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Step-by-Step Synthesis of the Endohedral Stannaspherene $[Ir@Sn_{12}]^{3-}$ via the Capped Cluster Anion $[Sn_9Ir(cod)]^{3-}$**

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

Abstract: The endohedral stannaspherene cluster anion $[Ir@Sn_{12}]^{3-}$ was synthesized in two steps. The reaction of K_4Sn_9 with $[IrCl(cod)]_2$ (cod: 1,5-cyclooctadienyl) in ethylenediamine (en) solution first yielded the $[K(2,2,2\text{-crypt})]^+$ salt (2,2,2-crypt: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) of the capped cluster anion $[Sn_9Ir(cod)]^{3-}$. Subsequently, crystals of this compound were dissolved in en, followed by the addition of triphenylphosphine or 1,2-bis(diphenylphosphino)ethane and treatment at elevated temperatures. $[Ir@Sn_{12}]^{3-}$ was obtained and characterized as the $[K(2,2,2\text{-crypt})]^+$ salt. The isolation of $[Sn_9Ir(cod)]^{3-}$ as an intermediate product establishes that the formation of the stannaspherene $[Ir@Sn_{12}]^{3-}$ occurs through the oxidation of $[Sn_9Ir(cod)]^{3-}$. Among the structurally characterized tetrel cluster anions, $[Ir@Sn_{12}]^{3-}$ is a unique example of a stannaspherene, and one of the rare spherical clusters encapsulating a metal atom that is not a member of Group 10. Single-crystal structure determination shows that the novel Zintl ion cluster has nearly perfect icosahedral I_h point symmetry.

Keywords: cluster compounds · intermetalloids · polyhedrons · synthesis design · Zintl anions

Introduction

Research on the synthesis of heteroatomic ligand-free clusters from homoatomic polyanions (Zintl ions) of the heavier tetrel elements has advanced greatly in the last decade and resulted in a series of cluster anions with fascinating polyhedral structures. Examples include spherical tetrel clusters encapsulating a late-transition-metal atom, namely $[Ni@Ge_9]^{3-}$,[1] $[Cu@E_9]^{3-}$ (E = Sn and Pb),[2] $[Ni@Pb_{10}]^{2-}$, and $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[3] as well as larger, nonspherical endohedral clusters containing more than one transition-metal atom, for example, $[Ni_2@Sn_{17}]^{4-}$,[4] $[Pt_2@Sn_{17}]^{4-}$,[5] $[Pd_2@Ge_{18}]^{4-}$,[6] $[Pd_2@Sn_{18}]^{4-}$,[7] and $[Ni_3@Ge_{18}]^{4-}$.[1a] Furthermore, there are polyanions, such as $[Au_3(Ge_9)_2]^{5-}$,[8] $[Hg_3(Ge_9)_4]^{10-}$,[9] and $^1{}_\infty[HgGe_9]^{2-}$,[10] that feature nine-atom germanium clusters linked by transition-metal atoms. The structural diversity exhibited by these anions was further extended by the pentagonal prismatic $[Co@Ge_{10}]^{3-}$,[11] the first nondeltahedral representative among these clusters, and the isostructural, probably paramagnetic, iron derivative $[Fe@Ge_{10}]^{3-}$[12] found shortly after. The current size record for this class of clusters was set by $[Au_3Ge_{45}]^{9-}$[13] with 45 Ge atoms, which exceeds even the largest of the homoatomic oligomers $[(Ge_9)_n]^{x-}$ ($n = 2$, 3, 4)[14] that are built up of covalently linked Ge_9 clusters and represents the largest isolated homoatomic tetrel polyanion known so far.

These ligand-free heteroatomic clusters are named intermetalloids,[15] according to "metalloid" clusters.[16] They might close the gap between the complex structures of interpenetrating or linked clusters, as they occur in neat intermetallic compounds, and rather simple species generated in the gas phase under high-vacuum conditions. The ongoing interest in ligand-free homoatomic and intermetalloid Zintl clusters largely stems from their (anticipated) ability to act as precursors or building blocks for the formation of nanomaterials, as has already been shown for the homoatomic clusters.[17] In this context, the ligand-free Zintl anions are remarkable analogous candidates[18] alongside well-known sys-

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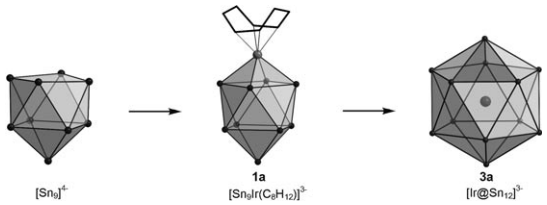
tems such as fullerenes and fullerides.[19] With respect to the possibility of covalent linkage between the cages and their ability to encapsulate other metal atoms, Zintl ions are even ahead of the fullerenes and fullerides.

In contrast to fullerenes,[20] the number of structurally characterized homoatomic cages of the heavier Group 14 elements E (E = Ge, Sn, and Pb) that encapsulate other metal atoms increases rapidly. These intermetalloid cluster anions can be obtained from reactions of $[E_9]^{4-}$ ions with the corresponding transition-metal complexes and are available in good yields. Many of the compounds containing these intermetalloid clusters can even be obtained in larger quantities than the endohedral fullerenes.[21] In the last few years, the icosahedral 12-atom clusters of Sn and Pb have attracted much interest because of their comparable size and symmetry (I_h) to the C_{60} fullerene. $[Sn_{12}]^{2-}$ and $[Pb_{12}]^{2-}$ were named stannaspherene and plumbaspherene, respectively, in view of this analogy, and the calculated diameters of these nearly spherical clusters are ~6.1 and ~6.3 Å for $[Sn_{12}]^{2-}$ and $[Pb_{12}]^{2-}$, respectively.[22] Their stability and their capability to host many different types of metal atoms are shown by recent studies based on photoelectron spectroscopy measurements of gas-phase species and quantum-chemical calculations.[23] The list of endohedral stannaspherene and plumbaspherene clusters that were subjected to these studies comprises clusters with encapsulated main-group metals, with $[Al@Pb_{12}]^{+}$ probably being the most prominent example,[24] numerous d-block transition-metal-atom-centered Sn_{12} and Pb_{12} clusters,[23,25] and various endohedral clusters containing f-block element atoms. In the case of centered plumbaspherenes, detailed theoretical studies have been performed even for species featuring centered actinide atoms such as Pu.[26] However, up to now only the plumbaspherene clusters with Group 10 central atoms $[M@Pb_{12}]^{2-}$ (M = Ni, Pt, Pd) have been obtained by wet-chemical synthesis and structurally characterized as their $[K(2,2,2\text{-crypt})]^{+}$ salts (2,2,2-crypt: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) by Eichhorn et al.[3] No crystal structure determination of any $[M'@Sn_{12}]^{x-}$ (M′ = metal atom) cluster has been reported so far. Some attempts to synthesize endohedral stannaspherene clusters resulted in the discovery of $[Pd_2@Sn_{18}]^{4-}$, a deltahedral 18-atom cage containing two endohedral transition-metal atoms, which can formally be described as the result of the fusion of two $[Pd@Sn_9]^{2-}$ fragments.[7] Despite the continually increasing number of structurally characterized intermetalloid clusters $[M_m@E_n]^{x-}$ (M = metal atom, E = Ge, Sn, and Pb) with $n > 9$, their formation from nine-atom clusters $[E_9]^{x-}$ remains unexplained.

Results and Discussion

In the context of our latest research on the synthesis of intermetalloid cluster compounds by the use of Group 14 Zintl ions,[2,11,27] the ligand-free iridium-centered icosahedral cluster $[Ir@Sn_{12}]^{3-}$ (**3a**) was obtained from the metal-capped cluster $[Sn_9Ir(cod)]^{3-}$ (**1a**; cod: 1,5-cyclooctadienyl), which was first yielded by the reaction of $[Sn_9]^{4-}$ with $[IrCl(cod)]_2$ (Scheme 1). The isolation of **1a** as an intermediate product provides remarkable experimental evidence for the stepwise



Scheme 1. Synthesis of $[Sn_9Ir(cod)]^{3-}$ (**1a**) and $[Ir@Sn_{12}]^{3-}$ (**3a**).

formation of the endohedral cluster anion **3a**. The anion **1a** was obtained from the reaction of K_4Sn_9 with $[IrCl(cod)]_2$ in ethylenediamine (en) solution in the presence of 2,2,2-crypt or 18-crown-6. The reaction at ambient temperature leads to the compounds $[K(2,2,2\text{-crypt})]_3[Sn_9Ir(cod)]$ (**1**) and $[K(18\text{-crown-6})]_3[Sn_9Ir(cod)]\cdot tol\cdot en$ (**2**; tol: 4-methylphenyl) in very good yields of about 80%. The salts have been characterized by single-crystal X-ray diffraction and energy-dispersive X-ray (EDX) analysis. The anionic clusters are well ordered and virtually identical in both compounds **1** and **2**.

The structure of the $[Sn_9Ir(cod)]^{3-}$ cluster (**1a**) corresponds to a Sn_9 monocapped square antiprism coordinating to the Ir atom of the {Ir(cod)} fragment through its open square face (Figure 1). The Sn–Sn distances along the edges of the polyhedron range from 2.9256(9) to 3.2035(9) Å and thus are close to those reported previously for Sn_9 clusters capped by transition-metal organometallic fragments such as $M''(CO)_3$ (M″ = Cr, Mo, W),[28] ZnPh,[29] and CdPh.[30] The Ir–Sn distances are in the range of 2.7605(7) to 2.7772(6) Å. Chemical bonding in **1a** can be discussed in analogy to the

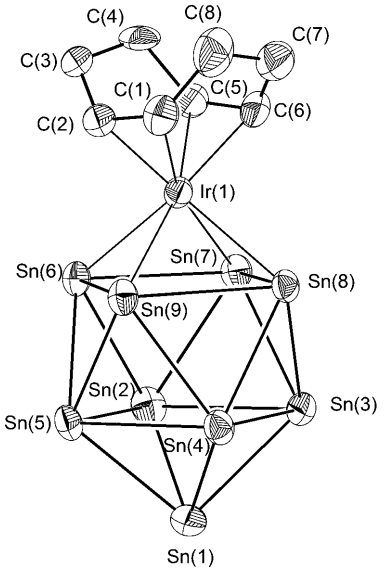


Figure 1. Structure of the $[Sn_9Ir(cod)]^{3-}$ ion (**1a**) in **1**. A virtually identical anion is present in **2**. Atomic displacements are shown at 50% probability level. For selected bond lengths and angles, see ref. [34].

organometallic compound $[CpIr(cod)]$[31] (Cp: C_5H_5) with the Cp^- ligand substituted by $[Sn_9]^{4-}$ which formally acts as a six-electron donor to an $\{Ir(cod)\}^+$ fragment. According to Wade's electron counting rules,[32] with its extension to the isolobal concept[33] (to account for the contribution from the transition-metal organometallic fragment), $[Sn_9Ir(cod)]^{3-}$ (**1a**) can be rationalized as a ten-vertex *closo* cluster with the required 22 ($2n+2$) skeletal bonding electrons provided by $[Sn_9]^{4-}$ (each Sn atom donating two electrons) and no electrons contributed by the $\{Ir(cod)\}^+$ fragment. Alternatively it is possible to count two skeletal electrons for each Sn atom, one electron for a neutral {Ir(cod)} fragment, and three electrons for the cluster's total charge, again adding up to 22 electrons ($9\times2+1+3$). The ^{119}Sn NMR spectrum reveals only one signal at $\delta=-1149$ ppm with satellites due to ^{117}Sn–^{119}Sn coupling (see the Supporting Information), and indicates a fast exchange of the Sn atoms. The shift is in the range of other intermetalloid clusters such as $[Cu@Sn_9]^{3-}$ ($\delta=-1431$ ppm, DMF)[2] and $[Pd_2@Sn_{18}]^{4-}$ ($\delta=-730$ ppm, DMF).[7]

Regarding the fact that $[Sn_9Ir(cod)]^{3-}$ (**1a**) can be a precursor for the endohedral stannaspherene $[Ir@Sn_{12}]^{3-}$ (**3a**), it is worth noting here that cod ligands are very labile in transition-metal complexes and easily provide ligand-free metal atoms as has been shown before for the reactions of $[Ni(cod)_2]$ with K_4Ge_9,[1] K_4Sn_9,[4] and K_4Pb_9.[3] Compound **1**, the $[K(2,2,2\text{-crypt})]^+$ salt of $[Sn_9Ir(cod)]^{3-}$ (**1a**), was used as starting material for the reaction that yielded $[Ir@Sn_{12}]^{3-}$ (**3a**). Crystals of **1** were dissolved in en, and subsequent addition of triphenylphosphine (PPh_3) or 1,2-bis(diphenylphosphino)ethane (DPPE) to this en solution of $[Sn_9Ir(cod)]^{3-}$ (**1a**), followed by heating to 80 °C, yielded the anion $[Ir@Sn_{12}]^{3-}$ (**3a**) which was isolated as the $[K(2,2,2\text{-crypt})]^+$ salt in the form of nicely shaped red single crystals of $[K(2,2,2\text{-crypt})]_3[Ir@Sn_{12}]\cdot$tol (**3**). ^{31}P NMR spectroscopy was employed to confirm that DPPE acts as an oxidizing agent during the reaction. The ^{31}P NMR spectrum of a sample of the en solution after the reaction of **1** and DPPE (see the Supporting Information) shows, in addition to the signal of DPPE at $\delta=-12$ ppm, two further resonance signals at $\delta=-2.9$ and -19.0 ppm which were assigned to the reduced species Ph_2P^- and $(Ph_2PCH_2CHPPh_2)^-$, respectively.[35] The role of phosphines as oxidizing agents has been suggested before.[3] The formation of a dark precipitate during the reaction was observed and is indicative of an insoluble by-product.

The compound $[K(2,2,2\text{-crypt})]_3[Ir@Sn_{12}]\cdot$tol (**3**) crystallizes in the monoclinic space group *C*2/*c*. The $[Ir@Sn_{12}]^{3-}$ anion (**3a**) features nearly perfect I_h point group symmetry, although the only crystallographically imposed symmetry element is a center of inversion (Figure 2). The Sn–Sn distances range from 3.0250(8) to 3.1004(9) Å with a mean value of 3.065 Å (d) and the Ir–Sn distances are in the very narrow range of 2.8828(5) to 2.9414(5) Å with a mean value of 2.922 Å (R). The R/d ratio for $[Ir@Sn_{12}]^{3-}$ (**3a**) is 0.953 and deviates only slightly from the ideal value of 0.951,[15,36] which was observed for the plumbaspherene $[Pt@Pb_{12}]^{2-}$.[3]

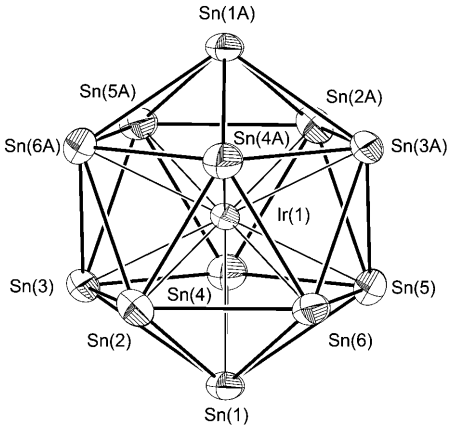


Figure 2. Structure of the $[Ir@Sn_{12}]^{3-}$ ion (**3a**) in **3**. Atomic displacements are shown at 50% probability level. For selected bond lengths and angles, see ref. [42].

The Sn–Sn distances in **3a** are in the range typically observed for polyhedral anionic Sn clusters[37] and the Ir–Sn distances are considerably larger than normal Ir–Sn single bonds.[38] Compared to the capped cluster in **1a**, this distance is enlarged by about 5%. Similar observations have been made for $[Bi_{10}]^{4+}$ clusters. Au–Bi distances in the filled cluster $[Au@Bi_{10}]^{5+}$ are also about 5% longer than in the bicapped cluster $[Au_2Bi_{10}]^{6+}$.[39]

Larger interatomic distances originate from the high coordination number and are indicative of weak interactions between Ir and Sn atoms if compared to single bonds. Generally, higher coordination numbers are frequent in intermetallic compounds such as Ir_3Sn_7 or the ternary compound $LiIrSn_4$, in which the Ir atoms are coordinated by eight Sn atoms in a square antiprismatic arrangement. The Sn–Sn distances in $LiIrSn_4$ are in the range of 2.940 to 3.121 Å;[40] these and also the Ir–Sn distances of 2.799 Å match well with those in the intermetalloid cluster $[Ir@Sn_{12}]^{3-}$ (**3a**). Interatomic distances in the same range also occur in binary Sn-rich Ir–Sn intermetallic phases.[41] Despite this intriguing match in interatomic distances of intermetallic compounds and intermetalloid clusters, differences exist in the nature of the chemical bond. Whereas delocalized metallic bonds are dominant in intermetallic compounds, the chemical bonding of the intermetalloid cluster **3a** is better described on the basis of a molecular orbital approach. According to Wade's rules, a 12-vertex polyhedron requires 26 ($2n+2$) skeletal electrons to form a *closo* cluster. The assumption of a stannaspherene $[Sn_{12}]^{2-}$ which encapsulates an Ir atom with the formal charge of -1, that is, a d^{10} electron configuration for the transition metal, leads to the required number of electrons. $[Sn_{12}]^{2-}$ provides the 26 electrons ($12\times2+2$) and the centered d^{10} transition metal does not contribute any skeletal bonding electrons. Similar findings with encapsulated d^{10} elements have been reported for both filled anionic and cationic intermetalloid clusters.[3,39a] Actually, up to now, the encapsulated transition metal in all structurally characterized deltahedral $[M@E_n]^{x-}$ (M = transition-metal atom; E =

Ge, Sn, Pb) clusters obtained from homoatomic tetrel Zintl anions is either a member of Group 10, as is the case for $[Ni@Ge_9]^{3-}$,[1] $[Ni@Pb_{10}]^{2-}$, and $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[3] or it shows a d^{10} configuration, namely $[Cu@E_9]^{3-}$ (E = Sn, Pb) which can be described as $[Cu^{+}@E_9]^{4-}$.[2] The encapsulated transition-metal atom with closed-shell d^{10} configuration does not contribute electrons to the skeletal electron count of the cluster. However, it provides orbitals for interaction with the cluster orbitals, thus leading to an overall stabilization of the cluster. The main contribution to this effect is attributed to the empty s and p orbitals.[1b,3a,39a] For $[Pt@Pb_{12}]^{2-}$ and $[Cu@Sn_9]^{3-}$ these interactions have been illustrated explicitly by molecular-orbital diagrams based on extended Hückel molecular orbital (EHMO) or DFT calculations, respectively.[2,3a]

To our knowledge the $[Ir@Sn_{12}]^{3-}$ anion has not yet been considered in any of the computational studies on endohedral stannaspherenes. Therefore, DFT calculations were performed on $[Ir@Sn_{12}]^{3-}$ (computational details are given in the Experimental Section). Structure optimizations led to a ground-state structure with icosahedral symmetry (I_h), consistent with the structure of $[Ir@Sn_{12}]^{3-}$ experimentally found in **3a**. A HOMO–LUMO gap of 2.28 eV is calculated for $[Ir@Sn_{12}]^{3-}$. The natural charge calculated for Ir in $[Ir@Sn_{12}]^{3-}$ is −1.07, which points towards the expected d^{10} configuration of Ir and supports a formal description of the cluster as $[Ir^{-}@Sn_{12}^{2-}]$. The calculated interatomic distances of 3.144 Å between neighboring Sn atoms and 2.990 Å between the central Ir atom and the Sn atoms are in good agreement with the mean crystallographically observed values of 3.065 and 2.922 Å, respectively. To compare the size of the endohedral cluster with that of an empty $[Sn_{12}]^{2-}$ anion, a structure optimization for $[Sn_{12}]^{2-}$ was carried out at the same level as the calculations for $[Ir@Sn_{12}]^{3-}$. The optimized Sn–Sn distance for icosahedral (I_h) $[Sn_{12}]^{2-}$ is 3.125 Å, in agreement with previously reported calculations.[22a] This value is only slightly smaller than that calculated for $[Ir@Sn_{12}]^{3-}$, thus indicating that the encapsulated Ir atom has little effect on the structure of the stannaspherene cluster.

Conclusion

It should be pointed out that only a few examples of structurally characterized ligand-free icosahedral clusters with I_h point symmetry exist. Except for the well-known icosahedron $(B_{12}H_{12})^{2-}$[43] and C_{60},[44] only $[As@Ni_{12}@As_{20}]$[45] and the Pb species $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt)[3] are described in the literature. Further examples, such as $[Cd@Tl_{12}]^{12-}$[46] and $[Tl@Tl_{12}]^{11-}$,[47] only exist in neat solids. To our knowledge, $[Ir@Sn_{12}]^{3-}$ (**3a**) represents the first structurally characterized stannaspherene Sn_{12} cluster and also the first observed encapsulation of a Group 9 element in a spherical tetrel deltahedron. Because $[Ir@Sn_{12}]^{3-}$ (**3a**) is yielded from $[Sn_9Ir(cod)]^{3-}$ (**1a**), this Sn_9 cluster capped by a transition-metal organometallic fragment seems to be a crucial intermediate during the formation of the transition-metal-centered cluster of higher nuclearity (**3a**). The reported reaction sheds new light on the directed synthesis of intermetalloids.

Experimental Section

Syntheses: All manipulations and reactions were performed in a purified Ar atmosphere, by using standard Schlenk-line or glove-box techniques. The intermetallic phase of nominal composition "K_4Sn_9" was synthesized by heating stoichiometric amounts of the elements K and Sn at 550 °C for 20 h in a stainless-steel tube. Ethylenediamine (Merck, 99 %) was distilled over CaH_2 and stored in an Ar-filled Schlenk tube; 2,2,2-crypt (Merck), 18-crown-6 (Merck), $[IrCl(cod)]_2$ (Heraeus, 98 %), and DPPE (Acros, 98 %) were dried under vacuum for 8–12 h.

$[K(2,2,2\text{-crypt})]_3[Sn_9Ir(cod)]$ (1): K_4Sn_9 (185 mg, 0.15 mmol) was dissolved in en (1.5 mL) in a Schlenk tube. The red solution was stirred for 30 min and filtered onto a mixture of $[IrCl(cod)]_2$ (50 mg, 0.075 mmol) and 2,2,2-crypt (225 mg, 0.6 mmol). The dark green solution was stirred for 3 h at ambient temperature, then filtered and layered with toluene to allow for crystallization. After one week, dark green prism-shaped crystals formed on the bottom of the Schlenk tube. Yield: ~82 % based on $[IrCl(cod)]_2$ (330 mg). Semiquantitative EDX spectra of the crystals were recorded with a JEOL 5900 LV scanning electron microscope equipped with a Röntec EDX detector, which showed the presence of the elements K, Ir, and Sn. ^{1}H NMR (400 MHz, CD_3CN): $\delta = 3.57$ (s, 36H; 2,2,2-crypt), 3.52 (m, 36H; 2,2,2-crypt), 2.53 (m, 36H; 2,2,2-crypt), 2.19 (br, 4H; 1,5-cod), 1.56 ppm (br, 8H; 1,5-cod).

$[K(18\text{-crown-}6)]_3[Sn_9Ir(cod)]\cdot tol\cdot en$ (2): The method was similar to the synthesis of **1** but 18-crown-6 was used instead of 2,2,2-crypt. Yield: ~80 % based on $[IrCl(C_8H_{12})]_2$ (290 mg).

$[K(2,2,2\text{-crypt})]_3[Ir@Sn_{12}]\cdot tol$ (3): $[K(2,2,2\text{-crypt})]_3[Sn_9Ir(C_8H_{12})]$ (**1**) (290 mg, 0.1 mmol) was dissolved in en (1.5 mL) in a Schlenk tube. The dark green solution was stirred for 30 min. After addition of DPPE (80 mg, 0.2 mmol), the solution was stirred for 1 h at ambient temperature and for 1 h at 80 °C. The final red solution was filtered and layered with toluene. After one week, red plate-shaped crystals appeared on the bottom of the tube. Yield: ~22 % (67 mg). Semiquantitative EDX analysis of the crystals showed the presence of the elements K, Ir, and Sn, with approximate ratios K:Ir:Sn = 3:1:12.

Structure determination: Single-crystal X-ray diffraction data for $[K(2,2,2\text{-crypt})]_3[Sn_9Ir(cod)]$ (**1**), $[K(18\text{-crown-}6)]_3[Sn_9Ir(cod)]\cdot tol\cdot en$ (**2**), and $[K(2,2,2\text{-crypt})]_3[Ir@Sn_{12}]\cdot tol$ (**3**) were collected on an Oxford Diffraction Xalibur3 diffractometer at 150(2) K with MoKα radiation. The crystals were selected under perfluoropolyalkylether and mounted on a glass fiber. The structures were solved by Direct Methods and refined on F^2 using the SHELXTL V6.1[48] package.

Structure determination of $[K(2,2,2\text{-crypt})]_3[Sn_9Ir(cod)]$ (1): Relative molecular mass $M_r = 2615.55$; crystal size $0.12 \times 0.10 \times 0.10$ mm; triclinic; space group $P\bar{1}$; $a = 14.8491(2)$, $b = 14.8987(2)$, $c = 23.6683(3)$ Å; $\alpha = 93.19(1)$, $\beta = 93.33(1)$, $\gamma = 112.60(1)°$; $V = 4808.6(4)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.806$ g cm^{-3}; $\mu = 3.86$ mm^{-1}; $T_{max}/T_{min} = 0.70/0.65$; $T = 150(2)$ K; $2\Theta_{max} = 50°$; 56373 measured reflections; 16024 independent reflections; $R_{int} = 0.036$. The en molecules are heavily disordered in the crystal structure. Thus, the SQUEEZE option of the PLATON program was used to model their contribution to the structure factors in the final refinement.[49] $R_1 = 0.038$ and $wR_2 = 0.102$ for $I > 2\sigma(I)$; $R_1 = 0.056$ and $wR_2 = 0.123$ for all data; min./max. residual electron density: −1.36/1.68 e Å^3.

Structure determination of $[K(18\text{-crown-}6)]_3[Sn_9Ir(cod)]\cdot tol\cdot en$ (2): $M_r = 2431.06$; crystal size $0.38 \times 0.13 \times 0.11$ mm; orthorhombic; space group $Pna2_1$; $a = 32.8723(4)$, $b = 15.4134(3)$, $c = 15.4432(2)$ Å; $V = 7824.7(2)$ Å^3; $Z = 4$; $\rho_{calcd} = 2.064$ g cm^{-3}; $\mu = 4.730$ mm^{-1}; $T_{max}/T_{min} = 0.62/0.27$; $T = 150(2)$ K; $2\Theta_{max} = 50°$. The crystal was an inversion twin with equal volume domains. 46925 measured reflections; 13581 independent reflections; $R_{int} = 0.039$; $R_1 = 0.047$ and $wR_2 = 0.118$ for $I > 2\sigma(I)$; $R_1 = 0.057$ and

$wR_2 = 0.121$ for all data; min./max. residual electron density: −2.44/2.70 e Å^3.

Structure determination of $[K(2,2,2\text{-crypt})]_3[Ir@Sn_{12}]\cdot tol$ (3): $M_r = 2955.38$; crystal size $0.20 \times 0.18 \times 0.12$ mm; monoclinic; space group $C2/c$; $a = 22.8031(3)$, $b = 18.2654(3)$, $c = 48.6766(6)$ Å; $\beta = 92.62(1)°$; $V = 20253.0(5)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.938$ g cm^{-3}; $\mu = 4.39$ mm^{-1}; $T_{max}/T_{min} = 0.62/0.47$; $T = 150(2)$ K; $2\Theta_{max} = 50°$; 114193 measured reflections; 17675 independent reflections; $R_{int} = 0.049$; $R_1 = 0.043$ and $wR_2 = 0.106$ for $I > 2\sigma(I)$; $R_1 = 0.070$ and $wR_2 = 0.113$ for all data; min./max. residual electron density: −1.03/1.17 e Å^3. One of the two crystallographically independent $[Ir@Sn_{12}]^{3-}$ clusters is subject to an orientational disorder. A rigid bond restraint to the U_{ij} components of the disordered atoms was applied to stabilize the refinement. The distortion of the en molecules was also handled by the SQUEEZE option of the PLATON program.[49] CCDC-750417, 750418, and 750419 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational methods: DFT calculations were performed by using the Gaussian 03 package of programs (Revisions D.01 and E.01).[50] Natural charges were calculated with Version 3.1 of the NBO program as implemented in Gaussian 03, Revision D.01.[51] To account for solvation effects, the polarizable continuum model (PCM) implemented in Gaussian 03 was used in all calculations. Because en is not among the solvents that can be specified routinely in Gaussian, dichloroethane was used because it has a dielectric constant that is very similar to that of en (ε_r(dichloroethane) = 10.36; ε_r(ethylendiamine) = 12.90). All DFT calculations were carried out by using the B3LYP functional.[52] Karlsruhe Def2-TZVP basis sets (triple-zeta valence basis sets augmented with polarization functions) were used with small-core effective core potentials (ECPs) for Sn and Ir.[53] Basis sets and ECPs were obtained from the EMSL Basis Set Exchange.[54]

For a preliminary structure optimization of $[Ir@Sn_{12}]^{3-}$, the atomic positions deduced from single-crystal X-ray analysis were used as a starting point and no constraints in symmetry were applied. This optimization led to a ground-state structure with near icosahedral symmetry, and thus the symmetry was restricted to I_h for the final structure optimization. Harmonic vibrational frequencies were calculated analytically for the optimized structures to characterize the nature of the stationary point on the potential energy surface.

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[1] a) J. M. Goicoechea, S. C. Sevov, *Angew. Chem.* **2005**, *117*, 4094–4096; *Angew. Chem. Int. Ed.* **2005**, *44*, 4026–4028; b) J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2006**, *128*, 4155–4161.

[2] S. Scharfe, T. F. Fässler, S. Stegmaier, S. D. Hoffman, K. Ruhland, *Chem. Eur. J.* **2008**, *14*, 4479–4482.

[3] a) E. N. Esenturk, J. Fettinger, Y. F. Lam, B. Eichhorn, *Angew. Chem.* **2004**, *116*, 2184–2186; *Angew. Chem. Int. Ed.* **2004**, *43*, 2132–2134; b) E. N. Esenturk, J. Fettinger, B. Eichhorn, *Chem. Commun.* **2005**, 247–249; c) E. N. Esenturk, J. Fettinger, B. Eichhorn, *J. Am. Chem. Soc.* **2006**, *128*, 9178–9186.

[4] E. N. Esenturk, J. C. Fettinger, B. W. Eichhorn, *J. Am. Chem. Soc.* **2006**, *128*, 12–13.

[5] B. Kesanli, J. E. Halsig. P. Zavalij, J. C. Fettinger, Y.-F. Lam, B. W. Eichhorn, *J. Am. Chem. Soc.* **2007**, *129*, 4567–4574.

[6] J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2005**, *127*, 7676–7677.

[7] a) Z. M. Sun, H. Xiao, J. Li, L. S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 9560–9561; b) F. S. Kocak, P. Zavalij, Y.-F. Lam, B. W. Eichhorn, *Inorg. Chem.* **2008**, *47*, 3515–3520.

[8] A. Spiekermann, S. D. Hoffmann, F. Kraus, T. F. Fässler, *Angew. Chem.* **2007**, *119*, 1663–1666; *Angew. Chem. Int. Ed.* **2007**, *46*, 1638–1640.

[9] M. S. Denning, J. M. Goicoechea, *Dalton Trans.* **2008**, 5882–5885.

[10] A. Nienhaus, R. Hauptmann, T. F. Fässler, *Angew. Chem.* **2002**, *114*, 3352–3355; *Angew. Chem. Int. Ed.* **2002**, *41*, 3213–3215.

[11] a) J. Q. Wang, S. Stegmaier, T. F. Fässler, *Angew. Chem.* **2009**, *121*, 2032–2036; *Angew. Chem. Int. Ed.* **2009**, *48*, 1998–2002; b) N. Korber, *Angew. Chem.* **2009**, *121*, 3262–3264; *Angew. Chem. Int. Ed.* **2009**, *48*, 3216–3217.

[12] B. Zhou, M. S. Denning, D. L. Kays, J. M. Goicoechea, *J. Am. Chem. Soc.* **2009**, *131*, 2802–2803.

[13] A. Spiekermann, S. D. Hoffmann, T. F. Fässler, I. Krossing, U. Preiss, *Angew. Chem.* **2007**, *119*, 5404–5407; *Angew. Chem. Int. Ed.* **2007**, *46*, 5310–5313.

[14] a) L. Xu, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 9245–9246; b) A. Nienhaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1752–1758; c) A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 10990–10991; d) A. Ugrinov, S. C. Sevov, *Inorg. Chem.* **2003**, *42*, 5789–5791; e) L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977–1981; f) L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149–1153.

[15] T. F. Fässler, S. D. Hoffmann, *Angew. Chem.* **2004**, *116*, 6400–6406; *Angew. Chem. Int. Ed.* **2004**, *43*, 6242–6247.

[16] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682–3704; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532–3554.

[17] T. F. Fässler, *Angew. Chem.* **2007**, *119*, 2624–2628; *Angew. Chem. Int. Ed.* **2007**, *46*, 2572–2575.

[18] a) T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347–377; b) D. Sun, A. E. Riley, A. J. Cadby, E. K. Richman, S. D. Korlann, S. H. Tolbert, *Nature* **2006**, *441*, 1126–1130; c) T. F. Fässler, *Angew. Chem.* **2001**, *113*, 4289–4293; *Angew. Chem. Int. Ed.* **2001**, *40*, 4161–4165.

[19] a) H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **1985**, *318*, 162–163; b) W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354–358; c) H. W. Kroto, A. W. Allaf, S. P. Balm, *Chem. Rev.* **1991**, *91*, 1213–1235; d) D. M. Guldi, F. Zerbetto, V. Georgakilas, M. Prato, *Acc. Chem. Res.* **2005**, *38*, 38–43.

[20] a) M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, H. Shinohara, *Nature* **1995**, *377*, 46–49; b) M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen, *Angew. Chem.* **2009**, *121*, 7650–7675; *Angew. Chem. Int. Ed.* **2009**, *48*, 7514–7538.

[21] S. Scharfe, T. F. Fässler, *Philosoph. Trans.*, DOI: 10.1098/rsta.2009.0270.

[22] a) L. F. Cui, X. Huang, L. M. Wang, D. Y. Zubarev, A. I. Boldyrev, J. Li, L. S. Wang, *J. Am. Chem. Soc.* **2006**, *128*, 8390–8391; b) L. F. Cui, X. Huang, L. M. Wang, J. Li, L. S. Wang, *J. Phys. Chem. A* **2006**, *110*, 10169–10172.

[23] a) L. F. Cui, X. Huang, L. M. Wang, J. Li, L. S. Wang, *Angew. Chem.* **2007**, *119*, 756–759; *Angew. Chem. Int. Ed.* **2007**, *46*, 742–745; b) X. Chen, K. Deng, Y. Liu, C. Tang, Y. Yuan, W. Tan, X. Wang, *J. Chem. Phys.* **2008**, *129*, 094301; c) X. Chen, K. Deng , Y. Liu, C. Tang, Y. Yuan, F. Hu, H. Wu, D. Huang, W. Tan, X. Wang, *Chem. Phys. Lett.* **2008**, *462*, 275–279.

[24] S. Neukermans, E. Janssens, Z. F. Chen, R. E. Silverans, P. von R. Schleyer, P. Lievens, *Phys. Rev. Lett.* **2004**, *92*, 163401–163404.

[25] X. Chen, K. Deng, Y. Liu, C. Tang, Y. Yuang, F. Hu, H. Wu, D. Huang, W. Tan, X. Wang, *Chem. Phys. Lett.* **2008**, *462*, 275–279.

[26] J.-P. Dognon, C. Clavaguera, P. Pyykkö, *Angew. Chem.* **2007**, *119*, 1449–1452; *Angew. Chem. Int. Ed.* **2007**, *46*, 1427–1430.

[27] a) L. Yong, S. D. Hoffmann, T. F. Fässler, S. Riedel, M. Kaupp. *Angew. Chem.* **2005**, *117, 2129–2133; Angew. Chem. Int. Ed.* **2005**, 44, 2092–2096; *Angew. Chem. Int. Ed.* **2005**, *44*, 2092–2096.

[28] a) B. W. Eichhorn, R. C. Haushalter, W. T. Pennington, *J. Am. Chem. Soc.* **1988**, *110*, 8704–8706; b) B. W. Eichhorn, R. C. Haushalter, *Chem. Commun.* **1990**, 937–938; c) B. Kesanli, J. Fettinger, B.

Eichhorn, *Chem. Eur. J.* **2001**, *7*, 5277–5285; d) J. Campbell, H. P. A. Mercier, H. Franke, D. P. Santry, D. A. Dixon, G. J. Schrobilgen, *Inorg. Chem.* **2002**, *41*, 86–107.
[29] J. M. Goicoechea, S. C. Sevov, *Organometallics* **2006**, *25*, 4530–4536.
[30] B. Zhou, M. S. Denning, T. A. D. Chapman, J. M. Goicoechea, *Inorg. Chem.* **2009**, *48*, 2899–2907.
[31] G. Pannetier, D. Tabrizi, R. Bonnaire, *J. Less-Common Met.* **1971**, *24*, 470–472.
[32] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.
[33] T. A. Albright, J. K. Burdett, M. H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, New York, **1985**, p. 404.
[34] Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.16(1), Ir(1)–C(2) 2.132(9), Ir(1)–C(5) 2.167(8), Ir(1)–C(6) 2.155(9), Ir(1)–Sn(6) 2.7772(6), Ir(1)–Sn(7) 2.7605(7), Ir(1)–Sn(8) 2.7700(7), Ir(1)–Sn(9) 2.7637(6), Sn(1)–Sn(2) 2.9530(9), Sn(2)–Sn(3) 3.2035(9), Sn(3)–Sn(4) 3.1185(8), Sn(5)–Sn(6) 3.0068(8), Sn(6)–Sn(7) 3.0591(8), Sn(7)–Sn(8) 3.1012(8), Sn(8)–Sn(9) 3.1129(8); C(1)-Ir(1)-C(2) 37.8(3), C(5)-Ir(1)-C(6) 38.5(4), Sn(7)-Ir(1)-Sn(8) 68.22(2), Sn(7)-Ir(1)-Sn(9) 103.26(2), Sn(8)-Ir(1)-Sn(9) 68.46(2).
[35] a) P. Brooks, M. J. Gallagher, A. Sarroff, *Aust. J. Chem.* **1987**, *40*, 1341–1351; J. Dogan, J. B. Schulte, G. F. Swiegers, S. B. Wild, *J. Org. Chem.* **2000**, *65*, 951–957.
[36] T. F. Fässler, *Angew. Chem.* **2001**, *113*, 4289–4293; *Angew. Chem. Int. Ed.* **2001**, *40*, 4161–4165.
[37] T. F. Fässler, M. Hunziker, *Z. Anorg. Allg. Chem.* **1996**, *622*, 837–844, and references therein.
[38] *d*(Ir–Sn) in $[Ir(C_7H_8)(PMe_3Ph)_2(SnCl_3)]$: 2.5867(6) Å (M. R. Churchill, K.-K. G. Lin, *J. Am. Chem. Soc.* **1974**, *96*, 76–84); in $[Ir(CO)_3(PCy_3)(SnPh_3)]$ (Cy: cyclohexyl): 2.6610(3) Å (M. A. Esteruelas, F. J. Lahoz, M. Olivan, E. Onate, L. A. Oro, *Organometallics* **1994**, *13*, 4246–4257); in $[Ir(CO)_3(SnPh_3)_2]^-$: 2.628 Å (J. M. Allen, W. W. Brennessel, C. E. Buss, J. E. Ellis, M. E. Minyaev, M. Pink, G. F. Warnock, M. L. Winzenburg, V. G. Young, *Inorg. Chem.* **2001**, *40*, 5279–5284); in $[Ir_2(cod)_2(SnCl_3)_2Cl_2(\mu\text{-}Cl)_2]$: 2.578(4) Å (J. Choudhury, S. Podder, S. Roy, *J. Am. Chem. Soc.* **2005**, *127*, 6162–6163); in $[MeSi\{SiMe_2N(p\text{-}tol)\}_2\{SiMe_2N(2\text{-}C_6H_3\text{-}4\text{-}CH_3)\}SnIr(cod)(H)(PPh_3)]$ (*p*-tol: 4-methylphenyl): 2.5798(8) Å (M. Kilian, H. Wadepohl, L. H. Gade, *Organometallics* **2008**, *27*, 524–533).
[39] a) B. Wahl, M. Erbe, A. Gerisch, L. Kloo, M. Ruck, *Z. Anorg. Allg. Chem.* **2009**, *635*, 743–752; b) B. Wahl, L. Kloo, M. Ruck, *Angew. Chem.* **2008**, *120*, 3996–3999; *Angew. Chem. Int. Ed.* **2008**, *47*, 3932–3935; c) B. Wahl, M. Ruck, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2267–2275.
[40] Z. Wu, R. D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1484–1488.
[41] *d*(Ir–Sn) in $IrSn_2$: 2.744 Å (H. Nowotny, K. Schubert, U. Dettinger, *Metallforschung* **1946**, *1*, 137–145); Ir_3Sn_7: 2.744–2.762 Å (M. Schlüter, U. Häussermann, B. Heying, R. Pöttgen, *J. Solid State Chem.* **2003**, *173*, 418–424); $IrSn_4$: 2.744–2.748 Å (E. L. Nordmark, O. Wallner, U. Häussermann, *J. Solid State Chem.* **2002**, *168*, 34–35).
[42] Selected bond lengths [Å] and angles [°]: Ir(1)–Sn(1) 2.9414(5), Ir(1)–Sn(2) 2.9229(6), Ir(1)–Sn(3) 2.8828(5), Ir(1)–Sn(4) 2.9363(6), Ir(1)–Sn(5) 2.9356(5), Ir(1)–Sn(6) 2.9115(6), Sn(1)–Sn(2) 3.1004(9), Sn(1)–Sn(3) 3.0429(7), Sn(1)–Sn(4) 3.0715(9), Sn(1)–Sn(5) 3.0636(8), Sn(1)–Sn(6) 3.0658(8), Sn(2)–Sn(3) 3.0609(9), Sn(2)–Sn(6) 3.0250(8), Sn(3)–Sn(4) 3.0632(9), Sn(4)–Sn(5) 3.0596(8), Sn(5)–Sn(6) 3.0954(9); Sn(3)-Ir(1)-Sn(2) 63.63(2), Sn(2)-Ir(1)-Sn(6) 62.46(2), Sn(2)-Ir(1)-Sn(1) 63.83(2), Sn(6)-Ir(1)-Sn(1) 63.17(2), Sn(3)-Sn(1)-Sn(2) 59.76(2), Sn(6)-Sn(1)-Sn(2) 58.76(2), Sn(2)-Sn(3)-Sn(4) 109.23(2), Sn(6)-Sn(2)-Sn(3) 107.25(3).
[43] J. A. Wunderlich, W. N. Lipscomb, *J. Am. Chem. Soc.* **1960**, *82*, 4427–4428.
[44] S. Liu, Y. J. Liu, M. M. Kappes, J. A. Ibers, *Science* **1991**, *254*, 408–410.
[45] M. J. Moses, J. C. Fettinger, B. W. Eichhorn, *Science* **2003**, *300*, 778–781.
[46] M. M. Tillard-Charbonnel, C. H. E. Belin, A. P. Manteghetti, D. M. Flot, *Inorg. Chem.* **1996**, *35*, 2583–2589.
[47] Z. C. Dong, J. D. Corbett, *J. Am. Chem. Soc.* **1995**, *117*, 6447–6455.
[48] SHELXTL, Version 6.1, G. M. Sheldrick, Brucker-Nonius AXS, Madison, **2000**.
[49] a) A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.
[50] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
[51] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison.
[52] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[53] a) Def2-TZVP basis sets for Sn and Ir: F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305; b) ECP28MDF for Sn: B. Metz, H. Stoll, M. Dolg, *J. Chem. Phys.* **2000**, *113*, 2563–2569; c) ECP60MWB for Ir: D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.
[54] Basis Set Exchange: A Community Database for Computational Sciences: K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052.

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