Synthesis of PtSn₄ and Ir₃Sn₇ Intermetallic Nanoparticles From Bimetallic Zintl Cluster Precursors

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Abstract

Controlled I₂ oxidations of preformed Zintl clusters [Pt₂Sn₉(PPh₃)]²⁻ and [Sn₉Ir(cod)]³⁻, give well ordered tin-rich intermetallic nanoparticles (NPs) of PtSn₄ and Ir₃Sn₇, respectively. The intermetallics were characterized by HR-TEM and XRD analysis. Both clusters have strong structural similarities with the final intermetallic, which appears to be an important factor in determining the phase of the resulting intermetallic NP. Despite the 1:9 (Ir:Sn) atomic ratio of the [Sn₉Ir(cod)]³⁻ cluster, ordered Ir₃Sn₇ NPs were formed instead of the compositionally-similar IrSn₄ phases. PtSn₄ is difficult to prepare and isolate due to the formation of other known Pt-Sn phases, such as PtSn, PtSn₂ and Pt₃Sn.

This paper is dedicated to Prof. Malcolm Chisholm (friend, colleague and mentor extraordinaire) on the occasion of his 70th birthday.

Keywords: Zintl clusters, intermetallics, PtSn phases, IrSn phases, catalysts, X-ray crystallography

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Bimetallic nanoparticles (NPs) of active Pt-group metals (PGMs) such as Rh, Ir, Pd and Pt are used in a variety of catalytic and electrocatalytic applications. While the PGMs provide the base activity of the catalyst, the secondary metals modify the PGM activity and / or impart tolerance to various poisons. For example, PtRu and PtFe bimetallic NP electrocatalysts show much higher tolerance to CO impurities in hydrogen fuel cell applications in comparison to pure Pt NPs.^{1,2} One drawback of PtM alloy catalysts is their low chemical and electrochemical stability relative to pure Pt. These instabilities can lead to catalyst degradation, phase separation and ion migration in electrochemical applications. In contrast, intermetallic NPs are often significantly more stable than alloys; especially in acidic media.³ Alloys and intermetallics differ in their crystal structures and, usually, the degree of atomic order. Alloys typically adopt the crystal structures of one (or both) of the metallic end members and contain random distributions of atoms in homogenous solid solutions. Intermetallics adopt crystal structures distinct from the metal end members and typically contain ordered atomic lattices with higher lattice energies. Atomic ordering in intermetallic NPs can also be exploited to alter reaction pathways as has been well documented in the PtBi and PtPb intermetallic electrocatalysts used in formic acid fuel cells.³⁻⁵

Due to the unique catalytic activity and enhanced stability of intermetallic catalysts, recent efforts have been devoted to preparing small intermetallic NPs to optimize surface area and atom economy. Polyol and seeded growth methods have been employed to prepare PtM NPs where M = Bi, Pb but these methods require moderate temperature annealing steps to induce crystallographic ordering (*i.e.* intermetallic formation), which can lead to undesirable particle growth.⁶ As a result, there are only a few known examples of small (< 8 nm) intermetallic NPs despite the promising properties of the catalysts.⁷⁻¹² For example, the hexagonalPtSn intermetallic electrocatalyst shows marked improvements in stability and CO tolerance in hydrogen electrooxidation applications when compared to the PtSn alloy or Pt NP catalysts of similar size.¹⁰ Likewise, the 2-3 nm PtBi intermetallics recently reported by Nazar show significantly higher mass activity for formic acid electrooxidation relative to other known catalysts.¹³

We report here the use of $\text{Sn}_9\text{Pt}_2(\text{PPh}_3)^{2-}$ and $\text{Sn}_9\text{Ir}(\text{cod})^{3-}$ molecular Zintl cluster precursors¹⁴⁻¹⁶ that give sub-8 nm intermetallic particles of PtSn_4 and Ir_3Sn_7 . The structures of the precursors are remarkably similar to the MSn_8 subunits that define the respective

intermetallic crystal lattices. These structural relationships between Zintl clusters and intermetallic phases have been well documented by Fässler.¹⁶ While the $\text{Sn}_9\text{Pt}_2(\text{PPh}_3)^{2-}$ cluster is also compositionally close to the PtSn_4 intermetallic ($\text{Pt}:\text{Sn} = 1 : 4.5$ versus $1 : 4$), the $\text{Sn}_9\text{Ir}(\text{cod})^{3-}$ precursor is significantly tin rich relative to the Ir_3Sn_7 phase ($\text{Ir}:\text{Sn} = 1 : 9$ versus $1 : 2.33$). Although the composition of $\text{Sn}_9\text{Ir}(\text{cod})^{3-}$ is much closer to the known IrSn_4 intermetallic,¹⁷ its structure is more akin to that of Ir_3Sn_7 . These results suggest that structural pre-organization of cluster precursors can be exploited to produce phase specific small intermetallic NPs.

Ordered 5 - 10 nm PtSn_4 intermetallic NPs were fabricated via the oxidation of the $[\text{Pt}_2\text{Sn}_9(\text{PPh}_3)]^{2-}$ cluster with elemental iodine at room temperature (eq. 1). The cluster precursor was prepared from a 1:1 mole ratio of K_4Sn_9 and $\text{Pt}(\text{PPh}_3)_4$ in ethylenediamine (en) in the presence of 2,2,2-crypt as previously reported.¹⁴ The PtSn_4 NPs were washed with hexanes, collected by centrifugation and characterized by TEM, EDX and XRD analysis (Figure 1).

Figure 1. (a) The High resolution TEM image and (b) X-ray diffraction experiment of ‘as-prepared’ sub-10 nm ordered PtSn_4 nanoparticles (PtSn_4 ; JCPDS 04-0744). The 2.32 Å d-spacing is associated with the 213 facet at 39.7° .

The XRD data of the as-prepared NPs clearly show the distinctive reflections associated with the PtSn_4 intermetallic (Figure 1b). EDX analysis gives a $1 : 4$ ratio of Pt to Sn and, although the cluster precursor is slightly Sn rich, we do not detect the excess tin in either the XRD studies or the TEM / EDX analysis and assume it to be amorphous. The excess Sn may

remain in solution and is effectively removed from the PtSn₄ NPs. The particles form agglomerates, most likely due to the absence of particle stabilizers that aid in colloidal dispersion.

Bulk-phase Pt-Sn bimetallics have high activity in several catalytic systems¹⁸ but Pt-Sn nanoparticles especially the Sn-rich NPs such as PtSn₄, are difficult to prepare due to differences in reduction potentials. In 2000, Jeitschko reported the single-crystal X-ray structure of PtSn₄ using crystals obtained from the reaction between powdered platinum and tin metal.¹⁹ The synthesis requires heating the elements in a Sn flux at 500 °C. The PtSn₄ intermetallic is isolated by dissolving the excess tin flux in dilute hydrochloric acid, resulting in low yields of PtSn₄ single crystals. PtSn₄ NPs are particularly difficult to isolate in pure form due to the presence of competing Pt₃Sn, PtSn, Pt₂Sn₃ and PtSn₂ phases.^{8,19} While Schaak has successfully prepared the Pt-rich intermetallic NPs,^{20,21} the corresponding PtSn₄ NPs have not previously been reported to our knowledge.

Similarly, ordered Ir₃Sn₇ intermetallic NPs were prepared via the oxidation of en solutions of [Sn₉Ir(cod)]³⁻ with toluene solutions of iodine at room temperature (eq. 2). The [Sn₉Ir(cod)]³⁻ precursor was prepared *in situ* through the reaction of en solutions of K₄Sn₉ and toluene solutions of [Ir(cod)Cl]₂ in the presence of 2,2,2-crypt.¹⁵ The synthesis and characterization of the [Sn₉Ir(cod)]³⁻ cluster were described previously. The as-prepared Ir₃Sn₇ NPs contain a preponderance of Sn metal as expected from the stoichiometry of eq. 2 (see Fig. 2). The Sn metal was removed with an HNO₃ wash (0.1 M) giving essentially amorphous Ir₃Sn₇ NPs (Figure S1). Annealing the NPs at 450 °C gives crystalline samples that retain their small size. The Ir₃Sn₇ NPs were washed with acetone, collected by centrifugation and characterized by XRD, EDS and TEM.

The Ir₃Sn₇ NPs form aggregates of 6-13 nm particles (Figure 2). The agglomeration presumably results from the lack of capping agents used in the synthesis process. The XRD analysis of the crude NP product clearly shows the presence of the Ir₃Sn₇ phase in the presence of the strong reflections of Sn metal (Figure 2). After the HNO₃ wash, some of the Ir₃Sn₇ diffraction lines are discernible (Figure S1) but there is no detectable Sn remaining in the sample.

However, the TEM images show only Ir₃Sn₇ NPs as indicated by the distinctive lattice fringes (Figure 2) with 200, 211, 222, and 330 facets (19.0°, 23.3°, 33.2°, and 40.9°, respectively); the most prominent corresponding to the 4.71 Å d-spacing associated with the 200.

Figure 2.(a) The high-resolution TEM image and (b) X-ray diffraction data of annealed intermetallic Ir₃Sn₇ nanoparticles. The particles for the TEM experiments were washed with nitric acid to remove the excess Sn (Ir₃Sn₇, JCPDS 01-072-4234).

Although the [Sn₉Ir(cod)]³⁻ precursor (Ir:Sn = 1 : 4.5) is closer in composition to the IrSn₄ intermetallic than that of the Ir₃Sn₇ (Ir:Sn = 1 : 2.3), IrSn₄ is not observed in our experiments. To further probe the effect of precursor composition, we studied the effect of stoichiometry to see if alternate phases could be produced. In all cases, the K₄Sn₉ and [Ir(cod)Cl]₂ precursors were pre-mixed in the presence of 2,2,2-crypt prior to oxidation, as is required for [Sn₉Ir(cod)]³⁻ cluster formation. Three different Ir:Sn ratios were investigated; 1:9, 1:4.5 and 3:7, but all reactions

gave exclusively Ir₃Sn₇ in the presence of large excesses of metallic Sn. In the absence of 2,2,2-crypt, only Sn metal was observed by XRD and no intermetallic formation was detected. These data suggest that the [Sn₉Ir(cod)]³⁻ cluster is a necessary intermediate in the formation of Ir₃Sn₇.

As further evidence for the Zintl cluster route of the synthesis of the two NPs, co-reduction experiments were conducted in attempts to isolate the materials through a more traditional method. In the case of the Ir₃Sn₇ phase, K₄Sn₉ and [Ir(cod)Cl]₂ precursors were reacted with an iridium-tin ratio of 3:7, in the presence of 2,2,2-crypt and sodium triethylborohydride as a reducing agent. Neither synthesis method afforded measureable amounts of the desired PtSn₄ or Ir₃Sn₇ phases by XRD experiments. In the case of the IrSn system, the same precursors were used as in the Zintl cluster route indicating the necessity of the synthesis of the [Sn₉Ir(cod)]³⁻ ion as a precursor due to its similarity in molecular structure to the crystal lattice of Ir₃Sn₇ (see below).

The PtSn₈ subunits that define the structures of the PtSn₄ intermetallic and the [Pt@Sn₉Pt(PPh₃)]²⁻ cluster are strikingly similar, as illustrated in Figure 3 and Table 1. The [Pt@Sn₉Pt(PPh₃)]²⁻ ion has C_{3v} point symmetry with a 9-coordinate endohedral Pt atom. However, the structure can be viewed as a distorted mono-capped square antiprism as is emphasized in Figure 3c. The crystal structure of PtSn₄, Figure 3a-b, contains very regular PtSn₈ square antiprism repeat units, which define the orthorhombic *Ccca* PtSn₄ lattice. The PtSn₄ structure contains two-dimensional arrays of the PtSn_{8/2}square antiprisms that share common edges in the x-y plane. The layers are linked by weak Sn-Sn bonds (*d*_{Sn-Sn} = 2.7(3) Å, ave.) along the z direction of the monoclinic cell.^{17,19} The 8 Pt-Sn contacts within the square antiprismatic subunits of both the PtSn₄ intermetallic and the [Pt@Sn₉Pt(PPh₃)]²⁻ are equivalent at 2.75(1) Å, ave.¹⁴ Aside from the slight trigonal elongation of the PtSn₈ subunit in the [Pt@Sn₉Pt(PPh₃)]²⁻ ion, the cluster is ideally pre-organized to form the PtSn₄ intermetallic.

Figure 3. (a) Crystal lattice of PtSn_4 (pink = Pt, blue = Sn); (b) atomic arrangement of Sn atoms about each Pt atom in PtSn_4 ; (c) the PtSn_8 subunit of the $[\text{Pt}@\text{Sn}_9\text{Pt}(\text{PPh}_3)]^{2-}$ cluster showing the similarity to the structure of PtSn_4 ; (d) the $[\text{Pt}@\text{Sn}_9\text{Pt}(\text{PPh}_3)]^{2-}$ cluster.^{14,19}

Structural similarities are also present between the Ir_3Sn_7 intermetallic and the $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ ion as shown in Figure 4. The monocapped square anti-prism in Figure 4c is also found in the crystal lattice of Ir_3Sn_7 as a repeating subunit (Figure 4b).^{22,23} The fundamental $\text{Ir}_2\text{Sn}_{12}$ structural subunit in the Ir_3Sn_7 crystal lattice contains two IrSn_8 square antiprisms that share a common face (Figure 4b). These $\text{Ir}_2\text{Sn}_{12}$ double prisms share common corners with other double prisms to make a cubic array with Im-3m crystal symmetry (Figure 4a).^{22,23} The structure of $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ contains an Ir-capped square antiprism but the endohedral Ir atom is missing. However, the IrSn_4 capped square prismatic subunits of the Ir_3Sn_7 intermetallic and the $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ cluster anion are quite similar with equivalent Ir-Sn contacts of 2.77(9) Å, ave (Figure 4, Table 1). The Sn-Sn contacts of $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ are more varied than those of Ir_3Sn_7 ; especially groups A and C (See table 1). These differences are not unexpected in view of the differences in composition and charge.

Figure 4. (a) Crystal lattice of Ir_3Sn_7 (green = Ir, blue = Sn); (b) the $\text{Ir}_2\text{Sn}_{12}$ subunit in the Ir_3Sn_7 crystal lattice; (c) IrSn_4 subunits in Ir_3Sn_7 ; (d) The IrSn_9 core of the $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ ion; (e) the $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ cluster anion.^{15,22,23}

Table 1. Average bond lengths of Zintl clusters and intermetallics (Å).

Subgroups	$\text{PtSn}_4^{(a)}$	$[\text{Sn}_9\text{Pt}_2(\text{PPh}_3)]^{2-(b)}$	$\text{Ir}_3\text{Sn}_7^{(c)}$	$[\text{Sn}_9\text{Ir}(\text{cod})]^{3-(d)}$
A (M-Sn) M=Pt,Ir	2.766	2.746(9)	2.762	2.770(9)
B (Sn-Sn)upper square	3.376	3.052(52)	3.307	3.110(27)
C (Sn-Sn)waist	3.390	3.291(68)	3.582	2.989(22)
D (Sn-Sn)lower square	3.376	3.543(4)	3.086	3.151(56)

(a) ref.¹⁸ (b) ref.^{14a} (c) ref.²² (d) ref.^{14b}

There are 3 forms of IrSn_4 ; α - IrSn_4 , β - IrSn_4 and HT- IrSn_4 . The latter 2 phases are very similar to the PtSn_4 structure but are only found at high temperature or pressure. α - IrSn_4 is the ambient phase but has a trigonal structure with distorted bisdisphenoid IrSn_8 subunits that are quite distinct from the PtSn_4 -type subunits.¹⁷ The presence of the IrSn_4 square pyramids throughout the Ir_3Sn_7 crystal lattice apparently leads to its selective formation over other phases in the oxidation of $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$.

The atomic pre-organization of $\text{Sn}_9\text{Pt}_2(\text{PPh}_3)]^{2-}$ and $[\text{Sn}_9\text{Ir}(\text{cod})]^{3-}$ provides a direct, facile route to the synthesis of ordered intermetallic NPs that are difficult to prepare by other methods. In the case of the Ir_3Sn_7 NPs, the importance of cluster structure over stoichiometry is particularly supported by the discrepancy in Ir:Sn ratios between the intermetallic and cluster. Despite the 1:9 atomic ratio, ordered Ir_3Sn_7 NPs were formed instead of the more stoichiometric IrSn_4 phases.

Many bimetallic Zintl clusters isolated to date are composed of elements pertinent to various catalytic applications including $[\text{Pt}@\text{Pb}_{12}]^{2-}$, $[\text{Pd}_2@\text{Sn}_{18}]^{4-}$, $[\text{Sn}_9\text{Ni}_2(\text{CO})]^{3-}$, and $[\text{Pb}_9\text{Ir}(\text{cod})]^{3-}$ to name a few.^{14,15,24-26} The facile room temperature synthesis of the PtSn_4 and Ir_3Sn_7 NPs is important because it provides a pathway to small, ordered NPs making them readily available for the first time. The findings of this study show that the synthesis method may possibly be extended to other transition metal-stannide systems currently under investigation that could potentially yield other catalytically active materials. The catalytic activity of these various NPs will be tested in future studies, while we also aim to compare and contrast the catalytic activity of the well-studied PtSn and Pt_3Sn phases.

Experimental Section

Chemicals: K_4Sn_9 was made by high-temperature fusion ($\sim 1000^\circ\text{C}$) of stoichiometric amounts of the elements. The chemicals were loaded into evacuated silica tubes and carefully heated with a natural gas/oxygen flame behind a blast shield. 4,7,13,16,21,24-Hexaoxa-1,10-diazobicyclo[8.8.8]hexacacosane (2,2,2-crypt) were purchased from Fisher. Bis(1,5-cyclooctadiene)diiridium(I) dichloride and iodine was purchased from Adrich. Anhydrous ethylenediamine (en) and pyridine (pyr) were purchased from Fisher, vacuum distilled from K_4Sn_9 , and stored under dinitrogen. Toluene was distilled from sodium/benzophenone under dinitrogen and stored under dinitrogen.

Synthesis of PtSn_4 nanoparticles: A previously published protocol¹⁴ was followed to synthesize $[\text{K}(2,2,2\text{-crypt})]_2[\text{Sn}_9\text{Pt}_2(\text{PPh}_3)]$ precursor. In vial 1, K_4Sn_9 (80 mg, 0.065 mmol) was dissolved in en (~ 2 mL), giving a dark red solution. Four equivalents of solid crypt (98 mg, 0.260 mmol) were added to the solution and allowed to stir for an hour. In vial 2, $\text{Pt}(\text{PPh}_3)_4$ (81 mg, 0.065

mmol) was dissolved in toluene (~2 mL) to produce yellow solution. The contents of vial 2 were slowly added to vial 1 and the reaction mixture was stirred for 2 h to yield a dark brown solution. The reaction mixture was then filtered through tightly packed glass wool in a pipet. Dark red crystals formed in the reaction vessel after 2 weeks. ^{31}P NMR (162.0 MHz, Pyr, 25°C) $\delta = 34.8$ ppm ($^1\text{J}(^{195}\text{Pt}, ^{31}\text{P}) = 4777$ Hz, $^2\text{J}(^{195}\text{Pt}, ^{31}\text{P}) = 296$ Hz). $[\text{K}(2,2,2\text{-crypt})]_2[\text{Sn}_9\text{Pt}_2(\text{PPh}_3)]$ crystals (10 mg, 0.004 mmol) dissolved and stirred in en for ten minutes. Elemental iodine (10 mg, 0.038 mmol) dissolved in minimal toluene was added to solution of $[\text{K}(2,2,2\text{-crypt})]_2[\text{Sn}_9\text{Pt}_2(\text{PPh}_3)]$ dropwise and stirred for an hour. Solution precipitates, giving a black solid. Solvent drained off and particles rinsed in hexanes, sonicated, and isolated via centrifugation.

Synthesis of Ir_3Sn_7 nanoparticles: A previously published protocol¹⁵ was followed to synthesize $\text{K}(2,2,2\text{-crypt})_3[\text{Sn}_9\text{Ir}(\text{cod})]$ precursor. In vial 1, K_4Sn_9 (54 mg, 0.044 mmol) was dissolved in en (~2 mL), giving a dark red solution. Three equivalents of solid crypt (50 mg, 0.133 mmol) were added to the solution and allowed to stir for an hour. In vial 2, $[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ (30 mg, 0.044 mmol) was dissolved in toluene (~2 mL) to produce an orange-yellow solution. The contents of vial 2 were slowly added to vial 1 and the reaction mixture was stirred for 2 h to yield a dark brown solution. The reaction mixture was then filtered through tightly packed glass wool in a pipet. Elemental iodine (10 mg, 0.038 mmol) dissolved in minimal toluene was added to the reaction solution dropwise and stirred for an hour. Solution precipitates, giving a black solid. Solvent drained off and particles rinsed in acetone, dispersed, and isolated via centrifugation. Excess tin removed by nitric acid rinse.

IrSn co-reduction: K_4Sn_9 (54 mg, 0.044 mmol), $[\text{Ir}(\text{C}_8\text{H}_{12})\text{Cl}]_2$ (57 mg, 0.085 mmol), and three equivalents of solid crypt (50 mg, 0.133 mmol) were mixed in 20 mL of phenyl ether under nitrogen and stirred. Temperature increased to 200°C and 1.0 M $\text{Na}(\text{BHEt}_3)$ carefully added to the reaction. Reaction mixture refluxed for 30 minutes then allowed to cool to RT. Solvent drained off of black solid and particles rinsed in ethanol, dispersed, and isolated via centrifugation.

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Supporting Information: X-ray data of acid washed material.

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