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Article

Hydrogen Polyphosphides $P_3H_2^{3-}$ and $P_3H_3^{2-}$: Synthesis and Crystal Structure of $K_3(P_3H_2)\cdot 2.3NH_3$, $Rb_3(P_3H_2)\cdot NH_3$, $[Rb(18\text{-crown-}6)]_2(P_3H_3)\cdot 7.5NH_3$, and $[Cs(18\text{-crown-}6)]_2(P_3H_3)\cdot 7NH_3$

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The incongruous solvation of polyphosphides and phosphanes or the direct reduction of white phosphorus in liquid ammonia leads to the hydrogen polyphosphides *catena*-dihydrogen triphosphide, $P_3H_2^{3-}$, and *catena*-trihydrogen triphosphide, $P_3H_3^{2-}$, in the crystalline compounds $K_3(P_3H_2)\cdot 2.3NH_3$ (1), $Rb_3(P_3H_2)\cdot NH_3$ (2), $[Rb(18\text{-crown-}6)]_2(P_3H_3)\cdot 7.5NH_3$ (3), and $[Cs(18\text{-crown-}6)]_2(P_3H_3)\cdot 7NH_3$ (4).

Introduction

Because of the many parallels to hydrocarbon chemistry, polyphosphanes, P_mH_n, are a class of intensively studied compounds,[1−4] and the same holds true for the polyphosphides, P_m^{n-}.[5,6] Far less is known about hydrogen polyphosphides, which can be seen as intermediates in protonation/deprotonation processes of polyphosphides or phosphanes, respectively. Most of the hitherto known hydrogen polyphosphides are thermally unstable, highly unstable to pH change, or both. Baudler and coworkers were the first who could identify several hydrogen polyphosphides using solution NMR methods.[7−15] Recently, direct synthetic routes to stable, crystalline hydrogen polyphosphides were elaborated and led to compounds with $P_7H_2^-$, P_7H^{2-}, and $P_{11}H^{2-}$ anions,[16−18] which were characterized by X-ray structure analysis. The reactions leading to these hydrogen polyphosphides were carried out by dissolving the corresponding alkali metal polyphosphides in liquid ammonia and protonating the anions under very controlled conditions in the presence of voluminous counterions. This rational access, however, is limited to polyphosphides that congruently dissolve in liquid ammonia. In the last several years, we extended the understanding of the chemistry of polyphosphides and phosphanes that are incongruently dissolving in liquid ammonia.[3,4,19−24] A first step in that direction was the in situ generation of a whole new class of hydrogen polyphosphides, namely, the *catena*-trihydrogen triphosphide anions,

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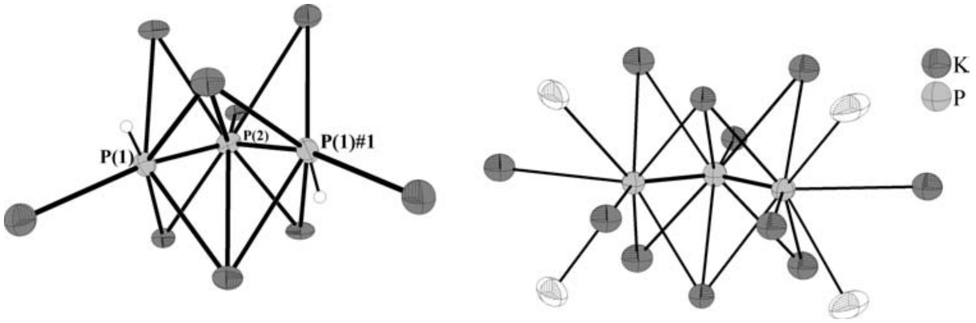

Figure 1. Foreshortened projection of the coordination sphere of the $P_3H_2^{3-}$ anion of (1) (left) and the coordination sphere of the P_3^{4-} anion in K_4P_3 (right) for comparison. The white ellipsoids are the additional potassium ions in K_4P_3. Thermal ellipsoids are drawn at 70% probability level.

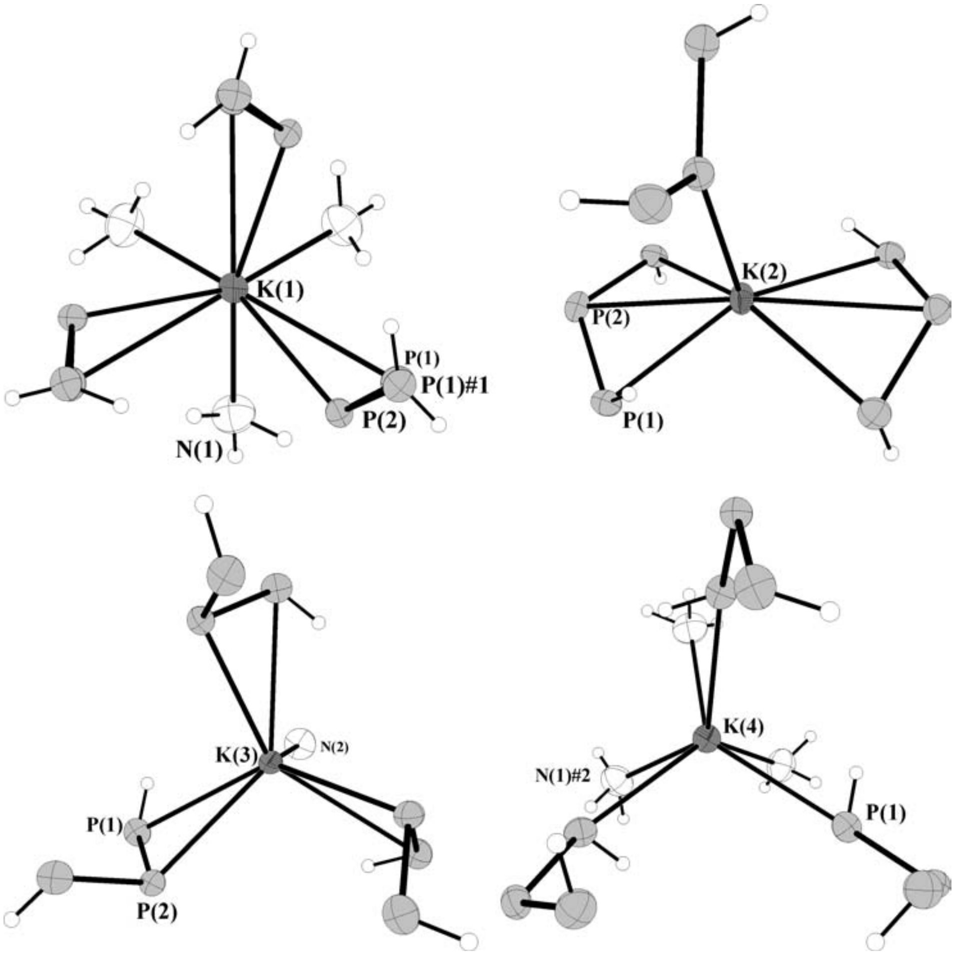

Figure 2. Projections of the coordination spheres of the potassium ions. Thermal ellipsoids are drawn at 70% probability level. Selected bond lengths (Å): P(1)−K(2) 3.329(4), P(1)−K(1) 3.388(4), P(1)−K(4) 3.427(4), P(1)−K(3) 3.444(4), P(2)−K(3) 3.355(3), P(2)−K(2) 3.612(4), P(2)−K(1) 3.614(4), N(1)−K(1) 3.022(8), N(2)−K(3) 3.118(7), K(4)−N(1)#2 2.894(8).

$P_3H_3^{2-}$, in $[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$,[25] which were synthesized by direct reduction of white phosphorus with alkali metal dissolved in liquid ammonia. To this completely new class of *catena*-trihydrogen triphosphides, $P_3H_3^{2-}$, of which only one member was known, we can now add the two compounds $[Rb(18\text{-crown-}6)]_2(P_3H_3)\cdot 7.5NH_3$ and $[Cs(18\text{-crown-}6)]_2(P_3H_3)\cdot 7NH_3$ synthesized by incongruous solvation of diphosphane (4), P_2H_4, and a cyclohexaphosphide, P_6^{4-}, respectively. Furthermore, we present the first two examples of the *catena*-dihydrogen triphosphide anion, $P_3H_2^{3-}$, obtained in the compounds $K_3(P_3H_2)\cdot 2.3NH_3$ and $Rb_3(P_3H_2)\cdot NH_3$. They were synthesized by direct reduction of white phosphorus and incongruous solvation of a cyclohexaphosphide in liquid ammonia, respectively. Organosubstituted derivatives of these delicate compounds are quite well known in the literature.[26,27] Finally, we discuss the

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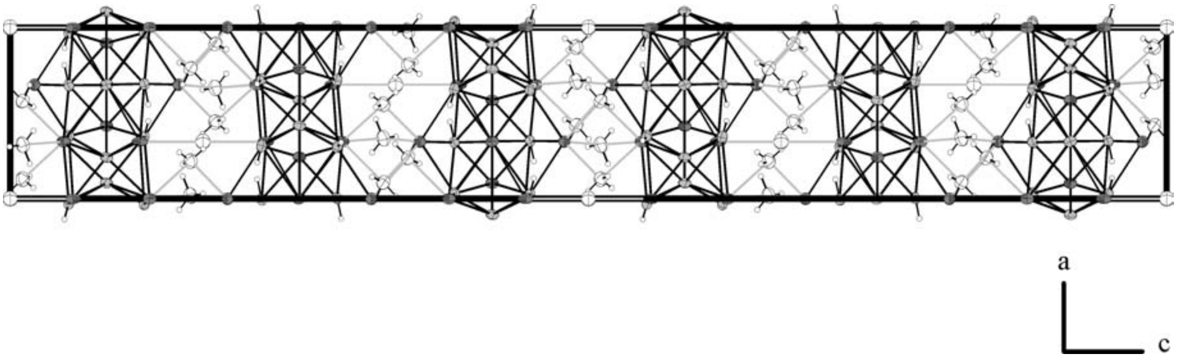

Figure 3. Projection of the unit cell of (1). Black bonds between phosphorus and potassium show the 2D infinite sheets that are interconnected by ammonia molecules (gray bonds between potassium and nitrogen). Thermal ellipsoids are drawn at 70% probability level.

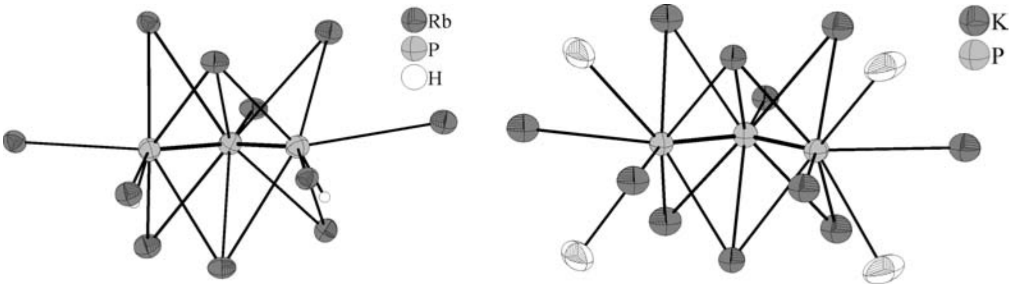

Figure 4. Comparison of the coordination spheres of the $P_3H_2^{3-}$ anion (left) in (2) with the P_3^{4-} anion (right) in K_4P_3. The four additional cations in the coordination sphere of K_4P_3 are shown as white thermal ellipsoids. Thermal ellipsoids are drawn at 70% probability level.

Table 1. Crystallographic Data of the Presented Structures

	$K_3(P_3H_2)\cdot 2.3NH_3$ (1)	$Rb_3(P_3H_2)\cdot NH_3$ (2)	$(Rb(18\text{-crown-}6))_2(P_3H_3)\cdot 7.5NH_3$ (3)	$(Cs(18\text{-crown-}6))_2(P_3H_3)\cdot 7NH_3$ (4)
empirical formula	$H_9K_3N_2P_3$	$H_5NP_3Rb_3$	$C_{24}H_{73.50}N_{7.50}O_{12}P_3Rb_2$	$C_{24}H_{72}Cs_2N_7O_{12}P_3$
mol mass (g/mol)	251.97	368.37	923.25	1009.62
cryst syst	trigonal	orthorhombic	monoclinic	monoclinic
space group	$R\bar{3}c$	$Pbca$	$C2$	$P2_1/c$
a (Å)	9.775(10)	12.971(2)	33.989(2)	10.1662(7)
b (Å)	9.775(10)	9.659(1)	10.0683(5)	30.577(2)
c (Å)	57.35(11)	15.085(3)	13.4933(9)	14.911(1)
α (deg)	90	90	90	90
β (deg)	90	90	97.319(8)	90.0(0)
γ (deg)	120	90	90	90
V (Å^3)	4746(12)	1890.0(5)	4579.9(5)	4635.1(5)
Z	18	8	4	4
ρ_{calc} (Mg/m^3)	1.587	2.589	1.339	1.447
T (K)	123	123	123	123
F(000)	2292	1344	1940	2064
μ(Mo Kα) (mm^{-1})	1.681	15.896	2.296	1.729
θ range (deg)	2.51−23.97	2.70−27.95	2.06−25.93	2.41−27.83
measured, independent, and observed ($I > 2\sigma(I)$) reflns	8216, 829, 696	30514, 2259, 1547	19620, 8615, 8067	12453, 7351, 5523
R_{int}	0.0570	0.1435	0.0417	0.0578
$R(F)$ ($I > 2\sigma(I)$, all data)	0.0775, 0.0871	0.0395, 0.0651	0.0266, 0.0289	0.0578, 0.798
$wR(F^2)$ ($I > 2\sigma(I)$, all data)	0.1981, 0.2107	0.0914, 0.0987	0.0615, 0.0648	0.1507, 0.1754

varying P−P−P bond angles in the *catena*-triphosphides and compare the experimental results with quantum chemically obtained results.

Results and Discussion

Structure of $K_3(P_3H_2)\cdot 2.3NH_3$ (1). The compound $K_3(P_3H_2)\cdot 2.3NH_3$ contains the new *catena*-dihydrogen triphosphide ion, $P_3H_2^{3-}$ (C_2 symmetry), with the central phosphorus atom P(2) on the 18*e* and the two symmetry equivalent phosphorus atoms P(1) on the 36*f* Wyckoff position of space group $R\bar{3}c$. The phosphorus−phosphorus bond length is 2.212(4) Å, which is in the range that is usually found for P−P single bonds in polyphosphides.[5,6] The P−P−P bond angle is 115.5(2)°. The hydrogen atom is bound to P(1) with a bond length of 1.30(5) Å, and the hydrogen atoms are in E conformation because of symmetry.[16,17] Figure 1 shows a foreshortened projection of the $P_3H_2^{3-}$, its coordination sphere, and a comparison to the coordination sphere of the P_3^{4-} anion in the compound K_4P_3.[28] The K−P distances in (1) are in the range of 3.24 to 3.61 Å, and the K−P distances in K_4P_3 are in a similar range of 3.33 to 3.57 Å. The coordination number of the central phosphorus atom is nine in both cases, but the outer

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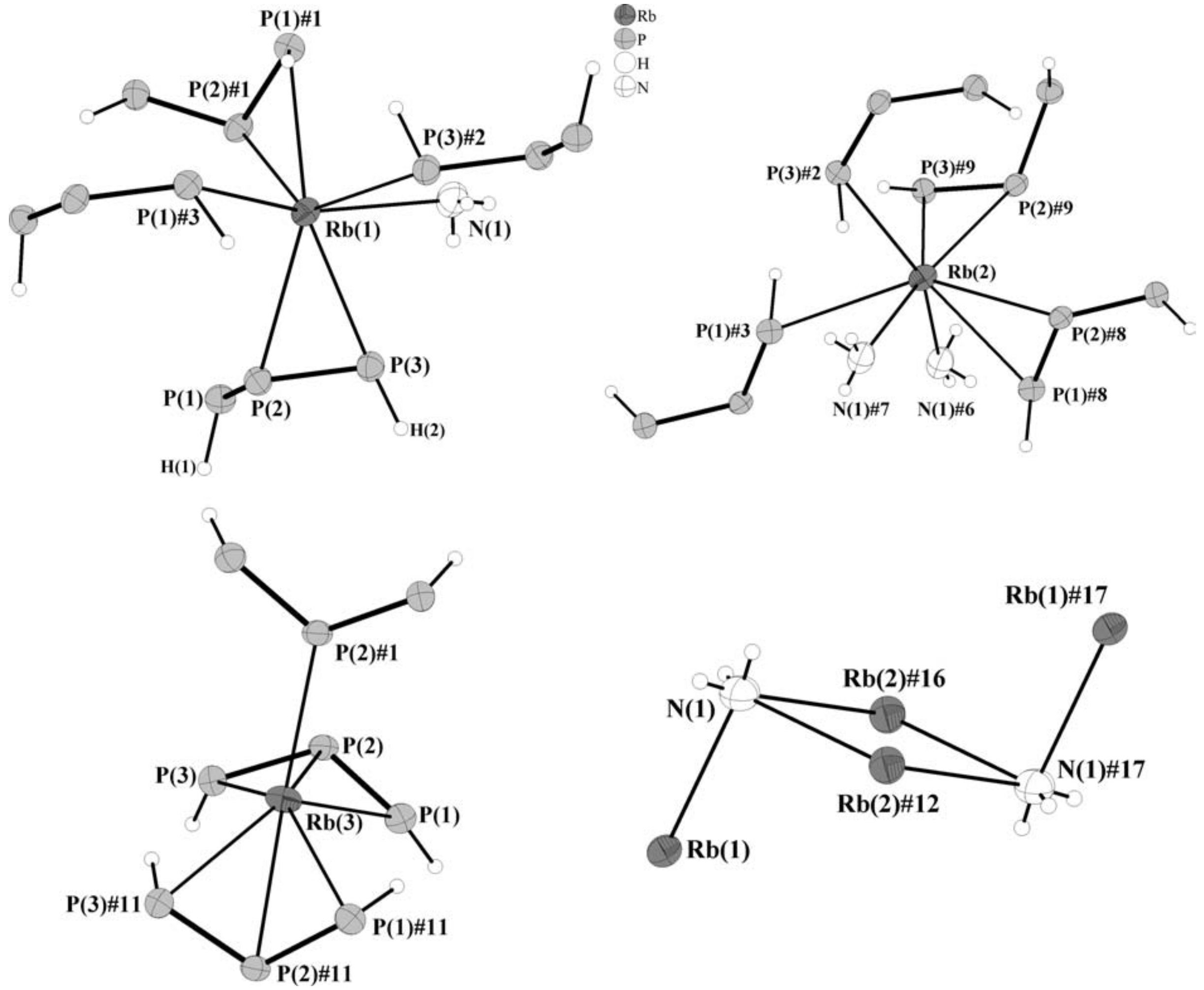

Figure 5. Coordination spheres of Rb(1), Rb(2), Rb(3) and of the nitrogen atom N(1) of the ammonia molecule in (2). Thermal ellipsoids are drawn at 70% probability level. Selected bond lengths (Å): Rb(1)−N(1) 3.210(7), Rb(1)−P(2)#1 3.461(2), Rb(1)−P(3) 3.4797(19), Rb(1)−P(3)#2 3.4872(19), Rb(1)−P(1)#3 3.5381(19), Rb(1)−P(1)#1 3.560(2), Rb(1)−P(2) 3.6505(19), Rb(2)−N(1)#6 3.258(7), Rb(2)−N(1)#7 3.307(7), Rb(2)−P(1)#8 3.5246(19), Rb(2)−P(3)#2 3.6204(19), Rb(2)−P(1)#3 3.700(2), Rb(2)−P(3)#9 3.704(2), Rb(2)−P(2)#8 3.7101(19), Rb(2)−P(2)#9 3.763(2), Rb(3)−P(1) 3.323(2), Rb(3)−P(3) 3.427(2), Rb(3)−P(2)#1 3.4733(19), Rb(3)−P(3)#11 3.5363(19), Rb(3)−P(1)#11 3.5502(19), Rb(3)−P(2)#11 3.5750(19), Rb(3)−P(2) 3.683(2), N(1)−Rb(2)#16 3.258(7), N(1)−Rb(2)#12 3.307(7).

phosphorus atoms are surrounded by only five potassium atoms in the case of the $P_3H_2^{3-}$ anion in (1) instead of seven potassium ions in K_4P_3 (Figure 1). The coordination number of the $P_3H_2^{3-}$ anion in (1) is 9, whereas the coordination number of P_3^{4-} in K_4P_3 is 15.

The potassium ions K(1), K(3), and K(4) reside on the special 12*c* position; potassium ion K(2) is located on the 18*e* position. Potassium ion K(1) is coordinated η^2-like by three symmetry equivalent $P_3H_2^{3-}$ anions with the phosphorus atoms P(1) and P(2) and three symmetry equivalent ammonia molecules with nitrogen atom N(1) yielding a coordination number of nine. Bond lengths are available in the caption of Figure 2. The coordination number of potassium ion K(2) is seven because it is coordinated η^3- and η^1-like by symmetry-equivalent $P_3H_2^{3-}$ anions. K(3) has a coordination number of seven; it is coordinated by three symmetry-equivalent $P_3H_2^{3-}$ anions and the nitrogen atom N(2) of an ammonia molecule. The coordination number of K(4) is six because it is surrounded by three symmetry-equivalent ammonia molecules with nitrogen atom N(1) and three symmetry-equivalent $P_3H_2^{3-}$ anions.

The interactions between cations and anions lead to 2D infinite sheets that are parallel to the *ab* plane (Figure 3). These sheets are interconnected by ammonia molecules, leading to the formation of a 3D infinite network (Figure 3).

Further details of the crystal structure are available in Table 1. Tables 4 and 5 in the Supporting Information hold selected atom coordinates and thermal displacement parameters.

Because of the low solubility of (1) in liquid ammonia no ^{31}P- or ^{1}H NMR could be obtained.

Structure of $Rb_3(P_3H_2)\cdot NH_3$ (2). All atoms occupy the 8*c* Wyckoff position of space group *Pbca*. The new *catena*-dihydrogen triphosphide anion, $P_3H_2^{3-}$, is present in the structure. The anion is coordinated by 11 rubidium cations of which some are equivalent by symmetry; in (1), the coordination number of the $P_3H_2^{3-}$ anion is 9 for comparison. The coordination sphere of the anion is again very similar to that in the compound K_4P_3[28] (space group *Cmcm*), where

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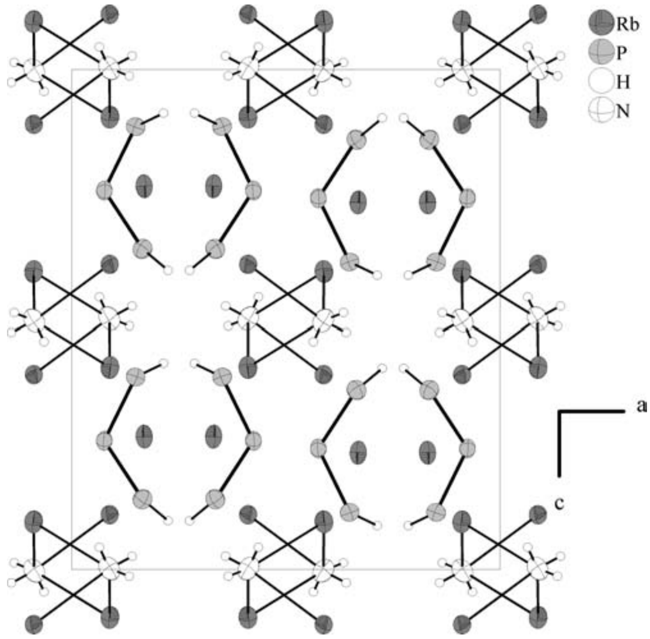

Figure 6. Projection of the unit cell of $Rb_3(P_3H_2)\cdot NH_3$ along the *b* axis. Thermal ellipsoids are drawn at 70% probability level.

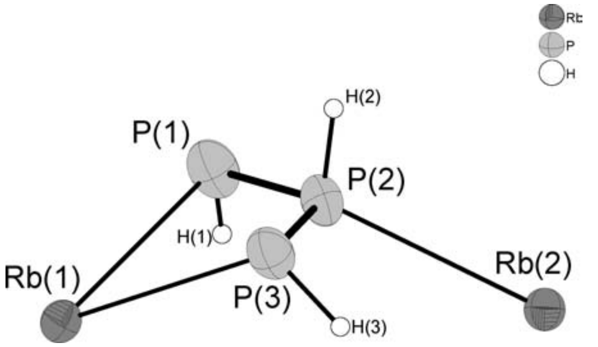

Figure 7. Projection of the *catena*-trihydrogen triphosphide anion, $P_3H_3^{2-}$, and its coordination to the rubidium cations Rb(1) and Rb(2) in (3). Thermal ellipsoids are drawn at 70% probability level. Selected bond lengths (Å) and angles (deg): P(1)−P(2) 2.2073(11), P(2)−P(3) 2.1947(11), P(1)−H(1) 1.41(4), P(2)−H(2) 1.39(4), P(3)−H(3) 1.46(6), P(3)−P(2)−P(1) 115.18(4), P(3)−P(2)−H(2) 97.5(17), P(1)−P(2)−H(2) 94.5(18), P(2)−P(3)−H(3) 94(2), Rb(1)−P(3) 3.5198(9), Rb(1)−P(1) 3.6288(8), Rb(2)−P(2) 3.7012(8).

the coordination number of the P_3^{4-} anion is 14. A comparison of the coordination spheres of the anions of $Rb_3(P_3H_2)\cdot NH_3$ and K_4P_3 is shown in Figure 4.

The P−P bond lengths in the $P_3H_2^{3-}$ anion are 2.236(2) Å for P(1)−P(2) and 2.222(2) Å for P(2)−P(3), with a bond angle of 112.2(1)°. In the case of K_4P_3, the P−P bond length is 2.183(2) Å with a bond angle of 118.07(7)°. The hydrogen−phosphorus bond lengths are in the usual range for P−H bonds in such compounds with 1.3(1) and 1.4(1) Å; the hydrogen atoms are in Z conformation.[16,17] The Rb−P distances in $Rb_3(P_3H_2)\cdot NH_3$ are in a range of about 3.33 to 3.77 Å, and the K−P distances in K_4P_3 are in the range of 3.33 to 3.57 Å. Figure 5 shows the coordination spheres of the rubidium ions Rb(1), Rb(2), Rb(3) and of the nitrogen atom N(1) of the ammonia molecule. The coordination number of Rb(1) and Rb(3) is seven, and the coordination number of Rb(2) is eight. Through the cation−anion interaction, a 3D infinite network is formed. Bond lengths are available in the caption of Figure 5. By coordination of the ammonia molecule to three rubidium cations Rb(1), Rb(2), and a symmetry equivalent, a trigonal pyramid is formed that is connected to a symmetry-equivalent one by sharing an edge. This leads to formal $[Rb_4(NH_3)_2]^{4+}$ units.

In Figure 6 a projection of the unit cell of $Rb_3(P_3H_2)\cdot NH_3$ along the *b* axis is shown. Tables 6 and 7 in the Supporting Information supply the atom coordinates and thermal displacement parameters. Table 1 holds further crystallographic details of the structure.

Because of the low solubility of compound (2) in liquid ammonia, ^{31}P and ^{1}H NMR spectra at −40 °C did not show any signals that could be assigned to the $P_3H_2^{3-}$ anion.

Structure of $[Rb(18\text{-crown-}6)]_2(P_3H_3)\cdot 7.5NH_3$ (3). Only one nitrogen atom, N(8), occupies the special 2*a* position of space group *C*2; all of the other atoms lie on the common 4*c* position. As the anion, the *catena*-trihydrogen triphosphide anion $P_3H_3^{2-}$ is present, which coordinates two rubidium cations to be η^1- and η^2-like (Figure 7). The bond lengths are 2.2073(11) Å for P(1)−P(2), 2.1947(11) Å for P(2)−P(3), 1.41(4) Å for P(1)−H(1), 1.39(4) Å for P(2)−H(2), and 1.46(6) Å for P(3)−H(3). The P−P−P bond angle is 115.18(4)°.

In addition to coordinating the outer phosphorus atoms of the $P_3H_3^{2-}$ anion, the rubidium cation Rb(1) is complexed by a molecule of 18-crown-6. The rubidium ion is shifted 1.1738(8) Å away from a least-squares plane defined by the oxygen atoms of the crown ether; Rb−O distances are available in the caption of Figure 8, and the coordination number of Rb(1) is eight. The rubidium cation Rb(2) is coordinated by the central phosphorus atom of $P_3H_3^{2-}$ in an η^1-like manner by two nitrogen atoms N(2) and N(4) of two ammonia molecules and is complexed by a molecule of crown ether. The Rb(2) cation is 1.3215(9) Å away from a least-squares plane defined by the oxygen atoms of the crown ether molecule, and its coordination number is nine (Figure 8).

The crystal structure features hydrogen bonds between the hydrogen atoms H(7), H(8), and H(9) of the ammonia molecule with nitrogen atom N(3) and the oxygen atoms O(8), O(9), O(10), and O(12) of a crown ether molecule (Figure 9). Furthermore, the nitrogen atom N(5)#1 of an ammonia molecule is bound via H(11)#1 to O(9) (Figure 9). The ammonia molecule with nitrogen atom N(7) displays N−H···N and N−H···O hydrogen bonding.

The mentioned coordinative interactions and hydrogen bonds lead to some voids in the structure, which are filled with the residual molecules of ammonia (Figure 10).

Again, we could not obtain ^{31}P or ^{1}H NMR spectra of the anion because of the low solubility of (3) in liquid ammonia at −40 °C. Tables 8 and 9 in the Supporting Information show selected atom coordinates and thermal displacement parameters of (3). Table 1 holds further crystallographic details of the structure.

Structure of $[Cs(18\text{-crown-}6)]_2(P_3H_3)\cdot 7NH_3$ (4). All atoms occupy the common 4*e* position of space group $P2_1/c$. The anionic moiety is the *catena*-trihydrogen triphosphide anion, $P_3H_3^{2-}$; the P−P bond lengths are 2.208(4) Å for

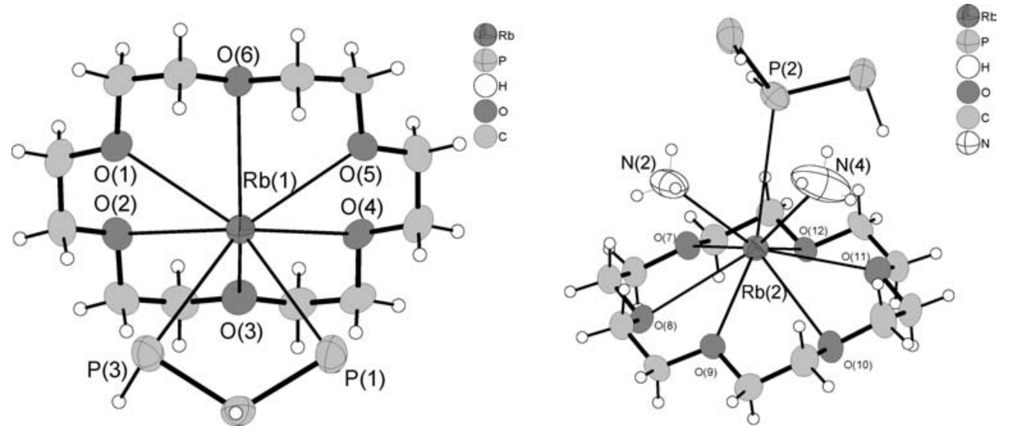

Figure 8. Projections of the coordination spheres of Rb(1) and Rb(2) in (3). Thermal ellipsoids are drawn at 70% probability level. Selected bond lengths (Å): Rb(1)−O(3) 2.958(2), Rb(1)−O(5) 2.9972(19), Rb(1)−O(1) 3.0335(18), Rb(1)−O(4) 3.078(2), Rb(1)−O(6) 3.1191(19), Rb(1)−O(2) 3.150(2), Rb(2)−O(7) 3.0172(19), Rb(2)−O(11) 3.0364(18), Rb(2)−O(9) 3.0485(19), Rb(2)−O(12) 3.115(2), Rb(2)−O(10) 3.218(2), Rb(2)−O(8) 3.2776(19), Rb(2)−N(2) 3.060(3), Rb(2)−N(4) 3.157(3).

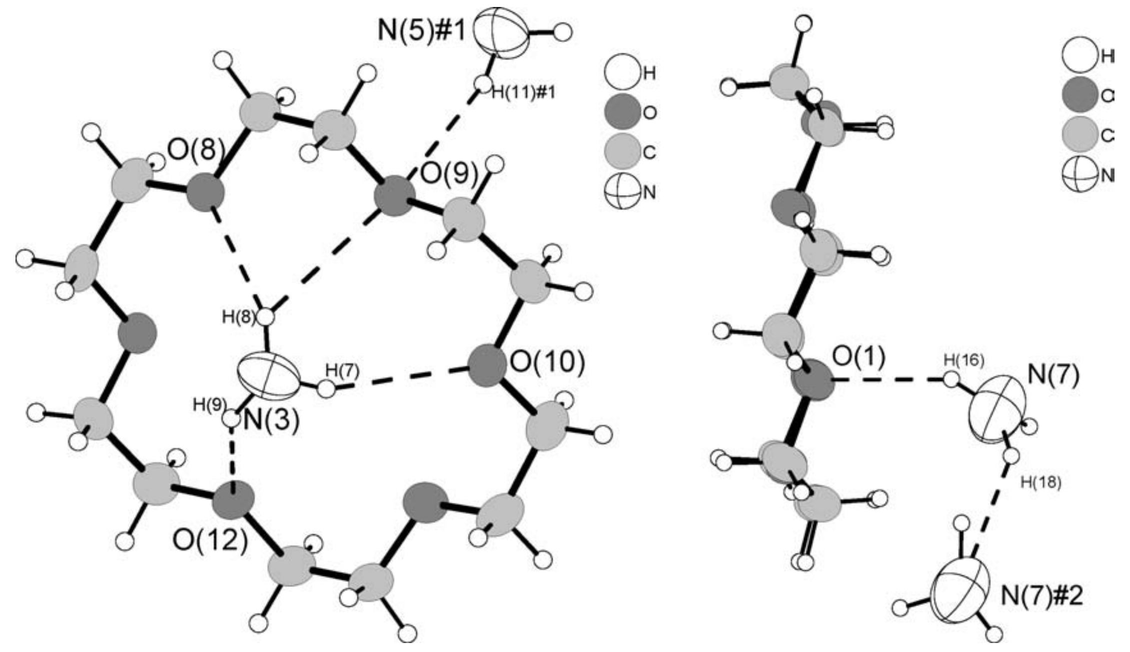

Figure 9. Projections of the N−H···O− and N−H···N− hydrogen bonds in (3). Thermal ellipsoids are drawn at 70% probability level. Selected hydrogen bond lengths (Å) and angles (deg): D−H···A, d(D−H), d(H···A), d(D···A), <(DHA): N(3)−H(7)···O(10), 0.88(6), 2.53(6), 3.353(4), 157(5); N(3)−H(8)···O(8), 0.91(5), 2.33(5), 3.184(4), 156(5); N(3)−H(8)···O(9), 0.91(5), 2.69(5), 3.363(4), 131(4); N(3)−H(9)···O(12), 0.98(5), 2.79(5), 3.576(4), 137(4); N(5)#1−H(11)#1···O(9), 0.80(5), 2.52(5), 3.216(4), 146(4); N(7)−H(16)···O(1), 0.95(5), 2.50(6), 3.352(5), 149(5); N(7)−H(18)···N(7)#2, 1.10(7), 2.42(8), 3.308(10), 137(7).

P(1)−P(2) and 2.178(4) Å for P(2)−P(3). The P−P−P bond angle is only 101.7(2)°, and the P−H distances are 1.29(2) Å for P(1)−H(1), 1.29(2) Å for P(2)−H(2), and 1.30(2) Å for P(3)−H(3) in the expected range (Figure 11). The anion is coordinated by two cesium cations above and below the P−P−P plane with Cs−P distances between 3.46 and 4.04 Å. Additionally, every cesium cation is coordinated by a molecule of 18-crown-6 and an ammonia molecule, yielding a total coordination number of 10 for each cesium ion (Figure 11). On the non-cesium coordinating side of the two crown ether molecules, molecules of ammonia with nitrogen atoms N(2) and N(5) are bound via N−H···O hydrogen bonding. Unfortunately the involved hydrogen atoms on N(2) and N(5) could not be localized. Furthermore, N(2) and N(5) act as hydrogen bond acceptors. N(3) donates its hydrogen atom to N(5), and the ammonia molecule with N(7) bridges with its hydrogen atoms between N(2) and N(5). More hydrogen bonds, their bond lengths, and angles are available in the caption of Figure 11.

By the bridging between the $(Cs(18\text{-crown-}6))_2(P_3H_3)$ moieties over N−H···O− and N−H···N− hydrogen bonds, 1D infinite zigzag strands result, running parallel to the *b* axis (Figure 12).

Because of low solubility, no ^{31}P or ^{1}H NMR spectra of the anion could be obtained in liquid ammonia at −40 °C. Tables 10 and 12 of the Supporting Information contain selected atom coordinates and thermal displacement parameters. Table 1 holds further crystallographic details of the structure.

Comparison of the *catena*-Triphosphides. The bond lengths and angles of the presented *catena*-dihydrogen triphosphides, $P_3H_2^{3-}$, and *catena*-trihydrogen triphosphides,

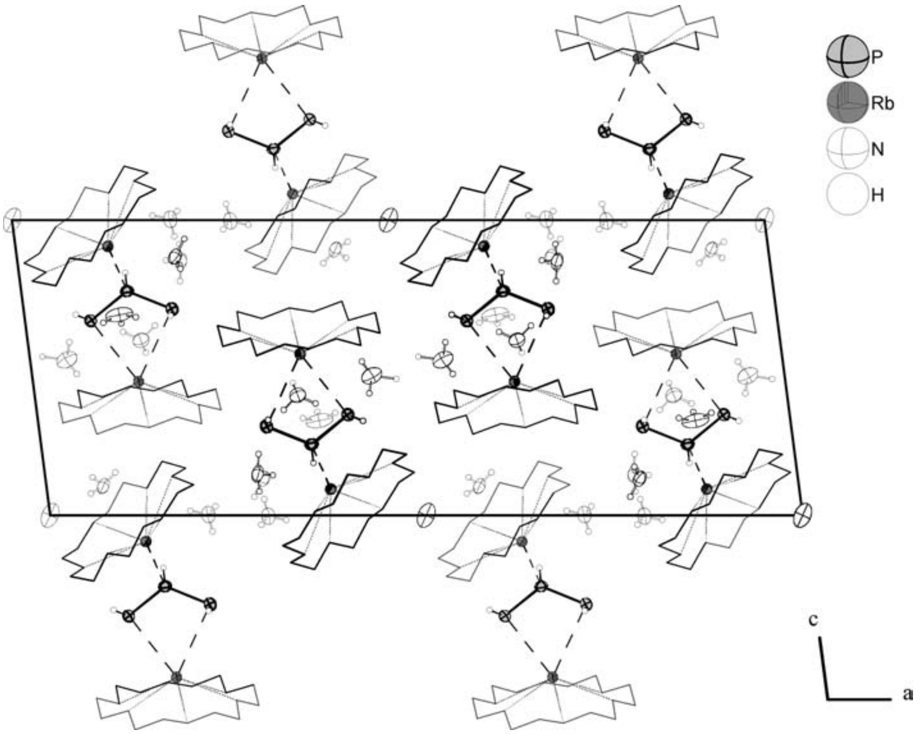

Figure 10. Projection of the unit cell of (3) along the *b* axis. Thermal ellipsoids are drawn at 70% probability level. Crown ether molecules are shown only as frameworks for the sake of clarity.

$P_3H_3^{2-}$, can be compared with the equivalent parameters in anions and compounds they can be formally derived from. These are the triphosphane(5), P_3H_5,[29−32] and the P_3^{5-} anion in the lanthanum phosphide, LaP_2,[5,33] which is the formal product of the full deprotonation of triphosphane(5). We further include the 19-electron radical P_3^{4-} of K_4P_3[28] in our comparison because we found very similar coordination spheres of the anions in K_4P_3 and the compounds (1) and (2). As one can see from Table 2, all P−P bond lengths are in the range that is usually found for phosphorus−phosphorus single bonds.[5,6] Furthermore, most of the P−P−P bond angles are larger than 112°; the only deviating compounds are LaP_2, P_3H_5, and (4) with 107.6(5), 104.5, and 101.7(2)°, respectively. The bond angle varies from 112.2(1) to 115.5(2)° in the *catena*-dihydrogen triphosphides, $P_3H_2^{3-}$, and from 101.7(2) to 115.18(4)° in the *catena*-trihydrogen triphosphides, $P_3H_3^{2-}$. Therefore, one may conclude that the P−P−P bond angles are relatively flexible depending on the coordination sphere and the counterions. K_4P_3, $Rb_3(P_3H_2)\cdot NH_3$ (2), and $K_3(P_3H_2)\cdot 2.3NH_3$ (1) show very similar coordination spheres with diminishing coordination numbers of the anions with 14, 11, and 9, respectively, but neither bond lengths nor angles show a trend.

Quantum chemical structure optimizations (Table 3) yield results that fit the measured values well, with the bond lengths being a little longer but the bond angles in the same range of larger than 110°. Calculations of vibration frequencies show the P−P−P flexing mode to be the second lowest one in energy with a low wavenumber of only 150 cm^{-1}. The potential of the vibration is almost a harmonic one and shows a force constant of only 0.026 $mE_h/°$. Therefore, the quantum chemical calculations support the flexibility of the P−P−P bond and the easy change of the P−P−P bond angle by different coordination of cations.

Experimental Section

Starting Materials. White phosphorus was obtained from Hoechst, dried in vacuo, and redistilled. Rb_4P_6 and Cs_4P_6 were synthesized from red phosphorus (Hoechst, 99.999%) and distilled rubidium/cesium in tantalum ampoules, according to the procedure described in the literature.[36−38] 18-crown-6 was obtained from Aldrich and sublimed. Lithium was distilled prior to use.

Synthesis, Structure Solution, and Refinement of (1). The compound was synthesized by reduction of white phosphorus (4.23 mmol) with distilled potassium (9.52 mmol) in dry liquid ammonia at −78 °C. After 2 weeks at −40 °C, the blue solution became yellow, and yellow plate-shaped crystals of (1) were obtained. A suitable crystal was mounted on a glass tip using a perfluorinated ether at temperature below −40 °C. The systematic extinctions

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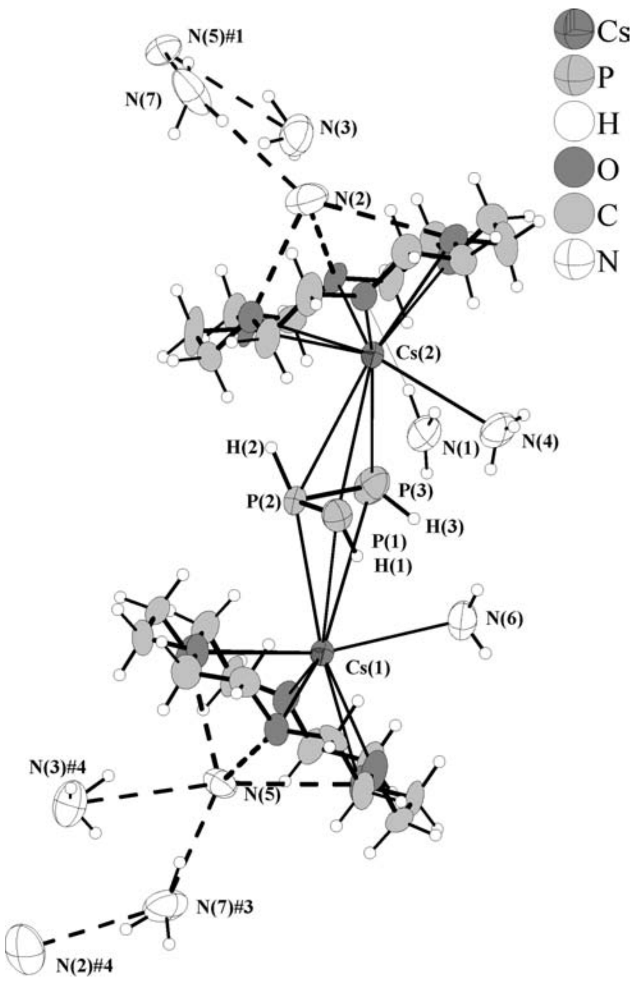

Figure 11. Projection of the $P_3H_3^{2-}$ anion in (4), its coordination by the cesium cations, and their coordination sphere. Hydrogen bonds are shown as dashed lines. Thermal ellipsoids are drawn at 70% probability level. Hydrogen bond lengths (Å) and angles (deg), D−H distance, H···A distance, D···A distance, D−H···A angle (D is donor, A is acceptor): N(1)−H(4)···O(7): D−H 1.11, H···A 2.38, D···A 3.469(10), D−H···A 166.8; N(3)−H(12)···N(2): D−H 0.88, H···A 3.31, D···A 3.705, D−H···A 109.5; N(3)−H(10)···N(5)#1: D−H 1.11, H···A 2.59, D···A 3.537(10), D−H···A 142.2; N(7)−H(16)···N(2)#2: D−H 1.03(6), H···A 2.60(7), D···A 3.538(17), D−H···A 150(7); N(7)−H(18)···N(5)#3: D−H 1.03(6), H···A 2.58(8), D···A 3.49(2), D−H···A 147(9).

showed the space group *R*-3*c* to be a proper choice. The structure was solved in space group *R*-3*c* using the direct methods implemented in SHELXS-97.[39] A full-matrix least-squares refinement on F^2 was then performed with SHELXL-97 in the same space group.[40] All atoms were anisotropically refined; hydrogen atoms were located, where possible, by Fourier cycling methods and were isotropically refined. An absorption correction was carried out using the DELrefABS algorithm of PLATON.[41] To account for the high residual electron density close to potassium ion K(4), several disorder models and twin refinements in lower space groups were tried without better results.

Synthesis, Structure Solution, and Refinement of (2). The compound was synthesized by the reaction of 422 mg distilled rubidium (4.94 mmol) and approximately 5 mL of diphosphane(4) P_2H_4. The next day, about 15 mL of ammonia was condensed onto the mixture, and after 1 year of storage at −40 °C, orange, cube-shaped crystals of (2) were obtained and subjected to X-ray analysis. A suitable crystal was mounted on a nylon loop using a perfluorinated ether at −40 °C. The structure was solved in space group *Pbca* using direct methods in SHELXS-97. A numerical absorption correction using X-RED/X-SHAPE[42,43] was applied. All non-hydrogen atoms were anisotropically refined in a full-matrix least-squares refinement against F^2 using SHELXL-97. Hydrogen atoms were located with Fourier cycling techniques and were refined either free or using same-distance restraints (hydrogen atoms of the ammonia molecules).

Synthesis, Structure Solution, and Refinement of (3). The compound was synthesized from rubidium cyclohexaphosphide (90.0 mg, 0.17 mmol), lithium (6.4 mg, 0.92 mmol), and sublimed 18-crown-6 (238 mg, 0.90 mmol) in 15 mL of liquid ammonia at −78 °C. At the beginning of the reaction, the reaction mixture was a yellow solution with a black precipitate. After 6 days of storage at −40 °C, transparent yellow plates of (3) were obtained, and a suitable crystal was subjected X-ray analysis. Without the reducing lithium, different products were obtained, which we reported elsewhere.[19] The crystal was mounted on a nylon loop using a perfluorinated ether. The structure was solved in space group *C*2 using direct methods implemented in SHELXS-97. The refinement was performed in the same space group using full-matrix least-squares refinement against F^2 in SHELXL-97. After absorption correction using DELrefABS in PLATON, all atoms except hydrogen atoms were anisotropically refined. The hydrogen atoms of the crown ether or of the rubidium-ion-coordinating ammonia molecules were localized and refined using a riding model, if possible. Not all of the hydrogen atoms of the free ammonia molecules of the structure could be localized and refined by using same-distance restraints.

Synthesis, Structure Solution, and Refinement of (4). The compound was synthesized by the reaction of 100 mg cesium cyclohexaphosphide (0.14 mmol), 2 mg lithium (0.28 mmol), and 74 mg 18-crown-6 (0.28 mmol) in about 15 mL of liquid ammonia at −78 °C. After a couple of minutes, the yellow-colored solution turned blue. After 1 day of storage at −40 °C, the solution was dark green, and after 5 more days, the solution became red, and red, needle-shaped crystals had developed. At the air and room temperature, the red crystals became yellow and decomposed to a yellow powder, and we smelled the evolution of phosphanes. Without the addition of the reductive lithium, the cyclotetraphosphide anion, P_4^{2-}, was quantitatively obtained.[19,23] When the red crystals were transferred to the cold (< −40 °C) perfluorinated ether oil, they also become yellow, but they did not seem to change otherwise. One of those was mounted on a nylon loop and subjected to X-ray analysis. The internal *R* values in the orthorhombic and monoclinic crystal systems were almost the same with 0.142 and 0.132, respectively. Because the extinction conditions in the orthorhombic system showed a only a two-fold screw axis clearly, but all of the extinction conditions did not lead to any space group, and solutions and refinements in $P2_12_12_1$ and $P222_1$ did not yield proper results, the solution with direct methods using SHELXS-97 was performed in the monoclinic system. The extinction condition suggested space group $P2_1/c$. During the full-matrix least-squares

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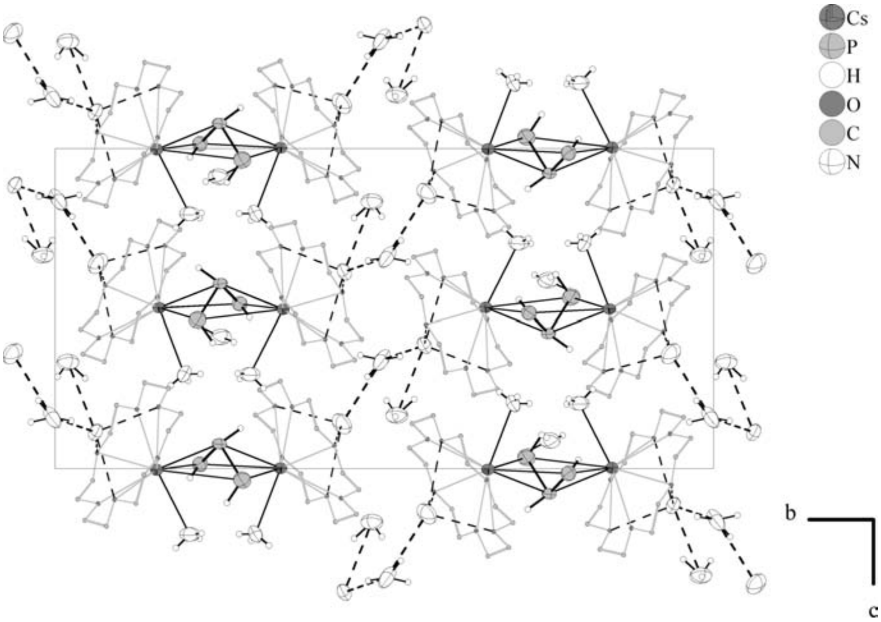

Figure 12. Projection of the unit cell of (4) along the *a* axis. Thermal ellipsoids are drawn at 70% probability level. For the sake of clarity, only a framework of the crown ether molecules is displayed.

Table 2. Comparison of Bond Lengths and Angles of *catena*-(Hydrogen)triphosphide Anions and Triphosphane (5)

compd	species	bond length (Å)	bond angle (deg)
LaP_2[33]	P_3^{5-}	2.21(2), 2.24(2)	107.6(5)
K_4P_3[28]	P_3^{4-}	2.183(1)	118.07(7)
$K[Li(NH_3)_4]_5(P_3H_2)_2$[34]	$P_3H_2^{3-}$	2.232(4)	113.30(4)
$K_3(P_3H_2)\cdot 2.3NH_3$ (1)	$P_3H_2^{3-}$	2.212(4)	115.5(2)
$Rb_3(P_3H_2)\cdot NH_3$ (2)	$P_3H_2^{3-}$	2.236(2), 2.222(2)	112.2(1)
$[Rb(18C6)]_2(P_3H_3)\cdot 7.5NH_3$ (3)	$P_3H_3^{2-}$	2.207(1), 2.195(1)	115.18(4)
$[Cs(18C6)]_2(P_3H_3)\cdot 7NH_3$ (4)	$P_3H_3^{2-}$	2.208(4), 2.178(4)	101.7(2)
$[Na(NH_3)_5][Na(NH_3)_3(P_3H_3)]$[25]	$P_3H_3^{2-}$	2.1977(6)	113.1(4)
P_3H_5 (Raman data)[2]	P_3H_5		104.5

Table 3. Quantum Chemically Calculated Bond Lengths and Angles of the $P_3H_3^{2-}$ and $NaP_3H_3^{2-}$ Anion

calculation[a]	anion	bond length (Å)	bond angle (deg)
HF/I	$P_3H_3^{2-}$	2.23	116.80
HF/II	$P_3H_3^{2-}$	2.24	116.73
B3LYP/I	$P_3H_3^{2-}$	2.26	118.19
B3LYP/II	$P_3H_3^{2-}$	2.27	118.63
MP2/I	$P_3H_3^{2-}$	2.22	116.98
MP2/II	$P_3H_3^{2-}$	2.27	117.35
HF/I	$NaP_3H_3^-$	2.24	111.19
HF/II	$NaP_3H_3^-$	2.25	111.94
MP2/I	$NaP_3H_3^-$	2.23	112.63
MP2/II	$NaP_3H_3^-$	2.24	112.18

[a] I: 6-311G (3df, 3pd); II: aug-VTZ.[35]

refinement against F^2 using SHELXL-97, the twin law $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$ was introduced, which improved the R_1 value from 0.21 to 0.15 and the wR_2 value from 0.50 to 0.25. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were localized and refined either freely a using a riding model. Not all of the hydrogen atoms could be localized with Fourier cycling methods. After the refinement converged, searches for additional and missed symmetry were performed using ADSYMM in PLATON[41] and KPLOT[44] but did not lead to another space group.

Outline of the Theoretical Procedures. The calculations were carried out using Gaussian98[45] on various levels of theory.

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Supporting Information Available: Atom coordinates and isotropic and anisotropic thermal displacement parameters of (1)−(4) and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 604804 and 604805 contain the supplementary crystallographic data for compounds (3) and (4). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Further details of the crystal structure investigations of compounds (1) and (2) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de; http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) upon quoting the deposition numbers CSD-416484 and -416485.

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