Inorg. Chem. **2003**, *42*, 5837

Inorganic Chemistry
Article

Structural Motifs in (*t*-butoxy)Zirconium Phosphinates, Arsinates, and Phosphates[†]

K. C. Kumara Swamy,*,[‡] Michael Veith,*,[§] Volker Huch,[§] and Sanjay Mathur[⊥]

School of Chemistry, University of Hyderabad, Hyderabad- 500046, India, Anorganische Chemie,
Fachbereich 8.11, Universität des Saarlandes, Gebäude 23, Postfach 151150,
D-66041 Saarbrücken, Germany, and CVD Division, Institut für Neue Materialien, Im Stadtwald,
Gebäude 43, 151150, D-66041 Saarbrücken, Germany

Received April 30, 2003

Reaction of zirconium tetrakis(*tert*-butoxide) (**1**) with dicylohexylphosphinic acid in toluene leads to the dinuclear compound $[Zr(\mu,\mu'\text{-}O_2P(cycl\text{-}C_6H_{11})_2)(O\text{-}t\text{-}Bu)_3]_2$ (**2**) in which the zirconium is pentacoordinated. An analogous reaction using diphenylphosphinic acid in tetrahydrofuran also leads to a dinuclear complex $[Zr(\mu,\mu'\text{-}O_2PPh_2)(THF)((O\text{-}t\text{-}Bu)_3]_2\cdot C_6H_5CH_3$ ($\mathbf{3}\cdot C_6H_5CH_3$), in which zirconium is hexacoordinated. A novel exchange of *tert*-butoxy and phenoxy groups occurs when **1** is treated with diphenyl phosphate $[(PhO)_2PO_2H]$ leading to the isolation of the exchange product $[Zr\{\mu,\mu'\text{-}O_2P(O\text{-}t\text{-}Bu)(OPh)\}(\mu\text{-}OPh)(O\text{-}t\text{-}Bu)_2]_2$ (**4**). In contrast to the above, trinuclear zirconium compounds $Zr_3(\mu,\mu'\text{-}O_2AsMe_2)_2(\mu_2,\mu'\text{-}O_2AsMe_2)(O\text{-}t\text{-}Bu)_7(\mu\text{-}O\text{-}t\text{-}Bu)_2$ (**5**) and $Zr_3(\mu,\mu'\text{-}O_2P(O\text{-}t\text{-}Bu)_2)_5(O\text{-}t\text{-}Bu)_7\cdot{}^1/_2C_6H_5CH_3$ ($\mathbf{6}\cdot{}^1/_2C_6H_5CH_3$) have been isolated from the reaction of **1** with cacodylic acid and di-*tert*-butyl phosphate, respectively. The X-ray structures of **2**, **3**, **5**, and **6** have been determined; although the X-ray structural analysis of **4** could not be satisfactorily finished, it reveals the disposition of the substituents. The solution state NMR data suggest that these compounds undergo structural changes in solution. Possible relationships among the various structures are discussed.

Introduction

In recent years there has been a burgeoning interest in molecular alkoxy−titanium and −zirconium phosphates and phosphonates which in part is due to the possible use of these compounds as precursors to solid-state materials.[1,2] The usefulness of metal alkoxides/phosphates as relevant to material science is well-known,[3] and in this connection we have been looking for the possibility of using some of these products in chemical vapor deposition (cvd) processes.[4] Two reactions which attracted our attention were those of $Ti(O\text{-}i\text{-}Pr)_4$ with $(t\text{-}BuO)_2P(O)OH$[1f] and $Zr(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_2$ with $Ph_2P(O)OH$[5] wherein compounds **I** and **II**, respectively, were characterized by X-ray crystallography. On the basis of NMR studies, it has been suggested that the structure of **I** is dynamic in solution although the exact nature of the species

---

* Corresponding authors. K.C.K.S.: e-mail, kckssc@uohyd.ernet.in; fax, +91-40-3012460. M.V.: e-mail, veith@mx.uni-saarland.de; fax, 0681-302-3995.

[†] The synthetic part (K.C.K.S.) of the experimental work was done at Saarbrücken (University of Saarlandes) during May−August 2000 with support from the Alexander von Humboldt foundation.

[‡] University of Hyderabad.

[§] Universität des Saarlandes.

[⊥] Institut for Neue Materialien.

(1) (a) *Inorganic Ion Exchange Materials*; Clearfield, A., Ed.; CRC Press: Boca Raton, FL, 1982. (b) Alvarez, C.; Llavona, R.; Garcia, J. R.; Suarez, M.; Rodriguez, J. *Inorg. Chem.* **1987**, *26*, 1045. (c) Errington, R. J.; Ridland, J.; Willett, K. J.; Clegg, W.; Coxall, R. A.; Heath, S. L. *J. Organomet. Chem.* **1998**, *550*, 473. (d) Wang, B.; Greenblatt, M.; Wang, S.; Hwu, S. *Chem. Mater.* **1992**, *5*, 32. (e) Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1992**, *31*, 1138. (f) Lugmair, C. G.; Tilley, T. D. *Inorg. Chem.* **1998**, *37*, 1821. (g) Guerrero, G.; Mehring, M.; Mutin, P. H.; Dahan, F.; Vioux, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1537. (h) Guerrero, G.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **2000**, *12*, 1268. (i) Clearfield, A.; Sharma, C. V. K.; Zhang, B. (P) *Chem. Mater.* **2001**, *13*, 3099 (review).

(2) (a) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801. (b) Horne, J. C.; Huang, Y.; Liu, G.-Y.; Blanchard, G. J. *J. Am. Chem. Soc.* **1999**, *121*, 4419. (c) Horne, J. C.; Blanchard, G. J. *J. Am. Chem. Soc.* **1999**, *121*, 4427.

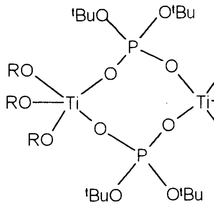
(3) Selected recent references: (a) Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater.* **1999**, *11*, 1615. (b) Yonezawa, T.; Matsune, H.; Kunitake, T. *Chem. Mater.* **1999**, *11*, 33. (c) Murugavel, R.; Sathiyendran, M.; Walawalkar, M. G. *Inorg. Chem.* **2001**, *40*, 427. (d) Fujdala, K. L.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123***,** 10133. (e) Sathiyendiran, M.; Murugavel, R. *Inorg. Chem.* **2002**, *41*, 6404.

10.1021/ic034458o CCC: $25.00

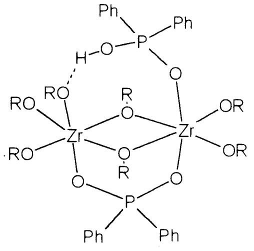
could not be ascertained. The zirconium compound **II** might be considered to be an intermediate in the formation of the dimer $[Zr(\mu,\mu'\text{-}O_2PPh_2)(O\text{-}i\text{-}Pr)_3]_2$, a species analogous to **I**. Thus, even in the 1:1 stoichiometric reaction of $M(OR)_4$ [M = Ti, Zr, Hf] with monobasic phosphinic/arsinic acids of type $R_2P(O)OH$ or $R_2As(O)OH$ depending on steric and electronic requirements, it is likely that diverse products could be obtained and it is this aspect which we planned to address in our studies. This is also in consonance with the experience in the chemistry of tin(IV), an element of group 14, wherein subtle variations in the substituents on phosphorus/arsenic stabilized different structural forms like cubane, hexagonal prismane (drum), O-capped trinuclear clusters, etc., for the monorganotin(oxo) phosphinates/phosphates/arsinates, suggesting that structural analogies could be productive in developing the cage chemistry of Ti and Zr, which belong to group 4.[6] In this paper, we report characterization of compounds $[Zr(\mu,\mu'\text{-}O_2P(cycl\text{-}C_6H_{11})_2P)(O\text{-}t\text{-}Bu)_3]_2$ (**2**), $[Zr(\mu,\mu'\text{-}O_2PPh_2)(THF)(O\text{-}t\text{-}Bu)_3]_2\cdot C_6H_5CH_3$ (**3**$\cdot C_6H_5CH_3$), $[Zr\{\mu,\mu'\text{-}O_2P(O\text{-}t\text{-}Bu)(OPh)\}(\mu\text{-}OPh)(O\text{-}t\text{-}Bu)_2]_2$ (**4**), and $Zr_3(\mu,\mu'\text{-}O_2AsMe_2)_2(\mu_2,\mu'\text{-}O_2AsMe_2)(O\text{-}t\text{-}Bu)_7(\mu\text{-}O\text{-}t\text{-}Bu)_2$ (**5**), all of which contain an equal number of zirconium and phosphorus/arsenic centers, but provide a structural variety that should be useful in further analyzing their hydrolysis/thermolysis products for future applications. In addition, we also report the synthesis and structure of $Zr_3(\mu,\mu'\text{-}O_2P(O\text{-}t\text{-}Bu)_2)_5(O\text{-}t\text{-}Bu)_7$ (**6**$\cdot{}^1/_2C_6H_5CH_3$). All of these have been prepared by starting with $Zr(O\text{-}t\text{-}Bu)_4$ (**1**).[4b,7] Whereas **2** has a structure analogous to the titanium compound **I**, compound **3** has hexacoordinated zirconium atoms with two symmetrically bridging diphenylphosphinate residues *unlike* structure **II**. Compounds **5** and **6** are unique in that they are trinuclear with unsymmetrical arsinate/phosphate bridges, albeit the fact that the empirical formula is still retained. In **4**, although we started with *diphenyl phosphate*, there has been an *exchange* of one of the phenoxy groups on phosphorus by a *tert*-butoxy group with concomitant transfer of the phenoxy group to zirconium.

Results and Discussion

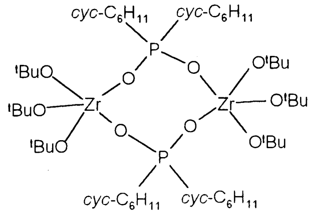
The reaction of **1** with $(C_6H_{11})_2PO_2H$, Ph_2PO_2H, $(PhO)_2PO_2H$, or Me_2AsO_2H gave products **2**−**5**, all with 1:1 ratios of Zr:P or Zr:As. The spectra recorded in C_6D_6 solutions changed over a period of several days, suggesting that there is a dynamic equilibrium in solution as observed for **I** by Tilley and co-workers.[1f] In the case of **4**, due to lack of a reference compound, it was not possible to predict the exchange of the phenoxy and *tert*-butoxy groups by means of the spectral features. Exchange of phenoxy groups in $(PhO)_2PO_2H$ with *tert*-butoxy groups did not take place in the presence of catalytic amounts of $Zr(O\text{-}t\text{-}Bu)_4$. Thus, it appears that initially a dimer similar to **2** had formed which then underwent ligand reorganization; species **III** is a possible intermediate.



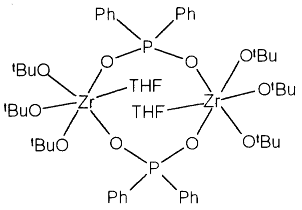
I (R = ⁱPr)



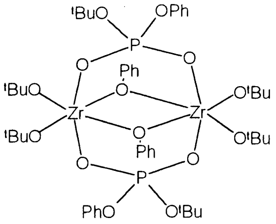
II (R = ⁱPr)



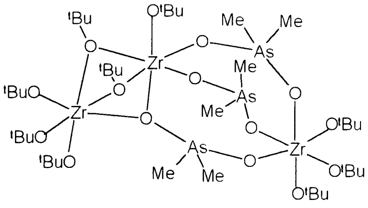
2



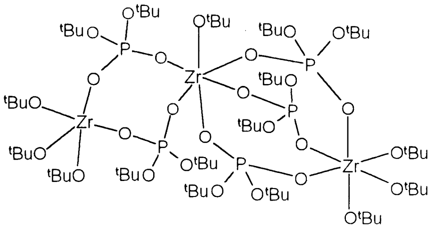
3



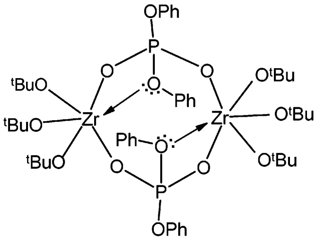
4



5



6



III

In the synthesis of di-*tert*-butyl phosphate compound **6**$\cdot{}^1/_2C_6H_5CH_3$, during the process of workup, some insoluble material was also obtained; this is most likely the reason for the observed zirconium-to-phosphate ratio of 3:5 in this

---

(4) (a) Veith, M. *J. Chem. Soc., Dalton Trans.* **2002**, 2423. (b) Veith, M.; Mathur, S.; Huch, V.; Decker, T. *Eur. J. Inorg. Chem.* **1998**, 1327 (μ_2- and μ_3-*tert*-butoxy-bridged zirconium compounds).

(5) Chakraborty, D.; Chandrasekhar, V.; Bhattacharjee, M.; Krätzner, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2000**, *39*, 23.

(6) (a) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (b) Burton, S. D.; Kumara Swamy, K. C.; Holmes, R. R.; Day, R. O. *Phosphorus Sulfur Silicon* **1989**, *41*, 467 (from proceedings of Fifth International Conference on Inorganic Ring Systems, Amherst, MA, 1988). (c) Kumara Swamy, K. C.; Schmid, C. G.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 223. (d) Kumara Swamy, K. C.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 4184. (e) Kumara Swamy, K. C.; Said, M. A.; Nagabrahmanandachari, S.; Poojary, D. M.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1998**, 1645.

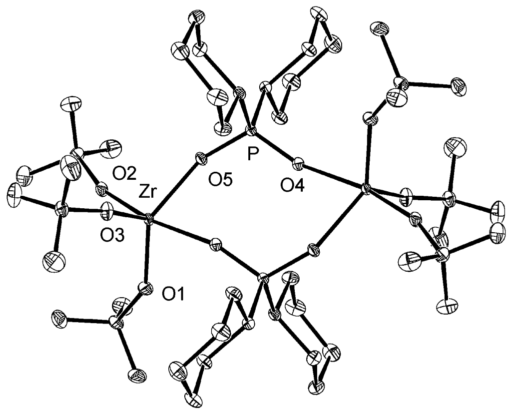


Figure 1. ORTEP drawing of **2**. Hydrogen atoms are omitted and only selected atoms labeled.

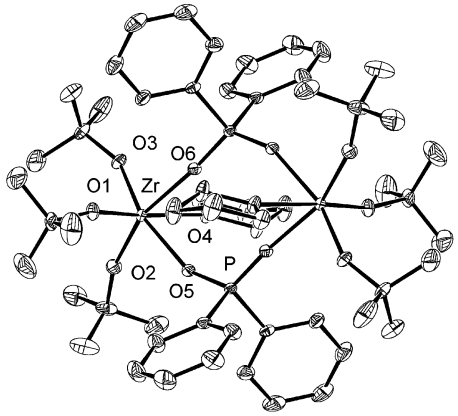


Figure 2. ORTEP drawing of **3**$\cdot C_6H_5CH_3$. Hydrogen atoms as well as the solvent are omitted and only selected atoms labeled.

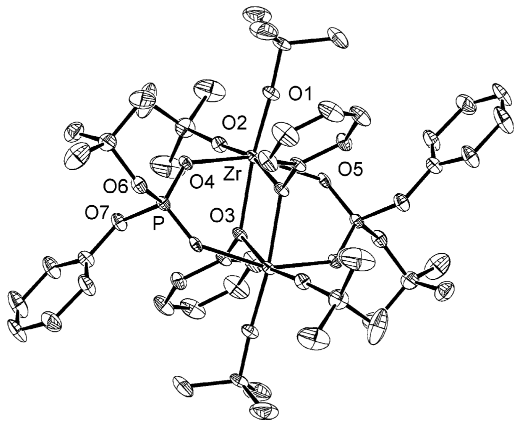


Figure 3. ORTEP drawing of **4**. Hydrogen atoms are omitted and only selected atoms labeled.

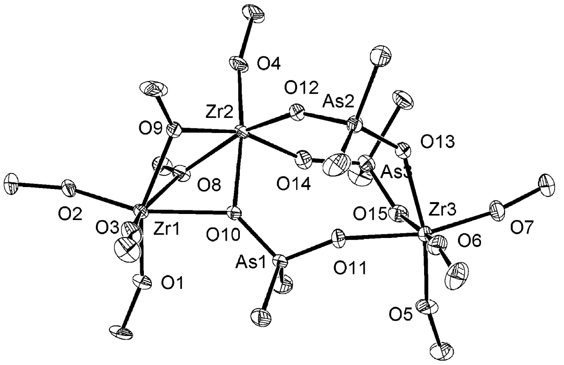


Figure 4. ORTEP drawing of **5**. Hydrogen atoms as well as the terminal *tert*-butoxy carbon atoms are omitted and only selected atoms labeled.

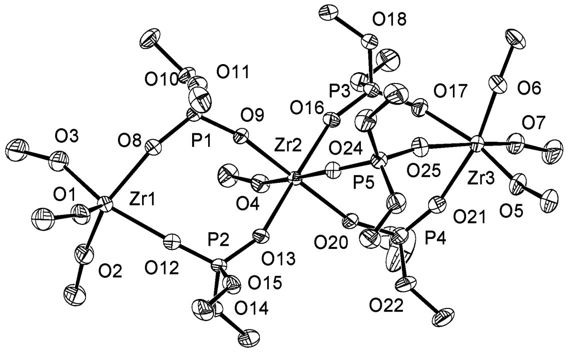


Figure 5. ORTEP drawing of **6**$\cdot {}^{1}/_{2}C_6H_5CH_3$. Hydrogen atoms, terminal *tert*-butoxy carbon atoms, and the solvent are omitted and only selected atoms labeled.

derivative. The solution state NMR spectra of this compound also changed with time, hampering a detailed assignment of the signals.

Compounds **2**−**4** exhibit a single peak in the ^{31}P NMR (immediately upon dissolution) consistent with the solid-state structure; in the case of **6**, three major signals (∼2:2:1 ratio) are observed showing that the phosphates are in different environments, but the exact assignment is difficult. In the ^{13}C NMR of **2** and **3** only one *C*Me$_3$ signal is observed, as expected. For **5**, the peaks for As*Me*$_2$ and C(*Me*)$_3$ signals for **5** are close together both in ^{1}H and ^{13}C NMR; out of a maximum of nine O*C*Me$_3$ signals possible, six distinct peaks of differing intensities are observed in the ^{13}C NMR for this compound. This is most likely due to the equivalence of some of the *tert*-butoxy groups on the terminal zirconium atoms.

The molecular structures of **2**−**6**, as revealed by X-ray crystallography, are shown in Figures 1−5, respectively. In the case of **4**, the structural features are clear despite the poor quality of the crystals. Compound **2** is a dimer similar to the titanium compound **I**, but it should be noted that for zirconium hexa- or higher coordination is more common and pentacoordinate compounds with five surrounding oxygens are rare.[8] The geometry around zirconium is that of a heavily distorted trigonal bipyramid with O(1) and O(4) at the apical positions. The Zr−O distances to the phosphinate oxygens are longer than those to the *tert*-butoxy oxygens. This is reasonable, as the oxygen bonded to phosphorus is involvedin further "mesomeric" bonding [i.e. the phosphorus also competes with Zr for the electron density of oxygen at P−O(Zr) bond, and hence, the corresponding Zr−O(P) bond is longer] in contrast to the oxygen connected to the *tert*-butyl group. Compound **3** is also a dimer, but here zirconium is hexacoordinate with the sixth position occupied by a THF molecule. The Zr−O(THF) distance is longer than Zr−O(phosphinate) which itself is longer than Zr−O(*tert*-butoxy)

---

(7) Bradley, D. C.; Thomas, I. M. *J. Chem. Soc.* **1960**, 3857.

(8) Examples in which zirconium is surrounded by only five oxygen are reported in: (a) Terry, K. W.; Lugmair, C. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 9745. (b) Chisholm, M. H.; Huang, J.-H.; Huffman, J. C.; Streib, W. E.; Tiedtke, D. *Polyhedron* **1997**, *16*, 2941.

Table 1. Selected Bond Distances and Angles with Esd's for Compounds **2**−**4**

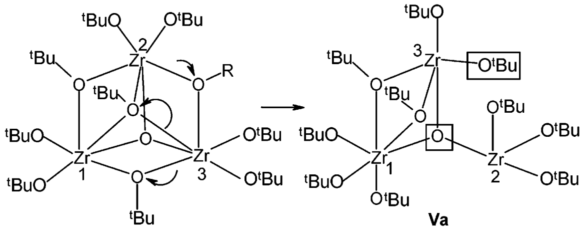
2		**3**·$C_6H_5CH_3$		**4**	
Zr−O(1)	1.9700(13)	Zr−O(1)	2.2132(18)	Zr−O(1)	2.227(4)
Zr−O(2)	1.9505(13)	Zr−O(2)	2.1836(18)	Zr−O(1)′	2.225(4)
Zr−O(3)	1.9225(15)	Zr−O(3)	2.3726(16)	Zr−O(2)	1.918(5)
Zr−O(4)	2.1656(13)	Zr−O(4)	1.9486(17)	Zr−O(3)	2.178(5)
Zr−O(5)	2.1413(12)	Zr−O(5)	1.9522(18)	Zr−O(4)	2.183(4)
		Zr−O(6)	1.9677(18)	Zr−O(5)	1.920(5)

2		**3**·$C_6H_5CH_3$		**4**	
O(1)−Zr−O(2)	95.89(6)	O(1)−Zr−O(2)	80.16(6)	O(1)−Zr−O(1)′	74.16(18)
O(1)−Zr−O(3)	112.99(6)	O(1)−Zr−O(3)	81.88(6)	O(1)−Zr−O(2)	91.47(19)
O(1)−Zr−O(4)	87.20(6)	O(1)−Zr−O(4)	96.15(8)	O(1)−Zr−O(3)	80.49(17)
O(1)−Zr−O(5)	129.91(6)	O(1)−Zr−O(5)	87.41(7)	O(1)−Zr−O(4)	79.38(17)
O(2)−Zr−O(3)	99.15(6)	O(1)−Zr−O(6)	162.86(7)	O(1)−Zr−O(5)	167.57(19)
O(2)−Zr−O(4)	166.18(5)	O(2)−Zr−O(3)	78.61(7)	O(1)′−Zr−O(2)	164.79(19)
O(2)−Zr−O(5)	87.11(5)	O(2)−Zr−O(4)	94.12(7)	O(1)′−Zr−O(3)	78.69(17)
O(3)−Zr−O(4)	91.97(6)	O(2)−Zr−O(5)	161.55(7)	O(1)′−Zr−O(4)	80.36(17)
O(3)−Zr−O(5)	115.82(6)	O(2)−Zr−O(6)	90.55(7)	O(1)′−Zr−O(5)	93.44(19)
O(4)−Zr−O(5)	80.64(5)	O(3)−Zr−O(4)	172.68(7)	O(2)−Zr−O(3)	94.3(2)
		O(3)−Zr−O(5)	86.23(8)	O(2)−Zr−O(4)	102.26(19)
		O(3)−Zr−O(6)	82.18(7)	O(2)−Zr−O(5)	101.0(2)
		O(4)−Zr−O(5)	100.76(9)	O(3)−Zr−O(4)	154.17(18)
		O(4)−Zr−O(6)	98.88(8)	O(3)−Zr−O(5)	98.2(2)
		O(5)−Zr−O(6)	97.78(8)	O(4)−Zr−O(5)	97.9(2)

distances. Although zirconium in **4** is also hexacoordinate, the sixth coordination site is provided by the μ_2-OPh group. Structures analogous to **4** are also observed in tin chemistry; an example is [n-BuSn(OH)($O_2P(C_6H_{11})_2)_2]_2$ (**IV**).[6c]

Compound **5** is a trinuclear zirconium cluster with all the zirconium atoms being hexacoordinate, but the structural motif is much different from that observed in **2** or **3**. The Zr−O(*t*-Bu) distance at the central zirconium Zr(2) is the shortest, followed by the nonbridging Zr−O(*t*-Bu) bonds to the Zr(1) and Zr(3). The Zr−O distances involving bridging arsinate/*tert*-butoxy are the longest. To our knowledge, this is the first structurally characterized Zr−O−As bridged compound. While there are three bridging arsinate ligands between Zr(1) and Zr(3), two bridging *tert*-butoxy and an arsinate ligand connect Zr(1) and Zr(2); only one of the arsinate oxygens on As(1) coordinates to the two zirconium atoms. It appears that lesser steric hindrance by the methyl groups in this arsinate ligand is responsible for this unique structural feature. It can however be noted that multiple oxy or alkoxy bridging is not uncommon for zirconium.[4(b), 9] Although formation of **5** looks serendipitous, a similar triply bridged structural motif is also observed in the di-*tert*-butyl phosphate species **6**. The two bridging *tert*-butoxy groups corresponding to O(8) and O(9) in **6** are replaced by the phosphates corresponding to P(1) and P(2); the type of additional coordination of As−O oxygen to Zr(1) is absent in the phosphate structure which leaves Zr(1) pentacoordinate.[10]

It can be noted that the structures of **5** and **6** are more open compared to that of $Zr_3(O)(O\text{-}t\text{-}Bu)_9(OR)$ [R = *t*-Bu, H] (**V**) which also have three zirconium atoms in the skeleton.[9c,9d] However, a part of the skeleton present in **5** may be generated quite readily from **V** (R = *t*-Bu) as shown in **Va**. Three arsinates need to replace an oxide and a *tert*-butoxy group followed by coordination adjustments to form **5** from **Va**.



V

R = H or t-Bu

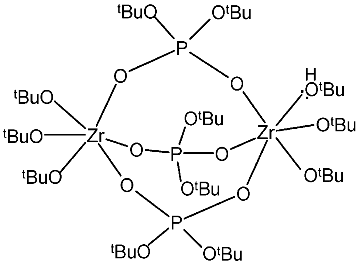
Va

To summarize, new structural forms for (*tert*-butoxy)-zirconium phosphinates/arsinates and phosphates that are

---

[9] (a) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 6289. (b) Teff, D. J.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 4030. (c) Evans, W. J.; Ansari, M. A.; Ziller, J. W. *Polyhedron* **1998**, *17*, 869. (d) Starikova, Z. A.; Turevskya, E. P.; Kozlova, N. I.; Turova, N. Ya, Berdyev, D. V.; Yanovsky, A. I. *Polyhedron* **1999**, *18*, 941. (e) Fleeting, K. A.; O'Brien, P.; Jones, A. C.; Otway, D. J.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1999**, 2853.

[10] We have isolated another compound with three bridging di(*tert*-butoxy)phosphates formulated as $Zr_2(O\text{-}t\text{-}Bu)_5(HO\text{-}t\text{-}Bu)(\mu,\mu'\text{-}O_2P(O\text{-}t\text{-}Bu)_2)_3$ (**7**), thus showing that such a feature is perhaps common for arsinates/phosphates. Compound **7** was obtained from a 1:2 stoichiometric reaction of **1** to di-*tert*-butyl phosphate in hexane, but no warming of the solution was done. Crystals were obtained from hexane at −10 °C. ^{1}H NMR: 1.41, 1.59, 1.70. ^{31}P NMR (C_6D_6): −21.56. ^{13}C NMR: 31.15, 31.23, 32.22, 33.59, 73.64, 79.70, 79.85. The spectra changed over a period of several hours and hence an exact assignment was not made. Other details including a Platon drawing are available as Supporting Information.



(**7**)

dynamic in solution are prepared in this study. Even in the 1:1 stoichiometric reactions, the structure of the final products formed would depend on the steric bulk as well as presence/absence of a coordinating solvent like THF (compounds **2** and **3**). It also appears that substitution of one alkoxy group by an arsinate/phosphate would make that particular zirconium center more prone for further attack (cf. compounds **5** and **6**). Reaction of Zr(O-*t*-Bu)$_4$ with diphenyl phosphate involves a unique ligand exchange between P−OPh and Zr−O-*t*-Bu groups (e.g., compound **4**). It would be interesting to see whether these multinuclear zirconium compounds (e.g., **6**) could be useful in the MOCVD process.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere using standard vacuum line techniques. Solvents were purified according to standard procedures and preserved over sodium wire.[11] Diphenyl phosphate, diphenyl phosphinic acid, and cacodylic acid were procured from Aldrich. Dicyclohexylphosphinic acid and di-*tert*-butyl phosphate were prepared according to literature procedures.[12] ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 200 MHz spectrometers with chemical shifts referenced to TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Elemental analyses were obtained using a LECO CHN 900 or a Perkin-Elmer 240C CHN analyzer.

Syntheses. Compound 2. To Zr(O-*t*-Bu)$_4$ (**1**)[4(b), 7] (0.304 g, 0.792 mmol) in toluene (8 mL) was added predried (0.1 mm/70 °C/3 h) dicyclohexylphosphinic acid (0.182 g, 0.792 mmol) slowly over a period of 5 min using a glass transfer tube with continuous stirring; the residual solid adhering to the transfer tube after dissolving in toluene (7 mL) was also transferred to the reaction flask. The contents were heated with continuous stirring at 70 °C for 24 h. After cooling, the solvent was completely removed in a vacuum and the solid obtained was dissolved in diethyl ether (ca. 4 mL). Cooling the solution to 0 °C afforded **2** as a crystalline solid after 6 d. Yield: 0.256 g (60%). Mp: 265−270 °C. ^{1}H NMR (C_6D_6): δ 1.49 (s, 54 H, *t*-Bu*H*), 1.00−2.20 (br m, 44 H, cyclohexyl-*H*). ^{13}C NMR (C_6D_6): δ 25.41, 25.47, 26.41, 26.50, 26.79, 33.26, 34.34, 36.28, 74.71 (br). ^{31}P NMR (C_6D_6): δ 42.64. The spectra changed over a period of 1 d, and in the ^{31}P NMR, an additional peak at 53.30 ppm was noticed. Anal. Calcd for $C_{48}H_{98}O_{10}P_2Zr_2$: C, 53.41; H, 9.08. Found: C, 52.82; H, 9.92.

Compound 3·$C_6H_5CH_3$. The reaction was performed by a procedure analogous to that for **2** using **1** (0.926 g, 2.41 mmol) in THF (10 mL) and predried (0.1 mm/70 °C/3 h) diphenyl phosphinic acid (0.53 g, 2.41 mmol). After cooling, the volatiles were completely removed in a vacuum and the residue was redissolved in a mixture of toluene and THF (10:1). Insolubles (ca. 0.3 g) were removed by filtration. The residue upon keeping at 0 °C for 3 d gave **3**·2THF·2$C_6H_5CH_3$ as thick needles. Yield: 0.72 g (40%). Mp: sweats at around 80 °C and completely melts at ∼200 °C. ^{1}H NMR (C_6D_6): δ 1.11−1.13 (m, 8 H, CC*H*$_2$), 1.54 (s, 54 H, *t*-Bu*H*), 2.11 (s, ca. 6H, Ar−C*H*$_3$), 3.81 (m, 8 H, OC*H*$_2$), 6.95−7.20 (m, ca. 22H, Ar-*H*), 8.38−8.47 (m, 8H, Ar-*H*). Since the crystals lost toluene quickly, this part of the integration could not be obtained accurately; the crystals had to be mounted along with some mother liquor for X-ray data collection. ^{13}C NMR (C_6D_6): δ 21.13, 24.67, 33.36, 70.19 (THF), 73.88, 125.39, 126.95, 127.27, 127.76, 129.04, 130.54, 132.43, 132.64, 135.93, 138.81. ^{31}P NMR (C_6D_6): δ 13.33. The spectra changed over a period of several days and in the ^{31}P NMR, a broad featureless peak in the region 15−28 ppm was noticed. Anal. Calcd for $C_{63}H_{98}O_{12}P_2Zr_2$: C, 58.52; H, 7.58. Found: C, 59.12; H, 7.27.

Table 2. Selected Bond Distances and Angles with Esd's for Compounds **5** and **6**

5		**6**·$^{1}/_{2}C_6H_5CH_3$	
Zr(1)−O(1)	1.967(4)	Zr(1)−O(1)	1.922(5)
Zr(1)−O(2)	1.945(4)	Zr(1)−O(2)	1.920(4)
Zr(1)−O(3)	1.937(4)	Zr(1)−O(3)	1.947(4)
Zr(1)−O(8)	2.326(4)	Zr(1)−O(8)	2.146(4)
Zr(1)−O(9)	2.303(4)	Zr(1)−O(12)	2.191(4)
Zr(1)−O(10)	2.328(4)	Zr(2)−O(4)	1.918(4)
Zr(2)−O(4)	1.918(4)	Zr(2)−O(9)	2.133(3)
Zr(2)−O(8)	2.154(4)	Zr(2)−O(13)	2.141(3)
Zr(2)−O(9)	2.131(4)	Zr(2)−O(16)	2.107(3)
Zr(2)−O(10)	2.278(3)	Zr(2)−O(20)	2.103(3)
Zr(2)−O(12)	2.071(4)	Zr(2)−O(24)	2.150(4)
Zr(2)−O(14)	2.067(4)	Zr(3)−O(5)	1.953(4)
Zr(3)−O(5)	1.958(4)	Zr(3)−O(6)	1.954(4)
Zr(3)−O(6)	1.996(5)	Zr(3)−O(7)	1.959(5)
Zr(3)−O(7)	1.949(4)	Zr(3)−O(17)	2.240(4)
Zr(3)−O(11)	2.187(4)	Zr(3)−O(21)	2.237(4)
Zr(3)−O(13))	2.227(4)	Zr(3)−O(25)	2.239(4)
Zr(3)−O(15)	2.228(4)		

5		**6**·$^{1}/_{2}C_6H_5CH_3$	
O(1)−Zr(1)−O(2)	95.89(6)	O(1)−Zr(1)−O(2)	95.89(6)
O(1)−Zr(1)−O(3)	95.89(6)	O(1)−Zr(1)−O(3)	95.89(6)
O(1)−Zr(1)−O(8)	95.89(6)	O(1)−Zr(1)−O(8)	95.89(6)
O(1)−Zr(1)−O(9)	95.89(6)	O(1)−Zr(1)−O(12)	95.89(6)
O(1)−Zr(1)−O(10)	95.89(6)	O(2)−Zr(1)−O(3)	95.89(6)
O(2)−Zr(1)−O(3)	101.32(19)	O(2)−Zr(1)−O(8)	146.5(2)
O(2)−Zr(1)−O(8)	95.25(16)	O(2)−Zr(1)−O(12)	87.52(17)
O(2)−Zr(1)−O(9)	96.59(15)	O(3)−Zr(1)−O(8)	88.11(17)
O(2)−Zr(1)−O(10)	160.73(15)	O(3)−Zr(1)−O(12)	160.7(2)
O(3)−Zr(1)−O(8)	157.83(16)	O(8)−Zr(1)−O(12)	80.07(14)
O(3)−Zr(1)−O(9)	93.69(18)	O(4)−Zr(2)−O(9)	90.94(16)
O(3)−Zr(1)−O(10)	92.50(16)	O(4)−Zr(2)−O(13)	93.80(15)
O(8)−Zr(1)−O(9)	69.67(14)	O(4)−Zr(2)−O(16).	93.08(15)
O(8)−Zr(1)−O(10)	68.26(13)	O(4)−Zr(2)−O(20)	94.98(16)
O(9)−Zr(1)−O(10)	68.91(13)	O(4)−Zr(2)−O(24)	178.06(15)
O(4)−Zr(2)−O(8)	102.28(18)	O(9)−Zr(2)−O(13)	87.67(13)
O(4)−Zr(2)−O(9)	101.65(19)	O(9)−Zr(2)−O(16)	90.69(13)
O(4)−Zr(2)−O(10)	172.79(15)	O(9)−Zr(2)−O(20)	173.71(15)
O(4)−Zr(2)−O(12)	95.93(19)	O(9)−Zr(2)−O(24)	87.20(14)
O(4)−Zr(2)−O(14)	96.4(2)	O(13)−Zr(2)−O(16)	172.95(14)
O(8)−Zr(2)−O(9)	76.22(15)	O(13)−Zr(2)−O(20)	89.83(13)
O(8)−Zr(2)−O(10)	72.14(14)	O(13)−Zr(2)−O(24)	86.70(13)
O(8)−Zr(2)−O(12)	160.99(16)	O(16)−Zr(2)−O(20)	91.10(14)
O(8)−Zr(2)−O(14)	94.23(16)	O(16)−Zr(2)−O(24)	86.38(13)
O(9)−Zr(2)−O(10)	72.83(14)	O(20)−Zr(2)−O(24)	86.90(14)
O(9)−Zr(2)−O(12)	94.94(16)	O(5)−Zr(3)−O(6)	99.0(2)
O(9)−Zr(2)−O(14)	161.02(15)	O(5)−Zr(3)−O(7)	96.6(2)
O(10)−Zr(2)−O(12)	89.25(15)	O(5)−Zr(3)−O(17)	169.12(17)
O(10)−Zr(2)−O(14)	88.71(14)	O(5)−Zr(3)−O(21)	90.2(2)
O(12)−Zr(2)−O(14)	89.06(16)	O(5)−Zr(3)−O(25)	91.13(19)
O(5)−Zr(3)−O(6)	98.99(19)	O(6)−Zr(3)−O(7)	97.3(2)
O(5)−Zr(3)−O(7)	101.17(19)	O(6)−Zr(3)−O(17)	88.95(17)
O(5)−Zr(3)−O(11)	91.41(17)	O(6)−Zr(3)−O(21)	167.33(17)
O(5)−Zr(3)−O(13)	165.53(17)	O(6)−Zr(3)−O(25)	90.07(18)
O(5)−Zr(3)−O(15)	87.23(18)	O(7)−Zr(3)−O(17)	89.69(18)
O(6)−Zr(3)−O(7)	97.6(2)	O(7)−Zr(3)−O(21)	90.2(2)
O(6)−Zr(3)−O(11)	88.46(16)	O(7)−Zr(3)−O(25)	168.4(2)
O(6)−Zr(3)−O(13)	89.82(17)	O(17)−Zr(3)−O(21)	80.86(16)
O(6)−Zr(3)−O(15)	169.57(16)	O(17)−Zr(3)−O(25)	81.40(15)
O(7)−Zr(3)−O(11)	164.96(18)	O(21)−Zr(3)−O(25)	81.02(17)
O(7)−Zr(3)−O(13)	88.93(17)		
O(7)−Zr(3)−O(15)	89.35(19)		
O(11)−Zr(3)−O(13)	77.27(15)		
O(11)−Zr(3)−O(15)	83.00(15)		
O(13)−Zr(3)−O(15)	82.49(15)		

---

(11) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, England, 1986.

(12) (a) Peppard, D. F.; Mason, G. W.; Andrejasich, C. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 697. (b) Zwierzak, A.; Kluba, M. *Tetrahedron* **1971**, *27*, 3163.

Table 3. Crystal Data for Compounds **2**, **3**, **5**, and **6**

compound	**2**	**3**·$C_6H_5CH_3$	**5**	**6**·$^1/_2C_6H_5CH_3$
emp formula	$C_{48}H_{98}O_{10}P_2Zr_2$	$C_{63}H_{98}O_{12}P_2Zr_2$	$C_{42}H_{99}As_3O_{15}Zr_3$	$C_{71.50}H_{157}O_{27}P_5Zr_3$
fw	1079.64	1291.79	1342.63	1877.48
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
A (Å)	10.273(2)	12.326(2)	20.329(4)	19.096(4)
b (Å)	11.148(2)	12.423(2)	12.025(2)	20.631(4))
c (Å)	25.830(5)	13.696(3)	27.685(6)	26.855(5)
α (deg)	90	67.00(3)	90	90
β (deg)	98.10(3)	71.89(3)	109.50(3)	92.43(3)
γ (deg)	90	67.50(3)	90	90
V (Å^3)	2928.6(10)	1751.2(6)	6380(2)	10571(4)
Z	2	1	4	4
D_{calcd} (g cm^{-3})	1.224	1.225	1.398	1.180
μ (mm^{-1})	0.457	0.396	2.076	0.426
F(000)	1152	682	2760	3988
no of data/restraints/param	4294/0/280	5024/13/388	9897/0/577	15851/14/953
S	1.062	1.045	1.008	1.007
R1 [$I > 2\sigma(I)$]^a	0.0232	0.0301	0.0510	0.0547
wR2 [all data]^a	0.0610	0.0846	0.1394	0.1624
max/min residual electron dens (e Å^{-3})	0.334/−0.239	0.762/−0.335	0.974/-−1.315	0.850/−0.713

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{0.5}$.

Compound 4. The procedure was analogous to that for **2** using **1** (0.611 g, 1.59 mmol) in toluene (10 mL) and predried diphenyl phosphate (0.400 g, 1.59 mmol). After cooling, the volatiles were completely removed in a vacuum and the residue was dissolved in hexane (6 mL). Upon preservation at −10 °C, a microcrystalline solid was obtained (ca. 0.35 g). This upon redissolving in a mixture of hexane and diethyl ether (10:1, ca. 5 mL) and preserving at −10 °C afforded **5** as hexagonal shaped crystals (0.15 g) after 7 d. [There were also a few rhombus-shaped crystals that could not be analyzed satisfactorily (by spectroscopy) because of the smaller amount.] We were not able to get more of **4** by further concentrating the mother liquor after removal of the microcrystalline solid. Yield: 0.15 g (17%). Mp: >280 °C. ^{1}H NMR (C_6D_6): δ 0.95 (s, 18H, PO-*t*-Bu*H*), 1.00−1.60 (br, ca. 36 H, ZrO-*t*-Bu*H*), 6.80−7.50 (br, ca. 10H, Ar*H*. ^{13}C NMR (C_6D_6): δ 29.98, 31.23, 127.00, 128.28 (other signals were of low intensity and buried in the noise). ^{31}P NMR (C_6D_6): δ −14.08. Anal. Calcd for $C_{48}H_{74}O_{14}P_2Zr_2$: C, 51.50; H, 6.62. Found: C, 51.15; H, 6.52.

Compound 5. The procedure was analogous to that for **2** using **1** (0.658 g, 1.70 mmol) in toluene (10 mL) and predried (0.1 mm/70 °C/3 h) cacodylic acid (0.237 g, 1.70 mmol) [***CAUTION*!** Cacodylic acid (dimethylarsinic acid) and its derivatives have to be handled with care inside an efficient hood and with sufficient protection]. After cooling, the volatiles were completely removed in a vacuum and the residue was dissolved in hexane (5 mL). Insolubles (ca. 0.05 g) were removed by filtration and the clear solution upon preserving at −10 °C gave **5** as irregular shaped crystals; more crystals were obtained after removing the first batch. Yield: 0.80 g (69%). Mp: >250 °C. ^{1}H NMR (C_6D_6): δ 1.33, 1.40, 1.45, 1.47, 1.60, 1.62, 1.64, 1.67 (s each, together 93 H, AsC*H*$_3$ + *t*-Bu*H*), 2.19 (s, 6 H, AsC*H*$_3$). ^{13}C NMR (C_6D_6): δ 19.46, 19.59, 21.71, 30.20, 32.15, 33.24, 33.55, 33.65, 33.73, 33.79, 33.93, 72.57, 73.01, 74.89, 75.61, 76.57, 76.89. The spectra changed over a period of several days, and after 10 days, the *tert*-butyl protons appeared as a broad peak and the As−CH$_3$ protons appeared essentially as a single peak at 1.14 ppm. Anal. Calcd for $C_{42}H_{99}O_{15}As_3P_3Zr_3$: C, 37.57; H, 7.38. Found: C, 37.16; H, 7.37.

Compound 6·$^1/_2C_6H_5CH_3$. A solution of (*t*-BuO)$_2$POOH (0.476 g, 2.27 mmol; dried in a vacuum for 6 h at 0.1 mmHg) in hexane (10 mL) was added dropwise (ca. 10 min) to a solution of **1** (0.869 g, 2.27 mmol) and the contents stirred overnight. Insoluble material (ca. 0.2 g) was filtered off and the solvent completely removed in vacuo at 40 °C. The crystalline material was redissolved in toluene (3 mL) with slight warming; a small amount of insoluble material (ca. 0.05 g) was again filtered off. Crystals of **6**·$^1/_2C_6H_5CH_3$ appeared after 12 h. Mp: >270 °C (loss of crystallinity at 210 °C). ^{1}H NMR: 1.53, 1.54, 1.57, 1.66, 1.69, 1.77; the spectrum of the crystal without drying showed a peak at 2.1 ppm due to toluene. ^{31}P NMR (C_6D_6): −23.12, −23.06, −21.20 (∼2:2:1 ratio). ^{13}C NMR: 31.38 (br), 33.35, 34.10, 73.50, 75.85. The spectra changed over a period of several hours, and hence, an exact assignment was difficult. Anal. Calcd for $C_{68}H_{153}O_{27}P_5Zr_3$ (after drying in vacuo for 2 h): C, 44.60; H, 8.42. Found: C, 45.15; H, 8.54.

All the above compounds (**2**−**6)** were unstable toward moisture; however, **2** could be handled for a few minutes in air.

X-ray Crystallography. Single crystals were selected from the bulk samples of compounds **2** and **4**−**6** and sealed in Lindemann capillaries under an atmosphere of nitrogen. For **3**·$C_6H_5CH_3$, a small amount of the solution of crystallization was also inserted inside the capillary before sealing. Data were collected using a Stoe IPDS diffractometer. Numerical absorption corrections were applied. The structures were solved by direct methods and refined by standard procedures.[13] The quality of the crystals (and hence the X-ray data) of **4** was not good despite repeated attempts and hence high residuals of 2.4 e Å^{-3} were observed close to zirconium; however, there was no ambiguity regarding the connectivity of the atoms. We have also tried to make a correction using Difabs, but the two ghost-peaks did not disappear.[14] In the case of **5** one of the methyl carbons of a *tert*-butoxy group [C(36)] is disordered. In **6**·$^1/_2C_6H_5CH_3$, the solvent toluene was heavily disordered, and hence, these carbon atoms were refined isotropically; the rest of the non-hydrogen atoms were refined anisotropically. Crystal data for **2, 3**, **5**, and **6** are provided in Table 3.

---

(13) Sheldrick, G. M. *SHELX-97: Programs for Crystal Structure Solution and Refinement;* University of Göttingen, Göttingen, Germany, 1997.

(14) Relevant crystal data for **4**: Emperical formula $C_{48}H_{74}O_{14}P_2Zr_2$, formula weight 1119.45, monoclinic, $C2/c$, $a = 21.387(4)$ Å, $b = 20.372(4)$ Å, $c = 13.294(3)$ Å, $\beta = 95.98(3)°$, $V = 5761(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.291$ g cm^{-3}, $\mu = 0.473$ mm^{-1}, $F(000) = 2336$, no. of data/restraints/parameters = 4468/0/307. $S = 1.021$, R1 [$I > 2\sigma(I)$] = 0.0920, wR2 [all data] = 0.2050, maximum/minimum residual electron density = 2.435/−01.339 e Å$^{-3.}$ Further data are available from the authors.

Acknowledgment. K.C.K.S. thanks the Alexander von Humboldt Foundation for financial support under the revisit program as well as for equipment.

Supporting Information Available: X-ray structure determination and crystal data for **2**, **3**, **5**, and **6** as CIF files, Figure 5, a Platon drawing of **7** with cell and bond parameters, and text giving crystal data for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034458O