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 diazaphospholines 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 of other rhodium-based systems such as those containing 1 or BIPHEMPhos (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.\(^1\) The catalyst was prepared in situ from [Rh(cacac)(CO)]\(_2\) (5 × 10\(^{-2}\) mol) and the phosphine (1.5–4.0 equiv, see Table 1) in toluene (2 mL) in a miniaturacleave 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-[Sn\(_3\)]\(^{6-}\) or closo-[Li\(_2\)Sn\(_3\)]\(^{4+}\)?**

**Synthesis and Characterization of A\(_2\)Li\(_2\)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\(_{11}\)\(^{2-}\), Tr\(_{10}\)\(^{4-}\), Tr\(_{9}\)\(^{6-}\), Tr\(_{8}\)\(^{8-}\), Tr\(_{7}\)\(^{10-}\), and Tr\(_{6}\)\(^{12-}\), and

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Tr$\text{II}$(Tr$\text{III})^{1-}$, where Tr (Triel = Group 13) is indium or thallium, were discovered.\textsuperscript{[3]}
Furthermore, it was found that the well-known nine-atom deltahedral Zintl ions $\text{T}_3^+$ (Tetrel = Group 14) characterized from solutions exist also in the corresponding precursor Zintl phases A$_3$T$_4$ (A = alkali metal).\textsuperscript{[3]}
This, for the first time, revealed relations between Zintl phases and Zintl ions.\textsuperscript{[3]}
In addition, even the nine-atom silicon clusters Si$_3^+$, previously unknown from solution studies, were characterized in the Zintl phase $\text{Rb}_3\text{LiSn}_3$.\textsuperscript{[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 *clos* species of ten atoms have not been unambiguously characterized yet either.\textsuperscript{[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, $\text{Rb}_3\text{LiSn}_3$ and $\text{K}_3\text{LiSn}_3$, 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 $\text{A}_3\text{Na}_5[\text{Tl}_{13}]$.\textsuperscript{[5]}
Similarly, the same mixture of cations combined with tin provides the new phase $\text{A}_3\text{Na}_5\text{Sn}_{13}$ 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 $\text{A}_3\text{Sn}_{13}$.\textsuperscript{[6]}
The compounds reported here, $\text{Rb}_3\text{LiSn}_3$ and $\text{K}_3\text{LiSn}_3$, were discovered in an attempt to make the Li analogue $\text{A}_3\text{Li}_5\text{Sn}_{13}$. They contain the unprecedented *arachno*-Sn$_8^{6-}$ clusters, stabilized by Li$^+$ as *clos*-[$\text{Li}_2\text{Sn}_4$]$^{6-}$ 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. $\text{Rb}_3\text{LiSn}_3$ crystallizes in $\text{P}1$ with $Z = 4$, while $\text{K}_3\text{LiSn}_3$ develops a superstructure ($\text{P}2_1/a$) with a fourfold larger cell and $Z = 16$. Since the two structures are otherwise virtually the same, only that of $\text{Rb}_3\text{LiSn}_3$ is described in detail here. It contains two crystallographically different but otherwise similar Sn$_8^{6-}$ clusters. They are almost perfect square antiprisms ($D_{4h}$) 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 *clos* derivative [Sn$_4$Cr(CO)$_3$]$_{n=7}$.

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)–4.578(3) Å, respectively. The clusters are well separated from each other; the shortest intercluster distance is 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.\textsuperscript{[9]}

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,\textsuperscript{[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 *clos* deltahedra of ten atoms, Li$_3$Sn$_3$ (Figure 1). Since the Li–Sn distances are similar to the Sn–Sn distances within the Sn$_3$ core (see above), the clusters are nearly ideal bicapped square antiprisms. Thus, instead of *arachno*-Sn$_8^{6-}$, the clusters can be viewed as *clos*-[$\text{Li}_2\text{Sn}_4$]$^{6-}$ species with 22 skeletal electrons that are iso electronic with the classical B$_2$H$_6$$^{2-}$. However, the isoelectronic relation is true only for the delocalized skeletal electrons, but not for the total number of electrons, which includes localized electrons of the B–H bonds in B$_2$H$_6$$^{2-}$ or the lone pairs in naked clusters. A naked *clos* cluster of 10 atoms should have 10 × 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 *clos* 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
Structure determination: Single crystals were selected from the initial reaction product and were sealed in capillaries. Data for a crystal of Rb$_2$Li$_2$Sn$_5$ (irregular shape, 0.12 x 0.10 x 0.08 mm) were collected on an Enraf-Nonius CAD-4 single-crystal diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation at room temperature (ω/2θ scans, a hemisphere with 2θ$_{max}$ = 52°, 8095 reflections) and were corrected for absorption by using the average of three ψ scans. Crystal data: triclinic, space group P1, a = 9.700(1), b = 14.794(3), c = 14.906(1) Å, α = 97.46(1), β = 103.461(19), γ = 102.49(2)°. V = 1994.1(6) Å$^3$, Z = 4, $μ$ = 193.4 cm$^{-1}$; $ρ_{calc}$ = 3.438 g cm$^{-3}$. The refinement of all tin atoms with anisotropic and all lithium atoms with isotropic thermal parameters converged to R1/wR2 (1 > 2σ) = 0.06370/0.1156 and R1/wR2 (all data) = 0.1405/0.1402 for 7780 independent reflections and 234 variables.

For a crystal of K$_3$Li$_2$Sn$_5$ (irregular shape, 0.16 x 0.10 x 0.06 mm) were collected on a Bruker SMART Apex CCD-based diffractometer with Mo$_{K\alpha}$ radiation at room temperature (ω scans of width 0.5°, a full sphere with 2θ$_{max}$ = 66.48°, 37158/13934 total/independent reflections). The data were corrected for absorption by using the empirical ellipsoidal model SADABS. Crystal data: monoclinic, space group P2$_1$/a, a = 18.9638(7), b = 22.0359(8), c = 18.9624(7) Å, β = 108.778(1)°, V = 7502.3(5) Å$^3$; Z = 16; $μ$ = 113.21 cm$^{-1}$; $ρ_{calc}$ = 3.996 g cm$^{-3}$. The final refinement of all atoms with anisotropic thermal parameters was carried out with interchanging $a$ and $c$ axes (winnings ratio of 0.405) and converged to R1/wR2 (1 > 2σ) = 0.04270/0.0562 and R1/wR2 (all data) = 0.06780/0.0599 for 9145 reflections and 257 variables. Both structures were solved by direct methods and were refined on $F$ with the SHELXTL 5.1 software package.

The reason for the $I$ centering in K$_3$Li$_2$Sn$_5$ (and the doubling of the volume) is that the almost equal $b$ and $c$ axes in the P1 cell of Rb$_2$Li$_2$Sn$_5$ of 14.794(3) and 14.906(2) Å, respectively, and the corresponding β and γ angles of 103.461(9) and 102.49(2)°, respectively, become exactly equal in K$_3$Li$_2$Sn$_5$. In addition, the 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 (Rb$_2$Li$_2$Sn$_5$) and CSD-411279 (K$_3$Li$_2$Sn$_5$).

Magnetic measurements: The magnetization of 40 mg of selected crystals of Rb$_2$Li$_2$Sn$_5$ 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 x 10$^{-4}$ and −1.96 x 10$^{-4}$ emu mol$^{-1}$. This is consistent with a diamagnetic compound.

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