Syntheses and Molecular Structures of Novel Alkali Metal Tetraorganylcyclopentaphosphanides and Tetraorganyltetraphosphane-1,4-diides[‡]

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In memoriam Professor Marianne Baudler

Keywords: Alkali metals / Phosphorus / P ligands / ^{31}P NMR spectroscopy / Tetraphosphane-1,4-diides

The reaction of sodium with $RPCl_2$ and PCl_3 (12:4:1) in THF gives Na[*cyclo*-(P_5R_4)] [R = *i*Pr (**1**), Ph (**2**)], while four equivalents of $RPCl_2$ [R = Ph, 2,4,6-$Me_3C_6H_2$ (Mes), *t*Bu] react with ten equivalents of sodium sand or elemental potassium in refluxing THF to yield the compounds [$Na_2(THF)_5(P_4Ph_4)$] (**3**), [$Na_2(THF)_4(P_4Mes_4)$] (**4**), and [$Na_2(THF)_4(P_4tBu_4)$] (**5**), or the potassium salt [$K_2(THF)_6(P_4Mes_4)$] (**6**). Recrystallizing **6** from 1,4-dioxane/pentane (1:3) also led to [{$K(L)_2$}$_2${$K(L)$}$_6$(P_4Mes_4)$_4$·0.5THF]$_\infty$ (L = 1,4-dioxane) (**7**). In the solid state, compounds **3**–**6** exist as isolated ion-contact complexes, in which the P_4 chain of the $(P_4R_4)^{2-}$ ligand has a *syn* arrangement, while a polymeric helical arrangement was observed for **7**. A minor product, [{K(pmdeta)(HP_3Mes_3)}$_2${K_2(P_4Mes_4)}]·0.25hexane (**8**), was isolated from the reaction of $MesPCl_2$ and K (1:2.5). Compound **8** contains the first structurally characterized example of a triphosphanide anion, $(HP_3Mes_3)^-$, besides $K_2(P_4Mes_4)$.

Introduction

Cyclooligophosphanes *cyclo*-$(PR)_n$,[1] which are isolobal with cycloalkanes have attracted the interest of chemists for a long time. Whereas the first example of this class of compounds, *cyclo*-$(PPh)_5$, was synthesized as early as 1877,[2] the first cyclooligophosphanide anions *cyclo*-$(P_nR_{n-1})^-$ were only reported approximately 100 years later.[3,4] Even today, the number of compounds readily accessible in pure form is still small.[5] Thus, the alkali metal compounds K[*cyclo*-(P_3tBu_2)],[3] K[*cyclo*-(P_5Ph_4)],[5] and Li[*cyclo*-(P_ntBu_{n-1})] ($n = 3-5$)[6,7] were only obtained as inseparable mixtures, and characterized by ^{31}P NMR spectroscopy. Only recently, we reported the targeted high-yield synthesis of Na[*cyclo*-(P_5tBu_4)] as well as preliminary results of its use in coordination chemistry.[8]

We have now employed the same synthetic approach for the preparation of other cyclopentaphosphanide anions Na[*cyclo*-(P_5R_4)], starting from *i*PrPCl$_2$, PhPCl$_2$ or MesPCl$_2$ (Mes = 2,4,6-$Me_3C_6H_2$), PCl$_3$, and Na (4:1:12). While Na[*cyclo*-(P_5R_4)] [R = *i*Pr (**1**), Ph (**2**)] are obtained, the tetraphosphane-1,4-diides $Na_2(P_4R_4)$ are the major products for R = Ph (**3**) and R = Mes (**4**).

While a large number of alkali metal phosphanides M(PRR′) (R, R′ = alkyl, aryl, H) have been synthesized and structurally characterized, their structures in solution are largely unknown.[9] In this respect, oligophosphanediides of the general formula $M_2(P_4R_4)$ (M = Li, Na, K; R = Me, Et, Cy, *t*Bu, Ph), which were first obtained by Issleib et al. by reduction of cyclooligophosphanes, *cyclo*-$(PR)_n$, with Li, Na, and K, are of special interest.[10] In contrast to alkali metal phosphanides, M(PRR′),[9] these compounds have been extensively studied by ^{31}P NMR spectroscopy, and their molecular structures in solution were proposed on the basis of the complex spin systems observed.[11] Independently from our own work, the solid-state structures of complexes of the general composition $Na_2(P_nPh_n)$ ($n = 2-4$), which were obtained from the reaction of PhPCl$_2$ and Na, were recently reported.[12]

Although linear and cyclic oligophosphanides are of interest as ligands in main group and transition metal

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chemistry, there are only a few reports where linear oligophosphanide ligands $(P_nR_n)^{2-}$ have been employed in coordination chemistry. These include the synthesis of metallocene triphosphane-1,3-diyl complexes $[Cp_2M(P_3R_3)]$ (M = Ti, Zr, Hf; R = Me, Et, Ph, *t*Bu),[13] a nickel tetraphosphane-1,4-diyl complex $[Ni(\eta^2\text{-}P_2tBu_2)(P_4tBu_4)]$,[14] the germatetraphospholanes[15] *cyclo*-$(P_4tBu_4GeR_2)$ (R = Et, Ph) and *cyclo*-$\{P_4tBu_4Ge(\eta^2\text{-}P_2tBu_2)\}$, and the stannatetraphospholanes[16] *cyclo*-$(P_4tBu_4SnR_2)$ (R = *t*Bu, *n*Bu, Ph) and *cyclo*-$\{P_4tBu_4Sn(Cl)nBu\}$. In addition, we have shown, that the cyclic oligophosphanide anion *cyclo*-$(P_5tBu_4)^-$ exhibits a rich and unprecedented chemistry.[8,17]

We now report the syntheses of the sodium cyclopentaphosphanides Na[*cyclo*-(P_5R_4)] [R = *i*Pr (**1**), Ph (**2**)], and improved syntheses of the alkali metal tetraphosphane-1,4-diides $[Na_2(THF)_5(P_4Ph_4)]$ (**3**), $[Na_2(THF)_4(P_4Mes_4)]$ (**4**), and $[Na_2(THF)_4(P_4tBu_4)]$ (**5**), and the potassium salts $[K_2(THF)_6(P_4Mes_4)]$ (**6**) and $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4\cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**). The structures of **3**−**6** in solution were established from ^{31}P NMR spectroscopic studies, and were compared with the solid-state structures.

A minor product from the reaction of $MesPCl_2$ and K (1:2.5) with an excess of pmdeta (pmdeta = pentamethyldiethylentriamine) and hexane, namely $[\{K(pmdeta)(HP_3Mes_3)\}_2\{K_2(P_4Mes_4)\}]\cdot 0.25$hexane (**8**), was isolated and structurally characterized. Compound **8** contains the first structurally characterized example of a triphosphanide anion, $(HP_3Mes_3)^-$, besides $K_2(P_4Mes_4)$.

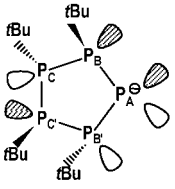
Results and Discussion

Synthesis and Spectroscopic Properties of Na[*cyclo*-(P_5R_4)] [R = *i*Pr (1), Ph (2)]

The reaction of sodium with $RPCl_2$ and PCl_3 (12:4:1) in THF gives Na[*cyclo*-(P_5R_4)] (R = *i*Pr (**1**), Ph (**2**)] in an amount of conversion of 61 and 32%, respectively (as determined by ^{31}P NMR spectroscopy). Besides **1** and **2**, signals of *cyclo*-$(PiPr)_4$,[18] $iPrPH_2$,[19] and $Na_2(P_2iPr_2)$[20] (for **1**) or $Na_2(P_4Ph_4)$ (**3**),[11] Na{PPhP(H)Ph},[20] $Na_2(P_3Ph_3)$,[11] and $Na_2(P_2Ph_2)$[20] (for **2**) were observed in the ^{31}P NMR spectra of the reaction mixtures. Compounds **1** and **2** are very air-sensitive, and even pyrophoric as finely divided powders. They dissolve readily in ethers, aliphatic, and aromatic organic solvents.

In the $^{31}P\{^1H\}$ NMR spectra, **1** and **2** exhibit signals for an ABB′CC′ spin system.[21] Only one conformational isomer was observed, which we propose to be the *all-trans* isomer by comparison with Na[*cyclo*-(P_5tBu_4)].[8] This is also in agreement with the observed coupling constants (Table 1).[5,11c,22]

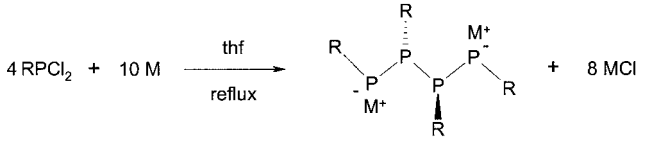
Table 1. $^{31}P\{^1H\}$ NMR parameters (C_6D_6, 25 °C, δ in ppm, *J* in Hz) of Na[*cyclo*-(P_5R_4)] (R = *i*Pr (**1**), Ph (**2**) or *t*Bu[8])



	*i*Pr	Ph	*t*Bu[8]
δ_A	−126.5(1)	−105.6(1)	−105.6(1)
$\delta_B = \delta_{B'}$	+66.3(1)	+72.8(1)	+82.7(1)
$\delta_C = \delta_{C'}$	+42.6(1)	+47.1(1)	+75.0(1)
$^1J_{AB} = {}^1J_{AB'}$	−352.1(1)	−403.2(1)	−379.2(1)
$^1J_{BC} = {}^1J_{B'C'}$	−293.9(2)	−312.3(1)	−317.3(1)
$^1J_{CC'}$	−324.8(2)	−334.2(1)	−309.4(1)
$^2J_{AC} = {}^2J_{AC'}$	−	+9.5(1)	−0.1(1)
$^2J_{BC'} = {}^2J_{B'C}$	−	+11.4(1)	−5.4(1)
$^2J_{BB'}$	−	+1.9(1)	−17.2(1)

Synthesis, Molecular Structures, and Spectroscopic Properties of $[Na_2(THF)_5(P_4Ph_4)]$ (3), $[Na_2(THF)_4(P_4Mes_4)]$ (4), $[Na_2(THF)_4(P_4tBu_4)]$ (5), $[K_2(THF)_6(P_4Mes_4)]$ (6), and $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4\cdot 0.5THF]_\infty$ (L = 1,4-Dioxane) (7)

The reaction of four equivalents of $PhPCl_2$ (**3**), $MesPCl_2$ (**4** and **6**), or $tBuPCl_2$ (**5**) with ten equivalents of sodium sand (**3**−**5**) or elemental potassium (**6**) in refluxing THF yields the compounds **3**−**6** in high purity and moderate yields (27 to 43%, Scheme 1). Compound **7** can be obtained upon recrystallization of **6** from dioxane/pentane (1:3).



Scheme 1. Synthesis of **3**−**6** [M = Na, R = Ph (**3**), Mes (**4**), *t*Bu (**5**); M = K, R = Mes (**6**)]

In the solid state **3**, **4**, **5**, and **6** exist as isolated ion-contact complexes, in which the P_4 chain of the $(P_4R_4)^{2-}$ ligand has a *syn* arrangement [torsion angles between the planes P1−P2−P3 and P2−P3−P4 or P1−P2−P2′ and P2−P2′−P1′: 32.1° (**3**), 72.7° (**4**), 8.8° (**5**), and 75.1° (**6**)], and is coordinated to two alkali metal cations (Figures 1−5). The coordination spheres of the alkali metal cations are completed by two (**4** and **5**) or three (**3** and **6**) THF molecules. In **3**, a bridging THF molecule can be observed [*d*(Na1−O3) = 301.3(8) pm]. This is a rare situation,[23] and has only been observed twice in the structures of alkali metal phosphanides.[24] Bridging THF molecules were also observed in the molecular structure of the tetrameric sodium and potassium fluorenone ketyls $[Na_4(OC_{13}H_8)_2(THF)_2(\mu_2\text{-}THF)_2(OC_{13}H_8)_4]$ [*d*(Na−O) = 239.1(7)−260.6(7) pm] and $[K_4(hmpa)_4(\mu_2\text{-}THF)(OC_{13}H_8)_4]$ (hmpa = $OP(NMe_2)_3$].[23] The P−P bond lengths, which range from 216.6(1)−226.2(2) pm, are in the typical range for single bond lengths.[25] In spite of these general similarities, there are significant differences between the coordination modes of

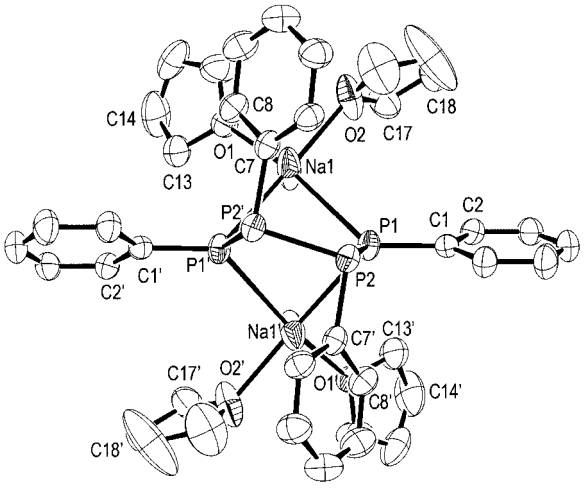


Figure 1. Molecular structure of $[Na_2(THF)_5(P_4Ph_4)]$ (**3**); the bridging THF molecule has been omitted for clarity

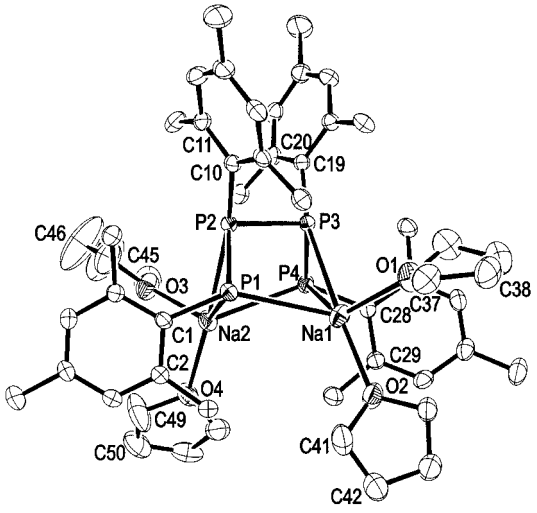


Figure 2. Molecular structure of $[Na_2(THF)_4(P_4Mes_4)]$ (**4**)

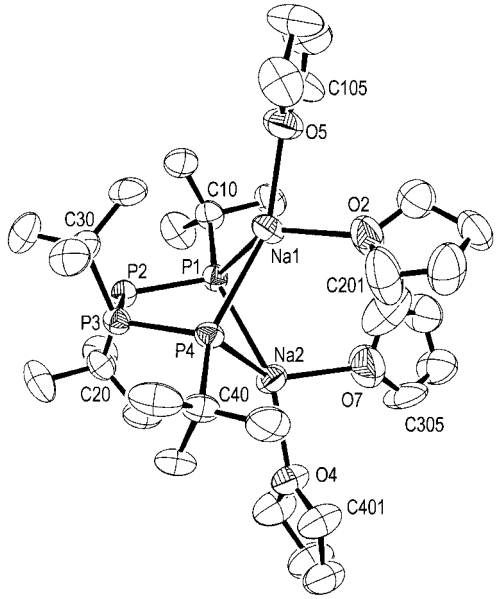


Figure 3. Molecular structure of $[Na_2(THF)_4(P_4tBu_4)]$ (**5**)

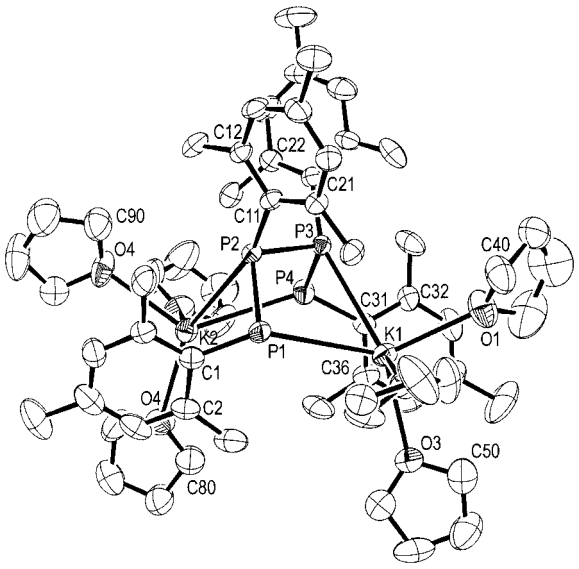


Figure 4. Molecular structure of $[K_2(THF)_6(P_4Mes_4)]$ (**6**)

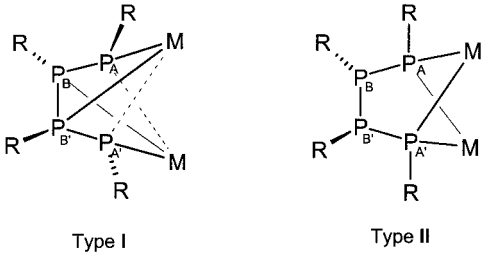


Figure 5. The two structural arrangements observed in the solid-state structures of **3** and **5** (type **II**), and **4** and **6** (type **I**)

Na and K. Whereas for **4** and **6** the phosphorus alkali metal distances are in the typical range for related sodium and potassium phosphanides[9] *both* for the internal and terminal phosphorus atoms of the chain [**4**: *d*(Na1−P1,P3), *d*(Na2−P2,P4) = 289.6(2)−316.6(1) pm, **6**: *d*(K1−P1,P3), *d*(K2−P2,P4) = 331.4(3)−359.8(2) pm], in **3** and **5** the Na cations are exclusively coordinated by the terminal phosphorus atoms [**3**: *d*(Na1−P1) = 290.1(2) pm, *d*(Na1−P1′) = 289.2(2) pm, **5**: *d*(Na1−P1,P4) = 281.9(1)−291.1(1) pm, *d*(Na2−P1,P4) = 284.0(1)−290.1(1) pm] (Figure 5). Thus, for **4** and **6**, the phosphorus atoms in the 1,3 positions coordinate and four-membered MP_3 chelate rings are formed. Additionally, longer contacts can be observed between the alkali metal and the second terminal phosphorus atom [**4**: *d*(Na1−P4) = 331.6(2), *d*(Na2−P1) = 317.3(2) pm, **6**: *d*(K1−P4) = 382.3(3) pm, *d*(K2−P1) = 385.1(2) pm]. The strong interaction with the inner phosphorus atoms is also reflected in the larger torsion angle of the $(P_4R_4)^{2-}$ chain (see above). Solvation of Na and K is completed by short contacts to carbon atoms of the mesityl substituents [**4**: d[Na(1)−C28,C29), *d*(Na2−C1,C2) = 289.6(3)−306.6(3) pm, **6**: *d*(K1−C31,C36), *d*(K2−C1,C2) = 314.2(5)−321.5(6) pm], indicating η^2 interactions of the aryl rings. Interestingly, short K−C contacts were not observed for the phenyl rings of **3**, whereas π coordi-

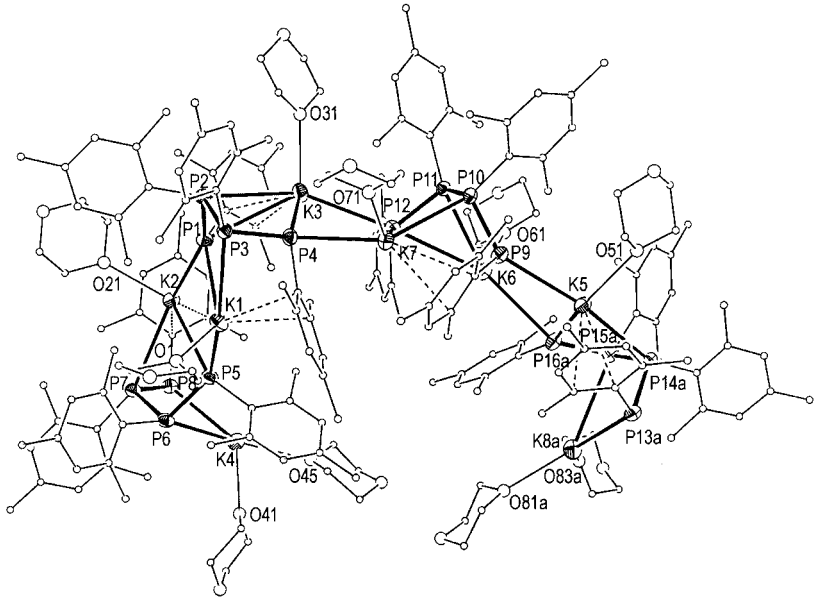


Figure 6. Molecular structure of $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4 \cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**); only one tetrameric unit is shown; the THF solvate molecule has been omitted for clarity; only K−P distances up to 363 pm are shown

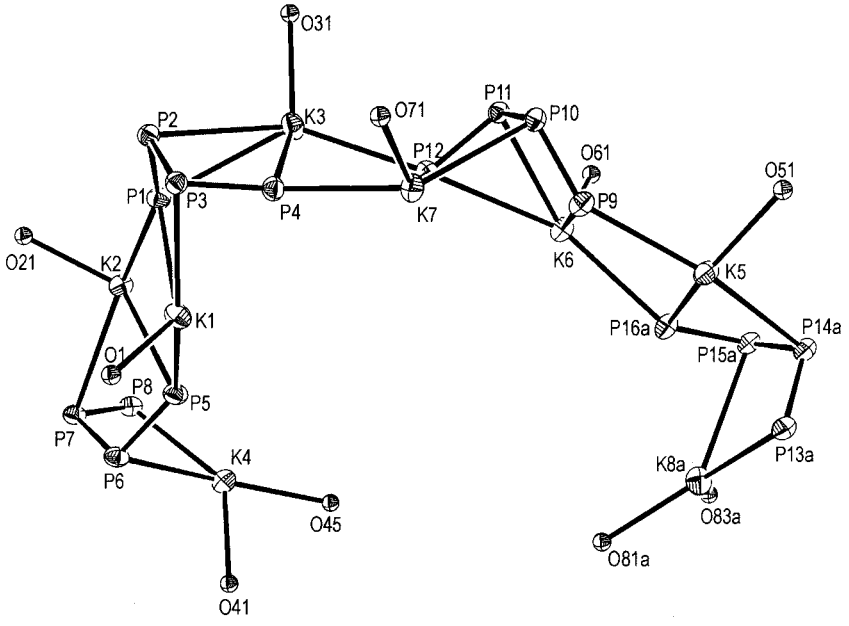


Figure 7. Molecular structure of the tetrameric unit in $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4 \cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**); only the central K, P, O framework and K−P distances up to 363 pm are shown

nation of arene ligands to potassium[26−30] and the heavier alkali metals[31] has often been observed.[32]

When $[K_2(THF)_6(P_4Mes_4)]$ (**6**) was recrystallized from a mixture of 1,4-dioxane and *n*-pentane (1:3), the orange crystalline compound $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4 \cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**) was formed. An X-ray crystal structure analysis revealed, that the asymmetric unit of **7** consists of two crystallographically independent units, $\{K_2(L)_3(P_4Mes_4)\}$ and $\{K_2(L)_2(P_4Mes_4)\}$, both of which are associated *via* K−P interactions. Thus, a tetrameric arrangement is formed in the solid state (Figure 6 and Figure 7), which aggregates *via* further K−P interactions to form a helical, 1-D coordination polymer (Figure 8).

Interestingly, the coordinative arrangement within the monomeric building blocks $\{K_2(L)_3(P_4Mes_4)\}$ and $\{K_2(L)_2(P_4Mes_4)\}$ of the polymeric chain resembles the pattern found in the monomeric THF adduct $[K_2(THF)_6(P_4Mes_4)]$ (**6**). Thus, the K−P distances between one terminal and one internal phosphorus atom are generally significantly shorter [*d*(K5−P16a,P14a;K8a−P15a,P13a) = 324.4(2)−358.9(2) pm, *d*(K6−P9,P11;K7−P10,P12) = 330.8(2)−345.6(2) pm, *d*(K1−P1,P3;K3−P2,P4) = 327.1(2)−355.1(2) pm, *d*(K2−

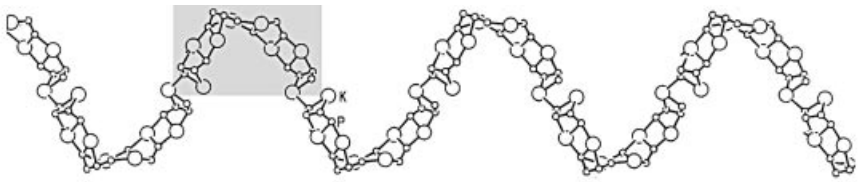


Figure 8. Polymeric helical arrangement in $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4 \cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**); the tetrameric unit is underlain in grey; only K−P distances up to 363 pm are shown

P5,P7;K4−P6,P8) = 323.6(2)−355.8(2) pm] than the K−P distance to the second terminal phosphorus atom [*d*(K8a−P16a;K5−P13a;K4−P5;K2−P8) = 346.5(2)−406.8 pm, *d*(K6−P12;K7−P9;K3−P1;K1−P4) = 360.8(2)−401.3(2) pm]. The torsion angles in the $(P_4Mes_4)^{2-}$ chains are in a range similar to those observed in **4** and **6** [torsion angles between the planes P5−P6−P7 and P6−P7−P8: 70.8°, P1−P2−P3 and P2−P3−P4: 74.4°, P9−P10−P11 and P10−P11−P12: 74.3°, P13a−P14a−P15a and P14a−P15a−P16a: 68.7°]. This seems to indicate the formation of four-membered chelate rings of the dianionic $(P_4Mes_4)^{2-}$ ligands with potassium, a situation that is analogous to the structures of **4** and **6**, and may be described as predominant coordination of the alkali metal by the phosphorus atoms in the 1,3 positions of the chain with additional (weaker) interactions bearing a further phosphorus atom in the terminal position of the chain. The monomeric $\{K_2(L)_3(P_4Mes_4)\}$ and $\{K_2(L)_2(P_4Mes_4)\}$ units are associated *via* a four-membered K_2P_2 ring motif displaying K−P interactions, which are close to the short contacts observed in the monomers themselves [*d*(K5,K6−P16a,P9) = 325.8(2)−340.7(2) pm, *d*(K7,K3−P4,P12) = 324.3(2)−345.6(2) pm, *d*(K1,K2−P1,P5) = 328.6(2)−338.2(2) pm]. In contrast, aggregation of the tetrameric units proceeds through only two K−P interactions [*d*(K8a−P8) = 360.4(2) pm, *d*(K4−P13) = 376.1(2) pm], which are in the upper range of the distances generally observed in related potassium phosphanides.[9] Six potassium atoms within the tetrameric framework are each solvated by one dioxane ligand, whereas the two potassium atoms at the termini of the tetramer are each coordinated by two dioxane ligands. It is noteworthy, that in all the dioxane molecules only *one* oxygen atom coordinates to potassium. Solvation is completed by additional close contacts of some of the potassium cations with the aromatic rings of the mesityl substituents, which may be described as η^2-interactions [(K1−C41,C46) = 308.4(5)−321.7(5) pm, *d*(K3−C11, C12) = 305.8(5)−309.6(5) pm, *d*(K7−C91,C92) = 312.6(5)−316.2(5) pm, *d*(K5−C131a,C132a) = 302.7(5)−309.5(5) pm, *d*(K2−C81,C86) = 302.7(5)−312.1(5) pm].[26−30]

Orange crystals of $[\{K(pmdeta)(HP_3Mes_3)\}_2\{K_2(P_4Mes_4)\}] \cdot 0.25$ hexane (**8**) were obtained from the concentrated reaction mixture of $MesPCl_2$ and K (1:2.5), which also contained an excess of pmdeta and hexane. The crystal structure of this compound displays a co-complex, containing a $[K_2(P_4Mes_4)]$ unit, which is in contact with two $(HP_3Mes_3)^-$ ligands and two K cations, the latter being additionally solvated in each case by one pmdeta ligand (Figure 9 and Fig-

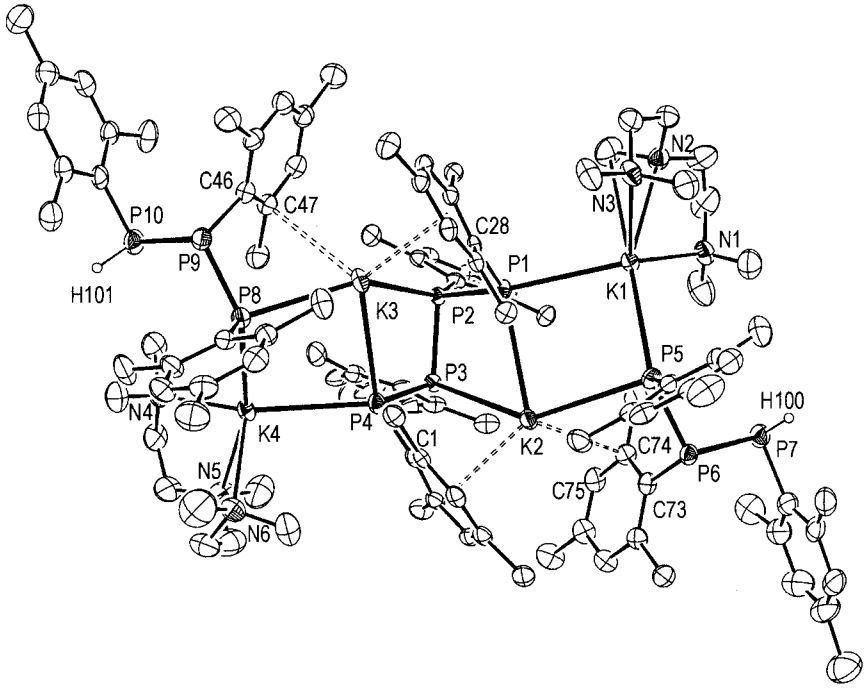


Figure 9. Molecular structure of $[\{K(pmdeta)(HP_3Mes_3)\}_2\{K_2(P_4Mes_4)\}] \cdot 0.25$hexane (**8**) (hexane not shown)

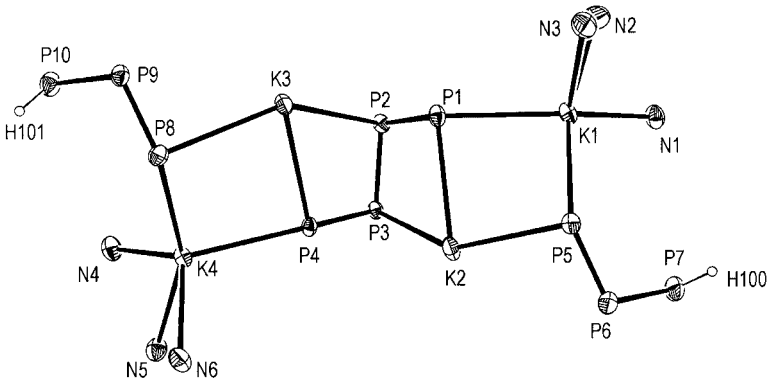


Figure 10. Molecular structure of $[\{K(pmdeta)(HP_3Mes_3)\}_2\{K_2(P_4Mes_4)\}]\cdot 0.25$hexane (**8**); only the central K,P,N framework and the P−H hydrogen atoms are shown.

ure 10). In spite of minor differences, the overall structural arrangement of the $[K_2(P_4Mes_4)]$ core in **8** is similar to those observed in the related compounds **4**, **6**, and **7**: the central $(P_4Mes_4)^{2-}$ dianion is in a *syn* arrangement with a slightly larger torsion angle than in the former structures [torsion angle between the planes P1−P2−P3 and P2−P3−P4: 91.1°]. The K−P distances are short between one terminal and one internal phosphorus atom of the chain and each potassium cation [*d*(K2−P1,P3) = 341.0(2)−342.5(2) pm, *d*(K3−P2,P4) = 339.4(2)−348.3(2) pm], but longer to the second terminal phosphorus atom [*d*(K2−P4) = 385.9(2), *d*(K3−P1) = 393.1(2) pm], indicating the formation of three-membered chelate rings (Figure 10). Additional solvation of the two central potassium cations by the aromatic substituents is indicated by short K−C contacts [*d*(K2−C28,C29,C30,C31,C32,C33) = 297.2(4)−342.3(5) pm, *d*(K2−C47) = 323.3 pm, *d*(K3−C1,C2,C3,C4,C5,C6) = 304.2(5)−334.9(5) pm, *d*(K3−C79) = 312.6 pm].[26−30]

The $[K_2(P_4Mes_4)]$ unit and the two $[K(pmdeta)(HP_3Mes_3]$ units are associated via four-membered K_2P_2 rings with short K−P interactions [*d*(K1,K2−P1,P5) = 321.7(2)−342.5(2) pm, *d*(K3,K4−P4,P8) = 328.5(2)−344.8(2) pm] (Figure 10). The catenated $(HP_3Mes_3)^-$ ligands coordinate to two potassium atoms (K1, K2 and K3, K8, respectively) through the anionic terminal phosphorus atom (P5 or P8), whereas the second terminal phosphorus atom (P7 or P10), which bears the proton of the chain, is uncoordinated. The bond angles about the internal phosphorus atom indicate sp^3 hybridization [angle P5−P6−P7: 107.41(9)°, angle P8−P9−P10: 108.20(8)°], and the P−P bond lengths within the anion are unremarkable [*d*(P5−P6), *d*(P6−P7), *d*(P8−P9), *d*(P9−P10) = 214.5(2)−224.6(2) pm].

The surprising observation of a three-membered monoprotonated $(HP_3Mes_3)^-$ anion in the structure of **8** may be explained by the fact that small amounts of the hitherto unknown compound $K_2(P_3Mes_3)$ were observed as a by-product in the synthesis of **6** when the stoichiometry of the reaction was slightly inaccurate. The anion $(HP_3Mes_3)^-$ may, therefore, have formed by reaction of the $(P_3Mes_3)^{2-}$ dianion with traces of water fortuitously present in the reaction mixture. Unfortunately, complete characterization of **8** was hampered by the impure nature of the isolated solid. Only further investigations will show if **8** can also be produced in a rational fashion.

A comparison of the structures **3**−**8** enables two different structural types to be distinguished: A "quasicyclic" arrangement, in which the ligands form five-membered chelate rings with the alkali metals, was observed for the structures of **3** and **5** (structural type **II**, Table 2 and Figure 5) − an arrangement, which has already been proposed by Baudler et al.[11a,11c] for **3** and related species, on the basis of their $^{31}P\{^1H\}$ NMR spectra (see below). In contrast, a different structural arrangement is present in **4**, **6**, **7**, and **8**, in which coordination occurs through both the internal and the terminal phosphorus atoms of the chain, and four-membered MP_3 chelate rings (M = Na, K) are the predominant structural features (structural type **I**, Table 2 and Figure 5).

Table 2. $^{31}P\{^1H\}$ NMR spectroscopic data (161.9 MHz, 25 °C, δ in ppm, *J* in Hz) of **3**−**6**

	3[11b]	**4**	**5**	**6**
$\delta_{AA'}$	−91.4	−113.1(1)	−78.1(1)	−110.5
$\delta_{BB'}$	−26.6	−13.7(1)	−5.2(1)	−12.6
$^1J_{BB'}$	−310.2(6)	−118.3(1)	−305.5(2)	−127.6(2)
$^1J_{AB} = {}^1J_{A'B'}$	−323.1(6)	−309.8(1)	−341.1(2)	−328.5(2)
$^2J_{AB'} = {}^2J_{A'B}$	−12.3(6)	+120.3(1)	−12.6(1)	+107.2(1)
$^3J_{AA'}$	+310.6(7)	+3.3(1)	+200.9(2)	+1.5(2)
Structural type	**II**	**I**	**II**	**I**

While the $^{31}P\{^1H\}$ NMR spectra of **4**−**6** display well resolved AA′BB′ spin systems at room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **3** exhibits broad signals. Only at −83 °C do signals showing the characteristic AA′BB′ spin system (ca. 80% intensity) appear. These signals compare well with the literature values.[11b] In addition, there are also resonances, which indicate the presence of a second species (δ = −25 to −30, −70; ca. 20% intensity). Since these multiplets were not well resolved, the nature of these

species could not be confidently ascertained. It seems likely, however, that these signals can be attributed to an ion-separated species $[Na(THF)_n][Na(THF)_m(P_4Ph_4)]$, which is in equilibrium with the ion-contact complex **3**.[12]

Nevertheless, the presence of only one AA′BB′ spin system for **3**−**6** clearly indicates the existence of only one diastereomer in solution. A summary of the chemical shifts and coupling constants of **3**−**6** is displayed in Table 2. While the chemical shifts of these species are in a similar range, a remarkable trend is observed for the coupling constants. Thus, whereas the $^3J(A,A')$ coupling constants (the coupling constants between the two terminal phosphorus atoms of the chain P_A and $P_{A'}$) of **4** and **6** are in the usual range expected for such long-range couplings, the corresponding coupling constants are dramatically larger for **3** and **5**. This unexpected strong coupling between the terminal phosphorus atoms, which has already been noted by Baudler et al. for **3** and related compounds, may indeed be explained by the presence of bridging alkali metal cations in a structure such as **II**, which may mediate an alternative pathway for coupling between the two terminal phosphorus atoms.[11a,11c] This, however, may not only be the case for an ion-contact structure such as **II**, but may also be consistent with alternative structures, such as an ion-separated cyclic arrangement with one bridging alkali metal cation, as suggested by Hoffmann and Caulton.[11b] To distinguish between these different possibilities, the $^2J(A,B')$ coupling constants are particularly informative. Interestingly, Baudler et al. noted that for related five-membered heterocycles *cyclo*-(P_4R_4X) (X = CH_2, R = Me, Cy, *t*Bu, Ph; X = S, Se, R = Ph; X = $P(CF_3)$, R = CF_3) a strict dependence of the $^2J_{P,P}$ coupling constant on structural features may be observed. If the substituents on the respective phosphorus atoms are in a *cisoid* arrangement, the coupling constants appear to attain significantly more positive values than if the substituents on the respective phosphorus atoms are in a *transoid* arrangement[11c] (a relationship, which is also valid for related sila-, stanna- and germatetraphospholanes).[15,16,33] A comparison of the $^2J(A,B')$ coupling constants in **3**−**6** revealed that **3** and **5** display similar negative $^2J(A,B')$ values. In contrast, the $^2J(A,B')$ coupling constants for **4** and **6** are significantly more positive. Hence, assuming that this rule is also valid for the related alkali metal complexes **3**−**6**, the different values for the $^2J(A,B')$ coupling constants may be due to different orientations of the organic substituents on the respective phosphorus atoms. A comparison of the solid-state structures of these compounds shows that a defined *cisoid* orientation of the Mes substituents of the internal and the terminal phosphorus atoms (i.e. between P_A,$P_{B'}$ and $P_{A'}$,P_B respectively) is indeed present in **4**, **6**, **7**, and **8**. However, the substituents on the terminal phosphorus atoms (P_A and $P_{A'}$) of **3** and **5** are approximately coplanar, with an almost coplanar arrangement of the four phosphorus atoms of the $(P_4R_4)^{2-}$ ligand. Thus, a proper *cis*/*trans* relationship between the substituents of P_A,$P_{B'}$ and $P_{A'}$,P_B was not observed for these structures. This characteristic feature of the solid-state structures of **3** and **5** may well be the underlying reason for the smaller values of the $^2J(A,B')$ coupling constants of these compounds in solution.

In general, the main features of the solid-state structures of **3**−**6** appear to reflect the trends observed for the P−P coupling constants of these species in solution quite clearly. This indicates, that the basic structural arrangements in the solid state are indeed retained in solution.

Interestingly, the ^{1}H NMR spectra of **4** and **6** [in C_6D_6 (**4**) and C_7D_8/[D_8]THF, 2:1, (**6**)] exhibit dynamic behavior. At room temperature, the resonances for the *ortho*-methyl groups of the Mes substituents of the terminal phosphorus atoms are inequivalent [**4**: δ = 2.47 (br) and 3.31 (br); **6**: δ = 2.36 and 3.22]. Upon warming the samples to 67 °C (**4**) and 60 °C (**6**), the broad, inequivalent peaks coalesce into a single broad resonance at ca. δ = 2.9 for **4**, while for **6** the previously sharp signals broaden severely, indicating that coalescence apparently requires a higher temperature. The inequivalence and the temperature dependence of the *o*-Me resonances may be the result of hindered rotation of the respective Mes groups in solution. Although a purely steric effect cannot be excluded on the basis of the NMR spectroscopic data alone, this might be caused by the presence of alkali metal-aryl interactions, which were also observed in the solid-state structures of these species.

Conclusions

Investigations of the reactions of *i*PrPCl$_2$, PhPCl$_2$ or MesPCl$_2$ with PCl$_3$ and Na (4:1:12) revealed that the cyclopentaphosphanide salts Na[*cyclo*-(P_5R_4)] [R = *i*Pr (**1**), Ph (**2**)] are formed in yields of 61% and 32%, respectively. In the reactions with PhPCl$_2$ and MesPCl$_2$, however, the catenated tetraphosphanediide salts $[Na_2(THF)_5(P_4Ph_4)]$ (**3**) and $[Na_2(THF)_4(P_4Mes_4)]$ (**4**) were obtained as the major products. Compounds **3**, **4**, $[Na_2(THF)_4(P_4tBu_4)]$ (**5**), and $[K_2(THF)_6(P_4Mes_4)]$ (**6**) were obtained more conveniently in a one-pot reaction of RPCl$_2$ (R = *t*Bu, Ph, Mes) with Na and K (1:2.5), and this represents a general, simplified route to tetraphosphanediide salts $[M_2(P_4R_4)]$.

In the solid state, two different types of coordination of the alkali metals were observed for **3**−**6**. All four phosphorus atoms are employed in the coordination of the alkali metal in **4** and **6**, whereas in **3** and **5**, coordination of Na occurs exclusively through the terminal phosphorus atoms of the chain. Recrystallization of **6** from 1,4-dioxane/pentane and pmdeta/THF/hexane solutions resulted in the isolation of $[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4\cdot 0.5THF]_\infty$ (L = 1,4-dioxane) (**7**) and $[\{K(pmdeta)(HP_3Mes_3)\}_2\{K_2(P_4Mes_4)\}]\cdot 0.25$hexane (**8**). The polymeric arrangement of **7** indicates that such compounds may also associate in the solid state, but the basic structural arrangement of the $[K_2(P_4Mes_4)]$ units, displaying four-membered KP_3 chelate rings, is preserved. This is also the case for the structure of **8**, in which one $[K_2(P_4Mes_4)]$ unit is associated with two [K(pmdeta)-(HP_3Mes_3)] moieties. A comparison of the structures of **3**−**8** and of the related compounds $[Na_2(tmeda)_2(P_4Ph_4)]$ and $[Na_2(dme)_3(P_4Ph_4)]$[12] indicates that the M_2P_4 frame-

works are structurally rather robust, even in the presence of chelating donors and for different modes of association.

The ABB′CC′ (for **1** and **2**) and the AA′BB′ coupling patterns in the ^{31}P NMR spectra of **3**−**6** were analyzed. A comparison of the resultant coupling constants of the latter indicates that the basic structural features of these species are preserved not only in the solid state, but also in solution.

Future investigations will focus on the further elaboration of the structural chemistry of alkali metal oligophosphanediides and on the use of these compounds in the synthesis of phosphorus-rich metal complexes.

Experimental Section

General Methods: All procedures were performed under an inert atmosphere of pure argon with vigorous exclusion of air and moisture. The NMR spectra were recorded with a Bruker AVANCE DRX 400 spectrometer. ^1H NMR (400.13 MHz), internal standard: solvent, external standard: TMS. ^{31}P NMR (161.9 MHz), external standard: 85% H_3PO_4. ^{13}C NMR (100.16 MHz), internal standard: solvent, external standard: TMS. The solvents were saturated with argon and stored over potassium mirrors. *i*PrPCl$_2$,[34] *t*BuPCl$_2$,[34] MesPCl$_2$[35] were prepared by literature methods. PhPCl$_2$ and PCl$_3$ are commercially available and were freshly distilled before use. Elemental analyses were performed on a Heraeus VARIO EL instrument. The melting points were determined in sealed capillaries under argon and are uncorrected.

Data Collection and Structural Refinements of 3−8: Data [λ(Mo-K_α) = 0.71073 Å] were collected with a Siemens CCD (SMART) diffractometer (for **3**−**6**), on a STOE IPDS (**7**) or on a Nonius Kappa CCD (for **8**). All observed reflections were used in the refinements (SAINT) of the unit-cell parameters. Empirical absorption corrections were carried out with SADABS (**3**−**6**) and SORTAV (**8**).[36] The structures were solved by direct methods (**3**−**7**: SHELXTL PLUS. **8**: SHELX-97).[37] Na, K, P, N O, and C atoms were refined anisotropically. Some C atoms of disordered solvent molecules were refined isotropically. H atoms were located using difference maps and refined isotropically. Table 3 lists crystallographic details. The thermal ellipsoids of the molecular structures in Figures 1−4 and 6−10 are shown at the 30% probability level. CCDC-222008 (for **3**), -222009 (for **4**), -222005 (for **5**), -222007 (for **6**), -222006 (for **7**), and -222004 (for **8**) 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 Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax (internat.): +44-1223-336-033 or E-mail: deposit@ccdc.cam.uk].

Na[*cyclo*-(P$_5$*i*Pr$_4$)] (1) and Na[*cyclo*-(P$_5$Ph$_4$)] (2): PCl$_3$ (2.51 g, 18.2 mmol, 1.6 mL) and Na (5.04 g, 219.0 mmol) were carefully added to *i*PrPCl$_2$ (10.6 g, 73.1 mmol) or PhPCl$_2$ (13.04 g, 72.6 mmol), respectively, in THF (150 mL). The mixture was heated to reflux for 5 days. After 1 day the initially colorless solution had become yellow-green, and after 2 days, dark brown. The solvent was removed under reduced pressure, and the dark brown residue extracted with *n*-pentane (250 mL). The solvent was re-

Table 3. Crystal data and structural refinements for **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
Formula	$C_{44}H_{60}Na_2O_5P_4$	$C_{52}H_{76}Na_2O_4P_4$	$C_{32}H_{68}Na_2O_4P_4$	$C_{60}H_{92}K_2O_6P_4$	$C_{186}H_{260}K_8O_{20.50}P_{16}$	$C_{109.50}H_{161.50}K_4N_6P_{10}$
M	838.78	934.99	686.72	1111.42	3631.26	2028.05
T [K]	208(2)	208(2)	218 (2)	218 (2)	203(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
Space group	*C*2/*c*	$P2_1/c$	$P2_1/n$	$Pna2_1$	$P2_1/c$	$P\bar{1}$
a [Å]	13.693(2)	19.379(4)	13.504(5)	16.021(5)	28.587(6)	12.544(3)
b [Å]	15.972(2)	19.040(4)	16.171(5)	25.135(5)	23.927(5	19.065(4)
c [Å]	21.196(2)	15.849(3)	19.307(5)	15.913(5)	33.789(7)	26.186(5)
α [°]	90	90	90	90	90	84.99(3)
β [°]	93.015(4)	113.679(4)	99.341(5)	90	105.98(3)	85.33(3)
γ [°]	90	90	90	90	90	89.51(3)
V [Å^3]	4629(1)	5356(2)	4160(2)	6408(3)	22219(8)	6218(2)
Z	4	4	4	4	4	2
Crystal size [cm]	0.4 × 0.4 × 0.4	0.4 × 0.4 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.4	0.15 × 0.15 × 0.10
ρ_{calcd} [Mg·m^{-3}]	1.204	1.160	1.096	1.152	1.086	1.083
F(000)	1784	2008	1496	2392	7728	2173
μ(Mo-K_α) [cm^{-1}]	0.223	0.198	0.232	0.292	0.323	0.315
hkl range	−10/17, −19/19, −24/26	11/26, −26/25, −21/20	−18/14, −21/20, −17/25	−19/19, −23/31, −19/19	−30/30, −25/25, −36/36	−14/14, −22/22, −29/31
$2\theta_{max.}$ (°)	52.74	58.76	58.76	52.12	45.00	50.16
Reflections collected/unique	14873/4730	32430/13365	25852/10112	34204/12380	95913/29035	54949/20231
R(int.)	0.0346	0.0485	0.0235	0.0651	0.0470	0.0830
Data/restraints/ parameters	4730/10/347	13365/0/768	10112/0/654	12380/7/658	29035/6/2225	20231/47/1215
Goodness of Fit on F^2	1.011	1.007	0.960	1.046	0.939	1.039
$R1/wR2$ [$I > 2\sigma(I)$]	0.0657/0.1616	0.0594/0.1259	0.0352/0.0883	0.0739/0.1432	0.0728/0.2037	0.0805/0.2076
$R1/wR2$ (all data)	0.1112/0.1922	0.1247/0.1492	0.0592/0.0996	0.1315/0.1632	0.1126/0.2234	0.1203/ 0.2333
Absolute structure parameter	/	/	/	0.49(7)	/	/
Largest diff. Peak/hole [e·Å^{-3}]	0.581/0.656	0.330/0.251	0.345/-0.186	0.213/−0.254	1.258/ −0.445	1.371/−0.564

moved under reduced pressure, and **1** and **2** were characterized by ^{31}P NMR spectroscopy (cf. Table 1).

$[Na_2(THF)_5(P_4Ph_4)]$ (3): $PhPCl_2$ (3.83 g, 21.4 mmol) was dissolved in THF (ca. 50 mL), and added to freshly prepared sodium sand (1.23 g, 53.5 mmol, prepared from Na in boiling toluene). The mixture was heated to reflux for 3 days. An orange suspension was formed that contained ca. 75% of **4**. Filtration and concentration of the THF solution to ca. 30 mL gave yellow crystals upon storage at −20 °C overnight. The yellow crystals were isolated and dried in vacuo for 45 min. Yield 1.97 g (48% ref. to **3**-THF); m.p. 101−103 °C. ^1H NMR (C_7D_8): δ = 1.32 (m, 16 H, THF), 3.36 (m, 16 H, THF), 6.38 (br., 2 H, *p*-H), 6.62 (br., 4 H, *m*-H), 6.78 (br., 2 H, *p*-H), 6.91 (br., 4 H, *o*-H), 7.29 (br., 4 H, *m*-H), 7.86 (br., 4 H, *o*-H). $^{13}C\{^1H,^{31}P\}$ NMR (C_6D_6): δ = 25.27 (THF), 67.55 (THF), 120.69 (4-C in Ph), 125.89 (4-C in Ph), 130.54 (2,6-C in Ph), 132.42 (2,6-C in Ph), 146.1 (1-C in Ph), 151.60 (1-C in Ph) (no P−C coupling observed, signals of 3,5-C overlap with solvent resonances at ca. 127 ppm). $^{31}P\{^1H\}$ NMR (C_7D_8, +25 °C): δ ≈ −23.0 (br), −74.6 (br), −88.0 (br). $^{31}P\{^1H\}$ NMR (C_7D_8, −83 °C): δ ≈ −25 to −30 (m, 2P), −26.5 (B part of an AA′BB′ spin system, 8P), ca. −70 (m, 2P), −90.7 (A part of an AA′BB′ spin system), cf. Table 2. $C_{40}H_{52}Na_2O_4P_4$ (766.72): calcd. C 62.7, H 6.80, P 16.2; found C 60.0, H 6.55, P 16.5.

$[Na_2(THF)_4(P_4Mes_4)]$ (4): $MesPCl_2$ (1.31 g, 5.9 mmol) was dissolved in THF (ca. 50 mL) and added to freshly prepared sodium sand (0.33 g, 14.5 mmol, prepared from Na in boiling toluene). The mixture was heated to reflux for 2.5 days. A red suspension was formed which was filtered. The solvent was completely removed, and the remaining yellow solid recrystallized from THF/hexane, 1:2. Yield 0.31 g (27% ref. to **4**−2THF); m.p. 238 °C decomp. to a brown solid. ^1H NMR (C_6D_6): δ = 1.51 (m, 8 H, THF), 2.04 (s, 6 H, *p*-CH_3 in Mes), 2.16 (s, 6 H, *p*-CH_3 in Mes), 2.47 (br., 6 H, *o*-CH_3 in Mes), 2.70 (s, 12 H, *o*-CH_3 in Mes), 3.31 (br., 6 H, *o*-CH_3 in Mes), 3.57 (m, 8 H, THF), 6.61 (br., 4 H, 3,5-H in Mes), 6.81 (br., 4 H, 3,5-H in Mes). $^{13}C\{^1H,^{31}P\}$ NMR (C_6D_6): δ = 20.43 (*p*-CH_3 in Mes), 20.56 (*p*-CH_3 in Mes), 23.56 (*o*-CH_3 in Mes), 24.47 (THF), 26.17 (*o*-CH_3 in Mes), 66.60 (THF), 128.13 (3,5-C in Mes at P_B), 129.41 (3,5-C in Mes at P_A), 135.03 (4-C in Mes at P_A), 137.34 (1-C in Mes at P_A), 141.43 (4-C in Mes at P_B), 141.89 (2,6-C in Mes at P_A), 145.09 (2,6-C in Mes at P_B), 150.40 (1-C in Mes at P_B) (no P−C coupling observed). $^{31}P\{^1H\}$ NMR (C_6D_6): cf. Table 2. $C_{52}H_{76}Na_2O_4P_4$ (935.05): calcd. C 66.80, H 8.20, O 6.80; found C 65.50, H 6.69, O 7.01.

$[Na_2(THF)_4(P_4tBu_4)]$ (5): $tBuPCl_2$ (5.71 g, 35.9 mmol) was dissolved in THF (ca. 50 mL), and added to freshly prepared sodium sand (2.10 g, 90.0 mmol, prepared from Na in boiling toluene). The mixture was heated to reflux for 5 days. A dark-green suspension formed, which contained ca. 53% of **5**. This was filtered, the filtrate reduced to ca. 10 mL, and layered with 20 mL of pentane. Light yellow crystals formed on storage at −20 °C and were isolated. The crystals still contained ca. 15% *cyclo*-$[Na(THF)_4(P_5tBu_4)]$ and were recrystallized from THF/hexane, 1:2 to give **5** in 95% purity. Yield 1.23 g (40% ref. to **5**-4THF); m.p. 240 °C decomp. to a brown solid. ^1H NMR (C_7D_8/[D_8]THF, 2:1): δ = 1.51 (br., 36 H, *t*Bu). $^{13}C\{^1H,^{31}P\}$ NMR (C_7D_8/[D_8]THF, 2:1): δ = 28.64 [2 $C(CH_3)_3$], 29.06 [2 $C(CH_3)_3$], 30.84 (6 CH_3 in *t*Bu), 37.81 (6 CH_3 in *t*Bu). $^{31}P\{^1H\}$ NMR (C_7D_8/[D_8]THF, 2:1): cf. Table 2.

$[K_2(THF)_6(P_4Mes_4)]$ (6): Potassium (1.12 g, 28.30 mmol) was added to a solution of $MesPCl_2$ (2.55 g, 11.51 mmol) in THF (40 mL). The mixture was heated to reflux for 3 h. The resultant dark red suspension was filtered, and the filtrate reduced to ca. 5 mL. A yellow precipitate formed, which redissolved on heating the solution. Dark-orange crystals formed on storing the saturated solution of **6** at ambient temperature. The orange-red, crystalline solid was isolated and dried in vacuo for 2 h. Yield 0.84 g (43% ref. to **6**−6THF); m.p. 200−201 °C. ^1H NMR (C_7D_8/[D_8]THF, 2:1): δ = 2.06 (s, 6 H, *p*-CH_3 in Mes), 2.11 (s, 6 H, *p*-CH_3 in Mes), 2.36 (s, 6 H, *o*-CH_3 in Mes), 2.62 (s, 12 H, *o*-CH_3 in Mes), 3.22 (s, 6 H, *o*-CH_3 in Mes), 6.41 (br., 4 H, 3,5-H in Mes), ca. 6.7 (br., 4 H, 3,5-H in Mes). $^{13}C\{^1H,^{31}P\}$ NMR (C_7D_8/[D_8]THF, 2:1): δ = 19.8 (*p*-CH_3 in Mes), 20.0 (*p*-CH_3 in Mes), 23.15 (*o*-CH_3 in Mes), 25.41 (*o*-CH_3 in Mes), 26.30 (*o*-CH_3 in Mes), 127.6 (3,5-C in Mes at P_A), 128.6 (3,5-C in Mes at P_B), 134.31 (4-C in Mes at P_A), 138.6 (1-C in Mes at P_A), 141.48 (2,6-C in Mes at P_A), ca. 141.4 (4-C in Mes at P_B), 144.68 (2,6-C in Mes at P_B), 153.5 (1-C in Mes at P_B) (no P−C coupling observed). $^{31}P\{^1H\}$ NMR (C_7D_8/[D_8]THF, 2:1): cf. Table 2.

$[\{K(L)_2\}_2\{K(L)\}_6(P_4Mes_4)_4\cdot 0.5THF]_\infty$ (L = 1,4-Dioxane) (7): A solution of **6** (0.21 g, 0.31 mmol) in 1,4-dioxane (5 mL) was layered with *n*-pentane (15 mL) and stored for 2 weeks at room temperature. Large orange crystalline plates formed, which were isolated and dried in vacuo for 1 h. Yield 0.15 g; m.p. 175−177 °C; the compound is insoluble in hydrocarbon solvents, but shows signs of decomposition when dissolved in THF (cf. ^{31}P NMR spectroscopic data). ^{31}P NMR ([D_8]THF): δ = −10.3 (br. m, 2P), −14.4 (B part of an AA′BB′ spin system of $(P_4Mes_4)^{2-}$, 4P), −83.6 (br., 4P), −85.3 [dd, 2P, $^1J_{P,P}$ = 376.3, $^1J_{P,H}$ = 204.4 Hz, MesPH of $K(HP_2Mes_2)$], −106.2 (br. m, 4P), −109.7 [A part of an AA′BB′ spin system of $(P_4Mes_4)^{2-}$, 4 P], −136.2 [d, 2 P, $^1J_{P,P}$ = 376.3 Hz, $MesP^-$ of $K(HP_2Mes_2)$], −143.2 [d, 1 P, $^1J_{P,H}$ = 163 Hz, K(HPMes)[28]].

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