

(18) Kottke, T.; Stalke, D. *Organometallics* **1996**, *15*, 4552−4558.

(19) Klinkhammer, K. W. *Chem.—Eur. J.* **1997**, *3*, 1418−1431.

(20) Wingerter, S.; Pfeiffer, M.; Baier, F.; Stey, T.; Stalke, D. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1121−1130.

Table 2. Crystallographic Data of **1**, **2**, and **3** and Details of the Structure Solution and Refinement Procedures

	1	**2**	**3**
formula	$C_{88}H_{168}K_4O_4P_4Si_4Zn_6$	$C_{148}H_{324}K_8O_{14}P_8Si_8Zn_8$	$C_{76}H_{168}Cs_4O_8P_4Si_4Zn_6$
fw (g mol^{-1})	2075.24	3636.31	2370.20
T (K)	200(3)	183(2)	200(3)
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	14.0515(3)	17.3763(5)	13.2359(3)
b (Å)	15.2891(4)	18.4589(4)	15.0135(3)
c (Å)	15.4475(5)	18.5341(6)	15.1417(3)
α (deg)	62.4254(9)	75.204(2)	115.2883(17)
β (deg)	69.291(1)	64.5460(10)	92.8817(10)
γ (deg)	70.318(1)	84.868(2)	104.3971(9)
V (Å^3)	2691.0(1)	5188.3(3)	2592.72(9)
Z	1	1	1
d_{calcd} (g cm^{-3})	1.281	1.164	1.518
μ (mm^{-1})	1.616	1.222	2.900
measured data	27 160	36 680	29 111
data with $I > 2\sigma(I)$	6839	14 478	6435
unique data (R_{int})	9321	23 584	9999
w$R_2{}^a$ (all data, on F^2)	0.1586	0.3174	0.1185
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0577	0.0941	0.0516

[a] Definition of the R values: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (xP)^2 + yP$ where $P = (F_o^2 + 2F_c^2)/3$.

how already small amounts of water lead to large cages thus binding a manifold stoichiometric amount of phosphanediides.

The formation of a heterocubane cage with strong deviations from the tetrahedral environment of the zinc atoms of the Zn_2O_2 plane is favored in comparison to oxygen-centered Zn_4 tetrahedrons. With monodentate ligands such as the trialkylsilylphosphandiide substituents that would be bound above the Zn···Zn edges, an adamantane-like structure would arise; however, all bonds from the zinc atom would show to the same side of the metal atom, with a vacant coordination site directed to the outside of the cage. Therefore, this structure is known only for $Sr_4(\mu_4\text{-}O)(\mu_2\text{-}P(SiR_3)_2)_6$, in which the vacant coordination site is occupied by agostic bonds to the alkyl group thus giving a strongly distorted trigonal bipyramidal coordination sphere for the strontium atoms.[21] With bidentate ligands such as carboxylates and phosphonates, the metal atoms in molecules such as $Zn_4(\mu_4\text{-}O)L_6$ are embedded in distorted tetrahedral environments.

Experimental Section

General. All experiments and manipulations were carried out under purified argon. Reactions were performed by using standard Schlenk techniques and dried, thoroughly deoxygenated solvents. Starting $H_2PSi\mathit{t}Bu_3$ was prepared by known literature procedures.[12] NMR spectra were recorded on JEOL spectrometers GSX270 and EX400. All NMR spectra were recorded at room temperature as [D$_6$]benzene solutions. A Perkin-Elmer Paragon 1000 PC spectrophotometer was used to record the IR spectra.

[(thf)(η^6-toluene)K$_2$]$_2$[(MeZn)$_4$Zn$_2$(μ$_3$-PSi*t*Bu$_3$)$_4$(μ$_4$-O)$_2$] (1). $ZnMe_2$ (1.12 mL of a 2 M solution in toluene, 2.25 mmol) was added to a colorless solution of 58.7 mg of potassium (1.5 mmol) and 350 mg of tri(*tert*-butyl)silylphosphane (1.5 mmol) in a solvent mixture of 10 mL of toluene and 5 mL of THF. After exchange of the inert gas atmosphere by air (by evacuating the Schlenk tube after freezing of the solution, warming up to room temperature, and then letting air into the Schlenk tube) and keeping an air stream for a minute, we stirred the reaction mixture for 5 days. The solution was then concentrated to a few milliliters. At 4 °C, 280 mg of colorless crystals (0.135 mmol, 36%) precipitated. Mp: >300 °C dec. ^{1}H NMR: δ −0.33 (s, ZnMe), 1.40 (s, *t*Bu). ^{13}C{^{1}H} NMR: δ 24.3 (s, C$_q$), 32.5 (s, *t*Bu). ^{31}P NMR: δ −248.5 (s). Anal. Calcd for $C_{74}H_{152}K_4P_4O_4Si_4Zn_6$, 1866.11 g mol^{-1} (without toluene): C, 47.02; H, 8.10. Found: C, 47.08; H, 8.19. IR (cm^{-1}): ν 1605 w, 1495 m, 1478 vs, 1469 vs, 1387 vs, 1366 s, 1244 s, 1198 s, 1059 vs, 1031 vs, 1006 vs, 962 vs, 934 vs, 818 vs, 742 w, 728 m, 694 m, 627 s, 611 s, 558 m, 508 s, 491 s, 477 vs, 462 vs, 414 m.

[Zn(PSi*t*Bu$_3$)$_2$K$_4$(thf)$_6$]$_2$[(MeZn)$_4$Zn$_2$(μ$_3$-PSi*t*Bu$_3$)$_4$(μ$_4$-O)$_2$] (2). A solution of 1.0 mmol of $ZnMe_2$ (0.5 mL of a 2 M solution in toluene) was added to a colorless solution of 1.0 mmol of potassium (39.1 mg) and 1.0 mmol of tri(*tert*-butyl)silylphosphane (233 mg) in a solvent mixture of 10 mL of toluene and 5 mL of THF. After exchanging the inert gas atmosphere by air, we stirred the reaction mixture for 5 days. The volume of the solution was then reduced to a few milliliters. At 4 °C, a few colorless crystals were obtained. ^{31}P{^{1}H} NMR: δ −251.0 (s, KP(Si*t*Bu$_3$)Zn), −246.0 (s, ZnMePSi).

[(thf)$_3$Cs$_2$]$_2$[(MeZn)$_4$Zn$_2$(μ$_3$-PSi*t*Bu$_3$)$_4$(μ$_4$-O)$_2$] (3). $ZnMe_2$ (1.50 mmol, 0.75 mL of a 2 M solution in toluene) was added to a colorless solution of 133 mg of cesium (1.0 mmol) and 233 mg of tri(*tert*-butyl)silylphosphanide (1 mmol) in a solvent mixture of 10 mL of toluene and 5 mL of THF. After exchange of the inert gas atmosphere by air and keeping an air stream for a minute, we stirred the reaction mixture for 5 days. The volume of the solution was reduced to a few milliliters. After cooling and storage of the solution at 4 °C, we obtained 182 mg of colorless crystals (0.077 mmol, 31%). Mp: >270 °C dec. ^{13}C{^{1}H} NMR: δ 23.3 (s, C$_q$), 31.9 (s, *t*Bu). ^{29}Si{^{1}H} NMR: δ 28.8 (br s, SiP). ^{31}P{^{1}H} NMR: δ −242.1 (s). ^{31}P NMR: δ −242.1 (s). Anal. Calcd for $C_{76}H_{168}Cs_4P_4O_8Si_4Zn_6$, 2370.34 g mol^{-1}: C, 38.72; H, 6.46. Found: C, 37.72; H, 7.15. IR (cm^{-1}): ν 1562 w, 1478 vs, 1469 vs, 1444 m, 1388 s, 1383 s, 1365 m, 1306 m, 1245 vs, 1186 m, 1133 m, 1062 m, 1062 m, 1044 m, 1029 m, 1012 s, 985 s, 963 s, 943 s, 934 s, 815 vs, 772 w, 752 w, 736 w, 727 w, 696 w, 650 vw, 604 s, 569 s, 510 s, 473 s, 458 s.

Structure Determinations. Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) using oil-coated rapidly cooled single

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(21) Westerhausen, M.; Digeser, M. H.; Nöth, H.; Knizek, J. *Z. Anorg. Allg. Chem.* **1998**, *624*, 215−220.

crystals. Crystallographic parameters, details of data collection, and refinement procedures are summarized in Table 2.

All structures were solved by direct methods with the programs SIR97[22] and SHELXS 97,[23] and refined with the software package SHELXL-97.[23] Neutral scattering factors were taken from Cromer and Mann,[24] and from Stewart et al. for the hydrogen atoms.[25] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding carbon atoms. The quality of the structure determination of **2** is rather poor because of very small crystals that became dull during handling and mounting on the diffractometer. In addition, rather large motion of the bulky tri(*tert*-butyl)silyl groups and nonresolved disordering damages the data set and leads to artificial distortions of these groups. Nevertheless, the structural motif of **2** is clearly deduced from this structure determination, and the standard deviations of the structural parameters show no unusually large uncertainty within the inner core.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-279302 for **1**, CCDC-278847 for **2**, and CCDC-279303 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. E-mail: deposit@ccdc.cam.ac.uk.

IC0515195

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(22) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(23) Sheldrick, G. M. *SHELXL*-93; Universität Göettingen: Göettingen, Germany, 1993; *SHELXL-97* and *SHELXS-97;* Universität Göttingen: Göttingen, Germany, 1997

(24) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *24*, 321−324.

(25) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175−3187.