Synthesis and Structures of Boron- and Aluminum-Containing Spirocycles with P-P Units

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The reaction of aluminum trichloride with $(t\mathrm{BuP})_2\mathrm{K}_2$ affords the potassium salt of the candy-like tricylic compound $[(t\mathrm{BuP})_8\mathrm{Al}_2]^{2-}$ **3**.With boron trifluoride–dimethyl etherate the bicyclic spiropentane derivative $(t\mathrm{BuP})_3(t\mathrm{BuPMe})\mathrm{B}$ **1** is formed. Obviously, cleavage of the dimethyl ether has occurred. The formation of **1** is accompanied by a boron-phosphorus macrocyclic compound resulting from THF cleavage. All structures have been confirmed by single crystal X-ray crystallography. $\mathrm{BP}_4\mathrm{R}_4$ compounds were investigated by DFT methods.

Introduction

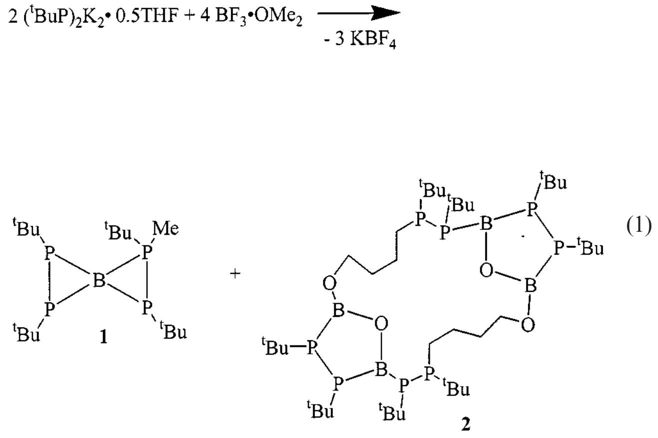
The chemistry of heterocyclic compounds of phosphorus with elements of group 13 has been investigated extensively in the past decades. This is especially true for the chemistry of boron.[1] In the case of aluminum four-membered ring compounds of type $(\mathrm{R_2AlPR'_2})_2$ are the most common;[2] they are considered as dimeric phosphanylalanes. In recent years the monomeric phosphanylalanes[3] have attracted interest in the investigation of possible p-p(π) interactions between atoms of group 13 and 15. With $(\mathrm{MesAlPPh})_3$ [4] the first AlP heterocycle with three coordinated aluminum and phosphorus atoms was synthesized. Comparatively little work has been done on heterocycles of these elements with P-P groups. Only diphospaboriranes $(t\mathrm{BuP})_2\mathrm{BNEt}_2$ [5] and the bicyclobutane derivative $\mathrm{tmpBP_2Btmp}$[6] (tmp = 2,2,6,6-tetramethylpiperidino) and 1,2,3,4-diphosphadiboretanes such as $(t\mathrm{BuP})_2(\mathrm{BNMe}_2)_2$ [7] have been structurally characterized.

On the other hand, butadiene analogues $\mathrm{R_2B{-}(PR')_2{-}BR_2}$ have been used in the discussion on the correlation of hybridization and bond length.[8] Recently, we reported the gallium analogue $\mathrm{tmp_2Ga}(\mathrm{P}t\mathrm{Bu})_2\mathrm{Gatmp_2}$.[9] Here we present the results of reactions of the dipotassium salt of the diphosphandiide $(t\mathrm{BuPP}t\mathrm{Bu})^{2-}$ [10] with halides of boron and aluminum.

Results and Discussion

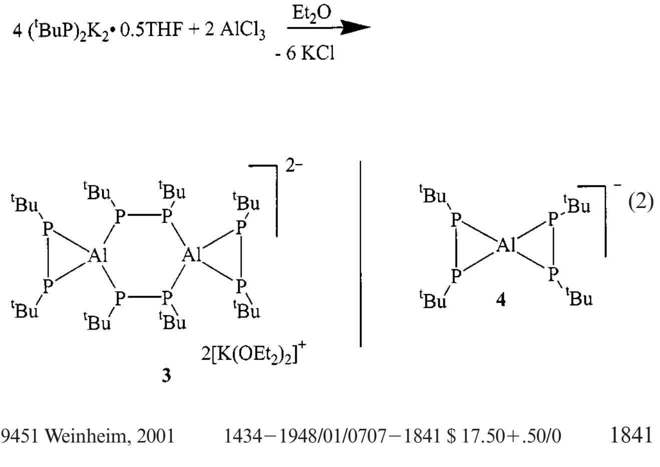
Reactions

If boron trifluoride-dimethyl etherate is reacted with $(t\mathrm{BuP})_2\mathrm{K}_2{\cdot}0.5\mathrm{THF}$ [Equation (1)] the expected product of simple substitution of the fluoride groups at the boron center is not observed. Compound **1** is isolated instead in good yields.



This compound is the product of the cleavage of dimethyl ether by a proposed intermediate such as $[(t\mathrm{BuP})_4\mathrm{B}]^-$. Neither an expected by-product of the type $\mathrm{X_2BOMe}$ nor the product of cleavage of $\mathrm{Me_2O}$ by a Lewis acidic boron compound could be observed in the reaction mixture by means of $^{11}\mathrm{B}$ NMR spectroscopy. The macrocycle **2** is a minor by-product of this reaction. It is formed by cleavage of THF instead of dimethyl ether at the Lewis acidic boron centers and nucleophilic phosphorus atoms.

With aluminum trichloride and $(t\mathrm{BuP})_2\mathrm{K}_2$ the dianionic spirocycle **3** is obtained [Equation (2)]. No products of ether cleavage could be identified. In contrast to the BP_4



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derivative **1** the tricyclic Al_2P_8 compound **3** contains a six-membered AlP ring in addition to three-membered rings. Thus, **3** might be viewed as a dimer of the hypothetical AlP_4 compound **4**.

Crystal Structure Analyses

Compound **1** crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$ (Table 1). The boron atom in the spirocyclic molecule (Figure 1) is coordinated in a distorted tetrahedral fashion. There is a three-membered ring formed by a $(t\mathrm{BuP})_2$ unit and a boron atom. A second three-membered ring is made up by the boron center and a *t*BuP−P(Me)*t*Bu unit. Thus, at first glance **1** may be viewed as a phosphane adduct of a trisphosphanyl borane. Both of the three-membered rings are orthogonal to one another, as is expected for a spiropentane analogue.

The boron-phosphorus bond lengths to the three-coordinate phosphorus atoms are between 194 and 198 pm. This distance is as expected for boron phosphorus bonds between tetracoordinate boron and λ^3 phosphorus atoms, for example in $(Et_2P)_2B(\mu\text{-}PEt_2)_2B(PEt_2)$.[1] The B(1)−P(4) bond (i.e. the λ^4-B−λ^4-P bond) is only 189 pm long. This is remarkable, because at the first glance this bond is expected to be the longest one. Actually, a short bond length like this is typical for bonds between three-coordinate boron and phosphorus atoms. Other examples of three-membered rings are $(t\mathrm{BuP})_2\mathrm{BNEt}_2$ [$d_{\mathrm{BP'}}$ = 189 pm][5] and $(\mathrm{tmpB})_2\mathrm{P}_2$ [d_{BP} = 190.5 (av.)].[6] In **1** two different P−P bond lengths are observed; the P(1)−P(2) bond [d_{PP} = 219.4(2) pm] is 4 pm longer than the P(3)−P(4) bond [d_{PP} = 215.6(2) pm]. Again, the bond involving the λ^4 phosphorus atom is the shorter one. A possible explanation may be found by inspecting the formal charges in **1**. If these are taken as real charges, the P(4)−B(1) bond is shortened by electrostatic attraction. This is discussed more precisely in the following subsection. In comparison to other compounds with P−P bonds, the P-P units in **1** show quite short bonds. For example, in $\mathrm{Et_2NB}(\mathrm{P}t\mathrm{Bu_2})_2$ the P−P bond is longer [d_{PP} = 223 pm]. In contrast with this, even shorter P−P bonds [d_{PP} = 210 pm] are observed in open chain diboryldiphosphanes.[8]

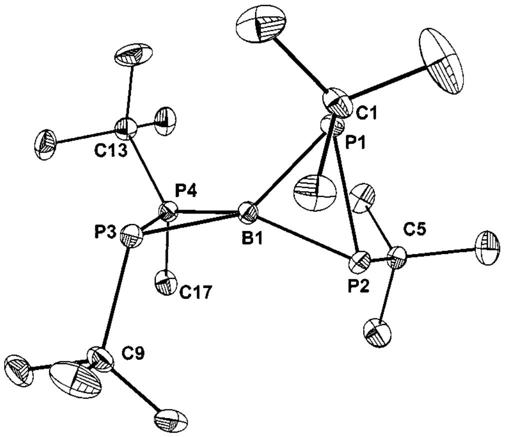


Figure 1. ORTEP view of a molecule of **1**; selected bond lengths [pm] and angles [°]: B(1)−P(1) 193.5(5), B(1)−P(2) 193.7(5), B(1)−P(3) 197.7(5), B(1)−P(4) 188.9(5), P(1)−P(2) 219.4(2), P(3)−P(4) 215.6(2); P(1)−B(1)−P(2) 69.0(2), P(3)−B(1)−P(4) 67.7(2), B(1)−P(1)−P(2) 55.5(2), B(1)−P(3)−P(4) 54.2(2), B(1)−P(4)−P(3) 58.1(1), B(1)−P(2)−P(1) 55.45(1)

Table 1. X-ray structure determination

	1	**3**
Mol. formula	$C_{17}H_{39}BP_4$	$C_{48}H_{112}Al_2K_2O_4P_8$
Cryst. size [mm]	0.2 × 0.15 × 0.15	0.6 × 0.4 × 0.4
Cryst. syst.	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Mol. wt.	378.2	1133.3
a [pm]	959.2(6)	1092.9(2)
b [pm]	1498.3(7)	1806.4(2)
c [pm]	1621.4(9)	1785.3(3)
β [deg]		92.95(3)
V [nm^3]	2.330(2)	3.520(1)
Z	4	2
D (calcd.), [gcm^{-3}]	1.078	1.069
F(000)	824	1232
μ [mm^{-1}]	0.320	0.374
2θ range [°]	14−48	5−45
No. of collcd. rflns	10425	6199
No. of unique rflns	3482	4580
No. of obsd. rflns [$I > 2\sigma(I)$]	3074	3115
GOF	1.178	1.003
Parameters	212	305
*wR*2(all data)	0.098	0.108
*R*1	0.052	0.040
Largest diff. peak [eÅ^{-3}]	0.273	0.298

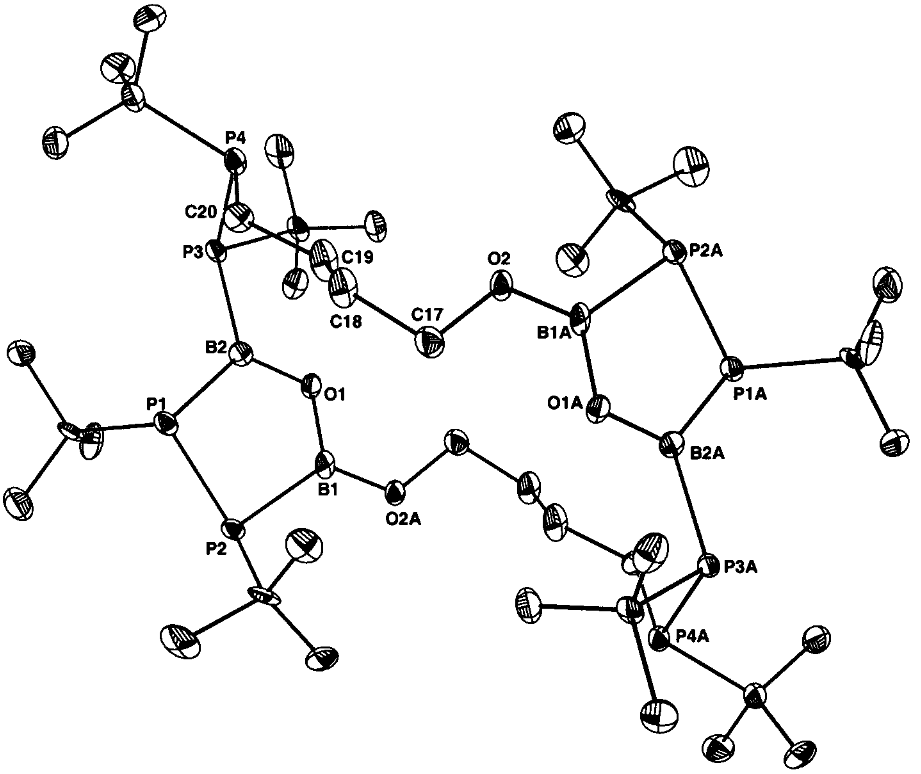


Figure 2. ORTEP view of a molecule of **2**

Compound **2** crystallizes triclinically in the space group $P\bar{1}$.[11] The molecule (Figure 2) consists of a central large 20-membered ring, consisting of four boron, four phosphorus, four oxygen and eight carbon atoms. The boron and oxygen atoms are also part of fused five-membered B_2OP_2 rings. Due to the low quality of the X-ray structure determination no bonding parameters will be discussed.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$. The centrosymmetric molecule (Figure 3) consists of two three-membered and one six-membered aluminum phosphorus ring in a chair conformation. In this spirocycle, the three-membered P_2Al rings and the AlP_2 units of the six-membered ring show an interplanar angle of only 70°. The aluminum atoms reside in a distorted tetrahedral array of four phosphorus atoms. The P(3)−Al−P(4) angle within the three-membered ring is very acute [54.72(4)°]; the corresponding one, P(1)−Al−P(2)A, in which the phosphorus atoms involved are part of the six-membered ring, is near the tetrahedral angle [107.26(5)°]. Consequently, the P−Al−P angles out of the rings are wider than 109°. The central Al_2P_4 ring adopts a chair conformation. P(2) and P(3) are coordinated in a trigonal pyramidal fashion by aluminum, carbon and phosphorus centers, the sum of angles being 337.2° at P(2) and 295.0° at P(3). P(1) and P(4) have contacts to a potassium cation [d_{KP} = 322 and 323 pm]. Consequently, P(1) and P(4) have longer Al−P bonds than P(2) and P(3). The distance K−P(2) is longer by 55 pm [$d_{K-P(2)}$ = 376.7 pm]. Thus, it is longer than the sum of the van der Waals radius of a phosphorus atom (190 pm) and

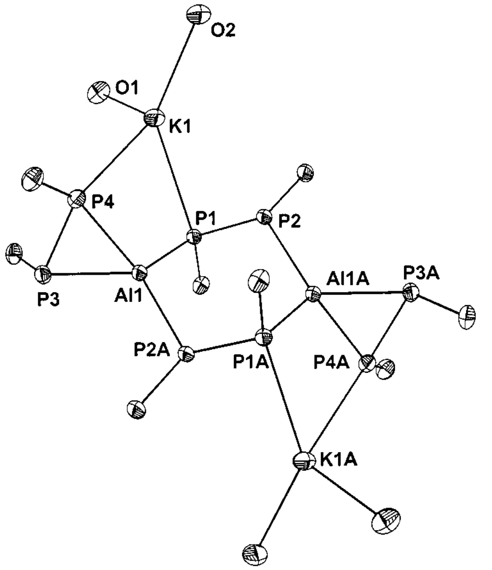
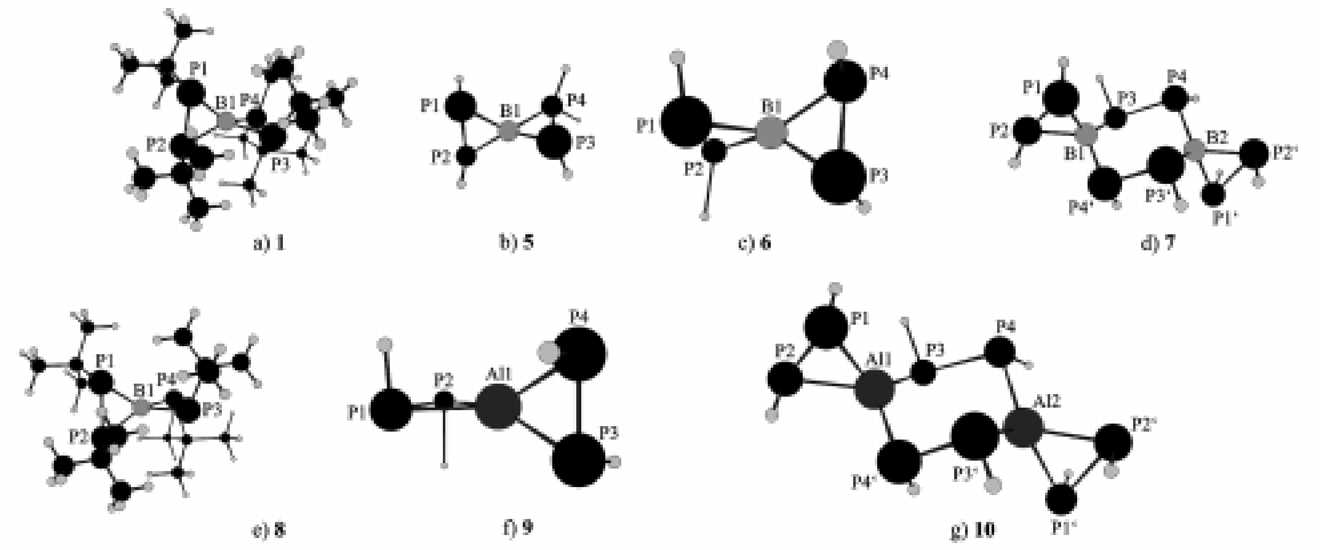


Figure 3. ORTEP view of a molecule of **3**; methyl and ethyl groups have been omitted for clarity; selected bond lengths [pm] and angles [°]: K−P(4) 322.05(14), K−P(1) 323.2(2), Al−P(1) 238.64(14), Al−P(3) 236.89(14), Al−P(2)A 237.28(14), Al−P(4) 239.1(2), P(1)−P(2) 217.05(13), P(3)−P(4) 218.8(2), P(3)−Al−P(1) 121.05(5), P(3)−Al−P(4) 54.72(4), P(1)−Al−P(4) 105.64(5), P(3)−P(4)−Al 62.12(5), P(3)−Al−P(2)A 119.48(5), P(2)A−Al−P(1) 107.26(5), P(2)A−Al−P(4) 141.68(6), P(2)−P(1)−Al 98.19(5), P(1)−P(2)−AlA 114.20(6), P(4)−P(3)−Al 63.16(4)



a) **1** b) **5** c) **6** d) **7** e) **8** f) **9** g) **10**

Figure 4. View of a molecule of: a) **1**, b) **5**, c) **6**, d) **7**, e) **8**, f) **9** and g) **10**, as predicted by RI-DFT calculations

Table 2. Selected DFT-calculated bond lengths [pm] for **1** (exp.) to **10**

	1 (exp·)	**5**	**6**	**7**	**8**	**9**	**10**	**3 (exp.)**
B(1)−P(1)	195.2 (193.5)	194.1	196.0−196.1	199.0−201.1	196.2−196.7	(Al−P) 236.9−237.1	239.8−241.7	236.9−239.1
B(1)−P(2)	196.0 (193.7)	195.7	−	−	−	−	−	−
B(1)−P(3)	200.1 (197.7)	196.6	−	197.8−198.3	−	−	−	−
B(1)−P(4)	191.3 (188.9)	193.2	−	−	−	−	−	−
P(1)−P(2)	223.1 (219.4)	227.1	227.7	226.5	223.2−223.7	235.5−235.6	232.4	218.8
P(3)−P(4)	220.1 (215.6)	223.1	−	227.8	−	−	227.6	217.1

the effective ionic radius of a potassium cation (150 pm). The potassium centers can be considered to be coordinated distorted tetrahedrally by two phosphorus atoms and two diethyl ether molecules. The P−P bonds in the three- and six-membered rings do not differ very much and are similar to those in **1**. The Al−P distances are between 236.9 and 239.2 pm long. This is shorter than in oligomeric phosphanylalanes $(R_2AlPR'_2)_n$ (range 243.3−247.5 pm).

Results of DFT Calculations

The most striking feature in the unusual spiropentane derivative **1** is the short λ P−B bond. Therefore, **1** and related compounds have been investigated by Density Functional methods. All calculations were done with the Turbomole program package[12] (**5a, b**) with RI approximation, the BP86 functional and SV(P) bases for all atoms.

For both, **1** and **5** a good agreement was found between the experimentally determined and the calculated structures (see Figure 4 and Table 2).

In **1** and in the all-hydrogen substituted spiropentane derivative **5** the λ^4 P−B bond is the shortest one and the other B−P bond, which is part of the same three-membered ring, is the longest one in the molecule. Obviously, steric arguments do not apply when explaining this observation. In the anionic compounds **6** and **8** four identical B−P bonds are expected and this is verified by the calculations. These B−P distances are similar to those in the $(RP)_2B$ rings in **1** and **5**.

By inspecting the atomic charges obtained from an Ahlrich−Heinzmann population analysis, a negative charge is found on the tetracoordinated boron atoms of **1** (−0.74), **5** (−0.75), **6** (−0.73) and **8** (−0.73) and a nearly equal positive charge on the tetracoordinated phosphorus atoms in **1** (+0.65) and **5** (+0.41). This is in line with the formal charges on these atoms and explains the short bond lengths. All other phosphorus atoms have very small charges (<+0.14). According to the shared electron numbers (SEN) obtained from this population analysis all B−P bonds are to be regarded as single bonds (SEN = 1.25−1.35). In particular, the short λ^4 PB bond has an SEN similar to the other B−P bonds; the longest B−P bonds in **1** and **5** have the smallest SEN, as expected. This is in line with the electrostatic interpretation of the bond shortening. The P(3)−P(4) bond in **1** and **5** is shorter than the λ^3[P(1)−P(2)] bond by 4 pm. A possible explanation may be found by inspecting the results of a natural bond orbital analysis. According to this, the P1−P2 bond acts as an electron donor into the σ*(B1P3) and σ*(B1P4) orbitals. Hereby a stabilization of 58 kJ·mol^{-1} is achieved. The P3−P4 bond is a weaker donor. By donation of electrons into the σ*(B1P1) and σ*(B1P2) orbitals a stabilization of only 36 kJ·mol^{-1} results.

The possible dimerization of **6** to afford **7** is endothermic (ΔH_{Dim} = 140 kJ·mol^{-1}). The B−P bonds in the dimer are longer than those in **6** by 4 pm. The P−P bonds are almost unaffected.

For the aluminum homologue **9**, the dimerization to **10** is also endothermic, but only by 64 kJ·mol^{-1}. Taking into account that **3** is not a free dianion as assumed for **10**, with the larger aluminum atom as spiro-center the dimeric structure is preferred over the monomer.

The Al−P bonds in **10** are similar to those in **3**, but longer than in **9**. Very striking are the long P−P bonds in **9**, which are in contrast to those in **3**. Here, the influence of substituents and the missing counterions is evident (compare P−P bond lengths in **1** and **5**−**8**). In a similar manner to **3**, the P−Al−P angles in **10** within the three-membered ring are 57.8°; within the six-membered rings they are 109.8° and 115.9°. Quantum chemical calculations are also helpful in assigning the NMR signals in **1**. For the calculated structure of **1** NMR shielding parameters can be calculated using the GIAO method[13] implemented in the Gaussian98 program. As reference points the shielding parameters for BF_3 and PH_3 were also calculated on the same level. The results, which are in good agreement with the experimentally observed data, and the assignment are summarized in Table 3. The ^{11}B NMR shift is in the typical range for tetracoordinated boron compounds. In the ^{31}P NMR spectrum a line-rich ABCX spin system is observed. The three chemically different P*t*Bu units are observed in a small range of 20 ppm as the tetracoordinated phosphorus atom is better shielded.

Table 3. ^{11}B and ^{31}P NMR shifts for **1** from GIAO calculations (BP86/6−31G*) and experimental values

	1 (DFT)	**1** (exp.)
δ^{11}B	−23.4	−25.9
δ^{31}P	−66 P(4)	−59.5
	−125 P(1)	−136.2
	−133 P(2)	−145.3
	−141 P(3)	−158.1

Conclusion

The group 13-phosphorus spirocycles **1** and **3** are new classes of heterocyclic small ring compounds. The larger covalent radius of aluminum compared to boron causes the different ring sizes in **1** and **3**.

Experimental Section

General Remarks: All experiments were performed under purified nitrogen or in vacuo with Schlenk techniques. All yields are referenced to $K_2P_2t\mathrm{Bu}_2$. Elemental analyses were performed in the microanalytical laboratory of the University of Karlsruhe. NMR: Bruker ACP200 and 250; Mass spectra: Varian MAT711; X-ray crystallography: Suitable crystals were mounted with a perfluorinated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data collections were performed with Mo-K_{α} radiation (graphite monochromator) on a STOE STADI4 diffractometer (**2**, **3**) in a ω-scan mode or on a Siemens Bruker P4 diffractometer with CCD detector (**1**). Structures were solved and refined with the Bruker AXS Shelxtl 5.1 program package. Refinement in full-matrix against F^2. All non-hydrogen atoms were included as a riding-model with fixed isotropic *U* values in the final refinement. For further data see Table 1.
Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-152829 (**1**) and -152830 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Quantum chemical calculations: The program packages TURBOMOL[12] and Gaussian98W[13] were used for the RI-DFT calculations[14] (BP86 functional,[15] SV(P)base), the NBO and GIAO calculations

(*t*BuP)$_2$B(P*t*Bu)P(*t*Bu)Me (1) and (2): $t\mathrm{Bu}_2P_2K_2$·0.5THF (0.48 g, 1.65 mmol) was suspended in 15 mL of diethyl ether and a solution of BF_3·OMe_2 (0.50 g; 4.40 mmol) in 25 mL diethyl ether was added dropwise at ambient temperature. After stirring for 12 h all volatiles were removed in vacuo. The residue was then taken up in 30 mL of pentane. KBF_4 (0.43 g) was separated by filtration. The solution was concentrated to a volume of 5 mL. At −30 °C colorless plates of **1** crystallized; yield: 0.14 g (45%), m.p. 72−74 °C. From the reduced mother liquor (2 mL) some colorless crystals of **2** were isolated, 0.02 g (5%).
1: ^{1}H NMR (C_6D_6): δ = 1.05 (d, $^2J_{\mathrm{PH}}$ = 18 Hz, PMe), 1.28 (d, $^3J_{\mathrm{PH}}$ = 12 Hz, *t*Bu), 1.40 (m, 3*t*Bu). − ^{31}P NMR(C_6D_6): δ = −158.1 (m, *N* = 253 Hz, P*t*Bu), −145.3 (m, *N* = 665.8 Hz, *t*Bu), −136.2 (m, *N* = 170 Hz, P*t*Bu), −59.5 (m, *N* = 407 Hz, PMe*t*Bu). − ^{11}B NMR: δ = −25.9 ("d", $^1J_{\mathrm{BP}}$ = 40 Hz). − MS (70 eV, EI): *m*/*z* (%) = 378 (38) [M$^+$], 321 (28) [M − *t*Bu]$^+$, 265 (30) [M − *t*Bu − C_4H_8]$^+$, 207 (100) [MeBP$_4$*t*Bu]$^+$. − $C_{17}H_{39}BP_4$ (378.2): calcd. C 53.99, H 10.39; found C 52.09, H 10.18.

Al_2(P*t*Bu)$_8$$K_2$·($OEt_2$)$_4$ (3): A solution of $AlCl_3$ (0.11 g, 0.83 mmol) in 10 mL diethyl ether was added dropwise at ambient temperature to a suspension of $t\mathrm{Bu}_2P_2K_2$·0.5THF (0.36 g, 1.24 mmol) in 25 mL diethyl ether. After stirring for 1 day the mixture was filtered and the colorless solution was reduced in volume to 20 mL. On standing at ambient temperature colorless plates of **3** crystallized; yield: 0.24 g (68%, ref to $t\mathrm{Bu}_2P_2K_2$), m.p. (dec.) >90 °C. Compound **3** is extremely pyrophoric and does not redissolve in common NMR solvents. Thus, analytical data given are incomplete (a ^{31}P NMR spectrum recorded from the reaction mixture exhibited several groups of signals between δ = −220 and −10 which could not be assigned unequivocally). − MS (70 eV, EI): *m*/*z* (%) = 499 (0.1) [Al(P*t*Bu)$_5$PH]$^+$, 494 (0.1) [Al_2(P*t*Bu)$_5$]$^+$, 352 (5) [(P*t*Bu)$_4$]$^{+\cdot}$, 264 (7) [P*t*Bu)$_3$]$^{+\cdot}$, 57 (100) [*t*Bu]$^+$.

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[11] Due to the low quality and waxy consistence of all crystals examined, the crystal structure analysis of **2** can only be used for getting a rough picture of the connectivities in the macrocycle. The X-ray structural data are: space group $P\bar{1}$, a = 977.0(2), b = 1184.2(2), c = 12.646(3) pm, α = 80.09(3)°, β = 77.49(3)°, γ = 73.08(3)°, no. of refl. $[I > 4\sigma(I)]$ = 3330(2299), param. = 265, R_1 = 0.160, wR_2 = 0.536.

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