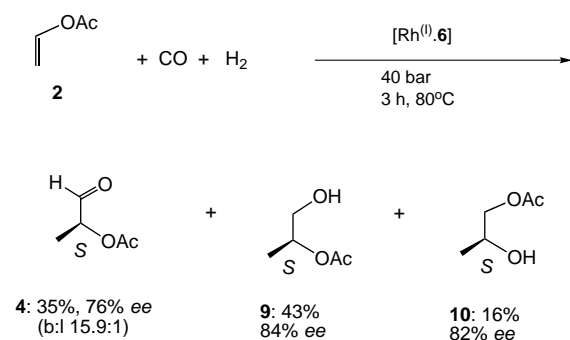


plexes of **6** and **7** are effective in styrene hydroformylation, the products in both cases were essentially racemic (Table 1, entries 13 and 14). This was unexpected, since most ligands are either good or bad for both substrates. It therefore appears that the presence of a coordinating group in the substrate is essential for high enantioselectivity when diazaphospholindines are used as ligands, somewhat analogous to asymmetric hydrogenation reactions with rhodium/diphosphane catalysts. However, it is possible that racemization may have followed an initially enantioselective reaction in the case of styrene, and we are currently investigating the causes of this unusual pattern of reactivity.

In some studies, we observed the formation of small quantities of alcohol products (from the reduction of the aldehyde **4**) when extended reaction times were employed in hydroformylation. Upon increasing the pressure and the temperature of the reaction, the alcohols **9** and **10** were formed in 43 and 16% yield, respectively, in both cases with 82–84% *ee* and identical configurations (Scheme 2; Table 1, entry 2). Clearly **9** is formed by the reduction of **4**, and **10** is a rearrangement product of **8**. This behavior contrasts with that



Scheme 2. Hydroformylation of vinyl acetate followed by reduction.

of other rhodium-based systems such as those containing **1** or BIPHEMPOS (**8**), which show no activity for aldehyde hydrogenation. Such hydrogenations must be carried out in a separate step. The quantity of **4** that remained unreduced (35%) had an *ee* of 76%, which is presumably the result of aldehyde racemization over the extended reaction times. Since both **9** and **10** can be hydrolyzed to the same product, this process provides a direct approach to the asymmetric synthesis of 1,2-diols, which are important reagents and intermediates for fine-chemicals manufacture. We are therefore currently examining the extension of our hydroformylation process to the synthesis of diols and low molecular weight epoxides.

In conclusion, we have described a novel class of chelating phosphorus-donor ligands for asymmetric hydroformylation reactions. Our results demonstrate the need for a bidentate rather than a monodentate structure and an unprecedented requirement for a coordinating group in the substrate to achieve high enantioselectivity. In addition, the same catalyst system can perform the hydrogenation of the aldehyde product and thus provides a route to chiral 1,2-propanediol precursors.

Experimental Section

The preparation of the ligands **6** and **7** has been described.^[3] The catalyst was prepared in situ from $[\text{Rh}(\text{acac})(\text{CO})_2]$ (5×10^{-5} mol) and the phosphane (1.5–4.0 equiv, see Table 1) in toluene (2 mL) in a miniautoclave fitted with a system for injection of substrate and for measuring kinetics at constant pressure. The autoclave was then flushed with CO/H_2 before pressurizing to several bar below the operating pressure. The temperature was raised with stirring to the desired operating temperature, styrene (1.0 g, 9.6×10^{-3} mmol) or vinyl acetate (1.0 g, 1.04×10^{-2} mmol) in toluene (2 mL) was injected, and the pressure was raised to the desired reaction pressure. The pressure was maintained with a mass flow controller. The autoclave stirring speed was 500 rpm. At the end of the reaction, the stirrer was stopped and the reactor cooled rapidly. The liquid products were analyzed by GC with a flame ionization detector (quantitative) and GC-MS (qualitative). The enantioselectivity of the reaction was determined by comparison with authentic product samples.

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arachno- $[\text{Sn}_8]^{6-}$ or closo- $[\text{Li}_2\text{Sn}_8]^{4-}$? Synthesis and Characterization of $\text{A}_4\text{Li}_2\text{Sn}_8$ (A = Rb, K)**

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Renewed interest in Zintl phases and Zintl ions in recent years has resulted in some major conceptual developments in these fields. Numerous isolated deltahedral clusters with unusual shapes, such as Tr_{11}^{7-} , Tr_4^{8-} , Tr_5^{7-} , Tr_6^{8-} , Tr_6^{6-} , and

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$\text{Tr}_{12}(\text{Tr})^{11-}$, where Tr (Triel = Group 13) is indium or thallium, were discovered.^[1] Furthermore, it was found that the well-known nine-atom deltahedral Zintl ions Tt_9^{4-} (Tetrel = Group 14) characterized from solutions exist also in the corresponding precursor Zintl phases A_4Tt_9 (A = alkali metal).^[2] This, for the first time, revealed relations between Zintl phases and Zintl ions.^[2] In addition, even the nine-atom silicon clusters Si_9^{4-} , previously unknown from solution studies, were characterized in the Zintl phase $\text{Rb}_{12}\text{Si}_{17}$.^[3] Despite this variety of clusters, isolated *arachno* species, that is, deltahedra with two missing vertices, were not known either in Zintl phases or as Zintl ions. For that matter *closo* species of ten atoms have not been unambiguously characterized yet either.^[4]

Here we report the synthesis and characterization of the first isolated *arachno* cluster of a main group element, namely, *arachno*- Sn_8^{6-} with the shape of a square antiprism. The cluster is found in two compounds, $\text{Rb}_4\text{Li}_2\text{Sn}_8$ and $\text{K}_4\text{Li}_2\text{Sn}_8$, both synthesized by direct fusion of the elements (see Experimental Section). The use of mixed alkali metals was not accidental. This approach is a very powerful tool for changing packing efficiency while keeping constant stoichiometry and charge, and we have used it in syntheses of other novel mixed-cation compounds. For example, mixing Na and Rb or Na and Cs is the only way to stabilize the silicon and germanium clathrate-II structures $\text{A}_8\text{Na}_{16}\text{Tt}_{136}$.^[5] Similarly, the same mixture of cations combined with tin provides the new phase $\text{A}_3\text{Na}_{10}\text{Sn}_{23}$ made of clathrate-II layers separated by a mixture of tin tetrahedra and cations, that is, an intergrowth of clathrate-II and the known phase A_4Sn_4 .^[6] The compounds reported here, $\text{Rb}_4\text{Li}_2\text{Sn}_8$ and $\text{K}_4\text{Li}_2\text{Sn}_8$, were discovered in an attempt to make the Li analogue $\text{A}_3\text{Li}_{10}\text{Sn}_{23}$. They contain the unprecedented *arachno*- Sn_8^{6-} clusters, stabilized by Li^+ as *closo*- $[\text{Li}_2\text{Sn}_8]^{4-}$ and separated by the larger Rb^+ or K^+ ions.

The structures of the two compounds were determined by single-crystal X-ray diffraction (see Experimental Section). Although they crystallize in different space groups and unit cells, their structures are nearly identical. $\text{Rb}_4\text{Li}_2\text{Sn}_8$ crystallizes in $P\bar{1}$ with $Z=4$, while $\text{K}_4\text{Li}_2\text{Sn}_8$ develops a superstructure ($I2/a$) with a fourfold larger cell and $Z=16$. Since the two structures are otherwise virtually the same, only that of $\text{Rb}_4\text{Li}_2\text{Sn}_8$ is described in detail here. It contains two crystallographically different but otherwise similar Sn_8^{6-} clusters. They are almost perfect square antiprisms (D_{4d}) with nearly flat and parallel bases (Figure 1). The deviations from planarity are less than 0.04 Å, and the dihedral angles between the bases are only 0.27(7) and 0.48(7)° for the two clusters. The Sn–Sn distances range from 2.947(3) to 3.037(2) Å (2.989(3)–3.044(2) Å in the square bases and 2.954(2)–3.026(2) Å in the waist) and are comparable with those in other deltahedral tin clusters such as *nido*- Sn_9^{4-} , which has a monocapped square antiprism structure, and its Cr-capped *closo* derivative $[\text{Sn}_9\text{Cr}(\text{CO})_3]^{4-}$.^[7]

The alkali metal cations cap faces, edges, and vertices, as expected, and provide six additional electrons per cluster. The Li–Sn and Rb–Sn distances are in the ranges 2.87(3)–3.20(3) and 3.561(3)–4.378(3) Å, respectively. The clusters are well separated from each other; the shortest intercluster distance is

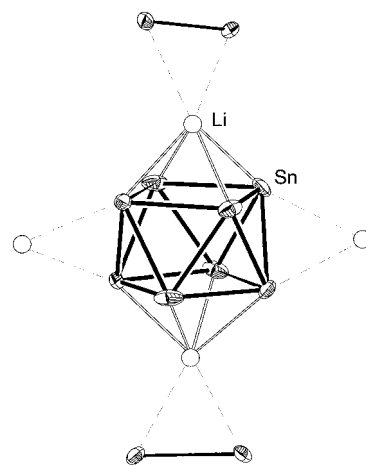


Figure 1. One of the two crystallographically independent *arachno*- Sn_8^{6-} clusters in $\text{Rb}_4\text{Li}_2\text{Sn}_8$ (50 % probability thermal ellipsoids) with the shape of a square antiprism (thick full bonds). Also shown are the two lithium atoms (open circles) that cap the square faces (Li–Sn 2.87(3)–3.03(4) Å) and “complete” the cluster to a *closo*- $[\text{Li}_2\text{Sn}_8]^{4-}$. They also interact with Sn–Sn edges of two other Sn_8^{6-} clusters in the same way as the shown cluster interacts with two other lithium atoms through two of its edges (broken lines, Li–Sn 3.03(3)–3.20(3) Å).

4.628(2) Å. The composition, the dark gray to black color, the brittleness, and, more importantly, the diamagnetism of the compound (see Experimental Section) suggest an electronically balanced compound, that is, a Zintl phase. The charge on the cluster is therefore 6– and is indicative of an *arachno* species according to Wade’s rules.^[8]

A second, more intriguing way to view the structure results from recognizing that lithium is: 1) an alkali metal with substantial covalency in its interactions,^[9] and 2) very specifically positioned with respect to the tin clusters in the structure. All lithium atoms cap the square faces of the antiprisms and thus “complete” them to *closo* deltahedra of ten atoms, Li_2Sn_8 (Figure 1). Since the Li–Sn distances are similar to the Sn–Sn distances within the Sn_8 core (see above), the clusters are nearly ideal bicapped square antiprisms. Thus, instead of *arachno*- $[\text{Sn}_8]^{6-}$ the clusters can be viewed as *closo*- $[\text{Li}_2\text{Sn}_8]^{4-}$ species with 22 skeletal electrons that are isoelectronic with the classical $\text{B}_{10}\text{H}_{10}^{2-}$. However, the isoelectronic relation is true only for the delocalized skeletal electrons, but not for the total number of electrons, which includes localized electrons of the B–H bonds in $\text{B}_{10}\text{H}_{10}^{2-}$ or the lone pairs in naked clusters. A naked *closo* cluster of 10 atoms should have $10 \times 2 = 20$ electrons for lone pairs in addition to the 22 skeletal electrons. This, however, is not the case here, since the lithium vertices clearly can not be expected to carry lone pairs, which would result in an enormous negative charge of more than two per lithium atom. The problem is solved very elegantly in this case by the formation of close contacts between a lithium vertex of one cluster and a Sn–Sn edge of another (Figure 1). Thus, instead of a lone pair of electrons, each lithium atom shares two pairs of electrons from the “lone pairs” of the two tin atoms of the nearby cluster in a three-center, four-electron bond. The MO diagram for this model is the same as for a bent H_3^- molecule (an open triangle). There is a low-lying bonding combination of all three atoms, a nonbonding combination of the two end atoms (the tin atoms

in our case), and an antibonding combination. The net result for four electrons is bonding, with two electrons responsible for the two Li–Sn interactions, and a pair of nonbonding electrons delocalized on the two tin atoms. Of course, one can view the bonding as totally localized and consider a resonance structure in which the lithium atom is bonded *exo* to one tin atom (and shares its pairs of electrons), while the second tin atom retains its nonbonding lone pair of electrons. Either way, the important consequence is that the two lithium atoms of one cluster are bonded to two other clusters, and in addition each cluster interacts with two lithium atoms of two other clusters. The clusters are linked to each other in flat layers (Figure 2) that are separated by the Rb^+ or K^+ ions. Thus,

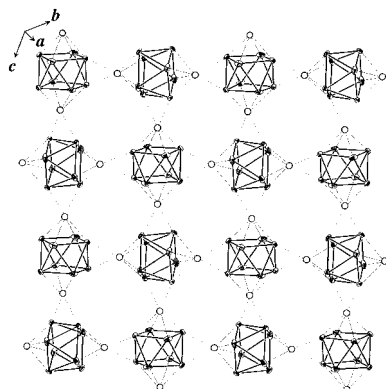


Figure 2. A layer of interconnected four-bonded $[\text{Li}_2\text{Sn}_8]^{4-}$ clusters. Each cluster is connected to two other clusters through its own two lithium atoms (open circles), and two more clusters are bonded to this cluster via their lithium atoms (broken lines). The Rb^+ or K^+ ions (omitted for clarity) are above and below the layer.

each cluster is bonded to four other clusters, whereby each bond carries two electrons, and therefore one electron per bond belongs to the cluster. As a result, the four-bonded *closio*- $[\text{Li}_2\text{Sn}_8]$ cluster requires 22 skeletal electrons (Wade's rules),^[8] four bonds \times one electron per bond = four electrons for intercluster bonding, and six lone pairs on the remaining six vertices \times two electrons per pair = 12 electrons. The total is 38 electrons, and since the number of provided electrons is $2\text{Li} \times 1 + 8\text{Sn} \times 4 = 34$, the cluster needs four additional electrons ($[\text{Li}_2\text{Sn}_8]^{4-}$), and these are provided by the four rubidium or potassium atoms. Attempts to bring the clusters into solution as Zintl ions are currently under way.

Experimental Section

Synthesis: All manipulations were performed in a nitrogen-filled glove box. The compounds were initially detected in the product of reactions of A, Li, and Sn (A = K, Rb) loaded in atomic ratio 3:10:23 in an attempt to produce the Li analogue of $\text{A}_3\text{Na}_{10}\text{Sn}_{23}$.^[6] The reactions were carried out in niobium containers sealed by arc-welding and enclosed in evacuated fused-silica ampoules at 400°C for 20 days followed by cooling in the turned-off furnace. After the structures and the stoichiometry of the compounds were elucidated from single-crystal X-ray diffraction, the corresponding stoichiometric mixtures were treated under similar reaction conditions. Nevertheless, the products contained impurities of poorly diffracting primitive hexagonal phases, most likely $\text{Rb}_{12}\text{Sn}_{17}$ ($a = 15.22(2)$, $c = 24.76(4)$ Å) and $\text{K}_{12}\text{Sn}_{17}$ ($a = 14.11(3)$, $c = 23.15(6)$ Å). Different temperature profiles did not improve the overall results. Much better yields were achieved when an excess of Sn was used, most likely due to flux effects that provide conditions for more facile reaction and crystal growth.

Structure determination: Single crystals were selected from the initial reaction product and were sealed in capillaries. Data for a crystal of $\text{Rb}_4\text{Li}_2\text{Sn}_8$ (irregular shape, $0.18 \times 0.10 \times 0.08$ mm) were collected on an Enraf-Nonius CAD-4 single-crystal diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation at room temperature ($\omega/2\theta$ scans, a hemisphere with $2\theta_{\text{max}} = 52^\circ$, 8095 reflections) and were corrected for absorption by using the average of three ψ scans. Crystal data: triclinic, space group $P\bar{1}$, $a = 9.700(1)$, $b = 14.794(3)$, $c = 14.906(1)$ Å, $\alpha = 97.46(1)^\circ$, $\beta = 103.461(9)^\circ$, $\gamma = 102.49(2)^\circ$; $V = 1994.1(6)$ Å³; $Z = 4$; $\mu = 195.14$ cm⁻¹; $\rho_{\text{calcd}} = 4.348$ g cm⁻³. The refinement of all tin atoms with anisotropic and all lithium atoms with isotropic thermal parameters converged to $R1/wR2$ ($I > 2\sigma_I$) = 0.0637/0.1156 and $R1/wR2$ (all data) = 0.1405/0.1402 for 7780 independent reflections and 234 variables.

Data for a crystal of $\text{K}_4\text{Li}_2\text{Sn}_8$ (irregular shape, $0.16 \times 0.10 \times 0.10$ mm) were collected on a Bruker SMART APEX CCD-based diffractometer with $\text{MoK}\alpha$ radiation at room temperature (ω scans of width 0.3° , a full sphere with $2\theta_{\text{max}} = 66.48^\circ$, 37158/13934 total/independent reflections). The data were corrected for absorption by using the empirical ellipsoidal model SADABS. Crystal data: monoclinic, space group $I2/a$, $a = 18.9638(7)$, $b = 22.0359(8)$, $c = 18.9624(7)$ Å, $\beta = 108.778(1)^\circ$, $V = 7502.3(5)$ Å³; $Z = 16$; $\mu = 113.21$ cm⁻¹; $\rho_{\text{calcd}} = 3.996$ g cm⁻³. The final refinement of all atoms with anisotropic thermal parameters was carried out with interchanging a and c axes (twinning ratio of 0.405) and converged to $R1/wR2$ ($I > 2\sigma_I$) = 0.0427/0.0562 and $R1/wR2$ (all data) = 0.0678/0.0599 for 9145 reflections and 257 variables. Both structures were solved by direct methods and were refined on F^2 with the SHELXTL 5.1 software package.

The reason for the I centering in $\text{K}_4\text{Li}_2\text{Sn}_8$ (and the doubling of the volume) is that the almost equal b and c axes in the $P\bar{1}$ cell of $\text{Rb}_4\text{Li}_2\text{Sn}_8$ of 14.794(3) and 14.906(2) Å, respectively, and the corresponding β and γ angles of $103.461(9)^\circ$ and $102.49(2)^\circ$, respectively, become exactly equal in $\text{K}_4\text{Li}_2\text{Sn}_8$. In addition, the a axis is doubled, and this also doubles the volume. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-411278 ($\text{Rb}_4\text{Li}_2\text{Sn}_8$) and CSD-411279 ($\text{K}_4\text{Li}_2\text{Sn}_8$).

Magnetic measurements: The magnetization of 40 mg of selected crystals of $\text{Rb}_4\text{Li}_2\text{Sn}_8$ was measured on a Quantum Design MPMS SQUID magnetometer at 3 T over the temperature range 10–280 K. The data were corrected for the holder and for ion-core diamagnetism. The corrected magnetic susceptibility is negative and temperature independent, and varies between -1.75×10^{-4} and -1.96×10^{-4} emu mol⁻¹. This is consistent with a diamagnetic compound.

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