



## Developing organo-Zintl deltahedral clusters as ligands for coordination to transition-metals via their organic tethers

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### ABSTRACT

Deltahedral Zintl ions  $\text{Ge}_n^{4-}$  are disubstituted with organic fragments that have various functional groups. Some of the latter are appropriate for coordination to transition-metals to eventually form coordination compounds where the organo-Zintl species act as ligands. Examples of  $[\text{Ge}_9\text{R}_2]^{2-}$  include  $\text{R} = -\text{CH}=\text{CH}-\text{Im}(\text{Me})$ ,  $-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OMe}$ ,  $-\text{CH}=\text{CH}-\text{Fc}$ ,  $-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{C}\equiv\text{CH}$ ,  $-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$ ,  $\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NH}_2$ ,  $\text{CH}=\text{CH}-\text{Py}$ ,  $-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{C}\equiv\text{N}$ ,  $-\text{CH}=\text{CHCH}(\text{OEt})_2$ ,  $-\text{C}(\text{CH}_3)_2\text{C}\equiv\text{CH}$ . Furthermore, the reported coexistence of  $[\text{Fe}(\text{en})_3]^{2+}$  and  $[\text{Ge}_9-(\text{CH}=\text{CH}-\text{Fc})_2]^{2-}$  in the structure of  $[\text{Fe}(\text{en})_3][\text{Ge}_9-(\text{CH}=\text{CH}-\text{Fc})_2]\cdot 3.5\text{en}$  shows that some transition metals in 2 + oxidation state may not oxidize the disubstituted clusters and could potentially coordinate to them.

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### 1. Introduction

The resurgence of Zintl chemistry over the last decade has been documented at several points [1]. The sheer volume of new cluster structures reported in such a highly-focused—and somewhat eclectic—field is impressive. As the discipline has matured, the discoveries have coalesced into several sub-categories, namely: intermetallic- [2], organometallic- [3], and organo-Zintl [3b,4] cluster chemistry.

From a historical perspective, the emergence of any one of these sub-fields is rather exceptional, as Zintl chemistry was long considered the sole purview of solid-state chemists. Reinforcing this notion was the belief that Zintl clusters were too reducing to be compatible with more mainstream types of chemistry. The latter belief follows from the Zintl-Klemm concept which views the bonding in these species as involving the complete transfer of electrons from the most electropositive metal (usually alkali or alkaline-earth) to the relatively electropositive main-group element (metal, metalloid, or non-metal) [5]. As a result, these species appear highly reduced, and are therefore assumed to be strong reducing agents.

This assumption has been evident as progress has been made in intermetallic Zintl chemistry. A wide array of structures and reactivity

patterns have emerged. (1) The Zintl cluster can act as a simple Lewis base coordinating to d-block metal, as seen in  $[\text{HgGe}_9]^{2-}$  [6],  $[\text{Hg}_3(\text{Ge}_9)_4]^{10-}$  [7],  $[\text{Au}_3(\text{Ge}_9)_2]^{5-}$  [8], and  $[\text{Ge}_{10}\text{Mn}(\text{CO})_4]^{3-}$  [3a]. (2) The Zintl clusters can be capped by a metal or an organometallic-metal fragment as in  $[\text{E}_9\text{M}(\text{CO})_3]^{3-}$  (where  $E = \text{Sn, Pb}$ ;  $M = \text{Cr, Mo, W}$ ) [9],  $[\text{E}_9\text{M-R}]^{3-}$  (where  $E = \text{Si, Ge, Sn, Pb}$ ;  $M = \text{Zn, Cd}$ ;  $R = \text{Ph, Mes, }^i\text{Pr}$ ) [3c–e],  $[\text{Ge}_9\text{Ni}(\text{CO})]^{3-}$  [3f], and  $[\text{E}_9\text{Ti}]^{3-}$  (where  $E = \text{Ge, Sn}$ ) [2d]. (3) The clusters can encapsulate transition metals of which there are several examples:  $[\text{Ni}@\text{Ge}_9]^{3-}$  [3f],  $[\text{Cu}@\text{E}_9]^{3-}$  (where  $E = \text{Sn, Pb}$ ) [2e]  $[\text{Ni}@\text{Pb}_{10}]^{2-}$  [10],  $[\text{M}@\text{Ge}_{10}]^{3-}$  (where  $M = \text{Co, Fe}$ ) [2f, g, i], as well as  $[\text{M}@\text{Pb}_{12}]^{2-}$  (where  $M = \text{Ni, Pd, Pt}$ ) [11], and  $[\text{Ir}@\text{Sn}_{12}]^{3-}$  [12]. (4) Some of the most dramatic examples include cage expansion and/or other more complex bonding motifs like  $[\text{Ni}@\text{Ge}_9\text{Ni}(\text{CO})]^{2-}$  [3f],  $[\text{Ni}@\text{Ge}_9\text{-Ni}(\text{PPh}_3)_2]^{2-}$  [13],  $[(\text{Pd}-\text{Pd})@\text{Ge}_{18}]^{4-}$  [14],  $[(\text{Pd}-\text{Pd})@\text{Sn}_{18}]^{4-}$  [15],  $[\text{Ni}_3@\text{Ge}_9]^{4-}$  [16], and  $[\text{M}_2@\text{Sn}_{17}]^{4-}$  (where  $M = \text{Ni, Pt}$ ) [2h,17].

What is notable about the synthesis of most of these clusters is that they use metals in 0 or 1 + oxidation states, e.g.  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  [3f,13],  $(\text{C}_6\text{H}_6)\text{Mo}(\text{CO})_3$  [9],  $\text{Pt}(\text{PPh}_3)_4$  [11],  $\text{Mn}_2(\text{CO})_{10}$  [3a],  $\text{Co}(\text{C}_8\text{H}_{12})(\text{C}_8\text{H}_{13})$  [2g,i],  $[\text{IrCl}(\text{cod})_2]$  [12], and  $(\text{Ph}_3\text{P})\text{AuCl}$  [18]. This approach is a subtle reflection of the Zintl clusters' behaviour as strong reducing agents. Noteworthy transition-metal exceptions are  $\text{Fe}^{\text{II}}\text{Ar}_2$  (where  $\text{Ar} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ ) [2f] and  $\text{Mn}^{\text{II}}_3(\text{Mes})_6$  [19], both by Goicoechea and co-workers. It should be noted that these metals are parts of organometallic compounds and are, therefore, divalent only in the formal sense. There are currently no Zintl clusters involved in complexes with true divalent metal cations of the Werner-type.

In contrast, we have recently demonstrated that Zintl clusters disubstituted with organic fragments—referred to as organo-Zintl

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clusters—are significantly more robust towards oxidation than previously anticipated. By exchanging the alkali metal counterions (present from the solid-state precursors) with tetraalkyl ammonium cations, these dianionic organo-Zintl clusters can be readily dissolved in conventional organic solvents such as benzene, toluene, ether, THF, etc. [4c]. Moreover, we have shown that the organo-Zintl clusters are compatible with water. The latter has been exploited to demonstrate that the organic substituents are capable of undergoing secondary organic transformations without any negative impact upon the cluster [20]. These discoveries are both unexpected and synthetically useful. One of our goals is to be able to use these organo-Zintl clusters as ligands for coordination to divalent transition metals via their organic tethers, thus forming neutral yet Zwitterionic complexes. To that end, we report herein the development of organo-Zintl clusters with organic substituents with coordinating functional groups. Moreover, crystallographic evidence demonstrates that the organo-Zintl clusters are compatible with Werner-type complexes of some divalent transition metals, specifically with  $\text{Fe}^{2+}$  in this case.

## 2. Experimental

### 2.1. General information and materials

#### 2.1.1. Materials

All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (en, Alfa Aesar, 99%) was distilled over sodium metal and stored in a gastight ampoule under nitrogen. 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane, Acros, 99%) and 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane, Acros, 98%) were used as received after careful drying under vacuum.  $\text{K}_4\text{Ge}_9$  was synthesized by heating a stoichiometric mixture of the elements (K: 99+%, Strem; Ge: 99.999%, Alfa Aesar) at 900 °C for 2 days in sealed niobium containers jacketed in evacuated fused-silica ampoules according to previously reported synthetic procedures [21].  $\text{ClC}(\text{CH}_3)_2\text{-C}\equiv\text{C-H}$  (3-chloro-3-methyl-1-butyne, Alfa Aesar, 97%),  $(3\text{-H}_2\text{NC}_6\text{H}_4)\text{C}\equiv\text{CH}$  (3-aminophenylacetylene, Acros, 98%),  $\text{HC}\equiv\text{C}(\text{CH}_2)_4\text{C}\equiv\text{CH}$  (1,7-octadiyne, Acros, 99%),  $\text{HC}\equiv\text{C}(\text{CH}_2)_3\text{C}\equiv\text{N}$  (5-hexynenitrile, Acros, 98%),  $(\text{EtO})_2\text{CHC}\equiv\text{CH}$  (propargylaldehyde diethyl acetal, Acros, 98%),  $\text{HC}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CH}$  (1,4-diethynylbenzene, Aldrich, 96%),  $\text{Me}_3\text{Si-C}\equiv\text{C-Im-CH}_3$  (5-[(trimethylsilyl)ethynyl]-1-methylimidazole, Aldrich, 99%), and  $(2\text{-C}_5\text{H}_4\text{N})\text{C}\equiv\text{CH}$  (2-ethynylpyridine, Aldrich, 98%) were all used as received.

#### 2.1.2. Mass spectrometry

Electrospray mass spectra were recorded from ethylenediamine solutions (0.03–0.4 M) on a Micromass Quattro-LC triple quadrupole mass spectrometer (100 °C source temperature, 125 °C desolvation temperature, 2.5 kV capillary voltage, and a 30 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 10  $\mu\text{L}/\text{min}$ . Spectra were taken in the negative-ion mode.

#### 2.1.3. NMR spectroscopy

Deuterated pyridine (Cambridge Isotope Labs, 99.9%) was stored over molecular sieves.  $^1\text{H}$  NMR spectra were recorded on a Varian 300 MHz spectrometer, locked on the deuterium signal of the deuterated pyridine, and referenced against the farthest downfield peak of the solvent residuals.

#### 2.1.4. Structure determination

Single-crystal X-ray diffraction data were collected on a Bruker X8 APEX-II diffractometer with a CCD area detector at 100 K with  $\text{Mo-K}\alpha$  radiation. All crystals were selected under Paratone-N oil,

mounted on fibres, and positioned in the cold stream of the diffractometer. The structures were solved and refined (on  $F^2$ ) with the aid of the SHELXTL V6.2 package [22].

### 2.2. Synthesis

#### 2.2.1. General method for organo-Zintl cluster synthesis

A general procedure, applicable for synthesizing  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-R})_2]^{2-}$  cluster anions where R = coordinating ligand, is described next.  $\text{K}_4\text{Ge}_9$  (close to 0.1 mmol) is dissolved in approximately 2 mL of ethylenediamine in a test tube with a magnetic stir bar. The appropriate alkyne ( $\text{H-C}\equiv\text{C-R}$ , 0.4 mmol) is then added dropwise slowly. (The use of excess alkyne ensures that the disubstituted cluster is isolated as the predominant product.) The reaction mixture is then stirred for 4 h, centrifuged, decanted, and filtered through a glass wool filter pipette. The potassium cations can then be either sequestered with 18-crown-6 or 2,2,2-crypt or exchanged for tetraalkyl ammonium cations.

#### 2.2.2. Synthesis of $[\text{K-crypt}]_3[\text{Ge}_9\text{-CH=CH-Ph-OMe}] \bullet 3.5\text{en}$ (1)

$\text{K}_4\text{Ge}_9$  (0.095 g, 0.117 mmol) was dissolved in ethylenediamine (2.0 mL) by stirring.  $\text{HC}\equiv\text{C-Ph-OMe}$  (0.016 g, 0.121 mmol) was dissolved in toluene (0.20 mL) and then added to this solution and stirred for 5 min. 2,2,2-crypt (0.155 g, 0.412 mmol) was dissolved in toluene (8 mL). The reaction mixture was filtered into a test tube, layered with the toluene/crypt solution, and left for crystallization. A single crystal suitable for X-ray diffraction studies was selected after approximately two weeks. ES-MS (en):  $m/z$  786  $[\text{Ge}_9\text{-CH=CH-Ph-OMe}]^-$ , 825  $\{[\text{K}^+][\text{Ge}_9\text{-CH=CH-Ph-OMe}]^{2-}\}^-$ , 919  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Ph-OMe})_2]^-$ , 958  $\{[\text{K}^+][\text{Ge}_9\text{-}(\text{CH}=\text{CH-Ph-OMe})_2]^{2-}\}^-$ .

#### 2.2.3. Synthesis of $[\text{K-crown}]_2[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ (2)

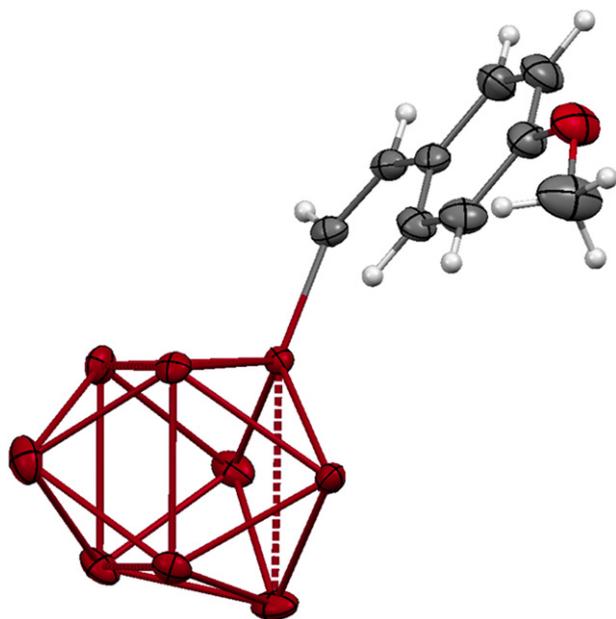
$\text{K}_4\text{Ge}_9$  (0.080 g, 0.099 mmol) was dissolved in 1.5 mL of ethylenediamine (red solution) in a test tube inside the glovebox.  $\text{Me}_3\text{Si-C}\equiv\text{C-Im-CH}_3$  (0.059 g, 0.33 mmol) was added and the reaction mixture was stirred for 4 h. The solution was centrifuged, filtered, and layered with a toluene solution (8 mL) of 18-crown-6 (0.198 g, 0.75 mmol). After diffusion, some red oil was isolated at the bottom of the test tube and dried under vacuum.  $^1\text{H}$  NMR ( $d_5$ -pyridine):  $\delta$  9.41 (s,  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ ), 7.50 (d, 14 Hz,  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ ), 7.48 (s,  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ ), 6.96 (d, 14 Hz,  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ ), 3.56 (s, crown), 3.16 (s,  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]$ ), 2.75 (s,  $-\text{CH}_2-$ , en), 2.23 (s,  $-\text{CH}_3$ , tol), 1.48 (br,  $-\text{NH}_2$  in en). ES-MS (pyridine, negative-ion mode):  $m/z$  = 867  $[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]^-$ , 906  $\{(\text{K}^+)[\text{Ge}_9\text{-}(\text{CH}=\text{CH-Im-CH}_3)_2]^{2-}\}^-$ .

#### 2.2.4. Synthesis of $[\text{Fe}(\text{en})_3][\text{Ge}_9\text{-}(\text{CH}=\text{CH-Fc})_2] \bullet 3.5\text{en}$ (3)

$\text{K}_4\text{Ge}_9$  (0.085 g, 0.105 mmol) was dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside the glovebox.  $\text{Fc-C}\equiv\text{CH}$  (0.052 g, 0.248 mmol) was added and the reaction mixture was stirred for 4 h. Separately,  $[\text{Fc}][\text{BF}_4]$  (0.136 g, 0.498 mmol) and  $\text{NaBPh}_4$  (0.186 g, 0.544 mmol) were each dissolved in 5 mL of THF and the solutions combined. The resulting  $\text{NaBF}_4$  was isolated by centrifuging, and the solution pumped down to isolate the  $[\text{Fc}][\text{BPh}_4]$ .  $[\text{Fc}][\text{BPh}_4]$  (0.060 g, 0.118 mmol) was added to the cluster solution from above. After stirring, the solution was filtered and layered with toluene (8 mL). After diffusion small black crystals were isolated and examined by X-ray diffraction.

### 2.3. Crystallographic data

Single-crystal X-ray diffraction data sets were collected on single crystals of  $[\text{K-crypt}]_3[\text{Ge}_9\text{-CH=CH-C}_6\text{H}_4\text{-OCH}_3]$  and  $[\text{Fe}(\text{en})_3][\text{Ge}_9\text{-}(\text{CH}=\text{CH-Fc})_2] \bullet 3.5\text{en}$ . Crystal data:  $[\text{K-crypt}]_3[\text{Ge}_9\text{-CH=CH-C}_6\text{H}_4\text{-OCH}_3] \bullet 3.5\text{en}$  - triclinic, P-1,  $a = 13.5808(9)$ ,



**Fig. 1.** Thermal ellipsoid plot of  $[\text{Ge}_9\text{-(CH=CH-C}_6\text{H}_4\text{-OCH}_3\text{)}]^{3-}$  (**1**) (ellipsoids shown at 33% probability).

$b = 15.0326(8)$ , and  $c = 25.5113(17)$  Å,  $\alpha = 77.190$ ,  $\beta = 83.352$ , and  $\gamma = 74.858(2)$ ,  $V = 4893.0(5)$  Å<sup>3</sup>,  $Z = 1$ ,  $R1/wR2 = 5.85/16.3\%$  for the observed data ( $I \geq 2\sigma_1$ ),  $R1/wR2 = 7.28/17.9\%$  for all data;  $[\text{Fe}(\text{en})_3][\text{Ge}_9\text{-(CH=CH-Fc)}_2] \cdot 3.5\text{en}$  - monoclinic,  $P2_1/n$ ,  $a = 13.0302(14)$ ,  $b = 15.0660(3)$ , and  $c = 47.9850(10)$  Å,  $\beta = 96.916(14)^\circ$ ,  $V = 9352.54(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $R1/wR2 = 3.84/9.4\%$  for the observed data ( $I \geq 2\sigma_1$ ),  $R1/wR2 = 5.2/10.6\%$  for all data. Further details of the crystal structures investigations are available free upon request from the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk); or [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html)) upon quoting depository numbers CCDC 877514 and 877515.

### 3. Results and discussion

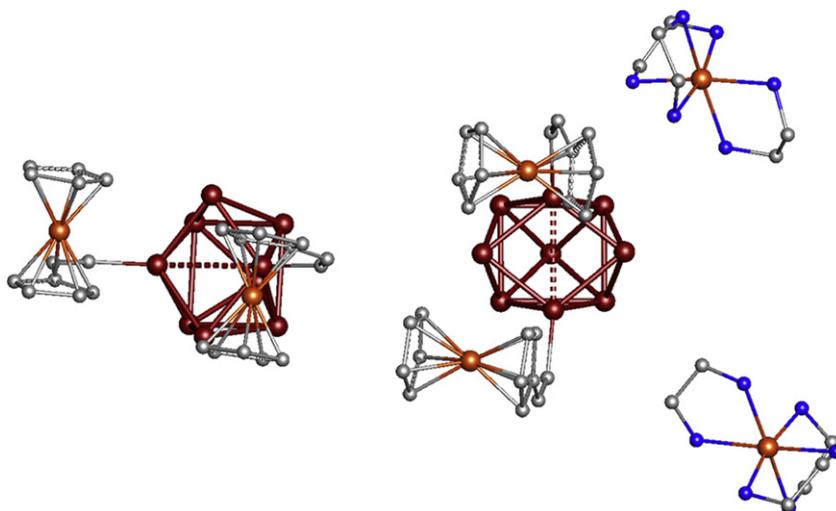
The reaction of  $\text{K}_4\text{Ge}_9$  with 4-ethynylanisole results in mono- and disubstituted clusters. As has been previously reported, the alkynes

undergo a nucleophilic addition reaction with the Zintl cluster, resulting in a reduction of the alkyne to an alkene and functionalization of the cluster. Previous studies have shown that the degree of functionalization (mono- versus di-) is stoichiometrically controlled. The electrospray mass spectrum of the reaction mixture of 4-ethynylanisole with  $\text{K}_4\text{Ge}_9$  in ethylenediamine (Figure S1) shows both the mono- and disubstituted product. Attempts to crystallize the disubstituted product only resulted in a red oil. When the reaction was run in a 1:1 ratio, a few small crystals of the monosubstituted product  $[\text{K-crypt}]_3[\text{Ge}_9\text{-CH=CH-C}_6\text{H}_4\text{-OCH}_3] \cdot 3.5\text{en}$  (**1**) were isolated and structurally characterized.

The nine-atom cluster in  $[\text{K-crypt}]_3[\text{Ge}_9\text{-CH=CH-C}_6\text{H}_4\text{-OCH}_3] \cdot 3.5\text{en}$  (**1**) exhibits the common tricapped trigonal prismatic geometry with one significantly elongate edge (Fig. 1). The latter distance is 3.387(3) Å in contrast to 2.765(4) and 2.780(6) Å for the other two edges of the prism. These distances compare well with those seen in  $[\text{Ge}_9\text{-(C}_5\text{H}_9\text{)}]^{3-}$  [**4e**], where the elongated edge has a distance of 3.349(2) Å, and 2.753(6) and 2.778(3) Å for the shorter two edges. In general, the elongated edge in organo-Zintl clusters is significantly longer for monosubstituted than disubstituted species. For example, in  $[\text{Ge}_9\text{-(CH=CH}_2\text{)}_2]^{2-}$ ,  $[\text{Ge}_9\text{-(CH=CH-CH}_2\text{NH}_2\text{)}_2]^{2-}$ , and  $[\text{Ge}_9\text{-(CH}_2\text{CH(CH}_2\text{)}_2\text{)}_2]^{2-}$  the elongated edge is 3.0950(3), 3.162, and 3.1127(4) Å, respectively, in contrast to the monosubstituted examples cited above. The Ge–C bond length in (**1**) is 1.984(7) Å which is similar to other monosubstituted organo-Zintl clusters such as  $[\text{Ge}_9\text{-(C}_5\text{H}_9\text{)}]^{3-}$  – 2.05(1) Å [**4e**],  $[\text{Sn}_8\text{Ge}_9\text{-(CH=CH}_2\text{)}]^{3-}$  – 1.974(6) Å, and  $[\text{Sn}_8\text{Ge}_1\text{-(CH=CH-CH(CH}_2\text{)}_2\text{)}]^{3-}$  – 2.019(9) Å [**4g**].

The crystal structure of  $[\text{Fe}(\text{en})_3][\text{Ge}_9\text{-(CH=CH-Fc)}_2] \cdot 3.5\text{en}$  (**3**) has two crystallographically unique clusters in the unit cell (Fig. 2). The diferrocenyl cluster has been reported previously [**4b**], and three prior structures (with varying counter-cation sequestering agents and co-solvents) have been characterized. The geometric parameters of the diferrocenyl substituted cluster in this structure are nearly identical to the previously reported structures. Like the  $[\text{Ge}_9\text{-CH=CH-C}_6\text{H}_4\text{-OCH}_3]^{3-}$  (**1**) structure above, the clusters are tricapped trigonal prisms with one elongated—though less so—edge. The elongated edges in the two crystallographically different clusters are 3.1374(16) and 3.1292(17) Å. The Ge–C distances are 1.950(9), 1.942(10), 1.967(10), and 1.958(13) Å—in strong agreement with the precedence.

There are two ferrocenyl-substituted clusters in the unit cell. In one of them, one of the ferrocenyl substituents is split over two crystallographic positions occupied in an 83:17 ratio (the same



**Fig. 2.** Unit cell of  $[\text{Fe}(\text{en})_3][\text{Ge}_9\text{-(CH=CH-Fc)}_2] \cdot 3.5\text{en}$  (**3**) showing two crystallographically unique  $[\text{Ge}_9\text{-(CH=CH-Fc)}_2]^{2-}$  clusters and two  $[\text{Fe}(\text{en})_3]^{2+}$  complexes (ethylenediamine solvent molecules removed for clarity).

disorder has been observed in previous structures). In one of the clusters, the two ferrocenyl groups point in the same direction (Fig. 3a) while in the second one they point in opposite directions (Fig. 3b). These variations have been observed before in different crystal structures but never within the same crystal structure. The different positioning of the substituents indicates free rotation around the Ge–C bonds in solution, and this is confirmed by the observed NMR spectra [4b]. In spite of the various orientations, however, the ferrocenyl substituents in all these structures are always offset in such a way that the cyclopentadienyl ring of one ferrocene can interdigitate with the iron centre of the other ferrocene. This is necessary, as evidenced by the space-filling diagram (Figure S2), to alleviate the steric strain.

It should be pointed out that when the ferrocenyl substituents point in opposite directions, the resulting ensemble exhibits axial chirality since its mirror image is non-superimposable as shown in Fig. 4 for the geometries found in two different structures. Although lacking an actual stereogenic carbon, this demonstrates the possibility of using the cluster backbone for building chiral ligands and thus chiral organometallic compounds, perhaps some with catalytic activity. This is very similar to the well-known chiral ligand and its derivatives, namely 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), where the steric bulk induces atropisomerism between the conformers. This chirality has been successfully and extensively employed in the BINAP ligand system.  $[\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]^{2-}$  and analogous disubstituted compounds exhibit similar geometric parameters—given the additional steric bulk—on which one could eventually build a chiral ligand scaffold [23,24].

As was noted in the introduction, it has been a long standing assumption that the deltahedral Zintl ions are too reducing to be compatible with oxidized transition metals. Nearly all of the intermetallic Zintl clusters characterized to date have been synthesized using zero- or mono-valent metals, and no structures with truly divalent transition metals have been characterized to date. In the exceptions noted above, namely organometallic precursors with Mn (II) [19], Fe (II) [2f], Zn (II) (3d,e), Cd (II) [3c], and Hg (II) [6,7] (the latter three being post-transition metals) the oxidation states of the metals are only formal designations given their organometallic nature. In fact, as Goicoechea recently commented [19], the majority of structures involve zerovalent,  $d^{10}$  metals, as in  $[\text{M}@\text{Pb}_{12}]^{2-}$  (where M = Ni(0), Pd(0), or Pt(0)) or  $[\text{Ni}@\text{Ge}_9]^{3-}$ . The corresponding electron counts are consistent with the Wade-Mingos rules for these *closo*-clusters [25]. In the more dramatic case of  $[\text{Ir}@\text{Sn}_{12}]^{3-}$ , where Ir is reported to be in the

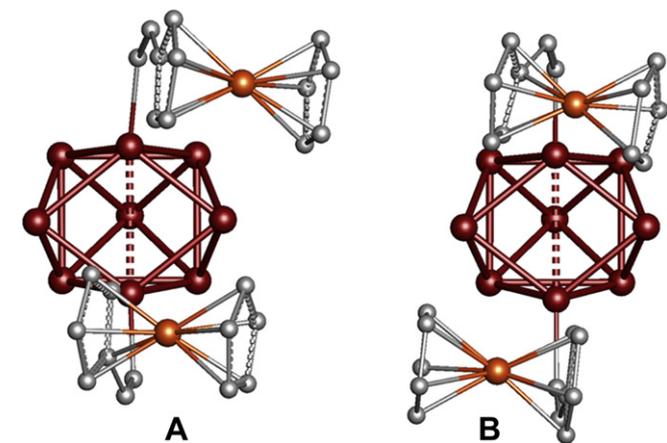


Fig. 3. Two orientations of the  $[\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]^{2-}$  clusters in the unit cell of  $[\text{Fe}(\text{en})_3][\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]$  (3) showing (A) The ferrocenyl groups pointing the same direction and (B) The ferrocenyl groups pointing opposite directions.

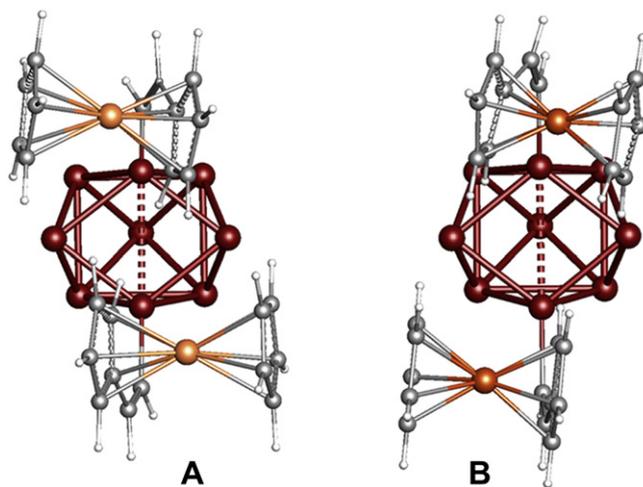


Fig. 4. Structure of  $[\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]^{2-}$  clusters in the solid-state showing the two non-superimposable conformers of the ferrocenyl substituents: (A)  $[\text{K}-(18\text{-crown-}6)]_2[\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]\cdot 2\text{en}$  and (B)  $[\text{Fe}(\text{en})_3][\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]\cdot 3.5\text{en}$ .

1- oxidation state, the transition-metal still has a closed-shell,  $d^{10}$  configuration [12].

In stark contrast to this, we report here for the first time, that a Zintl cluster can coexist with a cationic transition-metal complex,  $[\text{Fe}(\text{en})_3]^{2+}$ . The tris(ethylenediamine) iron (II) complex is a classical Werner complex, i.e. it is not notable for its structure by any means. What is notable is its compatibility with a dianionic organo-Zintl cluster. The compatibility of any pair of a Zintl cluster and a transition-metal complex will ultimately depend upon the reduction potentials of the two which, in turn, will be affected by the metal and the ligands. Nevertheless, this is the first example of an unambiguous divalent transition-metal coexisting with a Zintl cluster. This is a promising result, suggesting other combinations may follow.

The synthesis of  $[\text{Fe}(\text{en})_3][\text{Ge}_9(\text{CH}=\text{CH}-\text{Fc})_2]$  was quite divergent. In our pursuit of functional materials for electrochemistry, we sought to isolate a complex with both ferrocene and ferrocenium. The ligands in  $[\text{Fe}(\text{en})_3]^{2+}$  clearly came from the ethylenediamine solvent used in the reaction while the (probable) decomposition of ferrocenium  $[\text{Fc}]^+$  to  $[\text{Fe}(\text{en})_3]^{2+}$  may have been accelerated by the presence of the potassium amide formed by deprotonation of the solvent during the nucleophilic addition of clusters to the alkyne and/or unreacted  $\text{Ge}_9^{4-}$  or  $\text{Ge}_9^{3-}$ . The use of a non-coordinating solvent may eclipse this interference in the future. Investigations

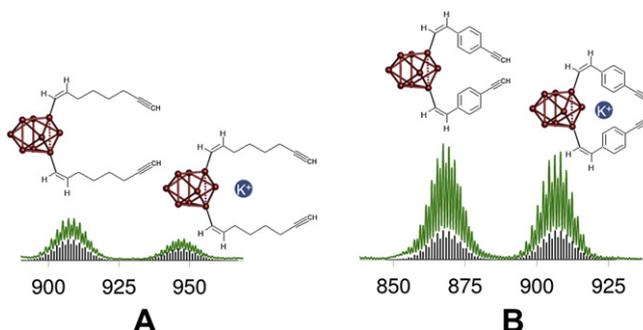
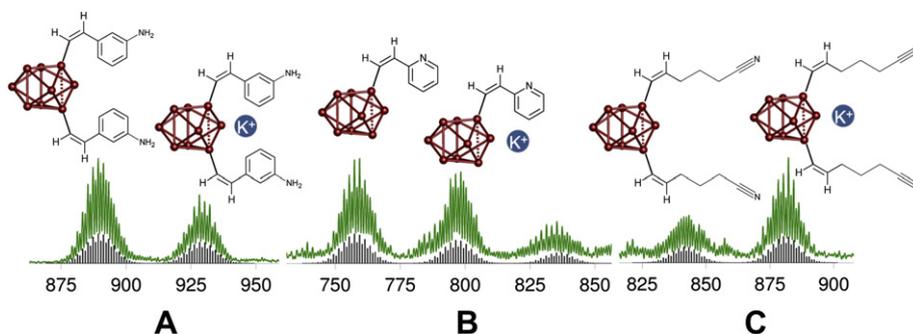


Fig. 5. Electrospray mass spectra of showing organo-Zintl clusters with representative carbon-based ligand substituents: (A)  $[\text{Ge}_9(\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{C}\equiv\text{C}-\text{H})_2]^{2-}$ ; (B)  $[\text{Ge}_9(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{H})_2]^{2-}$  (curve: experimental; bars: theoretical).



**Fig. 6.** Electrospray mass spectra of showing organo-Zintl clusters with representative nitrogen-based ligand substituents: (A)  $[\text{Ge}_9-(\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{NH}_2)_2]^{2-}$ ; (B)  $[\text{Ge}_9-(\text{CH}=\text{CH}-\text{C}_5\text{H}_4\text{N}_1)_2]^{2-}$ ; (C)  $[\text{Ge}_9-(\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{C}\equiv\text{N})_2]^{2-}$ ; (curve: experimental; bars: theoretical).

are currently underway to develop a more rational synthetic pathway for such complexes.

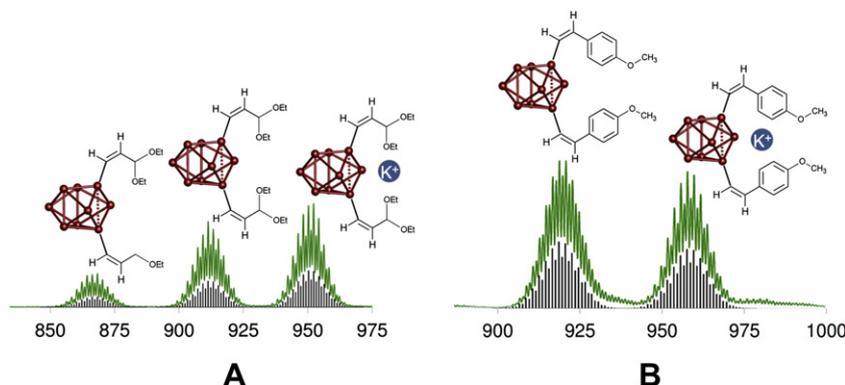
Two different synthetic pathways towards organo-Zintl clusters are known, e.g. the 'halide' and 'alkyne' routes [3b,4]. The former route can be utilized for addition of primary, secondary, tertiary, or alkenyl substrates to the Zintl clusters. The latter adds the cluster and a proton across terminal or internal triple bonds in alkynes to form alkenyl organo-Zintl clusters. The proton comes from either the solvent for internal triple bonds or the alkyne proton in the case of terminal triple bonds.

Both synthetic strategies have been employed here for the synthesis of organo-Zintl clusters with coordinating substituents. The addition of an organic fragment with a functional group of choice to the cluster results in a derivative with that same functional group as a pendant on the cluster. The compatibility of several types of coordinating functional groups have been demonstrated here, including amines, imines, nitriles, terminal alkynes, and ethers. Figs. 5–7 show the mass spectra of the reaction mixtures from the synthesis of each organo-Zintl cluster. The resulting compounds are representative of the types of coordinating functional groups that are compatible with organo-Zintl clusters. The alkynes and alkyl halides that were used were chosen because of their commercial availability, but provide a proof-of-concept that organo-Zintl scaffolds can be constructed for transition-metal coordination. There are well-established patterns in transition-metal chemistry and catalysis for the preference of certain metals and/or oxidation states with particular coordinating functional groups (e.g., the spectrochemical series). Given the large number of organic halides and alkynes that are either commercially or synthetically accessible, nearly any designer ligand can now be appended to the Zintl clusters.

Electrospray mass spectra show that organo-Zintl clusters with carbon- (Fig. 5), nitrogen- (Fig. 6), and oxygen-based (Fig. 7) coordinating functional groups can be synthesized. For example, the reaction of 2-ethynylpyridine with the Zintl precursor results in the 2-ethynylpyridine derivatized cluster (Fig. 6b). The pyridine family, particularly bipyridine and terpyridine have been extensively used in the design of transition-metal catalysts and optical materials [23,26].

The reaction of symmetrical dialkynes (e.g., 1,4-diethynylbenzene or 1,7-octadiyne) with  $\text{K}_4\text{Ge}_9$  in ethylenediamine results organo-Zintl clusters with terminal alkynes (Fig. 5). This is advantageous as the pendant alkyne can subsequently coordinate to transition-metals. The reaction with 3-chloro-3-methyl-1-butyne,  $\text{ClC}(\text{CH}_3)_2\text{C}\equiv\text{C}-\text{H}$  is particularly revealing, as the reagent contains both an alkyl halide and an alkyne. The product,  $[\text{Ge}_9-(\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}\equiv\text{CH})_2]^{2-}$ , shows that the  $\text{Ge}_9^{4-}$  cluster preferentially reacts with alkyl halides over alkynes (Fig. 8). This preference can be synthetically exploited to achieve organo-Zintl clusters whose substituents contain internal or terminal triple bonds.

The reaction of  $\text{K}_4\text{Ge}_9$  with 5-[(trimethylsilyl)ethynyl]-1-methylimidazole resulted in the imidazole functionalized cluster via the 'alkyne' route. This reaction (like the others) is stoichiometrically controlled, and the electrospray mass spectrum shows the clear formation of the disubstituted cluster (Figure S3). Although a crystal structure was not obtained, the  $^1\text{H}$  NMR spectrum is in agreement with the expected structure (Fig. 9). It shows a clear doublet for each of the olefinic hydrogens, coupled at 12 Hz reflecting the *cis* geometry around the double bond. Imidazole derivatives are excellent ligands for transition-metal coordination, and in addition to the coordinating substituents mentioned above, forms a nice library of compounds for



**Fig. 7.** Electrospray mass spectra of showing organo-Zintl clusters with representative oxygen-based ligand substituents: (A)  $[\text{Ge}_9-(\text{CH}=\text{CH}-\text{CH}(\text{OCH}_2\text{CH}_3)_2)_2]^{2-}$ ; (B)  $[\text{Ge}_9-(\text{CH}=\text{CH}-\text{C}_6\text{H}_4\text{OCH}_3)_2]^{2-}$  (curve: experimental; bars: theoretical).

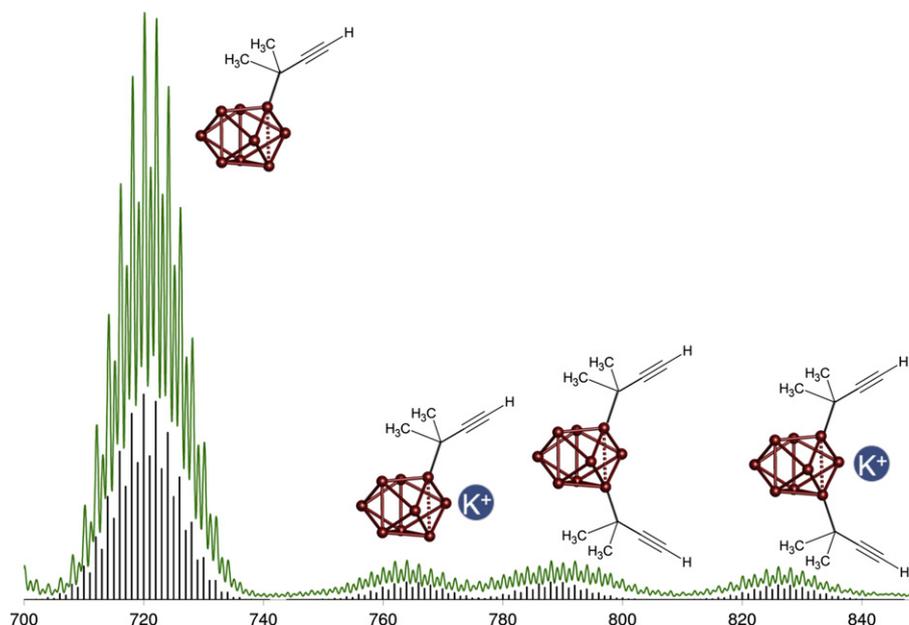


Fig. 8. Electrospray mass spectrum of reaction of  $K_4Ge_9$  with 4-chloro-4-methyl-1-butyne (curve: experimental; bars: theoretical).

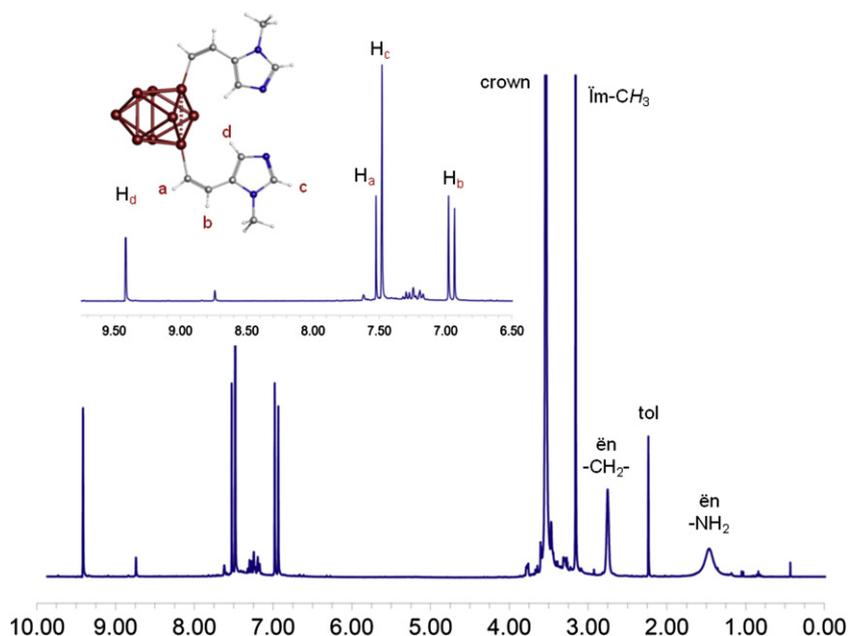


Fig. 9.  $^1H$  NMR spectrum of  $[K-(18\text{-crown-}6)]_2[Ge_9-(CH=CH\text{-Im-}CH_3)_2]$  in  $d_5$ -pyridine.

subsequent investigations into the formation of transition-metal/ organo-Zintl complexes.

#### 4. Conclusions

To date, Zintl chemistry has been precluded from utilizing transition metals in conventional oxidation states, namely 2+. The results presented here clearly establish the feasibility of using organo-Zintl clusters in transition-metal coordination. The structure of  $[Fe(en)_3][Ge_9-(CH=CH-Fc)_2]$  unequivocally demonstrates that organo-Zintl clusters can be married to divalent metals. Additionally, the wealth of coordinating ligands with which the clusters can be functionalized provides a *carte blanche* for the rational design of organo-Zintl/transition-metal

complexes. Independently, transition-metal complexes and Zintl clusters have rich optical and electrochemical properties, and these can now be combined in the pursuit of functional materials. For example, the direct coordination of a divalent metal by an organo-Zintl cluster would result in a neutral—albeit Zwitterionic—complex. Through the use of conjugated ligands, there is the potential for modulation of charge-transfer or optoelectronic properties. Particularly promising is the prospect of chiral organo-Zintl clusters, as seen in the conformers of  $[Ge_9-(CH=CH-Fc)_2]^{2-}$ , which could be used in catalyst design. Our recently reported  $[Ge_9-(CH=CH-CH_2NH_2)_2]^{2-}$  cluster can be coordinated on its own or be used to build a salen-like ligand [20]. Cumulatively, these results establish the entry into a new realm of organo-Zintl/transition-metal chemistry.

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## Appendix A. Supporting information

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.05.006.

## References

- [1] For successive summaries of the field see: (a) J.D. Corbett, *Chem. Rev.* 85 (1985) 383; (b) J.D. Corbett, *Struct. Bonding* 87 (1997) 157; (c) J.D. Corbett, *Angew. Chem. Int. Ed.* 39 (2000) 670; (d) T.F. Fässler, *Coord. Chem. Rev.* 215 (2001) 347; (e) S.C. Sevov, J.M. Goicoechea, *Organometallics* 25 (2006) 5678; (f) S. Scharfe, F. Kraus, S. Stegmaier, A. Schier, T.F. Fässler, *Angew. Chem. Int. Ed.* 50 (2011) 3630.
- [2] (a) M.M. Gillett-Kunnath, A. Munoz-Castro, S.C. Sevov, *Chem. Comm.* 48 (2012) 3524; (b) M.M. Gillett-Kunnath, A.G. Oliver, S.C. Sevov, *J. Am. Chem. Soc.* 133 (2011) 6560; (c) M.M. Gillett-Kunnath, J.I. Paik, S.M. Jensen, J.D. Taylor, S.C. Sevov, *Inorg. Chem.* 50 (2011) 11695; (d) D. Rios, M.M. Gillett-Kunnath, J.D. Taylor, A.G. Oliver, S.C. Sevov, *Inorg. Chem.* 50 (2011) 2373; (e) S. Scharfe, T.F. Fässler, S. Stegmaier, S.D. Hoffmann, K. Ruhland, *Chem. Eur. J.* 14 (2008) 4479; (f) B. Zhou, M.S. Denning, D.L. Kays, J.M. Goicoechea, *J. Am. Chem. Soc.* 131 (2009) 2802; (g) J. Wang, S. Stegmaier, T.F. Fässler, *Angew. Chem. Int. Ed.* 48 (2009) 1998; (h) B. Kesanli, J.E. Halsig, P. Zavalij, J.C. Fetting, Y.-F. Lam, B.W. Eichhorn, *J. Am. Chem. Soc.* 129 (2007) 4567; (i) J.-Q. Wang, S. Stegmaier, T.F. Fässler, *Angew. Chem.* 121 (2009) 2032.
- [3] (a) D. Rios, S.C. Sevov, *Inorg. Chem.* 49 (2010) 6396; (b) F.S. Kocak, P. Zavalij, Y.-F. Lam, B.W. Eichhorn, *Chem. Comm.* (2009) 4197; (c) B. Zhou, M.S. Denning, T.A.D. Chapman, J.M. Goicoechea, *Inorg. Chem.* 48 (2009) 2899; (d) B. Zhou, M.S. Denning, C. Jones, J.M. Goicoechea, *Dalton Trans.* (2009) 1571; (e) J.M. Goicoechea, S.C. Sevov, *Organometallics* 25 (2006) 4530; (f) J.M. Goicoechea, S.C. Sevov, *J. Am. Chem. Soc.* 128 (2006) 4155.
- [4] (a) M.W. Hull, A. Ugrinov, I. Petrov, S.C. Sevov, *Inorg. Chem.* 46 (2007) 2704; (b) M.W. Hull, S.C. Sevov, *Angew. Chem. Int. Ed.* 46 (2007) 6695; (c) M.W. Hull, S.C. Sevov, *Inorg. Chem.* 46 (2007) 10953; (d) D.J. Chapman, S.C. Sevov, *Inorg. Chem.* 47 (2008) 6009; (e) M.W. Hull, S.C. Sevov, *J. Am. Chem. Soc.* 131 (2009) 9026; (f) M.M. Gillett-Kunnath, I. Petrov, S.C. Sevov, *Inorg. Chem.* 49 (2010) 721; (g) C.B. Benda, J.-Q. Wang, B. Wahl, T.F. Fässler, *Eur. J. Inorg. Chem.* (2011) 4262; (h) F. Li, S.C. Sevov, *Inorg. Chem.* 51 (2012) 2706.
- [5] (a) S.M. Kauzlarich (Ed.), *Chemistry, Structure, and Bonding of Zintl Phases and Ions*, VCH Publishers, New York, 1996; (b) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, sixth ed. Wiley-Interscience, New York, 1999, pp. 40–42; (c) C.E. Housecroft, A.G. Sharpe, *Inorganic Chemistry*, second ed. Pearson/Prentice Hall, New York, 2005, pp. 219–221, 357–361.
- [6] A. Nienhaus, R. Hauptmann, T.F. Fässler, *Angew. Chem. Int. Ed.* 41 (2002) 3213.
- [7] M.S. Denning, J.M. Goicoechea, *Dalton Trans.* (2008) 5882.
- [8] A. Spiekermann, S.D. Hoffmann, F. Kraus, T.F. Fässler, *Angew. Chem. Int. Ed.* 46 (2007) 1638.
- [9] (a) B.W. Eichhorn, R.C. Haushalter, W.T. Pennington, *J. Am. Chem. Soc.* 110 (1988) 8704; (b) B.W. Eichhorn, R.C. Haushalter, *J. Chem. Soc. Chem. Commun.* (1990) 937; (c) B. Kesanli, J. Fetting, B.W. Eichhorn, *Chem. Eur. J.* 7 (2001) 5277; (d) L. Xu, S.C. Sevov, *J. Am. Chem. Soc.* 123 (2001) 4091; (e) J. Campbell, H.P.A. Mercier, F. Holger, D. Santry, D.A. Dixon, G.J. Schrobilgen, *Inorg. Chem.* 41 (2002) 86; (f) L. Yong, S.D. Hoffmann, T.F. Fässler, *Eur. J. Inorg. Chem.* (2005) 3663.
- [10] E.N. Esenturk, J. Fetting, B.W. Eichhorn, *Chem. Commun.* (2005) 247.
- [11] (a) E.N. Esenturk, J. Fetting, Y.-F. Lam, B.W. Eichhorn, *Angew. Chem. Int. Ed.* 43 (2004) 2132; (b) E.N. Esenturk, J. Fetting, B.W. Eichhorn, *J. Am. Chem. Soc.* 128 (2006) 9178.
- [12] J.-Q. Wang, S. Stegmaier, B. Wahl, T.F. Fässler, *Chem. Eur. J.* 16 (2010) 1793.
- [13] E.N. Esenturk, J. Fetting, B.W. Eichhorn, *Polyhedron* 25 (2006) 521.
- [14] J.M. Goicoechea, S.C. Sevov, *J. Am. Chem. Soc.* 127 (2005) 7676.
- [15] F.S. Kocak, P. Zavalij, Y.-F. Lam, B.W. Eichhorn, *Inorg. Chem.* 47 (2008) 3515.
- [16] J.M. Goicoechea, S.C. Sevov, *Angew. Chem. Int. Ed.* 44 (2005) 4026.
- [17] (a) E.M. Esenturk, J.C. Fetting, B.W. Eichhorn, *J. Am. Chem. Soc.* 128 (2006) 12.
- [18] A. Spiekermann, S.D. Hoffmann, T.F. Fässler, I. Krossing, U. Preiss, *Angew. Chem. Int. Ed.* 46 (2007) 5310.
- [19] B. Zhou, T. Kramer, A.L. Thompson, J.E. McGrady, J.M. Goicoechea, *Inorg. Chem.* 50 (2011) 8028.
- [20] M. W. Hull and S. C. Sevov, *Chem. Commun.* 48, in press.
- [21] V. Queneau, S.C. Sevov, *Angew. Chem. Int. Ed.* 36 (1997) 1754.
- [22] G.M. Sheldrick, *Acta Cryst A* 64 (2008) 112.
- [23] Q.-L. Zhou, *Privileged Chiral Ligands and Catalysts*, Wiley-VCH, Weinheim, Germany, 2011.
- [24] (a) R. Noyori, H. Takaya, *Acc. Chem. Res.* 23 (1990) 345; (b) H. Shimizu, I. Nagasaki, K. Matsumura, N. Sayo, T. Saito, *Acc. Chem. Res.* 40 (2007) 1385; (c) J. Wu, A.S.C. Chan, *Acc. Chem. Res.* 39 (2006) 711; (d) L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng, X.-L. Hou, *Acc. Chem. Res.* 26 (2003) 659; (e) G.C. Fu, *Acc. Chem. Res.* 39 (2006) 853.
- [25] (a) K.J. Wade, *Adv. Inorg. Chem. Radiochem.* 18 (1976) 1; (b) K.J. Wade, *Chem. Soc. D* 792 (1971); (c) D.M.P. Mingos, *Nat. Phys. Sci.* 99 (1972) 236; (d) D.M.P. Mingos, *Acc. Chem. Res.* 17 (1984) 311.
- [26] (a) J.J. Concepcion, J.W. Jurss, M.K. Brennaman, P.G. Hoertz, A.T.T. Patrocínio, N.Y.M. Iha, J.L. Templeton, T.J. Meyer, *Acc. Chem. Res.* 42 (2009) 1954; (b) T. Mutai, J.-D. Cheon, S. Arita, K. Araki, *J. Chem. Soc. Perkin Trans. 2* (2001) 1045; (c) F. Dumur, C.R. Mayer, E. Dumas, J. Marrot, F. Secheresse, *Tetrahedron Lett.* 48 (2007) 4143; (d) M. Maestri, N. Armadori, V. Balzani, E.C. Constable, A.M.W.T. Cargille Thompson, *Inorg. Chem.* 34 (1995) 2759; (e) J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni, V. Balzani, *Inorg. Chem.* 20 (1991) 4230; (f) A.M.W. Cargill Thompson, *Coord. Chem. Rev.* 160 (1997) 1; (g) K.C.D. Robson, B.D. Koivisto, T.J. Gordon, T. Baumgartner, C.P. Berlinguette, *Inorg. Chem.* 49 (2010) 5335.