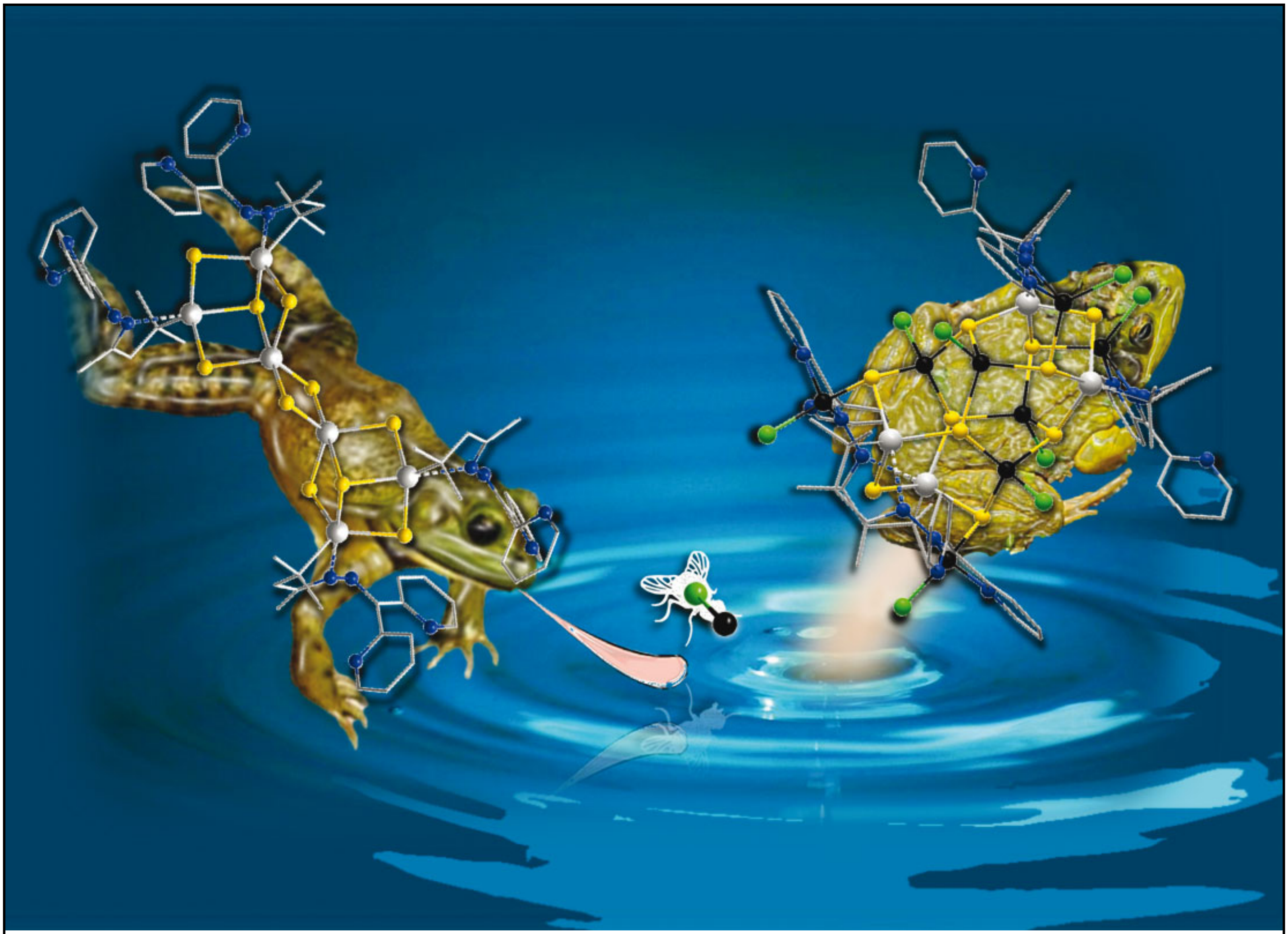
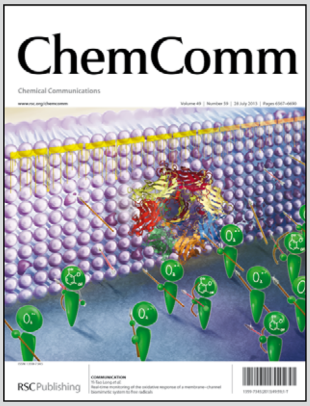


Showcasing research from Stefanie Dehnen's Laboratory/Fachbereich Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität, Marburg, Germany

Towards the installation of transition metal ions on donor ligand decorated tin sulfide clusters

Aiming at transition metal ion capturing on the surface of tetrelchalcogenide clusters, bispyridyl ligands were bonded to an organo-functionalized Sn/S complex. The chelate ligands trapped $[ZnX]^+$ units that were additionally incorporated in the cluster framework. Intermediates were identified by spectroscopy and/or X-ray diffraction to give insight into the formation processes.

As featured in:



ChemComm

Chemical Communications

RSC Publishing

See Stefanie Dehnen *et al.*, *Chem. Commun.*, 2013, **49**, 6590.

RSC Publishing

www.rsc.org/chemcomm

Registered Charity Number 207890

ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Towards the installation of transition metal ions on donor ligand decorated tin sulfide clusters†

Beatrix E. K. Barth, Eliza Leusmann, Klaus Harms and Stefanie Dehnen*

Cite this: *Chem. Commun.*, 2013, **49**, 6590

Received 15th May 2013,
Accepted 1st June 2013

DOI: 10.1039/c3cc43649g

www.rsc.org/chemcomm

Decoration of tetrelchalcogenide T–E clusters with chelating donor ligands was achieved to capture transition metal ions on their surfaces. We demonstrate that by covalent linking of bispyridyl ligands to an Sn–S complex, $[ZnX]^+$ units can be trapped and incorporated into the cluster framework. Intermediates that were identified using spectroscopy and/or X-ray diffraction gave insight into the formation processes.

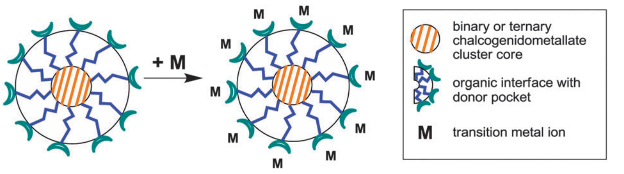
In the search for new compounds with desired properties, chemists and material scientists are continuously developing new connections between different fields of chemistry. One option is to combine inorganic core particles or clusters with functional organic ligand shells. For example, the functionalization of nanoparticles with suitable ligands offered the possibility to capture metal ions, as shown for gold nanoparticles with a shell of bipyridine ligands that produce a phosphorescent nanomaterial upon reaction with Eu(III) or Tb(III) ions.[1] Metals@ligands on inorganic surfaces are also present in photosensitive materials of dye-sensitized solar cells (DSSC);[2] this was achieved, for instance, by connecting terpyridine molecules to a silicon-surface, conversion of the material with Fe(II) ions and addition of a terminal ligand.[3]

Tetrelchalcogenide T–E and related ternary M–T–E systems (M = transition metal, T = tetrel, E = chalcogen) combine diverse structural, (opto-)electronic and magnetic properties to make them attractive for (photo-)catalysis and chemical sensing.[4] Further diversity is achieved by covalently binding organic moieties to these inorganic cores, to additionally include the chemical and physical properties of the organic substituent.

First investigations on organo-functionalized chalcogenidotetrelate cages $[(RT)_xE_y]$ were restricted to unreactive groups like R = Me, Ph, ^{t}Bu, CF_3, C_6F_5, $C(SiMe_3)_3$.[5] Aiming at the introduction of reactivity onto the cluster surfaces, we have recently synthesized species with functionalized ligands R^f, like $[(R^1Sn)_4S_6]$ (**A**; R^1 = CMe_2CH_2COMe), $[(HR^2Ge)_4S_6]$ (HR^2 = C_2H_4COOH) and $[(HR^{2,3}Ge)_4E_5]$ (E = Se, Te; HR^3 = $CH(CH_2COOH)_2$), by reactions of R^fTCl_3 with a chalcogenide source.[6,4e] Terminal keto groups in R^f readily react with hydrazines, leading to the generation of a variety of hybrid clusters, cages or cavitands.[6a,7] Reactions with transition metal compounds served to extend the inorganic core and to form multinary M–T–E clusters with organo-functionalized ligand shells.[6a,7a,b,8] First insight into the coordinating role of donor ligands on the cluster surface was gained *via* the carboxylate-decorated cluster $[(R^2Ge)_4S_6]$, which captured Mn^{2+} ions to generate a hybrid framework.[9a]

Different to the approaches on the micro- or nanoscale quoted above, it has so far not been possible to decorate molecular T–E or M–T–E clusters with chelating donor groups to trap transition metal complexes (Scheme 1). This approach differs from the previously reported synthesis of clusters surrounded by ferrocenyl (Fc) ligands,[8,10] since in that, Fe ions had never been introduced *a posteriori*, but the Fc units were rather installed as a whole. While we intend to eventually attach redox-active or catalytically active metal ions to the clusters, first investigations have been undertaken with redox-insensitive metal ions.

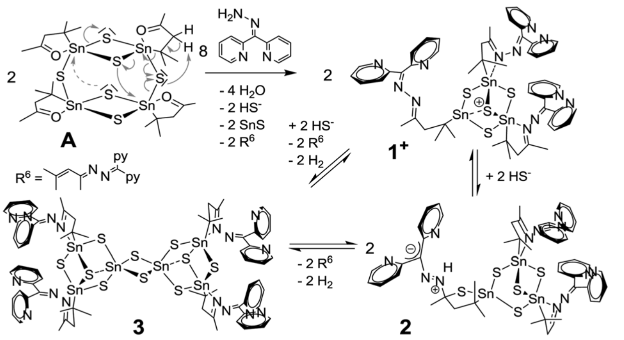
Since the introduction of N-donor chelate ligands in an R^fSnCl_3 precursor is not trivial, we employed condensation reactions of the ketone-functionalized cage **A** and corresponding hydrazine derivatives. Herein we present the first successful results of this approach, by attaching bispyridine ligands to Sn–S clusters.



Scheme 1 Metals@ligands on inorganic clusters with T–E or M–T–E cores (T = tetrel, E = chalcogen, M = transition metal).

Philipps-Universität Marburg, Fachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Hans-Meerwein-Straße, D-35043 Marburg, Germany. E-mail: dehnen@chemie.uni-marburg.de; Fax: +49 6421 2825653; Tel: +49 6421 2825751

† Electronic supplementary information (ESI) available: Details of the syntheses of **1–6**, X-ray diffraction, spectroscopy and spectrometry. CCDC 934166–934170. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc43649g



Scheme 2 Suggested formation of **1**$^+$, **2**, and **3** from **A**, indicating the re-arrangement of relevant electron pairs in the preliminary step; identified by-products are given. The scheme drawings refer to the exact atomic positions in the crystal structures of **A**, **2** and **3b**. For details see ESI;† the structure model of **1**$^+$ represents the most probable connectivity of the atoms within a defect-heterocubane geometry.

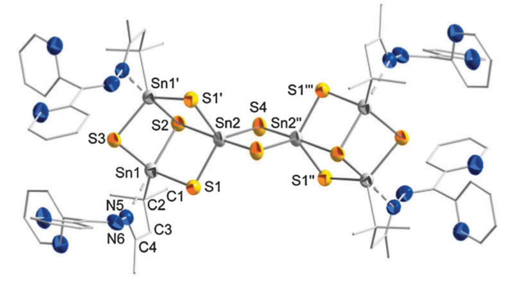


Fig. 1 Molecular structure of the bispyridine-decorated Sn–S cluster in **3b**. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

This led to the formation of the donor ligand-functionalized clusters $[(R^4Sn)_3S_4]^+$ (**1**$^+$, detected in solution) and $[(R^4Sn)_2(R^5SnS)S_4]$ (**2**), the second being obtained as single crystals besides the larger cluster $[(R^4Sn)_4Sn_2S_{10}]$ (**3**), upon layering of the reaction solution ($R^4 = CMe_2CH_2C(Me)NNC(2\text{-py})_2$, $R^5 = CMe_2CH_2C(Me)NHNC(2\text{-py})_2$, py = *o*-$C_5H_4N$). Reaction of **1**$^+$ with ZnX_2 salts proved the trapping capability of the new ligands, accompanied by coordinating sulfide ions of the re-arranged cluster core in the products $[(R^4Sn)_4S_{10}Zn_8X_8]$ (X = Cl, Br, I; **4–6**).

Cation **1**$^+$ was generated by the reaction of **A** with bispyridylhydrazone in CH_2Cl_2 (Scheme 2), as shown using electrospray ionization (ESI†) mass spectrometry of the reaction solution. The mass peak at 1321.0737 *m*/*z* (88% relative abundance) indicated **1**$^+$ to be the predominant species. Defect-heterocubane $[Sn_3E_4]$ scaffolds are common structural motifs in tin chalcogenide chemistry,[6a,7c,9b,c,11] thus the appearance of **1**$^+$ is probably not restricted to ESI-MS conditions. However, an ionic compound with the cationic cluster **1**$^+$ seems to have no crystallization tendency under the given conditions. In contrast, layering of the orange-brown reaction solution with *n*-hexane, or layering of a reaction solution in dioxane–methanol (2 : 1) with *n*-pentane, respectively, yielded crystals of $[(R^4Sn)_2(R^5SnS)S_4]$ (**2**) in small amounts besides triclinic crystals of $[(R^4Sn)_4Sn_2S_{10}]\cdot 5CH_2Cl_2$ (**3**·$5CH_2Cl_2$; **3a**), or monoclinic crystals of $[(R^4Sn)_4Sn_2S_{10}]$·1,4-dioxane·5MeOH (**3**·1,4-dioxane·5MeOH; **3b**), respectively.

Whereas **2** could not be detected by means of ESI-MS in the reaction solution, signals of **3** are found at 18% relative abundance (2150.7861 *m*/*z*) besides **1**$^+$ (88%, Fig. S13, ESI†). However, **1**$^+$ also represents the predominant species (100% relative abundance) in the ESI mass spectrum upon re-dissolving single-crystals of **3** in THF, whereas **3** is only found as a minor component (1%), suggesting an equilibrium between **1** and **3**. The neutral complex **2** (Fig. S16, ESI†) crystallized as heavily twinned crystals (monoclinic space group *C*2/*c*) besides **3a**‡ (see ESI†). **2** represents a derivative of **1**$^+$, by unprecedented expansion of the assumed defect-heterocubane motif of **1**$^+$. **2** might have been formed upon nucleophilic attack by an HS^- anion and transfer of the proton to one of the azine nitrogen atoms produced the zwitterionic organic moiety, which coordinates back to the Sn atom *via* the extra S atom. While this attack could occur at the strongly electrophilic azine C atom or directly at the Sn atom, the formation of the Sn–S moiety is clearly the first step towards the generation of the consecutive products **3** and **4–6** (see below).

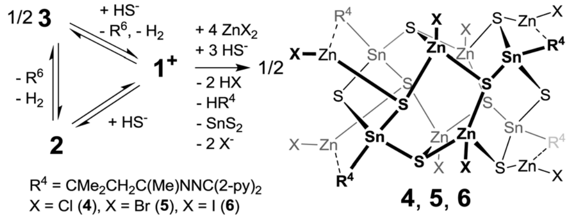
According to single-crystal X-ray diffraction,‡ the molecular structure of **3b** (space group *C*2/*m*, Fig. 1) comprises two (μ-S)$_2$-bridged $[\{(R^4Sn)_2Sn\}S_4]$ defect-heterocubanes. As previously observed in reactions of **A** with other bulky hydrazine derivatives,[6a,7c,d] the inorganic core underwent a re-arrangement into an $[Sn_6S_{10}]$ architecture.

Similar to the findings in the structure of **A**, with intramolecular Lewis acid–base interaction between the heteroatoms of the organic moiety with the parent Sn atom, the ketazine C=N–N=C groups in **3** coordinate back to the organo-substituted Sn atom. Five-membered SnC_3N rings are therefore generated, maintaining the coordination number (c.n.) five at the respective Sn atoms. The pyridine rings are twisted with respect to each other since they remain uncoordinated. The inner Sn_2S_2 ring leads to penta-coordination also at the purely inorganic $[SnS_5]$ units.

Although crystals **3a** or **3b** do not re-dissolve in CH_2Cl_2, ^1H and ^{13}C NMR spectra of the clear reddish-brown reaction solution yielding **3a** or **3b** indicate the presence of several species that point toward equilibria between various Sn–S species. A summary of the processes observed in the synthesis and transformations of the title compounds, which were additionally rationalized by spectroscopic methods (see ESI†), is sketched in Scheme 2.

In order to explore the ion capturing potential of the chelate-ligand decorated clusters **1**$^+$, **2** or **3**, which co-exist in solution as shown in Scheme 2, we have performed reactions with Zn^{2+} ions, which are known to form stable complexes with bispyridine ligands,[12] and which do not react with **A** or its derivatives reported previously.[6,7] Upon layering the reaction mixture that afforded compound **1**$^+$, **2** and **3** with a methanolic solution of ZnX_2 (X = Cl, Br, I), colorless crystals of compounds **4**, (X = Cl), **5** (X = Br) or **6** (X = I), respectively, were obtained within four days (Scheme 3).

Single crystal X-ray diffraction‡ revealed the following formulae, crystal systems and space groups: $[(R^4Sn)_4(Zn_8Cl_8)S_{10}]\cdot 2CHCl_3\cdot 2CH_2Cl_2$



Scheme 3 Formation of **4**, **5**, and **6** from equilibria between **1**$^+$, **2**, and **3**; identified by-products are given.

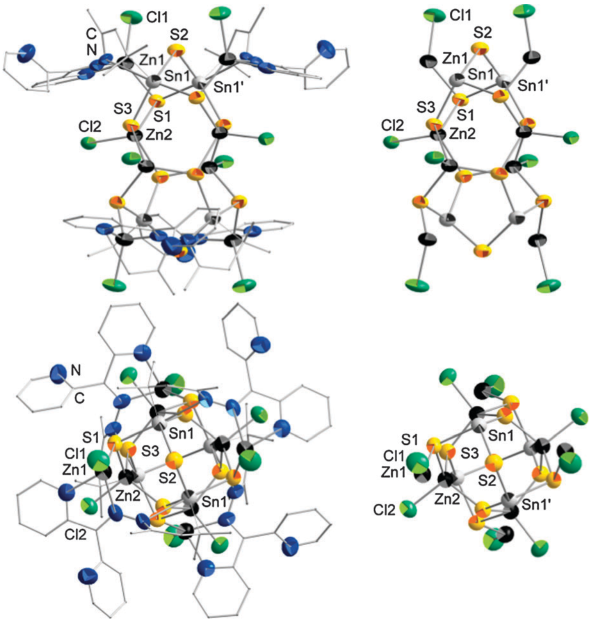


Fig. 2 Side view (top) and top view (bottom) of the molecular structure of **4** as an example for the isostructural motifs found in **4–6** (left hand side). Illustration of the inorganic $[Sn_4Zn_8X_8S_{10}]$ cluster core (right hand side). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

(**4**·$2CHCl_3·2CH_2Cl_2$, tetragonal, $I4_1/a$, Fig. 2), $[(R^4Sn)_4(Zn_8Br_8)S_{10}]$·$CHCl_3·CH_2Cl_2$ (**5**·$CHCl_3·CH_2Cl_2$, triclinic, $P\bar{1}$), and $[(R^4Sn)_4(Zn_8I_8)S_{10}]$·$1.25CHCl_3·0.75MeOH·0.5H_2O$ (**6**·$1.25CHCl_3·0.75MeOH·0.5H_2O$, triclinic, $P\bar{1}$). The discrete cluster cores in **4–6** possess the same topology and idealized D_{2d} symmetry; due to conformational freedom of the non-coordinating pyridine rings, this is reduced in the crystal structures to S_4 symmetry in **4**, and no symmetry (C_1) in **5** and **6**. The central part of the molecules consists of four Sn_2ZnS_3 and four $SnZn_2S_3$ six-membered rings that are annealed, to form a sulfur-capped, cylinder-shaped $[Sn_4Zn_4S_{10}]$ unit, with an inner volume of approximately 1.95 Å^3. Four further Zn atoms and one halide ligand per Zn atom complete an $[Sn_4Zn_8X_8S_{10}]$ inorganic core.

All Sn atoms have three sulfur neighbors and bind to an organic moiety; as in **2**, they show c.n. = 5 due to back-coordination by one of the N atoms of the ketazine group. The Zn atoms are all coordinated by one halide ligand. Four of the Zn atoms are part of the purely inorganic equator of the cluster and have a ZnS_3X coordination environment. The other four Zn atoms are coordinated by one pyridine N-donor atom of one of the two bispyridine ligands attached to the adjacent Sn atoms, and by the second N atom of the ketazine group, resulting in a $ZnSXN_2$ coordination. As for the formation of the equilibrium between compounds **1**$^+$, **2** and **3**, precipitation of insoluble powders indicates the formation of tin sulfide as a by-product during the formation of **4–6**. Based on the observation of a brown powder in the first reaction and an orange-yellow powder in this case, we assign the by-products to the compounds SnS and SnS_2, respectively, which is also in agreement with the spectroscopic findings (see ESI†).

The $[Sn_4Zn_8S_{10}]$ unit of **4–6** differs from all known clusters and frameworks that comprise the same elemental combination. Kanatzidis and co-workers reported P1-type supertetrahedral clusters as part of isostructural frameworks in $K_5ASn[Zn_4Sn_4S_{17}]$ (A = K, Rb, Cs),[13] and as discrete anions in $K_{10}Zn_4Sn_4S_{17}$.[14] Discrete T3-type supertetrahedral anions are present in $[Na_{10}(H_2O)_{32}][Zn_5Sn_5S_{20}]$.[15] In contrast to these supertetrahedra, which are based on barrelane-type or adamantane-type motifs, the structural condensation of six-membered rings is different in **4–6**. Besides the fact that the Zn^{2+} ions also contribute to the inorganic cluster core in **4–6**, these compounds are the first ones to demonstrate a successful trapping of metal ions by a terminal organic ligand on a semi-metal cluster surface. Thereby, they clearly point toward the possibility to form further examples of metals@ligands on inorganic clusters with T–E or M–T–E cores.

Notes and references

‡ X-ray crystallographic data: Data collection on a STOE IPDS2 diffractometer using graphite-monochromatized Mo K_α radiation (λ = 0.71073 Å) at 100 K. Structure solution and refinement by direct methods and full-matrix least-squares on F^2, respectively; SHELXTL software.[16] The crystallographic data are provided in the ESI.†

1 B. I. Ipe, K. Yoosaf and K. G. Thomas, *J. Am. Chem. Soc.*, 2006, **128**, 1907.
2 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
3 H. Maeda, R. Sakamoto, Y. Nishimori, J. Sendo, F. Toshimitsu, Y. Yamanoi and H. Nishihara, *Chem. Commun.*, 2011, **47**, 8644.
4 (*a*) P. Feng, X. Bu and N. Zheng, *Acc. Chem. Res.*, 2005, **38**, 293; (*b*) M. G. Kanatzidis, *Adv. Mater.*, 2007, **19**, 1165; (*c*) D. G. MacDonald and J. F. Corrigan, *Philos. Trans. R. Soc., A*, 2010, **368**, 1455; (*d*) S. Dehnen and M. Melullis, *Coord. Chem. Rev.*, 2007, **251**, 1259; (*e*) J. Heine and S. Dehnen, *Z. Anorg. Allg. Chem.*, 2012, **638**, 2425.
5 (*a*) C. Dörfelt, A. Janeck, D. Kobelt, E. F. Paulus and H. Scherer, *J. Organomet. Chem.*, 1968, **14**, P22; (*b*) H. Berwe and A. Haas, *Chem. Ber.*, 1987, **120**, 1175.
6 (*a*) Z. H. Fard, L. Xiong, C. Müller, M. Hołyńska and S. Dehnen, *Chem.–Eur. J.*, 2009, **15**, 6595; (*b*) Z. H. Fard, C. Müller, T. Harmening, R. Pöttgen and S. Dehnen, *Angew. Chem., Int. Ed.*, 2009, **48**, 4441; (*c*) S. Heimann, M. Hołyńska and S. Dehnen, *Chem. Commun.*, 2011, **47**, 1881.
7 (*a*) M. R. Halvagar, Z. H. Fard, L. Xiong and S. Dehnen, *Inorg. Chem.*, 2009, **48**, 7373; (*b*) M. R. Halvagar, Z. H. Fard and S. Dehnen, *Chem. Commun.*, 2010, **46**, 4716; (*c*) Z. H. Fard, M. R. Halvagar and S. Dehnen, *J. Am. Chem. Soc.*, 2010, **132**, 2848; (*d*) M. R. Halvagar, Z. H. Fard and S. Dehnen, *Chem.–Eur. J.*, 2011, **17**, 4371.
8 C. Pöhlker, I. Schellenberg, R. Pöttgen and S. Dehnen, *Chem. Commun.*, 2010, **46**, 2605.
9 (*a*) Z. H. Fard, R. Clérac and S. Dehnen, *Chem.–Eur. J.*, 2010, **16**, 2050; (*b*) C. Zimmermann, C. E. Anson and S. Dehnen, *J. Cluster Sci.*, 2007, **18**, 618; (*c*) Z. H. Fard, M. Hołyńska and S. Dehnen, *Inorg. Chem.*, 2010, **49**, 5748–5752.
10 (*a*) S. Ahmar, D. G. MacDonald, N. Vijayaratnam, T. L. Battista, M. S. Workentin and J. F. Corrigan, *Angew. Chem., Int. Ed.*, 2010, **49**, 4422; (*b*) D. G. MacDonald, C. Kübel and J. F. Corrigan, *Inorg. Chem.*, 2011, **50**, 3252; (*c*) D. G. MacDonald, A. Eichhöfer, C. F. Campana and J. F. Corrigan, *Chem.–Eur. J.*, 2011, **17**, 5890; (*d*) A. I. Wallbank, A. Borecki, N. J. Taylor and J. F. Corrigan, *Organometallics*, 2005, **24**, 788.
11 (*a*) W. S. Sheldrick, *Z. Anorg. Allg. Chem.*, 1988, **562**, 23; (*b*) W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch., B*, 1990, **46**, 1643; (*c*) K. Merzweiler and L. Weisse, *Z. Naturforsch., B*, 1990, **46**, 971; (*d*) K. Merzweiler and H. Kraus, *Z. Naturforsch., B*, 1993, **48**, 1009; (*e*) C. Wagner, R. Hauser and K. Merzweiler, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2001, **168**, 191.
12 (*a*) R. Sharma and D. Rawat, *J. Inorg. Organomet. Polym.*, 2011, **21**, 619; (*b*) B. F. Abrahams, T. A. Hudson and R. Robson, *Chem.–Eur. J.*, 2006, **12**, 7095; (*c*) C.-Y. Wong, G. S. M. Tong, C.-M. Che and N. Zhu, *Angew. Chem., Int. Ed.*, 2006, **45**, 2694; (*d*) P. J. Steel and C. J. Sumby, *Dalton Trans.*, 2003, 4505; (*e*) E. Katsoulakou, N. Lalioti, C. P. Raptopoulou, A. Terzis, E. Manessi-Zoupa and S. P. Perlepes, *Inorg. Chem. Commun.*, 2002, **5**, 719.
13 M. J. Manos, R. G. Iyer, E. Quarez, J. H. Liao and M. G. Kanatzidis, *Angew. Chem., Int. Ed.*, 2005, **44**, 3552.
14 (*a*) O. Palchik, R. G. Iyer, C. G. Canlas, D. P. Weliky and M. G. Kanatzidis, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2237; (*b*) O. Palchik, R. G. Iyer, J. H. Liao and M. G. Kanatzidis, *Inorg. Chem.*, 2003, **42**, 5052.
15 C. Zimmermann, C. E. Anson, F. Weigend, R. Clérac and S. Dehnen, *Inorg. Chem.*, 2005, **44**, 5686.
16 (*a*) G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112; (*b*) G. M. Sheldrick, *SHELXL-2013*, University of Göttingen, Germany, 2013.