Angewandte
International Edition Chemie

DOI: 10.1002/anie.201003441

Container Molecules

Ion Dynamics in Confined Spaces: Sodium Ion Mobility in Icosahedral Container Molecules**

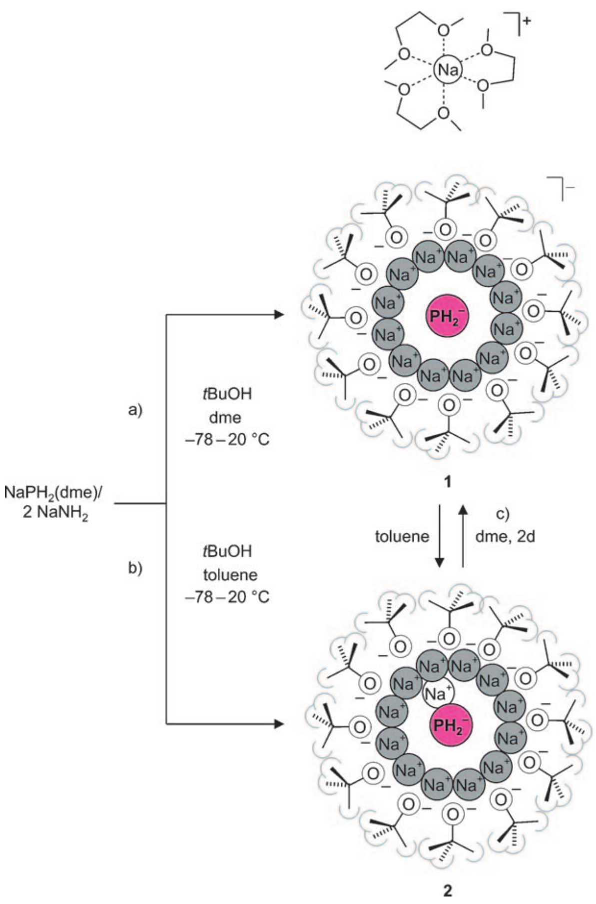
Maren Podewitz, Jacco D. van Beek, Michael Wörle, Timo Ott, Daniel Stein, Heinz Rüegger[†]*, Beat H. Meier,* Markus Reiher,* and Hansjörg Grützmacher**

Cation fluctuations within a molecular anionic ligand framework in crystals have rarely been observed. Veith et al. have studied local Li^+ ion fluctuations in crystalline lithium siloxyamides that contain either an anionic $(N\text{-}Si\text{-}O\text{-}Si\text{-}N)^{2-} = (X^{2-})$ or $(O\text{-}Si\text{-}N\text{-}Si\text{-}O)^- = (Z^-)$ skeleton.[1] In the crystalline $[Li_2(Z)_2]$ and $[Li_4(X)_2]$ species, the metal movements proceed in a concerted fashion, that is, the cations jump simultaneously from filled to empty positions as electrostatically coupled $(Li_2)^{2+}$ and $(Li_4)^{4+}$ clusters, and the movements are linked to phase transitions, rotations, and oscillations of atoms and atom groups. A partial dynamic disorder of Li^+ ions has also been reported in the "onion"-type spherical cluster $[Li_{24}OI_2(AsR)_{10}]$ ($R = Me_2(i\text{Pr}Me_2C)Si$).[2] To date, ion fluctuations in crystallized "molecular boxes" have only been observed for Li^+ ions.

We report herein on two compounds that are composed of a small central PH_2^- anion surrounded by a spherical outer shell consisting of twelve *tert*-butoxy anions. In this confined polyanionic space, that is, between the PH_2^- anion and the outer shell, 12 or 13 highly mobile sodium cations are embedded. One sodium ion can be reversibly added or removed to interconvert these aggregates.

Brandsma et al. reported the synthesis of sodium dihydrogenphosphide, $NaPH_2$, which uses the reduction of elemental phosphorus with sodium metal and subsequent addition of *tert*-butyl alcohol. This form of $NaPH_2$ is a versatile reagent for the preparation of organophosphorus compounds;[3] however, the nature of this "Brandsma reagent" was not known.

We treated a solution of sodium in a 1:1 (by volume) mixture of ammonia and dimethoxyethane (dme) with red or white phosphorus. A yellow-brown suspension is obtained after approximately 1.5 h. After evaporation of the ammonia, the crude mixture, containing $[NaPH_2(\text{solv})_x]$ and $[NaNH_2(\text{solv})_x]$ ($\text{solv} = NH_3$ or dme) suspended in dme, was treated with *tert*-butyl alcohol at −78 °C (Scheme 1 a). A clear solution is obtained at room temperature, which shows one triplet in the proton-coupled ^{31}P NMR spectrum at $\delta = -307.7$ ppm ($J = 145.0$ Hz) and a doublet at $\delta = -2.24$ ppm in the ^1H NMR spectrum ($J = 145.0$ Hz) for the PH_2^- ion. From this solution, colorless crystals of the composition $Na_{13}(dme)_3(PH_2)(OtBu)_{12}$ (**1**) were obtained.



Scheme 1. Syntheses of **1** and **2**.

When the crude $NaPH_2/NaNH_2$ mixture is evaporated to dryness and toluene is used as solvent for the reaction with *t*BuOH, a new species **2** is detected by ^{31}P and ^1H NMR spectroscopy in the clear solution. The PH_2^- ion is identified through a triplet at $\delta = -292.3$ ppm ($J = 142$ Hz) in the proton-coupled ^{31}P NMR spectrum and a doublet at $\delta =$

---

[*] Dr. M. Wörle, Dr. T. Ott, Dr. D. Stein, Dr. H. Rüegger,
Prof. Dr. H. Grützmacher
Laboratory of Inorganic Chemistry, ETH Zurich
8093 Zurich (Switzerland)
E-mail: hgruetzmacher@ethz.ch
M. Podewitz, Dr. J. D. van Beek, Prof. Dr. B. H. Meier,
Prof. Dr. M. Reiher
Laboratory of Physical Chemistry, ETH Zurich
8093 Zurich (Switzerland)
E-mail: beme@ethz.ch
markus.reiher@phys.chem.ethz.ch

[†] deceased 06-07-2009

[**] This work was supported by the Swiss National Science Foundation (SNF) and the ETH Zurich.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201003441.

−2.20 ppm ($J = 142$ Hz) in the ^{1}H NMR spectrum. Crystals from these solutions are free of dme and have the formula $Na_{13}(PH_2)(OtBu)_{12}$. The ^{31}P resonances of **1** and **2** are observed side by side in toluene solutions or toluene/dme mixtures containing up to 10% dme, thus indicating no or very slow exchange between the two aggregates on the time scale of NMR spectroscopy. When $Na_{13}(PH_2)(OtBu)_{12}$ (**2**) is dissolved in pure dme, the aggregate $Na_{13}(dme)_3(PH_2)(OtBu)_{12}$ (**1**) is quantitatively obtained after two days at room temperature. This route (Scheme 1c) yields pure **1** on a preparative scale. Similarly, when **1** is dissolved in toluene, the formation of **2** is detected. When [D$_9$]*t*BuOH was used in the synthesis of **1** and **2**, the partially deuterated species [D$_{108}$]**1** and [D$_{108}$]**2** were prepared.

Moisture- and air-sensitive single crystals of **1** and **2** were subjected to an X-ray diffraction study at 30 K.[4] The structure of **1** consists of a monoanionic cluster $[Na_{12}(PH_2)(OtBu)_{12}]^-$ and a $[Na(dme)_3]^+$ cation. Both are strongly disordered. The *tert*-butoxy residues are best described by a superposition of three independent groups with occupancies of 44, 37, and 19%. Figure 1a shows only one these possible orientations (44% occupancy factor); the disordered $[Na(dme)_3]^+$ counterion is not shown.

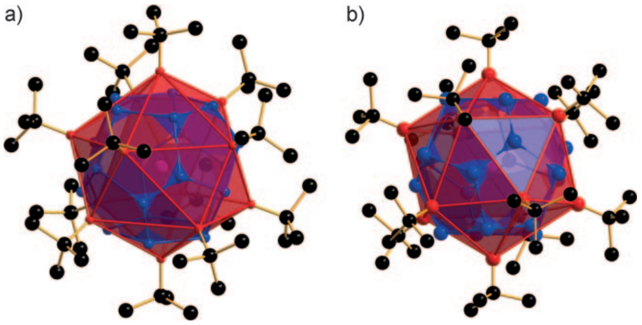


Figure 1. a) A representation of the anion $[Na_{12}(PH_2)(OtBu)_{12}]^-$ in **1**. Only one of the three possible orientations of the *tert*-butoxy groups (44% occupancy factor) is shown (hydrogen atoms are omitted for clarity). Interatomic distances at 30 K [Å]: P-Na 3.121(9)–3.214(6). b) A view of the cluster $Na_{13}(PH_2)(OtBu)_{12}$ (**2**) as determined in the space group *Pa*$\bar{3}$. Only one out of three possible orientations of the disordered *tert*-butoxy group is shown. Per molecule only 13 sodium atoms are located close to corners of a regular dodecahedron. Interatomic distances at 30 K [Å]: P-Na 3.127(6)–3.384(3), Na-O 2.150(8)–2.417(6). Na blue, O red, C black, P purple.

Despite cooling a crystal of **2** to 30 K, significant diffraction intensities could only be obtained to a resolution of 1 Å. This is consistent with the observation that even at this temperature, the molecules are highly disordered. A plot of **2** is depicted in Figure 1b showing only one of the three possible positions of the butoxy groups in $Na_{13}(PH_2)(OtBu)_{12}$. The packing of the individual molecules corresponds to an idealized CsCl type structure for **1** and an idealized face-centered cubic packing for **2**.

A free refinement of the occupancy factors of the Na$^+$ ions in **1** and **2** converged at a total number of 12.5(5) and 12.5(3) ions, respectively, which is in good agreement with the expected values of 12 and 13. The disorder observed even at low temperatures is consistent with temperature-dependent specific heat measurements, which gave no indications of phase transitions between 250 and 3 K. The X-ray studies indicate structures in which twelve *tert*-butoxy groups form an icosahedron that fully encapsulates the central PH_2^- anion. The twelve Na$^+$ ions in **1** or thirteen Na$^+$ ions in **2** can be modeled as statistically distributed on the twenty corners of a regular dodecahedron (shown in blue in the Figure 1). Both clusters can be viewed as "onionlike" aggregates showing subshells of ions of alternating charge within the cluster. The outermost shell is represented by the lipophilic *t*Bu groups, which completely cover the clusters and explain their relatively high solubility (about 20% by weight) in hydrocarbon solvents.[5]

Solid-state NMR spectroscopy at variable temperatures was subsequently used to study the structure and dynamics of the [Na$_{12}$] and [Na$_{13}$] clusters in the solid state, using deuterated *tert*-butoxy groups ([D$_{108}$]**1** and [D$_{108}$]**2**, dme protonated). The temperature dependence of the static ^{23}Na spectra of **1** and **2** (Figure 2) reveals a complex behavior for all sodium sites, except for the $[Na(dme)_3]^+$ counterion, which was found to be narrow, in accordance with its octahedral symmetry. It was possible to investigate **2** from room temperature down to 7 K, while the relaxation behavior of **1** limited

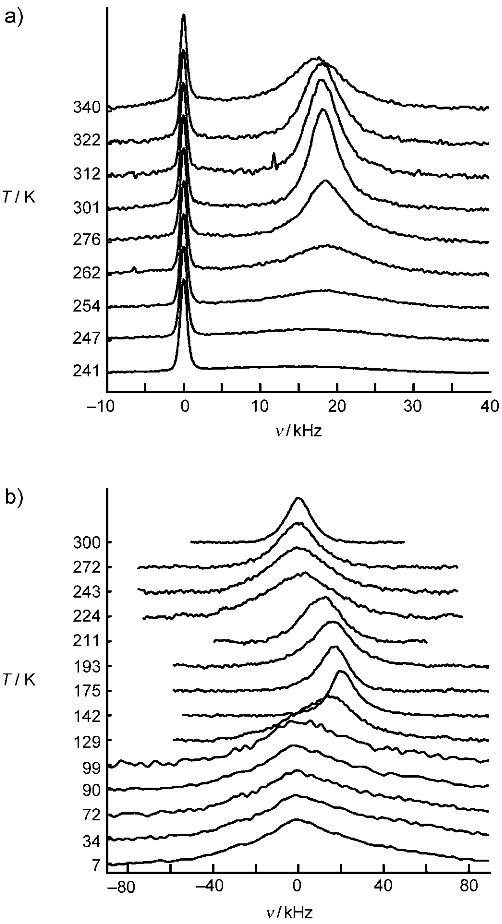


Figure 2. Temperature dependence of the ^{23}Na static NMR spectra for a) **1** and b) **2**. The narrow line obtained for the $[Na(dme)_3]^+$ cation was found at $\delta = -4$ ppm relative to a NaCl solution at room temperature.

the temperature range that could be studied to 240–340 K. From 300 down to 10 K the lineshape for **2** first displays broadening, then narrowing and shifting, and finally broadening again into a form that resembles a disordered quadrupolar tensor lineshape with a quadrupolar coupling constant C_{qcc} of approximately 6 MHz.

The observed behavior for **2** was successfully modeled by dynamics of sodium ions on an icosahedron, that is, an exchange of the 12 sites of an icosahedron, the rate constant of which is strongly dependent on the temperature. Crucially, the extreme narrowing of a large quadrupolar tensor displayed in Figure 2 can only be achieved by dynamical averaging at icosahedral or higher symmetry.[6] In this case, significant dynamics of the PH_2^- molecule is also required, the assumption of which we justify from temperature-dependent 1D ^{31}P NMR spectra. For **1**, slower sodium dynamics and a slightly higher degree of averaging of the quadrupolar interaction were detected. While the basic dynamical model still applies, the structure of **1** is expected to be closer to icosahedral symmetry and less frustrated than that of **2**.

This model is corroborated, for example, by ^{23}Na T_1 relaxation measurements (Figure 3) that support the conclusion of fast dynamics of the sodium nuclei. For **2**, a T_1 minimum of 7 μs was found at 230 K, whilst for **1**, an apparent minimum below 1 ms was outside the experimentally accessible conditions. The activation energies for sodium exchange were estimated to be roughly 30 and 10 kJ mol^{-1} for [Na$_{12}$] and [Na$_{13}$], respectively. For the minimum value of T_1 for [Na$_{13}$] a correlation time of 7.5×10^{-10} s was estimated for the sodium dynamics, which assumes the rapid correlation regime.[8]

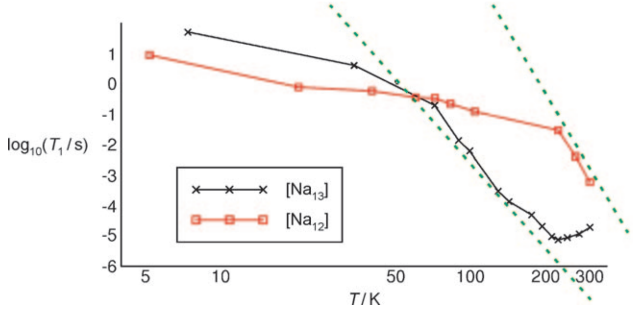


Figure 3. Temperature dependence of the ^{23}Na T_1 relaxation times in clusters **1** and **2**. The dashed lines indicate the slope from which the activation energies were estimated.[7]

The stability of various model structures for the anion of **1** and **2** was studied by BP86/TZVP[9] DFT structure optimizations.[9,10] A large number of distorted icosahedral cage structures of similar energy were found in these calculations. The clusters did not decompose upon structure optimization, and their cagelike structures were preserved even when the PH_2^- moiety was removed from the model or when the clusters were manually distorted.

The most stable [Na$_{12}$] cluster **1** and the most stable [Na$_{13}$] cluster **2** are shown in Figure 4. Focusing solely on the positions of the sodium atoms in **1**, it can be seen that they form a distorted icosahedron with Na–Na bond lengths between 2.982 and 3.834 Å. Removing the PH_2^- moiety changed the molecular structure only slightly, and the icosahedral arrangement of the sodium atoms was preserved, which can be seen on the right side of the upper panel of Figure 4. In the most stable [Na$_{13}$] cluster **2**, the 13 Na$^+$ ions form a monocapped and thereby distorted icosahedron.

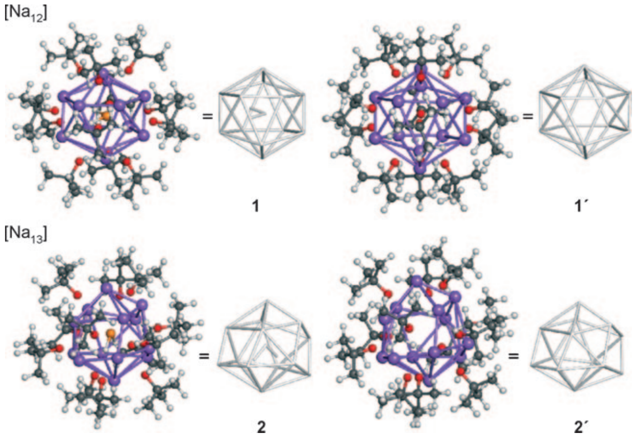


Figure 4. The optimized most stable [Na$_{12}$] and [Na$_{13}$] structures **1** and **2** (left) as well as the corresponding structures **1′** and **2′** optimized after the PH_2^- moiety was removed (right). For clarity, the Na polyhedra are also shown. It can be seen that the removal of the PH_2^- moiety does not affect the arrangement of the Na atoms in the polyhedra. The 12 oxygen atoms (red) also form an icosahedron, thus producing nested Na and O polyhedra.

To evaluate whether the stability of the [Na$_{12}$] and [Na$_{13}$] clusters is governed by steric hindrance, the bulky *tert*-butoxide anions of the most stable structures of **1** and **2** were substituted by a number of various smaller anions, such as methylate, hydroxide, and fluoride. All of these [Na$_{12}$] and [Na$_{13}$] model clusters were found to be stable during the optimization procedure, and their shell structure was preserved. Hence, the high stability of these cagelike structures is not solely due to steric hindrance by the bulky anions.

Based on the previous results the question arises whether the onionlike shell structure can be described by classical electrostatic interactions alone or whether covalent contributions must be considered. Therefore, we investigated the stability of NaX model clusters with small anions like fluoride on the basis of a simple electrostatic model. In the ionic model by Scheller and Cederbaum, the electronic energy of a LiF_3^{2-} molecule, assumed to be dominated by electronic interactions, is approximated by the Coulombic interactions between positive and negative point charges.[11] Additionally, a repulsive potential accounts for the repulsion of two oppositely charged ions at short distances. We have extended this model for the sodium clusters investigated herein, leading to the potential in Equation (1).

$$V = \sum_{i>j}^{N} \frac{q_i q_j}{R_{ij}} + \sum_{i>j}^{N} \frac{B}{R_{ij}^{n}} \tag{1}$$

The first term describes the classical Coulomb attraction and repulsion energies (q_i and q_j are the charges of the two particles, and R_{ij} is the distance between them),[12] while the second term accounts for repulsion energies between the oppositely charged ions at very short distances, in order to keep them at a distance. B and the Born exponent n are parameters that can be derived from crystal lattice theory.[13] These two constants were taken from the literature to be $B = 38.38$ a.u. and $n = 7$, although they had been determined for LiF.[13] By means of the potential energy function in Equation (1) a structure optimization was set up, and indeed, the icosahedral structures were preserved in the force-field structure optimization. The bond lengths of these optimized clusters are, however, shorter than in the case of the DFT structures because the electrostatic model overestimates the attraction between the oppositely charged ions. The DFT results were best reproduced for cluster **1** with a Born exponent $n = 5.5$ resulting in an increase of the repulsive forces between the oppositely charged ions. It is, however, noteworthy that the choice of the Born exponent n did not affect the shape of the optimized structures but only the bond lengths.

To summarize, using X-ray diffraction, solid-state NMR spectroscopy, and DFT calculations, we demonstrate that the crystalline forms of $Na_{13}(PH_2)(OtBu)_{12}$ and $[Na(dme)_3]^+$-$[Na_{12}(PH_2)(OtBu)_{12}]^-$ contain interlocked ionic cages of near-icosahedral symmetry with PH_2^- in the center of an inner sodium cage. At room temperature the sodium ions show fast dynamics with a correlation time of up to 7.5×10^{-10} s for $Na_{13}(PH_2)(OtBu)_{12}$ within the alkoxide cage. One sodium cation may be reversibly removed or added from the aggregates. Quantum-chemical calculations highlight that such onionlike arrangements of ions of opposite charge are energetically stable regardless of whether or not the PH_2^- ion is present inside the cage. A purely electrostatic model is able to account for all structural features of the complexes. Possibly, such systems may be of help in the development of nanoscaled Na^+ ion conductors.

Experimental Section

All syntheses were performed in dried glassware under an atmosphere of argon using standard Schlenk techniques and freshly distilled, oxygen- and water-free solvents. For further data see the Supporting Information.

1: In a thick-walled 100 mL Schlenk flask equipped with a Teflon valve, sodium (1.73 g, 75 mmol) and red phosphorus (0.78 g, 25 mmol) were suspended in DME (20 mL). Under agitation using a glass-mantled magnetic stirring bar, liquid ammonia (20 mL) was condensed at −78 °C, and the mixture warmed to 15 °C and stirred for 90 min behind an explosive-proof shield. The blue solution became yellow and the pressure in the flask rose to 7–8 bar. The ammonia was slowly evaporated and the DME removed in vacuum. The crude product is a mixture of $[Na(PH_2)(solv)]$ and $[NaNH_2(solv)]$ suspended in DME. After addition of *t*BuOH (3.71 g, 50 mmol, 2 equiv) over 5 min at −78 °C the flask was slowly warmed up to 20 °C to give a pale yellow suspension. After filtration, colorless crystals of **1** formed after two days at −30 °C (30–40 %). An almost quantitative yield (greater than 90 %)of **1** is obtained when **2** is recrystallized from dme. M.p.: 62 °C. ^1H NMR (250.1 MHz, $[D_8]$THF): $\delta = 1.37$ ppm (d, 2H, $J = 147.1$ Hz, PH_2). ^{31}P NMR (101.2 MHz, $[D_8]$THF): $\delta = -301.8$ ppm (t, $J = 147.1$ Hz, PH_2).

2: The crude mixture of $Na(PH_2)(solv)$ and $NaNH_2(solv)$ was suspended in toluene and *t*BuOH (3.71 g, 50 mmol) was added at −78 °C. The mixture was warmed to room temperature, and subsequently Na*Ot*Bu (22 g, 230 mmol) was added and the mixture stirred for 1 h at 80 °C in 100 mL toluene. In the ^{31}P NMR spectrum the reaction proceeds with quantitative yield. After filtration over Celite the solution was cooled to −30 °C, whereby large colorless crystals formed. 21 g (71 % yield). M.p.: 112 °C. ^{31}P NMR (121.49 MHz, $[D_8]$toluene): $\delta = -292.3$ (t, $^1J_{P,H} = 142.3$ Hz, PH_2). ^1H NMR (300.13 MHz, $[D_8]$toluene): $\delta = 1.48$ (s(br), 108 H, $OC(CH_3)_3$), −2.20 (d, 2 H, $^1J_{P,H} = 142.3$ Hz, PH_2^-).

Received: June 6, 2010
Published online: September 1, 2010

Keywords: cluster compounds · ionic aggregates · NMR spectroscopy · phosphorus · sodium

---

[1] a) M. Veith, *Eur. J. Inorg. Chem.* **2000**, 1883; b) M. Veith, M. Zimmer, K. Fries, J. Böhnlein-Maus, V. Huch, *Angew. Chem.* **1996**, *108*, 1647; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1529; c) M. Veith, M. Zimmer, V. Huch, *Z. Anorg. Allg. Chem.* **2009**, *635*, 674.

[2] a) M. Driess, R. Mulvey, M. Westerhausen in *Molecular Clusters of the Main Group Elements* (Eds.: M. Driess, H. Nöth), Wiley-VCH, Weinheim, **2004**, p. 391; b) M. Driess, *Acc. Chem. Res.* **1999**, *32*, 1017; c) M. Driess in *Advances in Inorganic Chemistry, Vol. 50*, Academic Press Inc, San Diego, **2000**, p. 235.

[3] Primary and secondary phosphanes, see: a) L. Brandsma, N. Gusarova, S. Arbuzova, B. Trofimov, *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *111*, 807; b) L. Brandsma, N. K. Gusarova, A. V. Gusarov, H. D. Verkruijsse, B. A. Trofimov, *Synth. Commun.* **1994**, *24*, 3219; c) L. Brandsma, J. A. Vandoorn, R. J. Delang, N. K. Gusarova, B. A. Trofimov, *Mendeleev Commun.* **1995**, *5*, 14; d) M. C. J. M. van Hooijdonk, University of Utrecht **1999**. Heterocycles, see: e) D. Stein, T. Ott, H. Grützmacher, *Z. Anorg. Allg. Chem.* **2009**, *635*, 682.

[4] Data sets were collected on an Xcalibur diffractometer (Oxford Diffraction) equipped with a CCD detector (Sapphire) and a Helijet cooling device. $[Na(dme)_3]^+[Na_{12}(PH_2)(OtBu)_{12}]^-$ **1**: $C_{60}H_{140}Na_{13}O_{18}P$ $0.3 \times 0.3 \times 0.3$ mm, cubic, space group $F\bar{4}3c$ (No. 219), $a = 26.083(3)$ Å, $V = 17746(4)$ Å^3, $Z = 8$, $\mu = 0.148$ mm^{-1}, $T = 30$ K, collected (independent) reflections = 19929 (786), $R_{int} = 0.0556$, 103 refined parameters and 31 restraints, $R1 = 0.0834$ with $I > 2\sigma$, $wR2 = 0.2566$ for all data, GooF on $F^2 = 1.025$, max./min. residual electron density = 0.201/−0.195 e Å^3. $Na_{13}(PH_2)(OtBu)_{12}$ **2**: $C_{48}H_{110}Na_{13}O_{12}P$ $0.52 \times 0.49 \times 0.48$ mm, cubic, space group $Pa\bar{3}$, $a = 19.3622(3)$ Å, $V = 7258.79(19)$ Å^3, $Z = 4$, $\mu = 0.161$ mm^{-1}; $T = 30$ K, collected (independent) reflections = 42818 (1549), $R_{int} = 0.0655$, 254 refined parameters and 573 restraints, $R1 = 0.0877$ with $I > 2\sigma$, $wR2 = 0.2510$ for all data, GooF on $F^2 = 1.091$, max./min. residual electron density = 0.454/−0.273 e Å^3. The refinement of the data sets is discussed in the Supporting Information. CCDC 773200 and CCDC 773201 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[5] In the solid state, Na*Ot*Bu shows a mixture of nonamers and hexamers, $Na(OtBu)_9$ and $Na(OtBu)_6$: a) T. Greiser, E. Weiss, *Chem. Ber.* **1977**, *110*, 3388; b) J. E. Davies, J. Kopf, E. Weiss, *Acta Crystallogr. Sect. B* **1982**, *38*, 2251. In solution, Na*Ot*Bu seems to form larger aggregates, but the presence of primarily cubic tetramers in THF was deduced from an analysis of the

vibrational spectra: c) P. Schmidt, L. Lochmann, B. Schneider, *J. Mol. Struct.* **1971**, *9*, 403 and mass spectroscopic investigations: d) E. Weiss, K. Hoffmann, H.-F. Grützmacher, *Chem. Ber.* **1970**, *103*, 1190, and references therein. For a mixed NaOH/NaO*t*Bu cluster, see: e) J. Geier, H. Grützmacher, *Chem. Commun.* **2003**, 2942.

[6] a) A. Samoson, B. Q. Sun, A. Pines in *Pulsed Magnetic Resonance: NMR, ESR and Optics*, Oxford Scientific Publications, Oxford, **1992**, p. 80; b) B. Q. Sun, J. H. Baltisberger, Y. Wu, A. Samoson, A. Pines, *Solid State Nucl. Magn. Reson.* **1992**, *1*, 267.

[7] N. Bloembergen, E. M. Purcell, R. V. Pound, *Phys. Rev.* **1948**, *73*, 679.

[8] a) A. Abragam, *Principles of Nuclear Magnetism*, Clarendon, Oxford, **1961**; b) K. Kanehashi, J. F. Stebbins, *J. Non-Cryst. Solids* **2007**, *353*, 4001.

[9] a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822; A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829; c) ftp://ftp.chemie.uni-karlsruhe.de/pub/basen; d) ftp://ftp.chemie.uni-karlsruhe.de/pub/jbasen; this is the def-TZVP basis set by Ahlrichs et al.

[10] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165.

[11] M. K. Scheller, L. S. Cederbaum, *J. Phys. B* **1992**, *25*, 2257.

[12] For the charges q_i and q_j integer unit charges, Mulliken partial charges or, in principle, any other kind of partial charges considered appropriate may be chosen.

[13] J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, Walter de Gruyter, New York, **1988**.