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Zintl Cluster Compounds

On the Formation of Intermetalloid Clusters: Titanocene(III)diammin as a Versatile Reactant Toward Nonastannide Zintl Clusters**

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

Abstract: *The reactivity of $TiCp_2Cl_2$ (d^0) towards Zintl clusters was studied in liquid ammonia (Cp = cyclopentadienyl). Reduction of $Ti^{IV}Cp_2Cl_2$ and ligand exchange led to the formation of $[Ti^{III}Cp_2(NH_3)_2]^+$, also obtainable by recrystallization of $[CpTi^{III}Cl]_2$. Upon reaction with $[K_4Sn_9]$, ligand exchange leads to $[TiCp_2(\eta^1\text{-}Sn_9)(NH_3)]^{3-}$. A small variation of the stoichiometry led to the formation of $[Ti(\eta^4\text{-}Sn_8)Cp]^{3-}$, which cocrystallizes with $[TiCp_2(NH_3)_2]^+$ and $[TiCp_2(\eta^1\text{-}Sn_9)(NH_3)]^{3-}$. Finally, the large intermetalloid cluster anion $[Ti_4Sn_{15}Cp_5]^{n-}$ (n = 4 or 5) was obtained from the reaction of $K_{12}Sn_{17}$ and $TiCp_2Cl_2$ in liquid ammonia. The isolation of three side products, [K([18]crown-6)]Cp, [K([18]crown-6)]Cp(NH_3), and [K([2.2]crypt)]Cp, suggests a stepwise elimination of the Cl^- and Cp^- ligands from $TiCp_2Cl_2$ and thus gives a hint to the mechanism of the product formation in which $[Ti(\eta^{4+2}\text{-}Sn_8)Cp]^{3-}$ has a key role.*

In recent years the bottom-up synthesis of intermetalloid clusters[1–8] from Zintl ions has been proven to be a powerful tool to generate macroscopic amounts of charged atom clusters of various compositions.[8,9] On one hand such heterometallic clusters are interesting candidates for material science with respect to catalysis and quantum dots, on the other hand they allow a better understanding of chemical bonding at the border of molecules and solids.[10]

A remarkable number of binary intermetalloid clusters formed in solutions such as $[Ni@Sn_9]^{4-}$, $[Cu@E_9]^{3-}$ (E = Sn, Pb), $[T@Pb_{10}]^{2-}$ (T = Ni, Pd, Pt), $[Pd_2@E_{18}]^{4-}$ (E = Ge, Sn), $[Pt_2@Sn_{17}]^{4-}$, $[Ir@Sn_{12}]^{3-}$, $[T@Pb_{12}]^{n-}$ (T = Mn, Ni, Pd, Pt and $n = 2$ or 3), $[Zn_9Bi_{11}]^{5-}$, and $[As@Ni_{12}@As_{20}]^{3-}$ have emerged in recent years.[11–20] However, the mechanism of the formation of larger clusters from Zintl ions is rather unexplored. Even though the formation of intermetalloid clusters in neat solids, which then can be transferred to solution, is known for a few examples,[21] the synthesis of clusters containing tetrel and transition metal atoms is generally achieved by reacting a homoatomic tetrel atom cluster E_9 (E = Si–Pb) with organometallic compounds TL_n (T = element of Group 8 to 12, L = various σ- and π-donor, aryl, or alkyl ligands).[17] In principle the generation of larger clusters can proceed through two pathways: a) stepwise ligand exchange reactions under the formation of $TL_{n-m}(E_9)$, $[T@E_9]$, and $[T_{1/2}E_{18}]$ complexes, and b) disproportionation reactions under fragmentation of the E_9 cluster (Scheme 1). Both reactions may also take place synchronously. The reaction of heteroatomic Zintl clusters generally follows the same reaction principles.[18]

Even though a full sequence for the same atom types E and T is not known yet, the reactions I to VI given in Scheme 1 are established through the individual examples **i**–**viii**. Whereas the reactions I to V lead to products **ii**–**v** and **vii** with intact or fused nine-atom clusters through ligand elimination reactions, the proposed reactions VI and VII to the products **viii** and **ix** involve a more complex reaction mechanism including cluster fragmentation followed by aggregation of these cluster fragments.

Remarkably, the major part of all reactions with organometallic precursors in solution reported so far involve transition metal complexes with late d block metals (Group 10 to Group 12),[22] and only a very limited number of examples of Group 6,[23] 7,[24] 8,[25] and 9[26] is known.

Reactions of tetrel cluster anions with compounds that contain early d-block elements (Groups 3–5) have not been described yet. Due to the high negative charge of these clusters a strong reducing power can be assumed, and in consequence exclusively organometallic compounds with electron-rich, late transition metals have been employed.[27] However, the recent discovery of stable compounds that contain $[Ge_9]^{4-}$ anions besides highly oxidized VO_4^{3-} and WO_4^{2-} groups[28,29] triggered us to investigate the reaction of tetrel cluster anions toward transition metal complexes of electron-poor metals such as the d^0 complex Cp_2TiCl_2. First, we investigated the behavior of $TiCp_2Cl_2$ in liquid ammonia solutions under reductive conditions.

The reaction of titanocene dichloride in liquid ammonia in the presence of the Zintl phases K_4E_9 (E = Ge, Sn, and Pb) showed that $TiCp_2Cl_2$ undergoes a ligand exchange reaction along with a partial reduction to Ti^{III} under formation of pale-blue crystals of $[Ti^{III}Cp_2(NH_3)_2]Cl(NH_3)$ (**1**). A further fragmentation of complex **1** under release of the Cp^- ligand became evident from the isolation of colorless crystals of $[K([18]crown\text{-}6)]Cp(NH_3)_n$ ($n = 0$, **2**; $n = 1$, **3**) and [K([2.2]crypt)]Cp (**4**) from reactions involving $TiCp_2Cl_2$ which were carried out in liquid ammonia solutions of various

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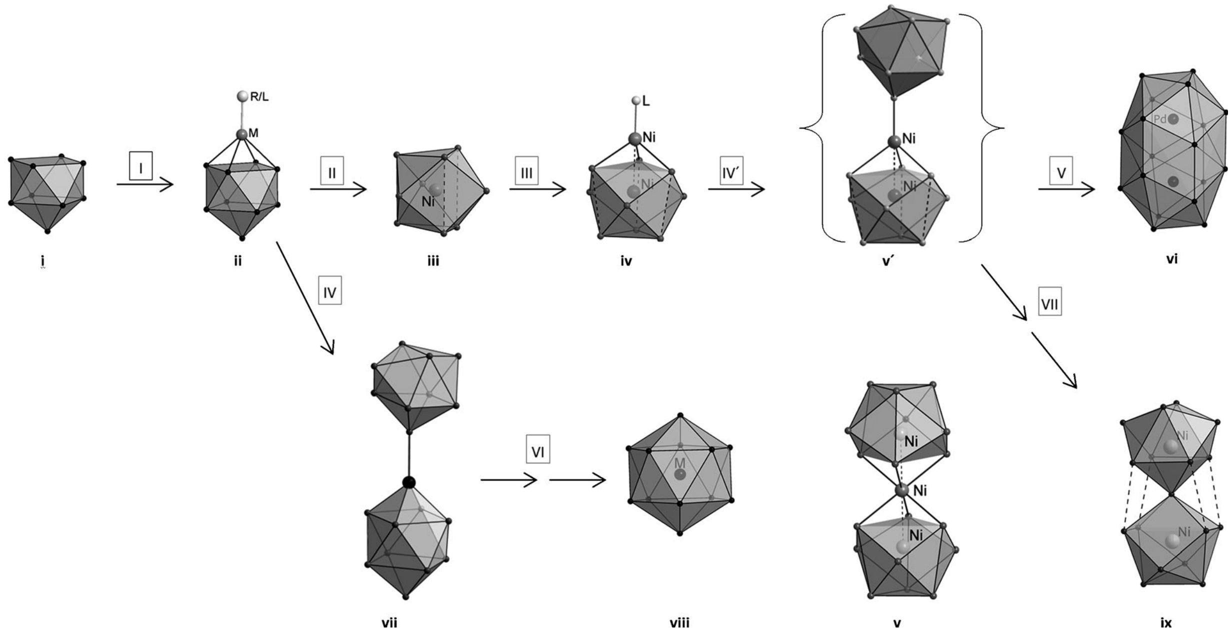
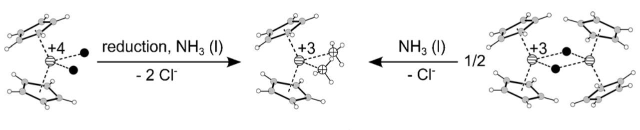


Scheme 1. Reaction routes to intermetalloid clusters from E_9 anions **i**. Known examples are **ii**: $[(CO)_3Cr(\eta^4\text{-}E_9)]^{4-}$ for E = Ge, Sn and Pb; $[PhZn(\eta^4\text{-}Ge_9)]^{3-}$ and $[iPr_3PCu(\eta^4\text{-}Ge_9)]^{4-}$, **iii**: $[Ni@Ge_9]^{4-}$ and $[Cu@E_9]^{3-}$ for E = Sn and Pb, and **iv**: $(PPh_3)Ni([(\eta^4\text{-}Ni@Ge_9)]^{2-}$ (reaction path I–III). **v′** with an endohedrally filled and empty cluster is not known; however, clusters with two filled and two empty clusters have been obtained with $[Ni_3@Ge_{18}]^{4-}$ (**v**) and $[(\eta^4\text{-}Ge_9)Cu(\eta^1\text{-}Ge_9)]^{7-}$ (**vii**), respectively. Cluster **v′** represents a possible intermediate for the formation of $[Pd_2@E_{18}]^{4-}$ (E = Ge, Sn) (**vi**) through reaction V or, through disproportionation reaction VII to form $[Pt_2@Sn_{17}]^{4-}$ (**ix**), whereas the fragmentation of **vii** may lead through reaction VI to clusters of type **viii** such as $[Ir@Sn_{12}]^{2-}$ or $[T@Pb_{12}]^{2-}$ (T = Pt, Pd).

Zintl phases (see Figures S3–S5 and Table S2 in the SI). The elimination of Cp^- from titanocene dichloride thus happens in analogy to the well-known Cp cleavage from metallocenes of the type MCp_2 (M = Mn, Fe, Co) in the presence of alkali metals.[30] Compound **1** is also quantitatively accessible simply by recrystallization of $[Ti^{III}Cp_2Cl]_2$ in liquid ammonia (Scheme 2). The crystal structure determination of **1** showed that $[TiCp_2(NH_3)_2]^+$ (**1a**; Figure S1, SI) adopts a distorted tetrahedral geometry with two Cp and two NH_3 ligands coordinated to the titanium atom. Ti–N distances of 2.221(2) and 2.197(2) Å are indicative for a Ti^{III} complex such as $[TiCp_2(C_5H_5N)_2][B(C_6H_5)_4]$ (d(Ti–N1) = 2.285(3) Å, d(Ti–N2) = 2.258(3) Å).[31] Ti^{IV} titanocene complexes show significantly shorter Ti–N distances.[32] The oxidation state + III was confirmed by an electron spin resonance (EPR) signal obtained from of a single crystal of compound **1** at 193 K (Figure S1, SI).

Besides compound **1**, black crystals of the composition $[K([18]crown\text{-}6)][K(NH_3)_6][TiCp_2(NH_3)_2]_4[Sn_9\text{-}(TiCp_2NH_3)]_2\text{-}(NH_3)_7$ (**5**) were isolated from the reaction mixture. The asymmetric unit of crystals of **5** consists of $[TiCp_2(\eta^1\text{-}Sn_9)\text{-}(NH_3)]^{3-}$ (**5a**, Figure 1) and the cations $[K([18]crown\text{-}6)\text{-}(NH_3)_2]^+$, $[K(NH_3)_6)]^+$, and $[TiCp_2(NH_3)_2]^+$ (**5b**, Figure S9, SI). The charge allocation of the cations is apparent for the K complexes present in **5**, and the structural similarity of **5b** with **1a** is also obvious (Table S5, SI). The anion **5a** is the result of the substitution of one NH_3 ligand in **1a** by an $[Sn_9]^{4-}$ cluster which acts as a two-electron donor through one of the lone pairs located at each of the tin atoms. Such a coordination of a deltahedral cluster is not very common, but has also been observed, for example, in $[(\eta^4\text{-}Ge_9)\text{-}Cu\text{-}(\eta^1\text{-}Ge_9)]^{7-}$ and $[E_6(M(CO_5)_6]^{2-}$ (M = Cr, Mo, W; E = Ge, Sn).[22] The Sn1–Ti distance in **5a** of 2.897(1) Å is longer than the sum of the covalent radii for single bonds of Ti and Sn (2.76 Å),[33] but compares well with the ones observed in intermetallic compounds such as $SnTi_3$ (2.953 Å).[34] Sn–Ti bonds in molecular compounds are comparably rare. Shorter bonds



Scheme 2. The reduction of titanocene dichloride forming $[TiCp_2\text{-}(NH_3)_2]^+$ (**1a**) in liquid ammonia in the presence of the Zintl phases K_4E_9 or $K_{12}Si_{17}$ (E = Ge, Sn, Pb) and from $[TiCp_2Cl]_2$. Ti, Cl, N, C, and H atoms are shown as striped, black, cross-hatched, grey, and white spheres, respectively.

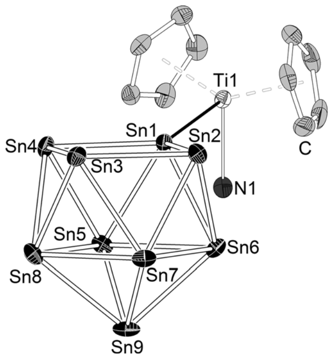


Figure 1. Structure of $[TiCp_2(\eta^1\text{-}Sn_9)(NH_3)]^{3-}$ (**5a**) in **5**. Anisotropic displacement ellipsoids are drawn at the 50% probability level at 120 K. Hydrogen atoms are omitted for clarity.

of 2.69 Å[35] have been observed in the titanocene stannylene phosphine $TiCp_2(SnSi_4(SiMe_3)_4(Me_4))(PEt_3)$ featuring, however, a Ti=Sn bond. In **5a** the Ti–Sn bond is best described as a donor–acceptor bond with the $[Sn_9]^{4-}$ unit acting as an electron donor. Due to the more bulky Sn_9 ligand in **5a** the Sn1-Ti-N angle $\alpha = 83.26(1)°$ is significantly larger than the N-Ti-N angle in **1a** (79.76(6)°). The mean Ct-Ti-Ct angle (Ct = center of the Cp ligand) of **1a** and **5b** with $\alpha_{\mathrm{mean}} = 135.2°$ is only slightly smaller than that in **5a** ($\alpha = 136.2°$) and is thus mostly unaffected by the substitution (Table S7, SI). The structure of the Sn_9 cluster derives from a slightly distorted monocapped square antiprism with a ratio of the diagonal lengths of the open square $d_1/d_2 = 1.09$ and a dihedral angle close to 180° (178.67(2)°). The Sn–Sn distances in **5a** range from 2.864(1) to 3.241(1) Å with the coordinated Sn1 atom having the shortest bonds to neighboring Sn atoms (Tables S6 and S7, SI).[36]

By variation of the stoichiometry of the mixtures of K_4Sn_9, $TiCp_2Cl_2$, and [18]crown-6 in liquid ammonia we also obtained the salt **6** with the rather multifarious composition $[K([18]crown\text{-}6)]_2(\eta^5{:}\eta^5\text{-}Cp)]_4[K([18]crown\text{-}6)(NH_3)_2][TiCp_2(NH_3)_2][TiCp_2(\eta^1\text{-}Sn_9)(NH_3)]\text{-}[Sn_8TiCp](NH_3)_{63}$. The single-crystal structure determination of **6** revealed that besides all the above-discussed ions $[TiCp_2(NH_3)_2]^+$, $C_5H_5^-$, and $[Sn_9TiCp_2(NH_3)]^{3-}$, compound **6** also contains the anion $[Ti(\eta^4\text{-}Sn_8)Cp]^{3-}$.

The novel cluster anion $[Ti(\eta^4\text{-}Sn_8)Cp]^{3-}$ (**6e**, Figure 2 and Figure S11, SI) comprises an Sn_8 fragment instead of the Sn_9 unit of the starting material. Sn–Sn bonds range from 2.859(2) to 3.108(2) Å and are thus in the typical region for deltahedral Sn clusters. The half-shell-type Sn_8 cluster coordinates with six Sn atoms of the rim of the open side to the Ti atom. Four shorter Ti–Sn bonds are in the narrow range from 2.929(4) to 2.951(4) Å (black solid bonds in Figure 2), and the Ti atom is located above the plane of these four atoms with a mean distance of 0.88 Å, whereas the longer bonds to Sn21 and Sn24 are 3.225(4) and 3.210(4) Å, giving rise to η^{4+2} coordination of the Sn_8 unit. All Ti–Sn bonds in **6e** are longer compared to those in **5a**, in agreement with the rule that higher coordination numbers of atoms correlate with longer bonds to neighboring atoms. The coordination sphere of the Ti atom is completed by the $(\eta^5\text{-}C_5H_5)^-$ ligand (Table S8, SI).

In cluster **6e** all ligands except for one Cp unit of the original Ti complex are substituted by Sn atoms, and the anion represents an interesting possible intermediate toward the formation of endohedrally filled clusters of the type $[Ir@E_{12}]^{3-}$ and $[T_2@E_{17}]^{n-}$ which both contain the E_8 fragment of **6e** as indicated by the circles in Figure 3.

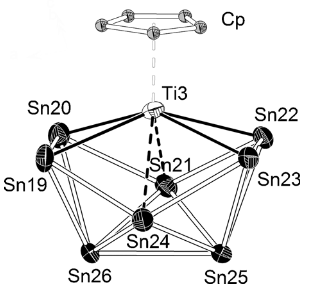


Figure 2. Molecular structure of $[Ti(Sn_8)Cp]^{3-}$ (**6e**) in **6**. Anisotropic displacement ellipsoids of Sn and Ti are drawn at the 50% probability level at 120 K. Hydrogen atoms are omitted for clarity. Cp represents the coordinating Cp ligand. C atoms are refined isotropically. Significantly longer Sn–Ti bonds are depicted as dashed black lines.

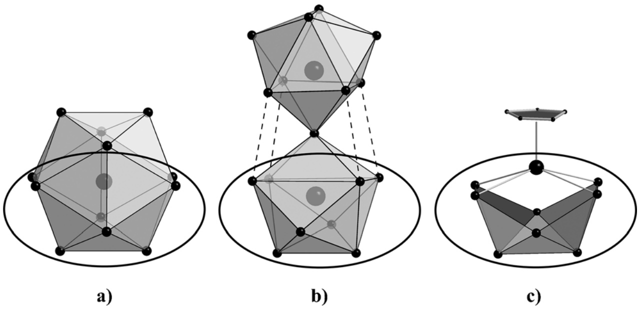


Figure 3. Examples of different intermetalloid clusters which exhibit an Sn atom framework (circles) similar to the cluster shown in c) $[Ti(Sn_8)Cp]^{3-}$ **6e**. a) $[Ir@Sn_{12}]^{3-}$[37] and b) $[(Sn_8)T(T@Sn_9)]^{n-}$ with T = Co ($n = 5$) and Ni ($n = 4$).[21,38]

Upon replacement of the starting material K_4Sn_9 with $K_{12}Sn_{17}$, crystals of compound **7** with the composition $K[K([18]crown\text{-}6)]_6[(\eta^5{:}\eta^5\text{-}Cp)[K(18\text{-}crown\text{-}6)]_2]_2\text{-}[Cp_5Ti_4Sn_{15}]_2(NH_3)_{40}$ (Figure 4 and Figure S8, SI) are obtained. Compound **7** contains the rather large intermetalloid anionic $Cp_5Ti_4Sn_{15}$ fragment, in which 15 Sn atoms are covalently connected and coordinated to four Ti atoms. The starting material $TiCp_2Cl_2$ appears in various fragments and with a large variety of bonding modes in the product: elimination of the two Cl ligands leads to a titanocenium cation "$TiCp_2^+$" as a coordinating fragment. The removal of one Cp ligand then results in the fragment "TiCp", which has also been found in **6e**. Finally, after all ligands have been removed, the coordination of a bare Ti atom occurs in **6e** as it is observed in the endohedrally filled Zintl ions mentioned above. Notice that the resulting by-products such as the released Cp ligands cocrystallize in the product **7**. The fragments disclose the large variety of different oxidation

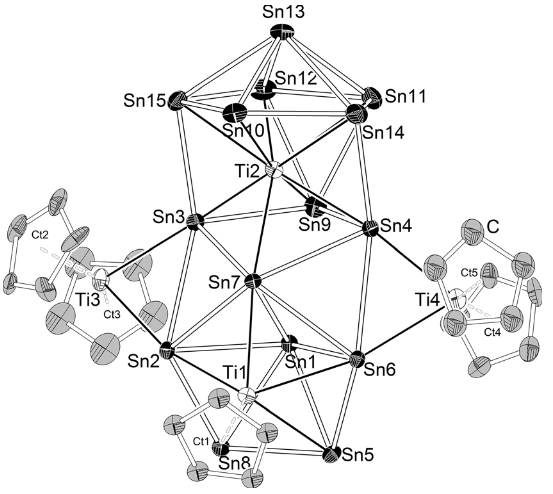


Figure 4. Structure of $[Ti_4Sn_{15}Cp_5]$ (**7a**) in $K[K([18]crown\text{-}6)]_6[(\eta^5{:}\eta^5\text{-}Cp)\text{-}[K(18\text{-}crown\text{-}6)]_2]_2[Cp_5Ti_4Sn_{15}]_2(NH_3)_{40}$ (**7**). Atoms are drawn at the 50% probability level at 120 K. Hydrogen atoms are omitted for clarity. Ct represents the center of the coordinating Cp ligands.

states and bonding modes of titanium, which stabilize the Sn_{15} unit in **7a**.

The leading structural motifs in **7a** are two Sn_6 fragments consisting of Sn atom-capped five-membered rings, which coordinate to the Ti atoms with an average distance $d(\mathrm{Sn–Ti1}) = 2.93$ Å in a η^5 fashion. The Sn–Sn distances within the two planar pentagons (angular sum is 539.7°) are set in a small limit with an average value of $d(\mathrm{Sn–Sn}) = 2.98$ Å, whereas slightly longer bonds of 3.08 Å appear between the ring atoms and the capping atoms Sn1 and Sn13 (see Table S9 in the SI for selected bond lengths). The coordination sphere of Ti1 is completed by a Cp ligand, and Ti2 coordinates to four additional Sn atoms (Figure 4). The two (η^5-Sn_6)Ti fragments are linked by three bridging Sn atoms (Sn3, Sn4, and Sn9).

Another view at the structure shows the presence of an Sn_8Ti fragment as it has been found in the anion **6e** (emphasized for Ti2 in Figure 5). It has a similar structure to the one in **6e** as it is shown in the inset at the top left corner in Figure 5. The planar Sn_5 ring at Ti1 in **7a** can also be found in **6e** as indicated in the inset at the bottom right corner in Figure 5, and the coordination of Ti2 to exclusively ten Sn atoms in **7a** can be regarded as an intermediate step toward the formation of an icosahedral M@Sn_{12} species.

For the evaluation of the charge of **7a**, a total of nine positive charges can be assumed for the cations per unit cell. ($1 \times K^+$, $6 \times [K([18]\text{crown-6})]^+$, and $2 \times [(\eta^5{:}\eta^5\text{-Cp})[K(18\text{-crown-6})]_2]^+$ thus negative charges have to be distributed among the two anions, which makes −4 for one and −5 for the other unit (an inversion center generates the second cluster **7a** per unit cell). Different charges for structurally very similar clusters have been observed previously in compounds with $[Sn_9]^{4-}$ and $[Sn_9]^{3-}$ clusters with a different electron count but with almost identical deltahedral structures.[39] **7a** contains even more atoms and thus may also form units that are identical by the center of inversion, but possess different charges. However, it is also possible that one of the two symmetry related clusters has an attached hydrogen atom as it has been observed for $[Ni@(HSn_9)]^{3-}$ and $[HSn_9]^{3-}$ [40] or that one of the numerous NH_3 molecules is an amide resulting in two clusters **7a** with charge −4. Although there is no doubt on the chemical composition as far as the heavy atoms in **7a** are concerned, the exact charge allocation has to be postponed to a forthcoming investigation due to lack of material.

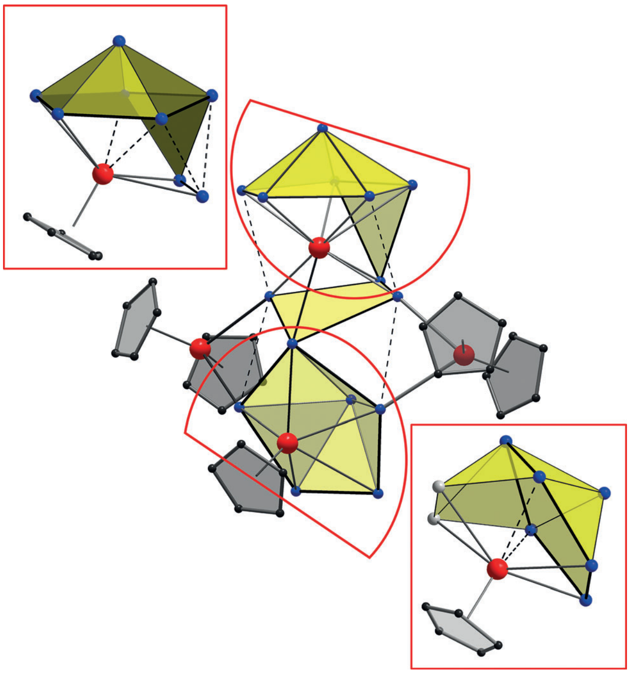


Figure 5. Structure of the anion **7a** and a comparison of its structural features with that of "CpTi(Sn_8)" (**6e**). Two representations of **6e** are given in the square insets showing their relationship to the encircled structure parts of **7a**. Ti, Sn, and C atoms are shown as red, blue or gray, and black spheres, respectively. Atom labeling according to Figure 4.

In summary, $TiCp_2Cl_2$ turned out to be a reactive source for organotitanyl fragments which then react in liquid ammonia with tin clusters and their fragments. Similar reactions in ethylenediamine, dimethylformamide, and acetonitrile have not been successful so far.

The compounds isolated in the course of these reactions allow a deeper insight into the mechanism of the formation of larger tetrel atom clusters: On the one hand the structure of the intermetalloid cluster [Sn_8Ti] (**6e**) perfectly matches a fragment of a Sn_{12} icosahedron (Figure 3), and thus represents an intermediate compound on the way to the formation of endohedral M@E_{12} clusters as they are known for $[Ir@Sn_{12}]^{2-}$ and $[T@Pb_{12}]^{n-}$ derivatives with T = Mn, Ni, Pd, or Pt.[41] On the other hand the structures of $[Sn_9TiCp_2(NH_3)]^{3-}$ (**5a**) and [$Ti_4Sn_{15}Cp_5$] (**7a**) with their variable Ti coordination modes manifest the participation of the transition metal on the formation of large intermetalloid clusters. A gradual replacement of the ligands in transition metal complexes allows different coordination modes of the tetrel atom cluster fragments: a) the cluster approaches the Ti atom and coordinates through a single atom (**5a**); b) the replacement of the second ligand and the formation of the "$TiCp_2$" fragment allows the Ti atoms to coordinate to further Sn atoms (as found for Ti3 and Ti4 in **7a**), c) the release of a Cp ligand as it occurs in **6e** and **7**, and d) the release of the second Cp ligand creates an endohedral transition metal atom as frequently found in endohedrally filled clusters.[1] Furthermore, the [Sn_8Ti] cluster in **6** represents a possible intermediate on the way to endohedral cluster anions like $[Ni_2@Sn_{17}]^{4-}$ and $[Co_2@Sn_{17}]^{5-}$.[21,38] Formally, the substitution of the Cp^- ligand in [Sn_8MCp] by an endohedral [M@Sn_9] cluster results in two endohedral clusters that are sharing one Sn vertex atom in [$M_2@Sn_{17}$] as shown in Figure 3 and Scheme 2. Even though Cp complexes of the transition metals Co, Ni, and Pt have not been employed for the synthesis of the endohedral cluster compounds mentioned above, the existence of **6e** in compound **6** clearly shows that eight-atom clusters can be present in solution.

A further interesting aspect is given by the isolation of $[TiCp_2(NH_3)_2]^+$ (**1a**), an easily accessible homogenous catalyst. Comparable cationic Ti^{III} complexes are used as effective catalysts for cross-selective titanium(III)-catalyzed reductive "umpolung" reactions or in particular intermolecular reductive cross-coupling reactions.[42]

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Keywords: cluster compounds · homogeneous catalysis · tin · titanium · Zintl anions

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