Phosphorus Radicals

"Naked" Phosphanediide Chains and their Fragmentation into Diphosphene Radical Anions**

*Jens Geier, Jeffrey Harmer, and Hansjörg Grützmacher**

Most multiple charged molecules are unstable in the absence of a stabilizing environment of opposite charge and decompose either under "Coulomb explosion", that is, under bond cleavage, and/or by electron detachment.[1] The latter process occurs easily in the case of polyanions because electrons are readily lost by tunneling through the barrier at the intersection of the X^{n-} and $X^{(n-1)-} + e^-$ (X = molecular fragment) potential energy surfaces. Numerous polyanions with phosphorus are found in the solid state as Zintl phases (M_nP_m), which generally show tight anion–cation contacts.[2] For example, in Ca_2P_2[3] or $[Cs_2P_4(NH_3)_2]$,[4] which contain the small $(P_2)^{4-}$ or the 6π aromatic $(P_4)^{2-}$ ions, the high concentration of negative charge is stabilized by the formation of bicyclobutane-type arrangements such as **A** in Figure 1. Such

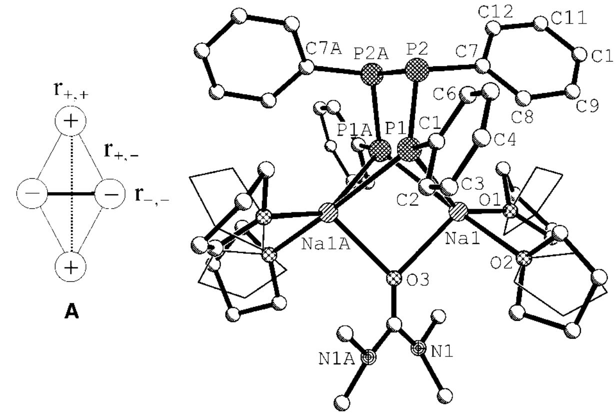


Figure 1. Bicyclobutane-shaped fragment **A** characteristic for $[(M^+)_2(X^{2-})]$ ion triples and structure of *rac*-[**1a**(thf)$_4$(tmu)]. Hydrogen atoms are omitted for clarity and the second orientation of the disordered THF molecules is shown in thin lines. Selected distances [Å] and angles [°]: Na1-P1 2.974(2), Na1-P1A 2.918(2), Na1-Na1A 3.491(4), Na1-O1 2.405(4), Na1-O2 2.326(4), Na1-O3 2.453(4), P1-P2 2.163(2), P2-P2A 2.206(2), P1-C1 1.809(4), P2-C7 1.850(5); C1-P1-P2 102.0(1), P1-P2-P2A 104.4(1), P1-P2-C7 107.4(1), C7-P2-P2A 98.8(2), C2-C1-C6 115.7(4), C8-C7-C12 117.3(4), P1-P2-P2A-P1A −31.9(1), C1-P1-P2-C7 88.8(2), C7-P2-P2A-C7A −170.6(3), normal angle (Na1,P1,P1A)/(Na1A,P1,P1A): 85.7(1).

---

[*] Dr. J. Geier, Dr. J. Harmer, Prof. Dr. H. Grützmacher
Department of Chemistry, HCI
ETH Hönggerberg
8093 Zürich (Switzerland)
Fax: (+41) 1-63-1032
E-mail: gruetzmacher@inorg.chem.ethz.ch

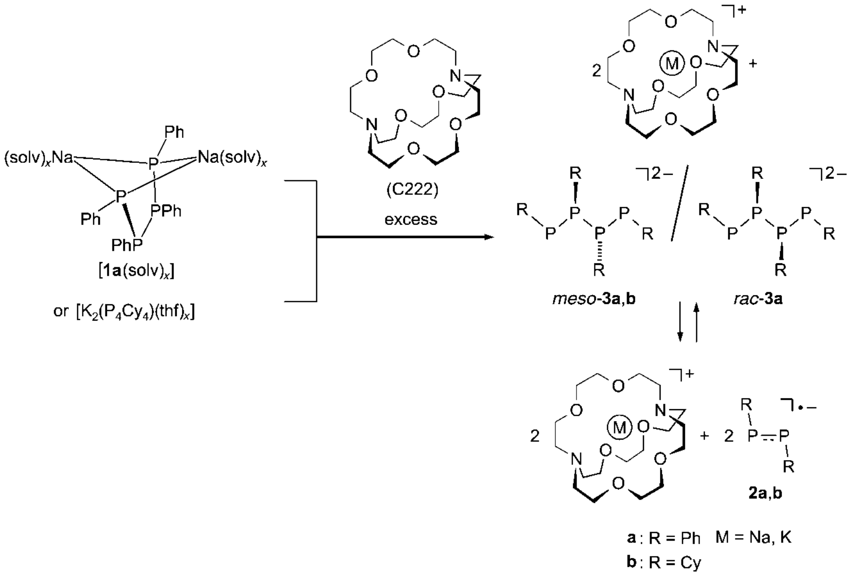
[**] This work was supported by the ETH Zürich and Ciba Speciality Chemicals.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200460130

arrangements are typical for ion triples[5] and are favored because they contain four attractive Coulombic interactions ($r_{+,-}$) but only two repulsive ones ($r_{-,-}$ and $r_{+,+}$), respectively. Exceptions are $[(BnMe_3N)^+_2(P_{11}H)^{2-}]$ and $[(EtMe_3N)^+_3(P_{11})^{3-}]$[6] which contain weakly coordinating large cations and the negative charges are delocalized over the σ framework of the P_{11} cage. Geminal dianions $(RP)^{2-}$ could be isolated in organophosphorus chemistry as cage compounds through intimate contacts with the countercations.[7] In the solid-state structures of bis(alkali metal)-*catena*-oligophosphane-α,ω-diides $[M_2(P_mR_m)(solv)_x]$ (M = Li, Na, K; $m = 2$, 3, 4; solv = M-bonded solvent molecules) ion triples with a M_2P_2-bicyclobutane-type arrangement were observed.[8,9] An example of such an ion triple is the C_2-symmetric disodium 1,2,3,4-tetraphenyltetraphosphane-1,4-diide $[Na_2(P_4Ph_4)(thf)_4(tmu)]$ (*rac*-[**1a**(thf)$_4$(tmu)], tmu = tetramethylurea; Figure 1).[10] This compound was obtained by reduction of phenylphosphonous acid dichloride with sodium metal in toluene/tetramethylethylenediamine (tmeda)[8a] and recrystallization of the product $[Na_2(P_4Ph_4)(tmeda)_2]$ from THF in the presence of tetramethylurea. The folding along the (P1,P1A) vector, caused by the bridging carbonyl oxygen atom of the strong tmu ligand, is particularly acute ($\Phi = 85.7°$), and consequently the Na···Na distance (3.491(4) Å) is relatively short compared with other $[Na_2P_nR_n]$ bicyclic structures ($n = 3$, 4). All other structural parameters lie within the typical range (Figure 1).[8,9] The terminal phenyl rings are only slightly tilted with respect to the adjacent P1–P2/P1A–P2A bonds (12.6°), and the terminal P–C bonds are shorter (P1–C1 1.809(4) Å) than the internal ones (P2–C7 1.850(5) Å), thus indicating charge delocalization from the formally negatively charged terminal phosphorus centers into the phenyl rings. The phosphorus centers at the central P–P unit of the P_4 chain in the $[M_2(P_4R_4)]$ ion triples has the *R*,*R*(*S*,*S*) configuration, that is, the P_4 chain is made of the sterically favored racemic *threo* isomer.

Would "naked" $(P_4R_4)^{2-}$ dianionic chains be stable? To answer this question we added an excess of the bicyclic sodium/potassium-complexing agent [2.2.2]cryptand (C222)[11] to (EPR-silent) solutions of *rac*-[**1a**(solv)] (solv = tmeda, dimethoxyethane (dme), thf; Scheme 1). A color change from yellow to red-orange occurred immediately and was accompanied by the precipitation of most of the phosphorus-containing species (> 90 %), firstly as a red oil which soon crystallized to give red and yellow crystals. Freshly prepared, inhomogeneous samples of the *rac*-[**1a**(solv)]/cryptand mixture gave a strong EPR signal ($g = 2.0089$) which appeared as a triplet (a_{iso}[P] = 115 MHz) as a result of hyperfine coupling with two identical ^{31}P nuclei. The signal is further split by smaller ^{1}H couplings to two nonequivalent *ortho* protons on each benzene ring (a_{iso}[H] = 8.5 MHz and a_{iso}[H′] = 4.0 MHz; Figure 2a).



Scheme 1. Syntheses of **2a**,**b** and *rac*-**3a**/*meso*-**3a**,**b**.

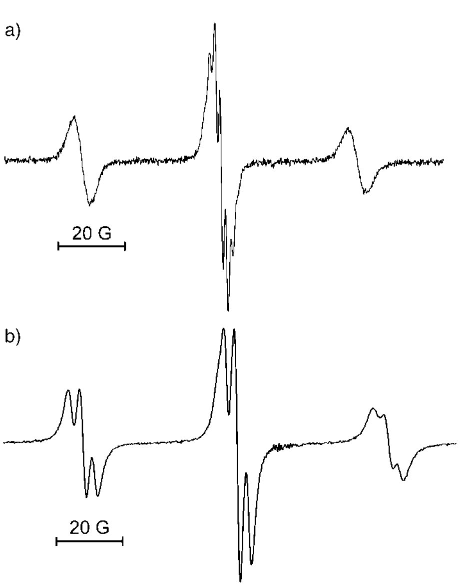


Figure 2. X-band EPR spectra of **2a** (a) and **2b** (b) in THF at room temperature. Spectra were measured with a microwave frequency of 9.7 GHz, a modulation amplitude of 0.05 mT, and a modulation frequency of 100 kHz.

This EPR spectrum is assigned to the free diphenyldiphosphene radical anion $(P_2Ph_2)^{\bullet-}$ (**2a**) formed by homolytic cleavage of the central P–P bond in the $(P_4Ph_4)^{2-}$ dianion upon removal of its charge-stabilizing contacts to the positive sodium counterions.[12] Dilute solutions of **2a** are remarkable stable, however, the same crystalline solids as formed in the reaction of *rac*-[**1a**(solv)] with (C222) were obtained upon concentration. These crystals were carefully washed with small portions of THF and then suspended in THF, which became slightly orange, thus indicating the complex was slightly soluble.

However, no ^{31}P NMR signal could be recorded; instead, **2a** was again detected by EPR spectroscopy. X-ray structure analyses were performed on both the red and yellow crystals. The red crystals, which are formed in a smaller amount, contain the 2*R*,3*S* diastereomer (*meso* or *erythro* isomer) of the "naked" $(P_4Ph_4)^{2-}$ chain (*meso*-**3a**)[10] (Figure 3 a) and the yellow ones the (2*R*,3*R*)/(2*S*,3*S*)-configured diastereomer *rac*-**3a**[10] (not shown here because the crystals of *rac*-**3a** were of poor quality and although the gross structural features could be unambiguously determined, a sufficient refinement of the data sets was impossible, see the Supporting Information for details and structure plots).

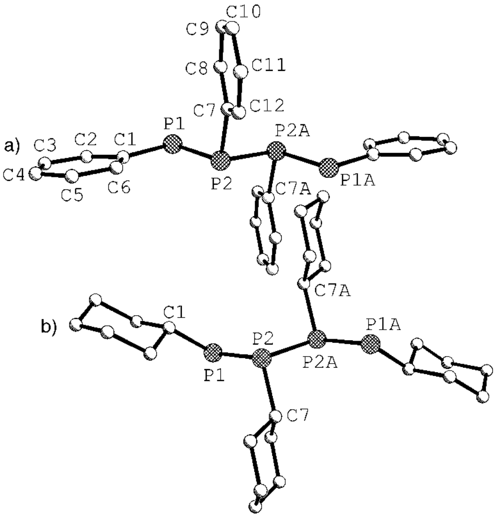


Figure 3. Solid-state structures of *meso*-**3a** (a) and *meso*-**3b** (b). Hydrogen atoms and countercations (*meso*-**3a**: [Na(C222)]$^+$, *meso*-**3b**: [K(C222)]$^+$) are omitted for clarity. Selected distances [Å] and angles [°]: a) P1-P2 2.178(1), P2-P2A 2.224(2), P1-C1 1.811(3), P2-C7 1.863(3); C1-P1-P2 99.8(1), P1-P2-P2A 97.4(1), P1-P2-C7 105.4 (1), C7-P2-P2A 97.7(1), C2-C1-C6 115.9(3), C8-C7-C12 117.3(3), P1-P2-P2A-P1A 180.0(0), C1-P1-P2-C7 −86.5(1), C7-P2-P2A-C7A 180.0(0); b) P1-P2 2.147(3), P2-P2A 2.210(4), P1-C1 1.866(7), P2-C7 1.876(8); C1-P1-P2 102.1(3), P1-P2-P2A 104.2(2), P2-P2-C7 106.2(3), C7-P2-P2A 96.3(3), P1-P2-P2A-P1A 180.0(0), C1-P1-P2-C7 121.7(4), C7-P2-P2A-C7A 180.0(0).

We also examined the reaction of the cyclohexyl (Cy) analogue $[K_2(P_4Cy_4)(thf)_x]$ [**1b**(thf)$_x$][13] (of unknown structure) with an excess of the [2.2.2]cryptand. As with *rac*-[**1a**(solv)], a strong EPR signal was observed ($g = 2.0099$) which indicates the formation of the radical anion $(P_2Cy_2)^{\bullet-}$ **2b** (Figure 2 b). In addition to the ^{31}P hyperfine couplings of $a_{iso}[P] = 127$ MHz, which are slightly larger than the ones in **2a**, couplings with the protons at the C1 atom were observed ($a_{iso}[H] = 10$ MHz). One sort of crystals precipitated from the THF solution and was subjected to X-ray structure analysis. The result (Figure 3 b) shows them to be composed of $[\{K(C222)\}_2^+](P_4Cy_4)^{2-}$. The "naked" $[P_4Cy_4]^{2-}$ chain corresponds to the 2*R*,3*S* diastereomer, that is, $[\{K(C222)\}_2^+](P_4Cy_4)^{2-}$ is denoted as *meso*-**3b**.

The centrosymmetric dianions in *meso*-**3a** and *meso*-**3b** provide the first structures for "naked" α,ω-dianions of chains made from main-group IV/V elements. The sodium ions in *meso*-**3a** and the potassium ions in *meso*-**3b** are completely encapsulated in the internal cavity of the cryptand. The shortest contacts between the formally negatively charged terminal phosphorus atoms P1 and P1A and the hydrogen atoms at the outside of the [M(C222)]$^+$ ions (M = Na, K) are about 2.88–3.05 Å. With exception of the C1-P1-P2-P2A torsion angles (*meso*-**3a**: −173.4(3)° , *meso*-**3b**: −137.2(3)°) the structural features of both P_4 chains are quite similar. For electrostatic reasons they adopt a planar 1,4-*anti* conformation to maximize the P1···P1A distance (5.139(2) Å in *meso*-**3a**, 5.289(2) Å in *meso*-**3b**) which is much shorter in the ion triple *rac*-[**1a**(thf)$_4$(tmu)] (3.475(2) Å). As in this latter complex, the terminal phenyl groups in *meso*-**3a** are almost coplanar with the P_4 chain (tilt angle 8.7°), and the distinctly shorter terminal P−C bonds (P1−C1: 1.811(3) Å versus P2−C7: 1.863(3) Å) may indicate some charge delocalization. This proposal is consistent with the observation of hindered rotation of the phenyl groups in the planar $(P_2Ph_2)^{\bullet-}$ radical anion[14] on the EPR time scale, that is, **2a** also profits from some π-type charge delocalization. Evidently, such effects are absent in the cyclohexyl-substituted analogues and the P−C bonds in *meso*-**3b** are almost identical (P1−C1: 1.866(7) Å and P2−C7: 1.876(8) Å). The most notable structural feature in *meso*-**3a,b** is that the stereochemistry at one of the central phosphorus atoms has been inverted when compared to the ion triples *rac*-[**1a**(solv)]. In view of the sizable inversion barriers at σ^3,λ^3-phosphorus centers in phosphanes (PR_3)[15] and the typical sum of bond angles at P2/P2A (*meso*-**3a**: 300.5°, *meso*-**3b**: 306.7°), it is reasonable to assume that the 2*R*,3*S*-configured P_4 chains in *meso*-**3a,b** result from a cleavage of the central P−P bond of the P_4 units in the ion triples into two $(P_2R_2)^{\bullet-}$ radical anions **2a,b** upon removal of the stabilizing anion–cation interactions. Subsequently, the radicals recombine to give the P_4 chains with the sterically favored *anti* arrangement of the internal substituents at P2 and P2A.[16] This process is reversible, that is, the ion triple *rac*-**1a** with its *R*,*R*(*S*,*S*)-configured P_4 units is reformed when crystals of *meso*/*rac*-**3a** are dissolved in a solution of sodium triflate (NaO_3SCF_3) in THF. No unusual P−P bond lengths are observed in *meso*-**3a,b**, and thus neither strain nor an especially weak central P−P bond is responsible for the dissociation process. The central P−P bond in the ion triple $[Na_2(P_4Ph_4)(thf)_4(tmu)]$ (*rac*-[**1a**(thf)$_4$(tmu)]) and the P_4 chains in *meso*-**3a,b** (*rac*-[**1a**(thf)$_4$(tmu)]: 2.206(2) Å; *meso*-**3a**: 2.224(2) Å; *meso*-**3b**: 2.210(4) Å) is only slightly longer than the terminal ones (*rac*-[**1a**(thf)$_4$(tmu)]: 2.163(2) Å; *meso*-**3a**: 2.178(1) Å; *meso*-**3b**: 2.147(3) Å). In contrast, the sterically overcrowded diphosphane $[(Me_3Si)_2CH]_2P{-}P[CH(SiMe_3)_2]_2$, which is cleaved into two $[(Me_3Si)_2CH]_2P^\bullet$ radicals upon melting, dissolution, or vaporization, shows a modestly elongated P−P bond (2.3103(7) Å) and considerable distortions in the geometry of the ligands.[17] The destabilizing energy which causes the dissociation of the "naked" $(P_4R_4)^{2-}$ chains in solution must have its origin mainly in the Coulombic repulsion between the negative charges. On the other hand, the electrostatic field in the crystals of *meso*-**3a,b** is clearly capable of allowing these weakly bonded or even unstable dianions to form quite normal oligophosphanes. While the neutral "phosphobenzene” PhP=PPh is unstable,[18] the phenomena described here allow the synthesis of the persistent free-radical anion $(P_2Ph_2)^{\bullet-}$ with partial P,P multiple bond character in solution. Such species must be considered in the chemistry of organophosphanides.[19]

Experimental Section

Inert conditions were maintained throughout all procedures. *rac*/*meso*-**3a**: Vacuum-distilled [2.2.2]cryptand (28 mg, 0.074 mmol) was added at room temperature in one portion to a solution of *rac*-[**1a**(tmeda)$_2$][8a] (25 mg, 0.035 mmol) in THF (0.5 mL) contained in a narrow (5 mm diameter) glass tube. The yellow solution became cloudy red-orange and a deep red oil separated which subsequently solidified over several hours to form a mixture of red, irregular-shaped (*meso*-**3a**) and yellow, needlelike (*rac*-**3a**) crystals (combined yield: >90%). The ratio of *rac*-**3a** to *meso*-**3a** was approximately 3:1—4:1 and increased further on using more dilute solutions. The orange-colored solution contained the radical **2a**, which was also observed in a lower concentration upon re-suspending the isolated (namely, rigorously THF-washed), sparingly soluble crystals of *meso*/*rac*-**3a** in THF. Addition of sodium triflate to *meso*/*rac*-**3a** in THF gave a clear yellow solution. The ^{1}H, ^{13}C, and ^{31}P NMR spectra for the $(P_4Ph_4)^{2-}$ section were identical to those of the starting material *rac*-[**1a**(tmeda)$_2$]. *Meso*-**3b** was prepared by addition of [2.2.2]cryptand (100 mg, 0.266 mmol) to a suspension of $[K_2(P_4Cy_4)(thf)_x]$[13] (70 mg, <0.13 mmol) in THF (20 mL). A clear red solution formed upon sonification and short (30 s) warming to 45 °C. Yellow crystals of *meso*-**3b** deposited on storing overnight (ca. 70%). M.p. 135 °C (decomp); IR (neat): $\tilde{\nu}$ = 2962w, 2886m, 2835m, 2824m, 2800m, 1479m, 1456w, 1445m, 1356m, 1295m, 1258m, 1166w, 1133m, 1095s, 1081s, 986w, 944s, 932s, 875w, 845w, 830m, 819w, 750w, 699w cm^{-1}. The solution contained the radical **2b**, which was also observed (in lower concentration) upon suspending the sparingly soluble, carefully washed crystals of *meso*-**3b** in THF. *rac*-[**1a**(thf)$_4$(tmu)]: Tetramethylurea (25 mg, 0.22 mmol) was added to *rac*-[**1a**(tmeda)$_2$] (150 mg, 0.21 mmol) in THF (10 mL). Large yellow crystals were isolated after concentration to 1/5 of the original volume and storing for one day at room temperature (47%; for spectroscopic data see the Supporting Information), m.p. 95 °C.

Received: March 26, 2004 [Z460130]

Keywords: EPR spectroscopy · ion pairs · phosphorus · radicals

---

[1] For a recent short review, see D. Schröder, *Angew. Chem.* **2004**, *116*, 1351; *Angew. Chem. Int. Ed.* **2004**, *43*, 1329.

[2] H.-G. von Schnering, W. Hönle, *Chem. Rev.* **1988**, *88*, 243.

[3] J. Getzschmann, P. Boettcher, W. Katurza, *Z. Kristallogr.* **1996**, *211*, 90.

[4] F. Kraus, J. C. Aschenbrenner, N. Korber, *Angew. Chem.* **2003**, *115*, 4162; *Angew. Chem. Int. Ed.* **2003**, *42*, 4030.

[5] A. Streitwieser, Jr., *Acc. Chem. Res.* **1984**, *17*, 353.

[6] N. Korber, J. Daniels, H.-G. von Schnering, *Angew. Chem.* **1996**, *108*, 1188; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1107.

[7] Reviews: a) K. Izod, *Adv. Inorg. Chem.* **2000**, *50*, 33; b) M. Driess, *Adv. Inorg. Chem.* **2000**, *50*, 236; c) M. Driess, *Acc. Chem. Res.* **1999**, *32*, 1017; [Mg(PR)] compounds: d) M. Westerhausen, M. Krofta, A. Pfitzner, *Inorg. Chem.* **1999**, *38*, 598; e) M. Westerhausen, S. Schneiderbauer, J. Knizek, H. Nöth, A. Pfitzner, *Eur. J. Inorg. Chem.* **1999**, 2215.

[8] a) J. Geier, H. Rüegger, M. Wörle, H. Grützmacher, *Angew. Chem.* **2003**, *115*, 4081; *Angew. Chem. Int. Ed.* **2003**, *42*, 3951; b) lithium compounds: D. Stein, M. Scherer, H. Grützmacher, unpublished results.

[9] R. Wolf, E. Hey-Hawkins, “Alkali Metal Salts of Catenated Oligophosphanes—Corresponding Structures in the Solid State and in Solution?”, lecture presented by R. Wolf at ALKCHEM-3, Würzburg, Germany, 30.09.2003.

[10] The data were collected on a Bruker AXS Smart Platform (*rac*-[**1a**(thf)$_4$(tmu)]) or an Apex (*meso*/*rac*-**3a**,**b**) CCD diffractometer and were corrected with the program SADABS version 2.03 (Bruker AXS). The structures were solved by direct methods and all atoms except hydrogen were refined anisotropically (SHELXTL version 6.12, Bruker AXS). *rac*-[**1a**(thf)$_4$(tmu)]: $C_{45}H_{64}N_2Na_2O_5P_4$; yellow cuboid, crystal size $0.63\times0.59\times0.51$ mm; monoclinic, space group $C2/c$, $a = 13.785(4)$, $b = 16.245(5)$, $c = 21.955(6)$ Å, $\beta = 90.695(4)°$, $V = 4916(2)$ Å^3, $Z = 4$, $\mu = 0.21$ mm^{-1}; $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 293$ K, $2\theta_{max} = 52.74°$, collected (independent) reflections = 18872 (5036), $R_{int} = 0.0289$; 259 refined parameters, $R_1 = 0.0823$ for 3021 reflections with $I > 2\sigma$, $wR_2 = 0.2790$ for all data, GOF on $F^2 = 1.036$, max./min. residual electron density = 0.53/–0.28 e Å^{-3}. Two orientations were refined for each of the disordered THF molecules with occupancies of 0.45/0.55 and 0.33/0.67 respectively. *Meso*-**3a:** $C_{60}H_{92}N_4Na_2O_{12}P_4$; red irregular crystal, crystal size $0.40\times0.32\times0.15$ mm; triclinic, space group $P\bar{1}$, $a = 11.254(1)$, $b = 12.674(1)$, $c = 14.259(1)$ Å, $\alpha = 98.248(1)$, $\beta = 112.408(1)$, $\gamma = 112.302(1)°$, $V = 1637.9(2)$ Å^3, $Z = 1$, $\mu = 0.19$ mm^{-1}; $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 293$ K, $2\theta_{max} = 52.74°$, collected (independent) reflections = 13289 (6630), $R_{int} = 0.0181$; 370 refined parameters, $R_1 = 0.0631$ for 4720 reflections with $I > 2\sigma$, $wR_2 = 0.1877$ for all data, GOF on $F^2 = 1.039$, max./min. residual electron density = 1.24/–0.36 e Å^{-3}. *Meso*-**3b**: $C_{60}H_{116}K_2N_4O_{12}P_4$; yellow irregular crystal, crystal size $0.19\times0.18\times0.15$ mm; triclinic, space group $P\bar{1}$, $a = 11.420(5)$, $b = 12.218(6)$, $c = 13.391(6)$ Å, $\alpha = 92.041(8)$, $\beta = 104.659(8)$, $\gamma = 106.041(7)°$, $V = 1726(1)$ Å^3, $Z = 1$, $\mu = 0.29$ mm^{-1}; $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $T = 293$ K, $2\theta_{max} = 43.92°$, collected (independent) reflections = 9153 (4160), $R_{int} = 0.1125$; 370 refined parameters, $R_1 = 0.0916$ for 1936 reflections with $I > 2\sigma$, $wR_2 = 0.2259$ for all data, GOF on $F^2 = 0.893$, max./min. residual electron density = 1.53/–0.62 e Å^{-3}. The structure of *rac*-**3a** could not be refined: $C_{60}H_{92}N_4Na_2O_{12}P_4$; yellow needle, crystal size $0.18\times0.06\times0.05$, triclinic, space group $P\bar{1}$, $a = 12.975(6)$, $b = 13.023(6)$, $c = 22.72(1)$ Å, $\alpha = 95.25(1)$, $\beta = 95.12(1)$, $\gamma = 95.54(1)°$, $V = 3786(3)$ Å^3, $Z = 2$.

[11] 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane: B. Dietrich, J.-M. Lehn, J.-P. Sauvage, J. Blanzat, *Tetrahedron* **1973**, *29*, 1629.

[12] Other persistent radical anions have been reported; $[P_2(2,4,6\text{-}t\text{Bu}_3\text{Ph})_2]^{\bullet-}$: a) B. Cetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, H. Goldwhite, *J. Chem. Soc. Chem. Commun.* **1982**, 691; $[P_2\{(Me_3Si)_3C\}_2]^{\bullet-}$: b) A. J. Bard, A. H. Cowley, J. E. Kilduff, J. K. Leland, N. C. Norman, M. Pakulski, G. A. Heath, *J. Chem. Soc. Dalton Trans.* **1987**, 249; c) M. Culcasi, G. Gronchi, J. Escudié, C. Cuoret, L. Pujol, P. Tordo, *J. Am. Chem. Soc.* **1986**, *108*, 3130; $[P_2(2,6\text{-Mes}_2\text{Ph})_2]^{\bullet-}$: d) S. Shaw, S. C. Burdette, S. Swavey, F. L. Urbach, J. D. Protasiewicz, *Organometallics* **1997**, *16*, 3395; $[P_2t\text{Bu}_2]^{\bullet-}$: e) H. Binder, B. Riegel, G. Heckmann, M. Moscherosch, W. Kaim, H.-G. von Schnering, W. Hönle, H.-J. Flad, A. Savin, *Inorg. Chem.* **1996**, *35*, 2119.

[13] a) This THF-insoluble compound was prepared in the reaction of P_4Cy_4 (from $CyPCl_2$ and $CyPH_2$[13b]) with potassium in THF according to: K. Issleib, K. Krech, *Chem. Ber.* **1965**, *98*, 2545; b) W. A. Henderson, Jr., M. Epstein, F. S. Seichter, *J. Am. Chem. Soc.* **1963**, *85*, 2462.

[14] A planar structure is also predicted by DFT calculations, which show that the planar *trans* isomer is preferred by about 8 kcal mol^{-1} over the *gauche* isomer: J. Geier, unpublished results; see also ref. [12d].

[15] Inversion barriers lie around 30–36 kcal mol^{-1}: R. D. Baechler, K. Mislow, *J. Am. Chem. Soc.* **1970**, *92*, 3090.

[16] Although the structure is not known, we assume that the $(P_4Cy_4)^{2-}$ chain in the ion triple $[K_2(P_4Cy_4)(thf)_x]$ ([**1b**(thf)$_x$]) has, like the $(P_4Ph_4)^{2-}$ chains in *rac*-[**1a**(solv)], the sterically favored *R*,*R*(*S*,*S*) configuration. We cannot definitively say that the intact $(P_4R_4)^{2-}$ chains are not present in solution together with the radical anions $(P_2R_2)^{\bullet -}$, although we have no spectroscopic indication that they are present. The observation that the racemic "naked" $(P_4Ph_4)^{2-}$ chain can be isolated as $[\{Na(C222)\}_2^+](P_4Ph_4)^{2-}$ (*rac*-**3a**) from *rac*-[**1a**(solv)] indicates that such a species may also have a short lifetime in solution. In this case, nucleophilic substitution reactions, that is for example, 2 *rac*-$(P_4Ph_4)^{2-} \rightarrow (P_6Ph_6)^{2-} + (P_2Ph_2)^{2-} \rightarrow 2$ *meso*/*rac*-$(P_4Ph_4)^{2-}$, or elimination processes involving neutral cyclooligophosphanes (in simplified form for example, *rac*-$(P_4Ph_4)^{2-} \rightarrow (PPh)_n{}^{2-} + (4-n)/m\ (PPh)_m \rightarrow$ *meso*/*rac*-$(P_4Ph_4)^{2-}$, $1 < n < 4$ and $3 \le m \le 6$) might also operate but $(PPh)_n{}^{2-}$ dianions with $n > 4$ have never been observed.

[17] a) S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. Voigt, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne, P. P. Power, *J. Am. Chem. Soc.* **2001**, *123*, 9045; b) S. L. Hinchley, C. A. Morrison, D. W. H. Rankin, C. L. B. Macdonald, R. J. Wiacek, A. H. Cowley, M. F. Lappert, G. Gundersen, J. A. C. Clyburne, P. P. Power, *Chem. Commun.* **2000**, 2045.

[18] This compound as originally formulated by Michaelis and Köhler in 1877 was shown to be $(PhP)_n$ ($n = 3$—6) in the 1960s. The first genuine diphosphene was prepared in 1981 and needed bulky substituents for kinetic stabilization: a) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higushi, *J. Am. Chem. Soc.* **1981**, *103*, 4587; this reference also cites older work; PhP=PPh itself could only be stabilized by transition-metal complexation, see for example: b) J. Borm, L. Zolnai, G. Huttner, *Angew. Chem.* **1983**, *95*, 1018; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 977.

[19] Chainlike tetraphosphanediides M-PPh-PPh-PPh-PPh-M (M = Li, K) in solution were proposed by: a) P. R. Hoffman, K. G. Caulton, *J. Am. Chem. Soc.* **1975**, *97*, 6370; however, these results were differently interpreted by: b) M. Baudler, D. Koch, E. Tolls, K. M. Diedrich, B. Kloth, *Z. Anorg. Allg. Chem.* **1976**, *420*, 146; c) M. Baudler, D. Koch, *Z. Anorg. Allg. Chem.* **1976**, *425*, 227.