AmB/**2**: MCl buffer), and 0.5 M NaOH (20 µL) were subsequently added. Usually 400 sec after the base pulse, 10% triton X-100 (50 µL) was added to determine complete collapse of the pH gradient (final pH 7.4). Relative transport efficiencies were calculated from the initial rate constants in comparison to that with external $K^+$ ($k = 1.6 \times 10^{-2}\,s^{-1}$), and are given in Figure 4. The CD, UV/Vis, and fluorescence quenching experiments were performed as reported before.[11]

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# Easy Access to Soluble Polyanions—Stabilization of the One-Dimensional Chain $^1_\infty[K_4Sn_9]$ by [18]Crown-6 in $[K_4Sn_9([18]crown\text{-}6)_3]\cdot$ethylenediamine**

Thomas F. Fässler* and Rudolf Hoffmann

*Dedicated to Professor Ernst Otto Fischer*
*on the occasion of his 80th birthday*

The reduction of metal salts provides an important way for the synthesis of element nanoparticles. Though routes for the generation of large transition metal clusters are well elaborated,[1] comparably little is known about analogous accesses to main group element clusters.[2] A general problem of the synthesis of nanoparticles is the broad distribution of particle size.[3] In contrast, a directed synthesis of small, charged main group element clusters of uniform size exists, and recently the chemistry of homoatomic clusters of Group 14 elements received new impulses through the synthesis and structure determination of the phases $Rb_{12}Si_{17}$,[4] $A_4Ge_9$ (A = K, Cs),[5, 6] $K_{12}Ge_{17}$,[5] and $K_4Pb_9$.[7] The crystalline compounds, which are synthesized from the elements at several hundred degrees, are Zintl phases with discrete nine-atom $E_9^{4-}$ clusters. In the case of the 12:17 phases additional tetrahedral $E_4^{4-}$ units are present. The crystal structure of the corresponding phase $A_4Sn_9$ or $A_{12}Sn_{17}$ (A = alkali metal) could not be elucidated due to poor crystal quality.[6] Though nine-atom clusters were observed in solution over 100 years ago[8] and the first structural characterization was carried out already in 1976,[9] only small amounts of well-defined products could be isolated from solution. In the course of our studies of soluble, homoatomic Zintl ions,[10] we report here a novel, very simple and efficient access to homoatomic polyanions from the elements at low temperatures.

We found that the alkali metals K, Rb, and Cs are soluble in the crown ether [18]crown-6, which is liquid at 40 °C.[11] The deep blue color of the melt indicates the formation of an alkalide or electride. The blue color vanishes after addition of an element of Group 14 to 16, indicating a reaction. To obtain crystalline products small amounts of solvent are added to the mixture. So far we were able to apply this procedure to the elements C (as $C_{60}$), Sn, Pb, As, Sb, Bi, and Te. Single-crystal structure analyses reveal the presence of the anions $C_{60}^{3-}$,[12a] $Sn_9^{4-}$, $Pb_9^{4-}$, $As_7^{3-}$, $Sb_7^{3-}$, and $Te_4^{2-}$.[12b] For As, Sb,[13] and Te,[14] the formation of larger homoatomic polyanions in solution from the elements and their isolation in crystalline form was already known. However, in the case of Sn and Pb crystalline products were only obtained by extraction of binary or ternary phases.[15] With the exception of $[Na_4(en)_7]Sn_9$, which was characterized by Kummer and Strähle and which contains disordered en molecules (en = ethylenediamine),[16] the struc-

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[*] Priv.-Doz. Dr. T. F. Fässler, R. Hoffmann
Laboratorium für Anorganische Chemie
der Eidgenössischen Technischen Hochschule
Universitätstrasse 6, CH-8092 Zürich (Switzerland)
Fax: (+41) 1-632-1149
E-mail: faessler@inorg.chem.ethz.ch

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tural characterization of nine-atom clusters was only accomplished on single crystals containing [A([2.2.2]crypt)]$^+$ (A = Na, K) as counter ions.[17, 18] Attempts to use other cations did not result in crystalline products.[19]

Following the experimental procedure introduced here, we obtained from the reaction of K and Sn in liquid [18]crown-6 different crystal types dependending on the workup process. X-ray single-crystal structure determinations[20] confirm that both crystal types contain four potassium ions for each Sn$_9$ polyhedron and that they differ in the ratio of K to [18]crown-6. The composition of four K atoms per cluster is in agreement with a fourfold negative charge for each polyanion. Whereas in [K([18]crown-6)]$_4$Sn$_9$ (**2**) only two of the four K atoms are in contact with the cluster (Figure 1), [K([18]crown-6)]$_3$KSn$_9\cdot$en (**1**) has a remarkable one-dimensional substructure of the composition K$_4$Sn$_9$ (Figure 2). A Zintl phase of such a composition has not yet been structurally described. In the title compound **1** the nine-atom tin clusters have contacts to all K atoms (Figure 1). Three K atoms are additionally coordinated to crown ether units in such way that in **1** the "saltlike intermetallic"[8b] chains $^1_\infty$[K$_4$Sn$_9$] are separated by organic molecules. Linear chains which exhibit alternating nine-atom clusters and noncomplexed K atoms are already known. However, in [K([2.2.2]crypt)]$_3$KSn$_9$ three K atoms have no contact with the anions due to full inclusion in the cryptand molecules.[21] In the present structure an uncharged unit K$_4$Sn$_9$ is formed. The compound is an intermediate between typical molecular (ionic) representatives and binary intermetallic phases (Zintl phases). The pronounced anisotropy of this structure should be reflected in the properties—semiconducting along the *a* axis and isolating in the perpendicular directions.

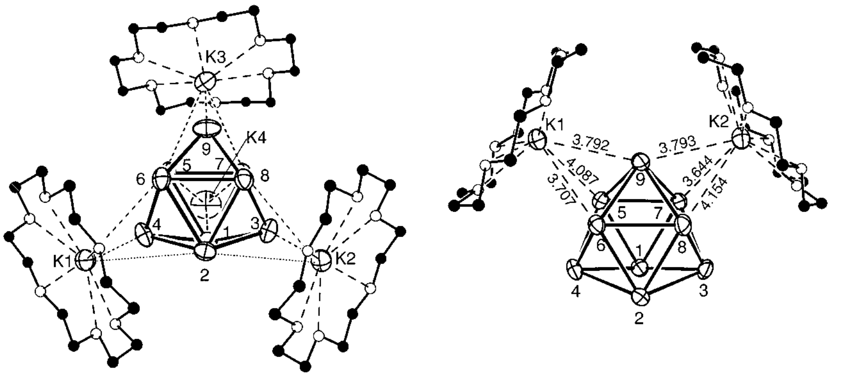


Figure 1. Details of the crystal structures of **1** (left) and **2** (right). The displacement parameters of the Sn and K atoms are shown with 50% probability ellipsoids. For reasons of clarity crown ether molecules are shown as stick-and-ball models. Distances in Å (standard deviation 0.005 Å). For further distances, see text and reference [30].

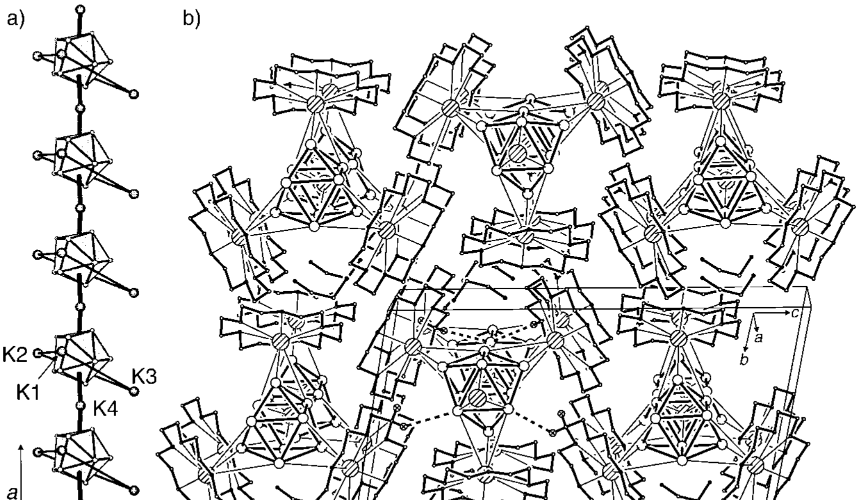


Figure 2. Larger sections of the structure of **1**. a) A one-dimensional moiety of the composition K$_4$Sn$_9$ aligns parallel to the *a* axis. b) Relative arrangement of ions and molecules as viewed down the *a* axis. Atom symbols: hatched circles: K, large and small open circles: Sn and C, respectively, filled circles: O and N. The shortest Sn$\cdots$H contacts of geometrically determined H positions (circles marked with crosses) are shown as dashed lines. The remaining H atoms are omitted.

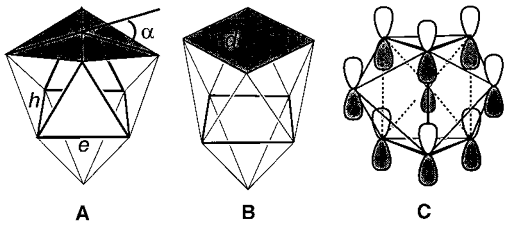
In **2** only two K atoms are directly bound to the polyanions (Figure 1). The K atoms of the two other [K([18]crown-6)] units possess significantly larger distances to nearest atoms of the polyanions (> 6.98 Å). The K–Sn distances of the [K([18]crown-6)] units in **1** and **2** are in the range of 3.535 to 4.154 Å (Figure 1) and vary around the values observed in the Zintl phase KSn.[22] Taking into account two slightly longer contacts in **1** (K1–Sn2 4.438(2) and K2–Sn2 4.353(2) Å) the polyanions set up $\eta^3$ coordination to the K atoms. The K4 atom, which is not coordinated to [18]crown-6, possesses a slightly distorted and elongated trigonal-prismatic coordination polyhedron of six Sn atoms with K–Sn distances of 3.603(3)–4.048(4) Å. The [K([18]crown-6)] entity proves to be an advantageous connecting device between intermetallic and organic networks. In addition to contacts of the K atoms, weak intermolecular interactions between the H atoms of the crown ethers and the atoms Sn1, Sn5, and Sn7 ($d$(Sn–H) = 3.13–3.17 Å)[23] enable the construction of the aggregate in **1** (Figure 2). The structure of **1** can therefore be regarded as a supramolecular arrangement of a "saltlike intermetallic" part of the composition K$_4$Sn$_9$ and an organic component.

The structures of the anions in **1** and **2** differ significantly from those of known Sn$_9^{4-}$ anions (Table 1). The classification of their structures to the polyhedra **A** and **B** can be accomplished according to the criteria in Scheme 1 and Table 1: An ideal threefold capped trigonal prism **A** with equal prism heights *h* and edge lengths *e* has an *h*/*e* ratio of 1.0 as well as three equal dihedral angles $\alpha$, whereas in an ideal monocapped square antiprism one angle $\alpha$ equals zero. The noncapped face in **B** possesses two diagonals of same length *d*. As predicted from Wade's rules[24] all previously structurally well characterized Sn$_9^{4-}$ anions exhibit nearly undistorted clusters of type **B**.[21, 25] More electron

Table 1. Structural parameters of nine-atom tin clusters (see Scheme 1).

| Compound[a] | $h_1, h_2, h_3$[b] | $h/e$[c] | $\alpha$ [°][d] | $d$ [Å][e] |
|---|---|---|---|---|
| $[K([2.2.2]crypt)]_6Sn_9Sn_9$[10a] | 1.10, 1.02, 1 | 1.08 | 13, 19, 23 | 3.315, 4.813 |
| $[K([2.2.2]crypt)]_3Sn_9$[25] | 1.04, 1.04, 1.02 | 1.08 | 17, 18, 18 | 3.501, 4.680 |
| $[K([2.2.2]crypt)]_3KSn_9$[21] | 1.29, 1.03, 1.00 | 1.19[f] | 2, 28, 29 | 4.129, 4.229 |
| $[Na([2.2.2]crypt)]_4Sn_9$[24] | 1.32, 1.04, 1.01 | 1.19[f] | 3, 29, 30 | 4.163, 4.205 |
| $[K([18]krone-6)]_3KSn_9$ **1** | 1.17, 1.06, 1.05 | 1.15 | 13, 22, 24 | 3.722, 4.506 |
| $[K([18]krone-6)]_4Sn_9$ **2** | 1.11, 1.08, 1.04 | 1.14 | 15, 17, 22 | 3.531, 4.673 |

[a] Formulae without solvent molecules. [b] Normalized heights of the trigonal prism **A** (reference value is the shortest height (3.194 Å) of the nondisordered anion in $[K\text{-}([2.2.2]crypt)]_6Sn_9Sn_9$). Heights $h_1-h_3$ correspond to the distances Sn7–Sn8, Sn5–Sn6, and Sn1–Sn2, respectively. [c] $h$ and $e$ are the mean values of the prism heights and the triangular edges, respectively. [d] Dihedral angles Sn3-Sn7-Sn8-Sn9, Sn4-Sn5-Sn6-Sn9, Sn3-Sn1-Sn2-Sn4. [e] Distances Sn7–Sn8 and Sn4–Sn9. [f] For the calculation, the shorter diagonal of the open square face in **B** is regarded as third prism height in **A**.



Scheme 1. Structures of nine-atom clusters as expected from Wade's rules: *closo*-type **A**, threefold capped trigonal prism ($D_{3h}$); *nido*-type **B**, singly capped square antiprism ($C_{4v}$). The parameters prism height $h$, dihedral angle $\alpha$ (angle which is defined by one prism height $h$ and the corresponding capping atoms), edge length $e$ of the triangles of the prism in **A** as well as the diagonal lengths $d$ in **B** characterize the two boundary structures. The energetically lowest unoccupied orbital (LUMO) **C** of a cluster with structure **A** and 20 skeletal electrons is antibonding along the prism heights.

deficient, paramagnetic $Sn_9^{3-}$ ions have structures which lie between the two boundary structures **A** and **B**. [10a, 26] The structure of these polyhedra are described as distorted variants derived from type **A**, that is, elongated prism with larger $h/e$ ratios than the ideal polyhedron **A** (Table 1). The origin of this distortion is the occupation of the LUMO **C** of a hypothetical *closo* cluster $Sn_9^{2-}$ with one electron (Scheme 1). The orbital interaction in **C** is antibonding along the prism heights. The $Sn_9^{4-}$ ions described here do not possess $C_{4v}$ point group symmetry. The deviation from a $C_{4v}$-symmetrical **B** is significant, as the parameter $\alpha$ and the different diagonal lengths $d$ demonstrate. Deduced from type **A**, they have even larger $h/e$ ratios than $Sn_9^{3-}$ anions, a fact expected from the occupation of orbital **C** with *two* electrons.[27] The anions display approximately $C_{2v}$ point group symmetry and can be described as threefold capped trigonal prisms, with one prism height about 10% longer than the other two.[18, 28] In comparison to other known anion structures the findings here demonstrate that a correlation of electron number and structure with respect to Wade's rules does not hold for naked main group element clusters.[31]

The reaction procedure reported here using crown ether as reaction medium offers the advantage of a "one-pot synthesis" that starts from the elements and which can be carried out at 40 °C in Schlenk tubes. The resulting reaction products are crystalline and soluble not only in amines but also in DMF and acetonitrile. This method should also be applicable using main group element and transition metal halides as reactants. The possible usage of polyethyleneoxides instead of cyclic crown ethers is currently under investigation.

## *Experimental Section*

**1**: [18]Crown-6 (800 mg, 3.0 mmol), K (98 mg, 2.5 mmol), and Sn (200 mg, 1.7 mmol) are mixed in a Schlenk tube (20 mL). The mixture is heated to 40–50 °C, just allowing the crown ether to melt, and stirred at this temperature for 1 h. Alternatively K and [18]crown-6 can be stirred at 40 °C, and Sn added in a second step to the deep blue melt. The color of the originally blue melt changes during the reaction from light gray to dark gray. Ethylenediamine (2 mL) is added to the cooled melt, and the mixture is sonicated for 15 min. Thereafter the solution is layered with toluene (4.5 mL). After one week **1** is obtained in the form of dark red, nearly black needles (yield: 120 mg, 31% based on employed Sn and 40% based on Sn undergoing reaction).

**2**: Analogously to the preparation of **1** [18]crown-6 (800 mg, 3.0 mmol), K (98 mg, 2.5 mmol), and Sn (475 mg, 4.75 mmol) are allowed to react. The dark red solution is filtered. After four weeks **2** is obtained in the form of brown plates (yield: 105 mg, 11% based on employed Sn).

Elemental analysis of the vacuum-dried products: **1** ($C_{36}H_{72}K_4O_{18}Sn_9$, 2017.56 g mol$^{-1}$): calcd (found) [%]: C 21.43 (20.58), H 3.60 (3.67), K, 7.75 (7.94), Sn 52.95 (51.05); **2** (($C_{48}H_{96}K_4O_{24}Sn_9$, 2282.06 g mol$^{-1}$): calcd (found) [%]: C 25.26 (25.00), H 4.24 (4.24), K 6.85 (7.20), Sn 46.82 (46.60).

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[20] Crystal structure determination: Crystals were mounted in glass capillaries. Structure solution (SHELXS-97) and refinement (SHELXL-97) was carried out with direct and full-matrix least-square methods based on $F^2$ for all atoms with anisotropic displacement parameters. **1**: crystal dimensions $0.12 \times 0.45 \times 0.50\ \mathrm{mm}^3$, lattice constants at 243 K: $a = 10.220(2)$, $b = 14.957(3)$, $c = 23.690(5)$ Å, $\alpha = 99.86(3)$, $\beta = 91.43(3)$, $\gamma = 103.79(3)^\circ$, $V = 3456(1)$ Å$^3$; space group $P\bar{1}$ (no 2), $Z = 2$, $\rho_{\mathrm{calcd}} = 1.996\ \mathrm{g\,cm^{-3}}$, $\mu = 3.489\ \mathrm{mm^{-1}}$; Data collection: STOE IPDS, $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation, $2\Theta_{\max} = 48.18^\circ$ (imaging plate distance 80 mm); of 20081 total reflections, 10171 were independent ($R_{\mathrm{int.}} = 0.052$); $R_1 = 0.046$ and $wR = 0.123$ for 620 parameters and 10168 reflections with $I > 2\sigma(I)$; max./min. residual electron density 1.57/ – 1.32 e Å$^{-3}$. **2**: crystal dimensions $0.24 \times 0.34 \times 0.46\ \mathrm{mm}^3$, lattice constants at 193 K: $a = 14.839(3)$, $b = 22.012(4)$, $c = 14.910(3)$ Å, $\beta = 108.97(3)^\circ$, $V = 4605(2)$ Å$^3$; space group $P2_1$ (no. 4), $Z = 2$, $\rho_{\mathrm{calcd}} = 1.645\ \mathrm{g\,cm^{-3}}$, $\mu = 2.631\ \mathrm{mm^{-1}}$; data collection: STOE IPDS, $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation, $2\Theta_{\max} = 48.18^\circ$ (imaging plate distance 80 mm); of 26456 total reflections, 13778 were independent ($R_{\mathrm{int.}} = 0.051$); $R_1 = 0.078$ and $wR = 0.209$ for 766 parameters and 13321 reflections with $I > 2\sigma(I)$; max./min. residual electron density 1.86/ – 1.05 e Å$^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102741 (**1**) and CCDC-102742 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[28] A cluster with a similar structure is also observed in $[\mathrm{Na_4(en)_7}]\mathrm{Sn_9}$[16] and for the isoelectronic cation $\mathrm{Bi_9^{5+}}$.[29]

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[30] Distances [Å] in **1**: Sn1–Sn2 3.355(2), Sn5–Sn6 3.412(2), Sn7–Sn8 3.722(2), Sn1–Sn5 3.116(1), Sn1–Sn7 3.014(1), Sn5–Sn7 2.951(1), Sn2–Sn6 3.081(1), Sn2–Sn8 2.993(1), Sn6–Sn8 3.019(1), Sn1–Sn3 2.915(1), Sn2–Sn3 2.985(1), Sn7–Sn3 2.939(1), Sn8–Sn3 2.944(1), Sn1–Sn4 2.925(1), Sn2–Sn4 2.975(1), Sn5–Sn4 2.932(2), Sn6–Sn4 2.940(1), Sn5–Sn9 2.952(1), Sn6–Sn9 2.938(2) Sn7–Sn9 2.942(1), Sn8–Sn9 2.906(1); K1–Sn2,Sn4,Sn6 4.438(2), 3.544(2), 4.074(3); K2–Sn2,Sn3,Sn8 4.353(2), 3.535(2), 4.072(2); K3–Sn5,Sn7,Sn9 4.039(3), 4.021(2), 3.542(3). Sn–Sn distances [Å] in **2** (same order as for **1**): 3.335(2), 3.450(2), 3.531(2), 3.045(2), 3.010(2), 2.990(2), 3.038(2), 3.030(2), 2.987(2), 2.974(2), 2.959(2), 2.930(2), 2.923(2), 2.958(2), 2.980(2), 2.930(2), 2.928(2), 2.942(2), 2.984(2), 2.982(2), 2.941(2).

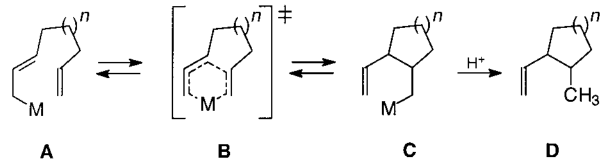
[31] For the controversial discussion on the charge allocation to the nonequivalent anions in $[\mathrm{K([2.2.2]crypt)}]_6\mathrm{Ge_9Ge_9}$, see C. H. E. Belin, J. D. Corbett, A. Cisar, *J. Am. Chem. Soc.* **1977**, *99*, 7163; T. F. Fässler, U. Schütz, *Inorg. Chem.*, in press; and references [10, 18].

# Chiral Induction by Elimination-Coupled Lithium–Ene Reaction: Synthesis of (+)-(3*R*,4*R*)-1,2-Dihydromultifidene**

Alexander Deiters and Dieter Hoppe*

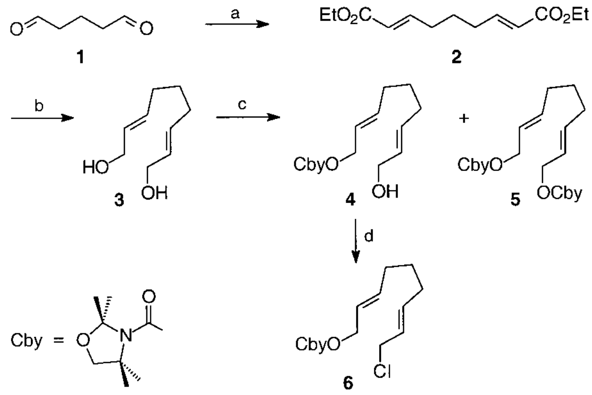
*Dedicated to Professor Bernt Krebs*
*on the occasion of his 60th birthday*

Intramolecular metallo–ene reactions are efficient methods for the construction of substituted ring systems.[1] As the Type 1 metallo–ene reaction illustrates, 2,($\omega$ – 1)-alkadienylmetal compounds **A** cyclize via the cyclic conjugated transition state **B** to form a (2-vinylcycloalkyl)methylmetal intermediate **C**, which is then protonated to give cycloalkanes **D** (Scheme 1). One problem is the poorly developed equilibrium state. Moreover, the previously described metallo–ene reaction where M = Li[2] and M = MgHal[3] give racemic products.[1, 4]



Scheme 1. Metallo–ene reaction of Type 1 ($n = 1, 2$; M = Li, MgHal).

We report here the first asymmetric lithium–ene reaction, the basis of which is the enantioselective (–)-sparteine-induced deprotonation of 2-alkenyl carbamates.[5, 6] We selected (2*E*,7*E*)-9-chloronona-2,7-dienyl carbamate (**6**)[7] as substrate in order to compensate for the unfavorable equilibrium state of the cyclization with an irreversible elimination step.[8] Compound **6** was obtained from pentanedial (**1**) by standard methods (Scheme 2). Treatment of **6** (*E*:*Z* = 98:2)



Scheme 2. Synthesis of **6**. a) $\mathrm{EtO_2CCH_2PO(OEt)_2}$ (2.2 equiv), $\mathrm{K_2CO_3}$ (5.0 equiv), $\mathrm{H_2O}$, 35 %;[9a] b) DIBAH (5.0 equiv), $\mathrm{PhCH_3}$, 92 %; c) NaH (1.1 equiv), CbyCl (1.0 equiv), THF, 19 % **3**, 39 % **4**, and 22 % **5**;[9b] d) LiCl (5.0 equiv), *n*BuLi (1.0 equiv), $\mathrm{CH_3SO_2Cl}$ (1.1 equiv), THF, 90 %.[26] DIBAH = diisobutylaluminum hydride.

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[*] Prof. Dr. D. Hoppe, Dipl.-Chem. A. Deiters
Organisch-chemisches Institut der Universität
Corrensstrasse 40, D-48149 Münster (Germany)
Fax: (+49) 251-8339772

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