

“n-Doping” of Deltahedral Zintl Ions

Miriam M. Gillett-Kunnath, Allen G. Oliver, and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

S Supporting Information

ABSTRACT: We report a simple and efficient method for replacing germanium atoms in deltahedral Ge_9^{4-} clusters with Sb or Bi. While reactions of Ge_9^{4-} with EPh_3 ($\text{E} = \text{Sb}, \text{Bi}$) at room temperature are known to produce mono- and disubstituted clusters $[\text{Ph}_2\text{E-Ge}_9\text{-Ge}_9\text{-EPh}_2]^{4-}$ and $[\text{Ph}_2\text{E-Ge}_9\text{-EPh}_2]^{2-}$, respectively, at elevated temperatures or with sonication they result in exchange of Ge cluster atoms with Sb or Bi. Structurally characterized from such reactions are the novel “n-doped” deltahedral Zintl ions $[(\text{EGe}_8)\text{-(Ge}_8\text{E)}]^{4-}$, $(\text{Sb}_2\text{Ge}_7)^{2-}$, and $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$.

Although the nine-atom deltahedral Zintl ions of Group 14 have been known for a century,¹ their redox chemistry is very young, just about 10 years old. Despite this short history, however, these cluster ions have already shown interesting and diverse reactivity.² Thus, they can be alkylated and alkenylated,³ metalated,⁴ functionalized with main-group and transition-metal organometallic fragments,^{5–7} oligomerized,⁸ polymerized,⁹ and centered by transition metals.¹⁰ The reactions of Ge_9^{4-} with EPh_3 for $\text{E} = \text{P}, \text{As}, \text{Sb},$ and Bi were among the very first redox reactions with such ions. While the lighter congeners PPh_3 and AsPh_3 cause mild oxidation and subsequent oligomerization of the clusters,^{8b} the heavier members produced the mono- and disubstituted species $[\text{Ge}_9\text{-EPh}_2]^{3-}$ (structurally characterized as a dimer of $[\text{Ph}_2\text{E-Ge}_9\text{-Ge}_9\text{-EPh}_2]^{4-}$) and $[\text{Ph}_2\text{E-Ge}_9\text{-EPh}_2]^{2-}$, respectively ($\text{E} = \text{Sb}, \text{Bi}$; Scheme 1).⁵ These reactions were carried out at room temperature for 1–2 h, and, at the time, were evaluated only by the crystalline compounds they produced. A more recent inspection of the same reactions by electrospray mass spectrometry (ES-MS, negative-ion mode) revealed the presence of species with mass corresponding to (EGe_8) in addition to the functionalized clusters described above. This led to further studies of the reactions by systematic variation of the reaction conditions in an attempt to improve the yield of the new species and to eventually isolate and structurally characterize them. As it turned out, higher temperatures or sonication at longer times results in virtually single-species products, namely nine-atom germanium clusters with one or more germanium cluster atoms exchanged for pnictogen atoms (Scheme 1). Herein we describe the synthesis and structural characterization of such “n-doped” clusters in the following compounds: $[\text{K}(2,2,2\text{-crypt})]_4[(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}] \cdot 3\text{en}$ (**1a**), $[\text{K}(18\text{-crown-6})]_4[(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}] \cdot 4\text{en}$ (**1b**), $[\text{Rb}(18\text{-crown-6})]_2(\text{Sb}_2\text{Ge}_7) \cdot \text{en}$ (**2**), $[\text{K}(2,2,2\text{-crypt})]_2[(\text{SbGe}_8)\text{-SbPh}_2]$ (**3**), and $[\text{K}(18\text{-crown-6})]_4[(\text{BiGe}_8)\text{-(Ge}_8\text{Bi)}] \cdot 5\text{en}$ (**4**). Subsequently, the clusters of **1** were alkenylated by a reaction with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ to produce

$[(\text{SbGe}_8)\text{-CH=CH}_2]^{2-}$ that was structurally characterized in $[\text{K}(2,2,2\text{-crypt})]_2[(\text{SbGe}_8)\text{-CH=CH}_2]$ (**5**).

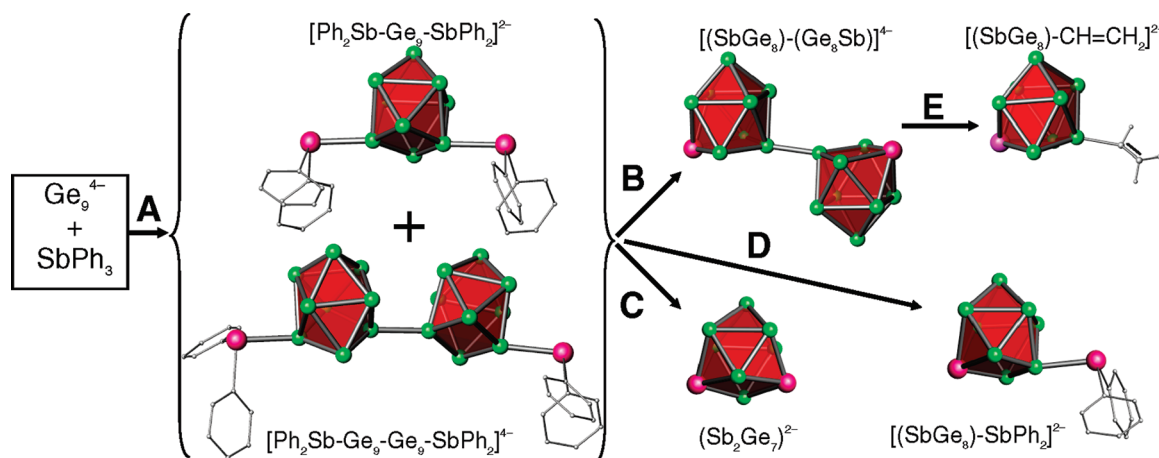
As already mentioned, the ES mass spectra (Figure S1 in Supporting Information) of the room-temperature reactions of Ge_9^{4-} (from a precursor with nominal composition K_4Ge_9 dissolved in ethylenediamine) with SbPh_3 show peaks with masses corresponding to $(\text{Ge}_9\text{-SbPh}_2)$, $(\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2)$, and (SbGe_8) . Present also is a small amount of Ge_{10}^{2-} , which is known to form upon mild oxidation with various reagents, in this case SbPh_3 (SbPh_2 and Ph-Ph anions are also seen in the spectra). Crystallized from this reaction are the reported compounds containing $[\text{Ph}_2\text{E-Ge}_9\text{-Ge}_9\text{-EPh}_2]^{4-}$ and $[\text{Ph}_2\text{E-Ge}_9\text{-EPh}_2]^{2-}$ (Scheme 1).^{8,9}

Next, the same reaction was carried out at 75 °C for 3 days. The corresponding ES mass spectrum (Figure S2) is dramatically different from that of the room-temperature reaction and is dominated greatly by the monoexchanged anion (SbGe_8) and its ion pair with potassium. Observed in very small quantities are also homo- and heteroatomic fragments with fewer than nine atoms, such as Ge_2Sb_2 , GeSb_3 , Ge_4Sb , Ge_7 , Ge_6Sb , Ge_7Sb , etc. Upon layering with toluene with 2,2,2-crypt or 18-crown-6 dissolved in it, the reaction solutions produced crystals of compounds **1a** and **1b**, respectively, containing the novel dimeric anion $[(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}]^{4-}$ (Scheme 1). Despite the dimeric nature of the anion in the solid state, the mass spectra of DMF solutions of crystals of **1a** and **1b** showed only monomers of (SbGe_8) (Figure S3).

The dimers $[(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}]^{4-}$ are isostructural and iso-electronic with the known homoatomic dimers $[\text{Ge}_9\text{-Ge}_9]^{6-}$.^{8a} As can be expected, the distances at the Sb atoms in the former, averages of 2.730 Å for **1a** and 2.744 Å for **1b**, are significantly longer than the average of 2.612 Å at the same vertex in the latter. Although $[(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}]^{4-}$ is isoelectronic with $[\text{Ge}_9\text{-Ge}_9]^{6-}$, its negative charge is lower because each substitution of a Group 14 with a Group 15 atom brings one additional electron to the cluster and reduces by one the number of external electrons needed for bonding. The (SbGe_8) clusters are mono-capped square antiprisms that are exo-bonded to each other via germanium atoms at the open square faces (Scheme 1). The antimony atoms are also in those square faces but are positioned diagonally opposite to the exo-bonded germanium atoms. The same positions, but occupied by germanium atoms in $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]^{4-}$, are the ones that are exo-bonded to the two SbPh_2 fragments. One possible path for the formation of the “doped” clusters is a high-temperature-driven intramolecular exchange of a cluster atom for a substituent atom within the parent clusters of $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]^{4-}$, i.e., $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]^{4-} \rightarrow [(\text{SbGe}_8)\text{-(Ge}_8\text{Sb)}]^{4-} + 2\text{Ge}^0\downarrow + 2\text{Ph-Ph}$

Received: January 23, 2011

Scheme 1



Legend: (A) room temp., 2 h; (B) 75 °C, 3 days; (C) 100 °C, 3 days; (D) sonication, 3 days; (E) rxn w/ TMS-C≡C-TMS

(small amounts of germanium precipitation are observed during the reaction). However, in light of the observed small Ge and Ge/Sb fragments in the mass spectra, eventual intermolecular reactions should not be ruled out.

The formation of $[(\text{SbGe}_8)-(\text{Ge}_8\text{Sb})]^{4-}$ at elevated temperatures suggested that raising the reaction temperature even higher may lead to exchange of more germanium atoms. Indeed, the same reaction with SbPh_3 but carried out at 100 °C produced $(\text{Sb}_2\text{Ge}_7)^{2-}$ with two exchanged germanium atoms (Scheme 1). The novel cluster was crystallized and structurally characterized in compound 2 with two Rb counterions sequestered by 18-crown-6 polyether. $(\text{Sb}_2\text{Ge}_7)^{2-}$ is isoelectronic and isostructural with Ge_9^{4-} (each Sb atom reduces the charge by one) and can be described again as a distorted monocapped square antiprism where the two Sb atoms are diagonally opposite in the open square face. However, since the cluster is found in three equally occupied orientations related by a pseudo-three-fold axis, it is more appropriately viewed as a tricapped trigonal prism (a common alternative description). The prism is made of six germanium atoms, while two antimony and one germanium are the capping atoms (Scheme 1). Rotation around the pseudo-three-fold axis of the trigonal prism results in mixed occupancy of the three capping positions, which are then refined each as made of 2/3 Sb and 1/3 Ge. ES mass spectra of the crystals clearly show only (Sb_2Ge_7) species and confirm the stoichiometry (Figure S4). A similar but highly disordered cluster of $[\text{Bi}_2\text{Sn}_7]^{2-}$ was recently reported as a minor impurity in a reaction between the known tetrahedra of $[\text{Sn}_2\text{Bi}_2]^{2-}$ and ZnPh_2 .¹¹

As for the proposed formation of the dimers of $[(\text{SbGe}_8)-(\text{Ge}_8\text{Sb})]^{4-}$ from the parent $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]^{4-}$ by an intramolecular reaction, it can be speculated here that $(\text{Sb}_2\text{Ge}_7)^{2-}$ is similarly generated by an intramolecular reaction from the known disubstituted parent species $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]^{2-}$, i.e., $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]^{2-} \rightarrow (\text{Sb}_2\text{Ge}_7)^{2-} + 2\text{Ge}^0 + 2\text{Ph-Ph}$. The ES mass spectra of these reactions at 100 °C are dominated by $(\text{Sb}_2\text{Ge}_7)^{2-}$ as expected (Figure S5). Interestingly, the only other fairly strong peak corresponds to its SbPh_2 -functionalized version $[(\text{Sb}_2\text{Ge}_7)\text{-SbPh}_2]^-$ (Figure S5). We speculated that if the pathways for the observed atom exchanges are indeed intramolecular, then we may be able to (a) convert the “intermediate” $[(\text{Sb}_2\text{Ge}_7)\text{-SbPh}_2]^-$ to the corresponding triply exchanged clusters $(\text{Sb}_3\text{Ge}_6)^-$ at even higher temperatures and (b) trap other “intermediates” at

appropriate conditions. It turned out that the former takes place at refluxing conditions (118 °C) for 4 days. The mass spectrum clearly indicates the presence of $(\text{Sb}_3\text{Ge}_6)^-$ species in addition to some unidentified higher-mass peaks (Figure S6). As far as trapping other intermediates is concerned, we found out that sonication for 3 days does exactly that (Scheme 1). The reaction produced crystals of compound 3 (upon layering with toluene and 2,2,2-crypt) containing the singly exchanged monosubstituted species $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$. This anion can be viewed as an “intermediate” between the parent disubstituted homoatomic clusters $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]^{2-}$ and $(\text{Sb}_2\text{Ge}_7)^{2-}$ with two exchanged cluster atoms, i.e., $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]^{2-} \rightarrow [(\text{SbGe}_8)\text{-SbPh}_2]^{2-} + \text{Ge}^0 + \text{Ph-Ph} \rightarrow (\text{Sb}_2\text{Ge}_7)^{2-} + 2\text{Ge}^0 + 2\text{Ph-Ph}$. Interestingly, the Ph_2Sb substituent in $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$ is bonded to the cluster at exactly the same germanium position that is found exchanged for antimony in $(\text{Sb}_2\text{Ge}_7)^{2-}$ (Scheme 1). The Ge–Sb exo-bond distance, 2.655(7) Å, is virtually the same as those distances in $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]$, $[\text{Ph-Ge}_9\text{-SbPh}_2]$, and $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]$.⁵

Exchange reactions were also carried out with BiPh_3 . Structurally characterized from these reactions were the dimers $[(\text{BiGe}_8)-(\text{Ge}_8\text{Bi})]^{4-}$ in compound 4, while the ES mass spectrum of the reaction showed the corresponding monomeric species (BiGe_8) (Figure S7). The Bi atoms take the same positions as the Sb atoms in $[(\text{SbGe}_8)-(\text{Ge}_8\text{Sb})]^{4-}$. The reaction conditions were varied in attempts to isolate the corresponding doubly exchanged species $(\text{Bi}_2\text{Ge}_7)^{2-}$, but only very small amounts were seen in the mass spectra.

Finally, the reactivity of the “doped” clusters was tested with one of the well-studied reactions for homoatomic Ge_9^{4-} clusters,^{4–6} that with alkynes to produce alkenylated clusters. Thus, the reaction solutions that produced crystals with $[(\text{EGe}_8)-(\text{Ge}_8\text{E})]^{4-}$ anions were reacted with $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ and $\text{PhC}\equiv\text{CH}$. Both reactions showed the presence of the corresponding alkenylated clusters in the mass spectra (Figures S8 and S9). Crystallized from the reaction with $\text{Me}_3\text{SiC}\equiv\text{C-SiMe}_3$ was compound 5 with vinyl-functionalized antimony-exchanged clusters $[(\text{SbGe}_8)\text{-CH=CH}_2]^{2-}$. The latter are analogous to the known $[\text{Ge}_9\text{-CH=CH}_2]^{3-}$ made by the same reaction but with the homoatomic Ge_9^{4-} clusters.

The observed exchange of germanium cluster atoms with antimony atoms can be viewed as a stepwise process of “n-doping” of the clusters that starts with the formation of the

previously known $[\text{Ph}_2\text{Sb-Ge}_9\text{-SbPh}_2]^{2-}$ and $[\text{Ph}_2\text{Sb-Ge}_9\text{-Ge}_9\text{-SbPh}_2]^{4-}$, followed by the incorporation of one Sb atom from one SbPh_2 fragment per cluster and formation of $[(\text{SbGe}_8)\text{-SbPh}_2]^{2-}$ and $[(\text{SbGe}_8)\text{-}(\text{Ge}_8\text{Sb})]^{4-}$, respectively, and ends with one more incorporation from the second SbPh_2 fragment in the former to form $(\text{Sb}_2\text{Ge}_7)^{2-}$. The new heteroatomic nine-atom clusters reported here add to the very short list of known species, namely $[\text{Sn}_2\text{Bi}_2]^{2-}$, $[\text{Sn}_2\text{Sb}_2]^{2-}$, $[\text{Sn}_3\text{Sb}_4]^{6-}$, $[\text{Pb}_2\text{Sb}_2]^{2-}$, $[\text{InBi}_3]^{2-}$, $[\text{GaBi}_3]^{2-}$, $[\text{In}_4\text{Bi}_5]^{3-}$, $[\text{TlSn}_9]^{3-}$, $[\text{TlSn}_8]^{3-}$, and $[\text{Tl}_2\text{Te}_2]^{2-}$.¹² The major difference for all of them is that they were made by direct dissolution of the corresponding tertiary precursors $\text{A}_x\text{B}_y\text{C}_z$ where A is an alkali metal and B and C are the corresponding p-elements. The clusters reported here, on the other hand, are made by postsynthetic modification of the homoatomic nine-atom clusters in reactions with organometallic compounds.

■ ASSOCIATED CONTENT

S Supporting Information. Detailed experimental preparation, ES-MS spectra, crystallographic information, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author
ssevov@nd.edu

■ ACKNOWLEDGMENT

We thank the National Science Foundation for their continuous financial support (CHE-0742365) and for the purchase of a Bruker Microtof-II mass spectrometer (CHE-0741793). We also thank Bill Bogges and the Center for Environmental Science and Technology at Notre Dame for providing advice, service, and facilities.

■ REFERENCES

- (1) Reviews:(a) Corbet, J. D. *Chem. Rev.* **1985**, *85*, 383. (b) Fässler, T. F. *Coord. Chem. Rev.* **2001**, *215*, 347.
- (2) Reviews:(a) Sevov, S. C.; Goicoechea, J. M. *Organometallics* **2006**, *25*, 5678.(b) Sevov, S. C. In *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Davies, A. G., Gielen, M., Pannell, K. H., Tiekink, R. T., Eds.; John Wiley & Sons Ltd: Chichester, UK, 2008; p 138. (c) Scharfe, S.; Fässler, T. F. *Philos. Trans. R. Soc. A* **2010**, *368*, 1265.
- (3) (a) Hull, M.; Ugrinov, A.; Petrov, I.; Sevov, S. C. *Inorg. Chem.* **2007**, *46*, 2704. (b) Hull, M.; Sevov, S. C. *Angew. Chem. Int. Ed.* **2007**, *46*, 6695. (c) Hull, M.; Sevov, S. C. *Inorg. Chem.* **2007**, *46*, 10953. (d) Chapman, D. J.; Sevov, S. C. *Inorg. Chem.* **2008**, *47*, 6009. (e) Hull, M.; Sevov, S. C. *J. Am. Chem. Soc.* **2009**, *131*, 9026. (f) Kocak, F. S.; Zavalij, P. Y.; Lam, Y.-F.; Eichhorn, B. W. *Chem. Commun.* **2009**, 4197. (g) Gillett-Kunnath, M. M.; Petrov, I.; Sevov, S. C. *Inorg. Chem.* **2010**, *48*, 721.
- (4) (a) Nienhaus, A.; Hauptmann, R.; Fässler, T. F. *Angew. Chem. Int. Ed.* **2002**, *41*, 3213. (b) Spiekermann, A.; Hoffmann, S. D.; Kraus, F.; Fässler, T. F. *Angew. Chem. Int. Ed.* **2007**, *46*, 1638. (c) Spiekermann, A.; Hoffmann, S. D.; Fässler, T. F.; Krossing, I.; Preiss, U. *Angew. Chem. Int. Ed.* **2007**, *46*, 5310. (d) Boeddinghaus, M. B.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2338. (e) Wang, J.-Q.; Wahl, B.; Fässler, T. F. *Angew. Chem. Int. Ed.* **2010**, *49*, 6592. (f) Scharfe, S.; Fässler, T. F. *Eur. J. Inorg. Chem.* **2010**, *8*, 1207. (g) Yong, L.; Boeddinghaus, M. B.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2010**, *636*, 1293.
- (5) (a) Ugrinov, A.; Sevov, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 2442. (b) Ugrinov, A.; Sevov, S. C. *J. Am. Chem. Soc.* **2003**, *125*, 14509.
- (6) Ugrinov, A.; Sevov, S. C. *Chem. Eur. J.* **2004**, *10*, 3727.
- (7) (a) Kesanli, B.; Fettinger, J.; Eichhorn, B. *Chem. Eur. J.* **2001**, *7*, 5277. (b) Kesanli, B.; Fettinger, J.; Gardner, D. R.; Eichhorn, B. W. *J. Am. Chem. Soc.* **2002**, *124*, 4779. (c) Campbell, J.; Mercier, H. P. A.; Holger, F.; Santry, D.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2002**, *41*, 86. (d) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Eur. J. Inorg. Chem.* **2005**, 3663. (e) Esenturk, E. N.; Fettinger, J.; Eichhorn, B. *Polyhedron* **2006**, *25*, 521. (f) Rios, D.; Sevov, S. C. *Inorg. Chem.* **2010**, *49*, 6396. (g) Downing, D. O.; Zavalij, P.; Eichhorn, B. W. *Eur. J. Inorg. Chem.* **2010**, 890.
- (8) (a) Xu, L.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 9245. (b) Ugrinov, A.; Sevov, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 10990. (c) Ugrinov, A.; Sevov, S. C. *Inorg. Chem.* **2003**, *42*, 5789. (d) Hauptmann, R.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2266. (e) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977. (f) Yong, L.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2004**, *631*, 1149. (g) Suchentrunk, C.; Daniels, J.; Somer, M.; Carrillo-Cabrera, W.; Korber, N. *Z. Naturforsch.* **2005**, *60b*, 277. (h) Nienhaus, A.; Hoffmann, S. D.; Fässler, T. F. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1752.
- (9) (a) Downie, C.; Tang, Z.; Guloy, A. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 338. (b) Downie, C.; Mao, J.-G.; Parmer, H.; Guloy, A. M. *Inorg. Chem.* **2004**, *43*, 1992. (c) Ugrinov, A.; Sevov, S. C. *C. R. Chim.* **2005**, *8*, 1878.
- (10) (a) Esenturk, E. N.; Fettinger, J.; Lam, Y.-F.; Eichhorn, B. *Angew. Chem. Int. Ed.* **2004**, *43*, 2132. (b) Goicoechea, J. M.; Sevov, S. C. *Angew. Chem. Int. Ed.* **2005**, *44*, 4026. (c) Goicoechea, J. M.; Sevov, S. C. *J. Am. Chem. Soc.* **2005**, *127*, 7676. (d) Esenturk, E. N.; Fettinger, J.; Eichhorn, B. W. *Chem. Commun.* **2005**, 247. (e) Goicoechea, J. M.; Sevov, S. C. *J. Am. Chem. Soc.* **2006**, *128*, 4155. (f) Esenturk, E. N.; Fettinger, J.; Eichhorn, B. W. *J. Am. Chem. Soc.* **2006**, *128*, 12. (g) Esenturk, E. N.; Fettinger, J.; Eichhorn, B. W. *J. Am. Chem. Soc.* **2006**, *128*, 9178. (h) Kocak, F. S.; Zavalij, P.; Lam, Y. F.; Eichhorn, B. W. *Inorg. Chem.* **2008**, *47*, 3515. (i) Scharfe, S.; Fässler, T. F.; Stegmaier, S.; Hoffmann, S. D.; Ruhland, K. *Chem. Eur. J.* **2008**, *14*, 4479. (j) Wang, J.-Q.; Stegmaier, S.; Fässler, T. F. *Angew. Chem. Int. Ed.* **2009**, *48*, 1998. (k) Zhou, B.; Denning, M. S.; Kays, D. L.; Goicoechea, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 2802. (l) Wang, J.-Q.; Stegmaier, S.; Wahl, B.; Fässler, T. F. *Chem. Eur. J.* **2010**, *16*, 1793.
- (11) Lips, F.; Dehnen, S. *Angew. Chem. Int. Ed.* **2009**, *48*, 6435; *Angew. Chem.* **2009**, *121*, 6557.
- (12) (a) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627. (b) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2804. (c) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1982**, *21*, 3286. (d) Critchlow, S. C.; Corbett, J. D. *Inorg. Chem.* **1985**, *24*, 979. (e) Xu, L.; Sevov, S. C. *Inorg. Chem.* **2000**, *39*, 5383. (f) Lips, F.; Schellenberg, I.; Pöttgen, R.; Dehnen, S. *Chem. Eur. J.* **2009**, *15*, 12968.