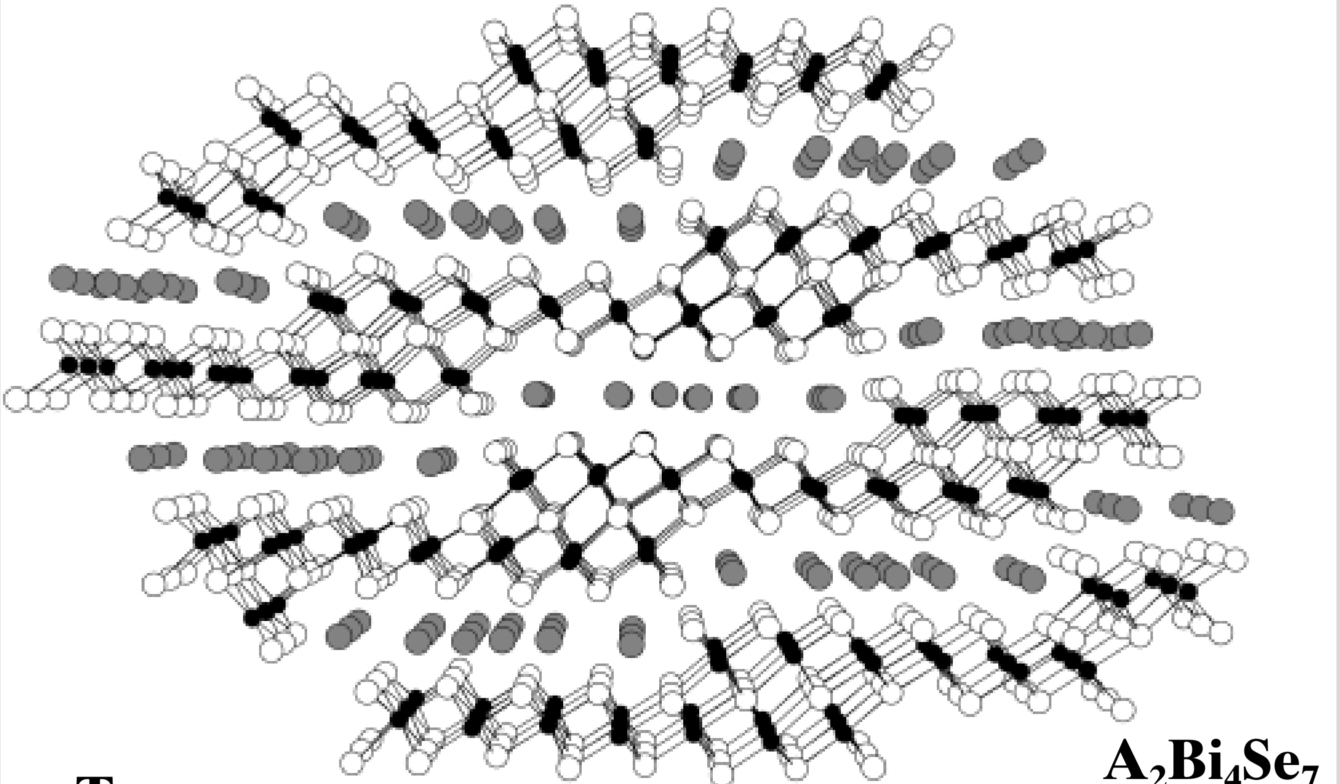
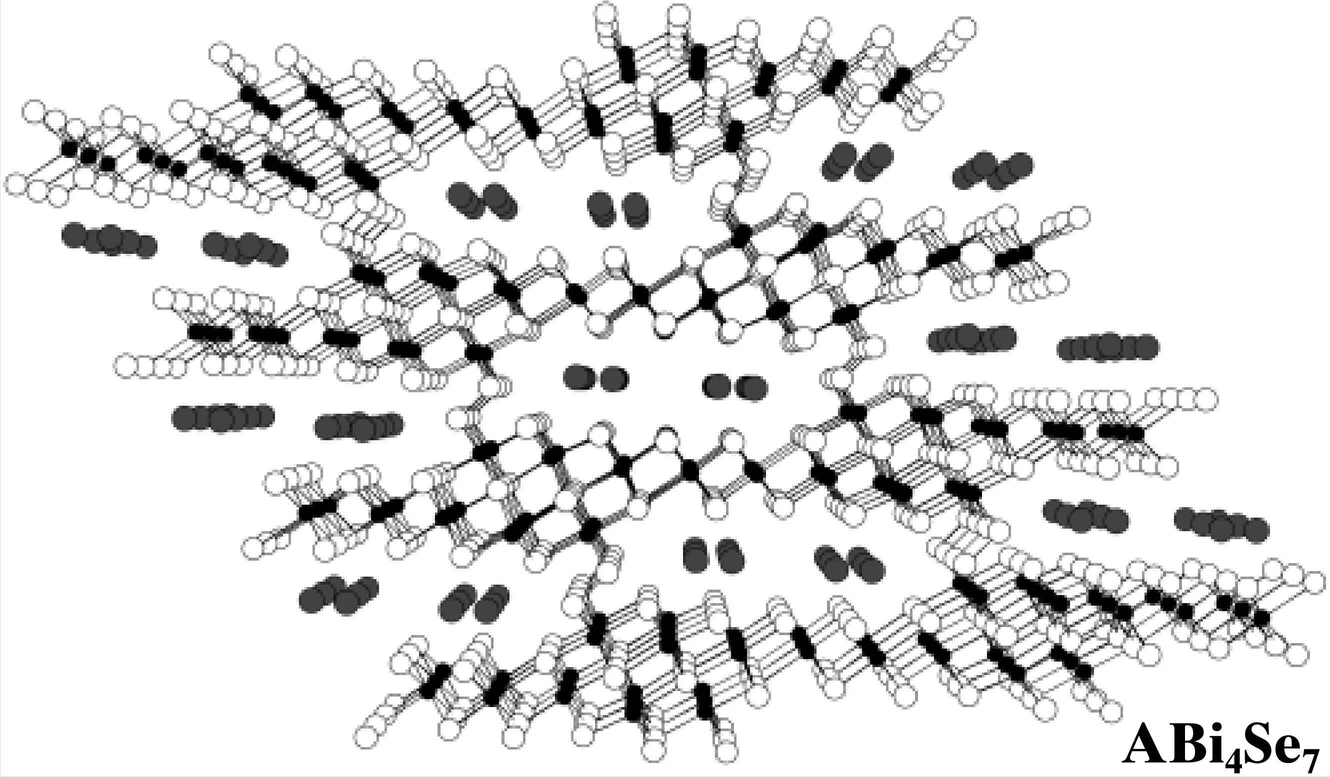


$A_2Bi_4Se_7$

Two rows of Se atoms belonging to two adjacent $[Bi_4Se_7]^{2-}$ layers come together in an oxidative zipper-like manner to give a single row of diselenide groups.

Oxidant

Find out more on the following pages.



ABi_4Se_7

Redox-Induced “Zipper” Action in $Rb_2Bi_4Se_7$ and $Cs_2Bi_4Se_7$: Coupling of Slabs to a Three-Dimensional Framework through Single-Crystal to Single-Crystal Conversion**

Lykourgos Iordanidis and Mercouri G. Kanatzidis*

The number of known topotactic single-crystal to single-crystal solid-state transformations is limited. Most of the reported cases involve the dimerization or polymerization of organic or organometallic[1] molecules by heat or light, or loss of solvent from coordination complexes[2] or rigid framework structures[3] without the collapse of the rest of the structure. One well-studied solid-state example is the topotactic reduction of γ-MnO_2 to MnO(OH) with hydrazine.[4] Our interest in exploring new solid-state chemistry in the A/Bi/Se (A = alkali metal) systems led us to the discovery of the new layered isostructural phases $Rb_2Bi_4Se_7$ and $Cs_2Bi_4Se_7$. The behavior of these phases is very different from any other A/Bi/Se phases studied by us before[5] in that they exhibit a remarkable redox transformation in the solid state. This conversion, of which we know of no other examples, involves the topotactic oxidative coupling of entire rows of Se^{2-} ions to give Se_2^{2-} groups in a cooperative way reminiscent of the closing action of a zipper. This remarkable process involves the rapid expulsion of alkali ions from the crystals and results in the daughter compounds $RbBi_4Se_7$ and $CsBi_4Se_7$, in which the original layers are stitched into a three-dimensional framework. The facility with which the zipperlike action transforms the starting compounds is attested by the clean and quick conversion of whole single crystals from one phase to the next without loss of crystallinity.

$Rb_2Bi_4Se_7$ is a two-dimensional (2D) layered structure made of Bi_2Te_3-type and CdI_2-type blocks (Figure 1 a).[6] The Rb atoms reside between the layers in trigonal prismatic sites. The $[Bi_4Se_7]^{2-}$ framework consists of edge-sharing distorted Bi octahedra. A key characteristic of the structure is that adjacent layers come in close, nonbonding contact through the Se5 atoms, which are at a distance of 3.336(6) Å. As seen in Figure 1 b the Se5 atoms in each layer form parallel rows that approach one another side by side so that the Se atoms in one row are staggered with respect to those in the other row. Rb1 has a bicapped trigonal prismatic coordination with bonds varying between 3.445(5) and 3.733(4) Å. Rb2 and Rb3 have similar trigonal prismatic coordination and are disordered over certain sites in the space provided between the layers.

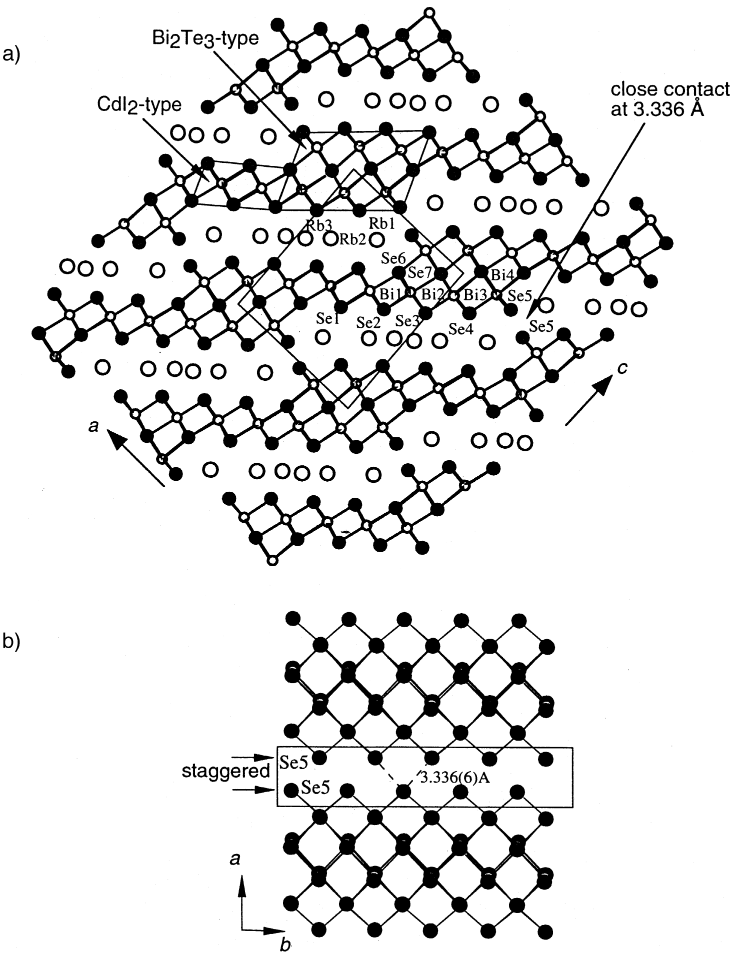


Figure 1. Projection of the structure of $Rb_2Bi_4Se_7$ down the *b* axis. The Bi1 and Bi2 octahedra are distorted with Bi–Se bond lengths between 2.870(3) – 3.061(3) Å. The octahedra around Bi3 and Bi(4) are more distorted with Bi–Se bond lengths varying between 2.808(4) and 3.205(3) Å. In each Bi octahedron there is a short bond *trans* to a long bond. For example, in the Bi4 octahedra there are two short Bi–Se bonds of 2.792(2) Å *trans* to two long bonds of 3.205(3) Å. The bond angles for Bi1 and Bi2 octahedra are more regular, varying between 86.74(8) – 92.58(9)° for Bi1 and 86.55(8) – 93.47(9)° for Bi2, while they are less regular in the Bi3 and Bi4 octahedra varying between 82.06(8) – 94.64(9) and 82.05(8) – 97.8(1)°, respectively.

Preparations of $Rb_2Bi_4Se_7$ and $Cs_2Bi_4Se_7$ give homogeneous-looking samples with thin, long plate morphology. We noticed that fresh batches of the compound tended to become “wet” and stuck to the vial walls when stored in air, yet no obvious decomposition of the compound was evident. We monitored the X-ray powder diffraction pattern of fresh samples of $Rb_2Bi_4Se_7$ and found them to be changing with time (small but significant shifts in the positions of a few reflections) upon exposure of the sample to ambient conditions. We concluded that an oxidative, probably topotactic, transformation was under way. Surprisingly, the structure of the “aged” products could be solved from data collected on the transformed crystals. Thus, we discovered the presence of diselenide (Se_2^{2-}) groups and a composition of $RbBi_4Se_7$ not $Rb_2Bi_4Se_7$. This process occurs also in $Cs_2Bi_4Se_7$ regardless of the crystal size. It is important to note that the structures of ABi_4Se_7 (A = Rb, Cs) were determined employing the same specimens used to determine the structures of $A_2Bi_4Se_7$.

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The two structure types are closely related,[7] which proves that their redox interconversion is fully topotactic. The structure of ABi_4Se_7 contains the same $[Bi_4Se_7]$ slabs of $A_2Bi_4Se_7$, but now they are connected through Se–Se bonds to form a 3D structure (Figure 2a). Compared to $A_2Bi_4Se_7$, the slabs in ABi_4Se_7 have shifted with respect to each other so that the Se5 atoms in two adjacent rows move from a staggered to an eclipsed position to form an infinite row of single Se5–Se5 bonds with a length of 2.354(9) Å (Figure 2b). This process resembles a zipperlike closing action. The Rb atoms in $RbBi_4Se_7$ show a diffuse character (high-temperature factors) as a result of the transformation process. Rb1 and Rb2 are now the only alkali atoms remaining in the tunnels and spread over the entire available space. The Cs analogue behaves correspondingly. A schematic representation of the "zipper" action is shown in Figure 3.

The interconversion of the pair $A_2Bi_4Se_7/ABi_4Se_7$ can be readily effected with the proper oxidants and reductants. Whereas the reaction with ambient oxygen is difficult to control and depends on the relative humidity, the reaction with I_2 in wet CH_3CN is facile and transforms the samples, usually within one hour [Eq. (1)]. The formation of Se–Se bonds can also be confirmed by Raman spectroscopy through observation of its symmetric stretching mode at 233 cm^{-1}.

$$2\,Rb_2Bi_4Se_7 + I_2 \rightarrow 2\,RbBi_4Se_7 + 2\,RbI \qquad (1)$$

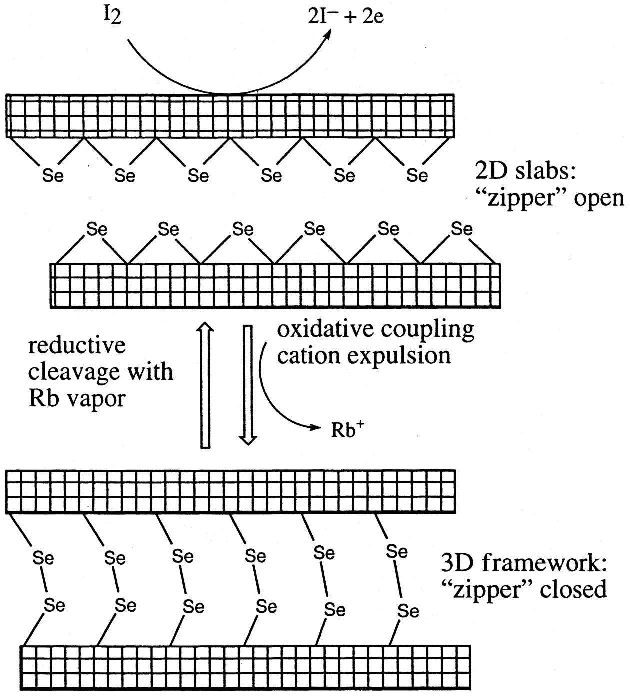

Figure 3. Schematic diagram showing the oxidative zipperlike couples of two rows of Se atoms belonging to two adjacent $[Bi_4Se_7]^{2-}$ layers into a single row of diselenide groups. This process happens for all such rows over the entire single crystal.

To reverse the process ("zipper" open), ABi_4Se_7 can be heated at moderate temperatures (200–300 °C) with a stoichiometric amount of alkali metal to give back $A_2Bi_4Se_7$.

This rare example of very long-range topotactic chemistry in the solid state is exceptional because the individual Se atoms that become diselenide groups are not actually accessible to oxygen for steric reasons. The fact that the oxidative coupling occurs in the presence of water suggests that the process is electrochemical in nature. The fact that all pertinent Se^{2-} atoms couple to give Se_2^{2-} groups even though the $A_2Bi_4Se_7$ phases are dense, and not porous, supports the electrochemical route. For "zipper" closing, electrons must be removed through the conductive $[Bi_4Se_7]^{2-/1-}$ framework, generating holes, which apparently migrate to the $Se5^{2-}$ atoms and cause them to form Se–Se bonds across the layers. These bonds therefore represent a form of hole localization in these materials. Alkali metal atoms are simultaneously expelled to maintain electroneutrality. The narrow energy band gaps present in $A_2Bi_4Se_7$ and ABi_4Se_7 (< 0.55 eV) allow adequate electron transport to complete the transformation.

In conclusion, an unparalleled all solid-state, topotactic oxidative coupling has been discovered, which generates rows of Se–Se bonds, a process that resembles the closing action of a zipper. The process is reversible as the "zipper" can also open by reduction with alkali metal vapor. $A_2Bi_4Se_7$ have the unique characteristic of oxidatively transforming to produce

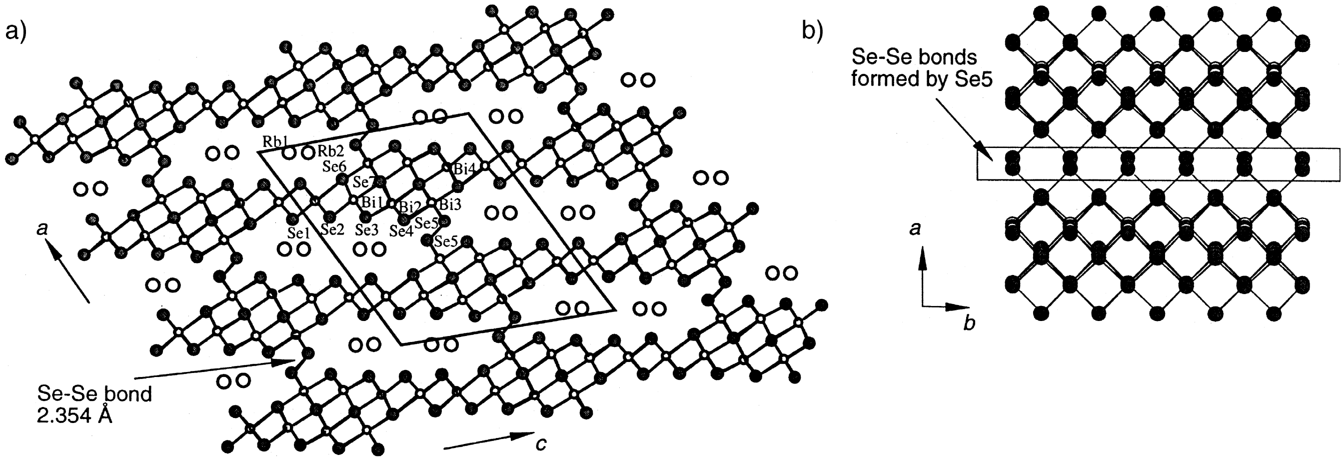

Figure 2. Projection of the structure of $RbBi_4Se_7$ down the *b* axis. Atoms Bi1 and Bi4 have bond lengths between 2.703(5)–3.260(5) and 2.883(4)–3.050(4) Å, respectively, while their angles are closer to that of a normal octahedron varying between 88.1(1)–92.0(1)° for Bi1 and between 88.4(1)–91.9(1)° for Bi4. In the case of Bi2 and Bi3 the Bi–Se bond lengths vary between 2.801(4)–3.097(4) and 2.776(4)–3.173(4) Å, respectively. The angles around Bi2 and Bi3 are between 87.2(1)–96.1(1) and 83.43(9)–96.5(1)°, respectively.

ABi_4Se_7 in a single-crystal to single-crystal fashion. We anticipate that the zipperlike action in these materials will also be feasible using electrochemical means.

Experimental Section

$Rb_2Bi_4Se_7$: A mixture of Rb_2Se (0.060 g, 0.240 mmol) and Bi_2Se_3 (0.314 g, 0.480 mmol) was transferred to a carbon-coated silica tube which was flame-sealed under vacuum. The tube was heated at 810 °C for 6 d, then cooled to 510 °C at 7 °Ch^{-1} and to 50 °C over 10 h. The product consisted of silver-gray long laths. Semiquantitative energy-dispersive analysis (EDS) using a scanning electron microscope (SEM) on several needles gave an average composition of $Rb_2Bi_4Se_{6.8}$. $Cs_2Bi_4Se_7$: The procedure was similar to the one above but using a mixture of Cs_2Se (0.060 g, 0.174 mmol) and Bi_2Se_3 (0.228 g, 0.348 mmol). A single-phase product was obtained. The optical band gaps of these two compounds were measured spectroscopically and are 0.53 and 0.56 eV, respectively.

ABi_4Se_7 (A = Rb, Cs): $Rb_2Bi_4Se_7$ (0.1 g, 0.064 mmol) was ground into powder and added to a 2.5 mM solution of I_2 in degassed, wet CH_3CN (100 mL) at 23 °C. The mixture was continuously stirred under an N_2 atmosphere. The oxidation to ABi_4Se_7 was complete in less than 1 h. The optical band gaps of both compounds are ~0.4 eV.

A Bruker SMART Platform CCD diffractometer using graphite monochromatic $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) was used for data collection in all cases. Several different sets of frames, covering a random area of the reciprocal space, were collected using 0.3° steps in ω. The SMART[8a] software was used for data acquisition and the SAINT[8a] program for data extraction. The absorption correction was carried out with SADABS[8a] and the structure solution (direct methods) and refinement (full-matrix least squares on F^2) were done with the SHELXTL[8a] and/or the SHELX97[8b] package of crystallographic programs.

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[1] a) K. Cheng and B. M. Foxman, *J. Am. Chem. Soc.* **1979**, *99*, 8102; b) K. Honda, F. Nakanishi, N. Feeder, *J. Am. Chem. Soc.* **1999**, *121*, 8246; c) M. Leibovitch, G. Olovsson, J. R. Scheffer, J. Trotter, *J. Am. Chem. Soc.* **1998**, *120*, 12755, and references therein; d) M. Leibovitch, G. Olovsson, J. R. Scheffer, J. Trotter, *J. Am. Chem. Soc.* **1997**, *119*, 1462; e) T. Suzuki, *Pure Appl. Chem.* **1996**, *68*, 281.

[2] a) S. Rabe, U. Müller, *Z. Anorg. Allg. Chem.* **1999**, *625*(8), 1367; b) U. Englert, B. Ganter, T. Wagner, W. Klaeui, *Z. Anorg. Allg. Chem.* **1998**, *624*(6), 970.

[3] a) C. J. Kepert, M. J. Rosseinsky, *Chem. Commun.* **1999**, 375; b) H. Li, M. Eddaoudi, M. O'Keefe, O. M. Yaghi, *Nature* **1999**, *402*, 276.

[4] W. Feitknecht, H. R. Oswald, U. Feitknect-Steinmann, *Helv. Chim. Acta* **1960**, *43*, 1947.

[5] a) T. J. McCarthy, S.-P. Ngeyi, J.-H. Liao, D. C. DeGroot, J. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1993**, *5*, 331; b) D.-Y. Chung, K.-S. Choi, L. Iordanidis, J. L. Schindler, P. W. Brazis, C. R. Kannewurf, B. Chen, S. Hu, C. Uher, M. G. Kanatzidis, *Chem. Mater.* **1997**, *9*, 3060; c) D.-Y. Chung, L. Iordanidis, K.-S. Choi, M. G. Kanatzidis, *Bull. Korean Chem. Soc.* **1998**, *19*, 1283.

[6] a) $Rb_2Bi_4Se_7$: Crystal dimensions 0.65 × 0.025 × 0.025 mm^3, space group $P2_1/m$, $a = 13.062(2)$, $b = 4.2072(5)$, $c = 15.301(2)$ Å, $\beta = 93.137(2)°$, $V = 839.61(17)$ Å^3, $Z = 2$, $\rho_{calcd} = 6.169$ gcm^{-3}, $2\theta_{max} = 50.18°$, $T = 173(2)$ K, 3887 reflections collected, 1689 independent, 1201 observed $[I > 2\sigma(I)]$, $\mu = 62.69$ mm^{-1}, $T_{max/min} = 0.064/0.029$, 85 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.066$, $wR2 = 0.16$, max/min residual electron density 6.60/−3.15 e Å^{-3}. b) $Cs_2Bi_4Se_7$: Crystal dimensions 0.5 × 0.025 × 0.015 mm^3, space group $P2_1/m$, $a = 13.227(1)$, $b = 4.1857(4)$, $c = 15.556(2)$ Å, $\beta = 94.592(2)°$, $V = 858.49(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 6.400$ gcm^{-3}, $2\theta_{max} = 56.92°$, $T = 173.1(1)$ K, 5978 reflections collected, 2224 independent, 1975 observed $[I > 2\sigma(I)]$, $\mu = 59.86$ mm^{-1}, $T_{max/min} = 1.00/0.43$, 86 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.036$, $wR2 = 0.094$, max/min residual electron density 3.79/−3.03 e Å^{-3}.

[7] $RbBi_4Se_7$: Data on this compound were collected on two different crystals. One of them was the same crystal (now transformed) initially used to determine the structure of $Rb_2Bi_4Se_7$. The other was selected from a converted batch of sample: Crystal dimensions 0.35 × 0.025 × 0.025 mm^3, space group $C2/m$, $a = 22.286(5)$, $b = 4.1760(8)$, $c = 19.794(4)$ Å, $\beta = 116.89(3)°$, $V = 1642.9(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 5.960$ gcm^{-3}, $2\theta_{max} = 50.44°$, $T = 293(2)$ K, 4127 reflections collected, 1651 independent, 1186 observed $[I > 2\sigma(I)]$, $\mu = 61.13$ mm^{-1}, $T_{max/min} = 1.00/0.51$, 80 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.082$, $wR2 = 0.209$, max/min residual electron density 5.64/−3.75 e Å^{-3}. $CsBi_4Se_7$: Crystal dimensions 0.42 × 0.02 × 0.02 mm^3, space group $C2/m$, $a = 22.224(7)$, $b = 4.178(1)$, $c = 19.742(6)$ Å, $\beta = 116.384(1)°$, $V = 1642.2(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 6.154$ gcm^{-3}, $2\theta_{max} = 57.16°$, $T = 173.1(1)$ K, 7393 reflections collected, 2154 independent, 1201 observed $[I > 2\sigma(I)]$, $\mu = 60.39$ mm^{-1}, $T_{max/min} = 1.00/0.46$, 80 parameters, final R indices $[I > 2\sigma(I)]$: $R1 = 0.053$, $wR2 = 0.123$, max/min residual electron density 6.11/−3.59 e Å^{-3}. 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-411071, -411072, -411073, and -411074).

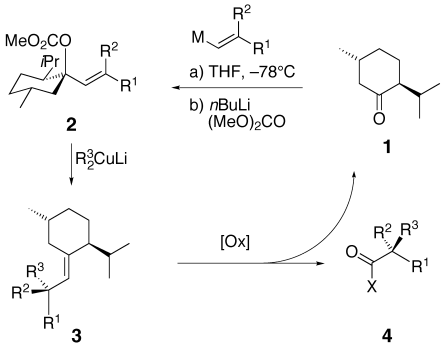
[8] a) SMART versions 4 and 5 (1996–1998), SAINT versions 4, 5, and 6 (1994–1999), SADABS, SHELXTL V-5, Bruker Analytical Xray Systems Inc. Madison, Wisconsin 53719 USA; b) G. M. Sheldrick, University of Göttingen, Germany.

A Novel Method To Generate Chiral Quaternary Carbon Centers of High Enantiomeric Purity Using a Highly Stereoselective Addition of Vinylalanes to a Chiral Aldehyde[**]

Claude Spino[*] and Christian Beaulieu

In memory of Larry Weiler

We recently reported on a novel alternative to the alkylation of chiral enolates using the S_N2' addition of cuprates to chiral carbonates **2** derived from menthone (**1**, Scheme 1).[1] Oxidative cleavage of **3** furnished aldehydes, carboxylic acids, or alcohols having a tertiary α-chiral center ($R^2 = H$) with enantiomeric purities greater than 99%.



Scheme 1. Generation of tertiary chiral carbon centers from menthone (**1**).

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