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Synthesis of a Cyclic Co_2Sn_2 Cluster Using a Co^- Synthron

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S Supporting Information

ABSTRACT: $[\text{Ar}'\text{SnCo}]_2$ (**1**, $\text{Ar}' = \text{C}_6\text{H}_3-2,6\{\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2\}_2$), a rare metal–metal bonded cobalt–tin cluster with low-coordinate tin atoms, was prepared by the reaction of $[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2]$ ($\text{cod} = 1,5\text{-cyclooctadiene}$) with $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2]$. This reaction illustrates a promising synthetic strategy to access uncommon metal clusters. The structure of **1** features a rhomboidal Co_2Sn_2 core with strong metal–metal bonds between tin and cobalt and a weaker tin–tin interaction. Reaction of **1** with white phosphorus afforded $[\text{Ar}'_2\text{Sn}_2\text{Co}_2\text{P}_4]$ (**2**), the first molecular cluster compound containing phosphorus, cobalt and tin.

Tin compounds have played a pivotal role in the chemistry of multiple bonded heavier main group species.¹ The ability of heavy p-block elements to form isolable homodinuclear multiple bonds was first demonstrated by the structural characterization of the distannene $\text{R}_2\text{Sn} = \text{SnR}_2$ ($\text{R} = \text{CH}\{\text{SiMe}_3\}_2$) by Lappert and co-workers in 1976.² Distannylene $\text{Ar}'\text{SnSnAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3-2,6\{\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2\}_2$), one of the first heavier group 14 element alkyne analogues, was described in 2002.³ Moreover, homo- and heterometallic Zintl ions,⁴ metalloid cages $[\text{SnR}]_n$ ⁵ and metalloid clusters $[\text{Sn}_n\text{R}_m]$ ($n > m$)⁶ have attracted significant attention. Various transition metal stannyl and stannylidene complexes were reported, while stannylidyne complexes and metallostannylenes are still scarce.^{1,7} Known examples such as A–C (Figure 1a) are stabilized by phosphane, cyclopentadienyl or carbonyl ligands.

Here, we describe a new strategy for the synthesis of unusual p-block/d-block element clusters. Pioneering work by Jonas and Ellis established the synthesis and reactivity of $[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2]$ (**D**, $\text{cod} = 1,5\text{-cyclooctadiene}$)⁸ and many related alkene and polyarene metalates.^{9,10} However, such anions were employed mainly in redox-neutral ligand exchange reactions.^{10,11} We now show that anion **D** can be used to obtain the unusual $[\text{Ar}'\text{SnCo}]_2$ cluster (**1**), which features a cyclic Co_2Sn_2 core with three coordinate tin atoms. In addition, reactivity studies of **1** with white phosphorus afforded $[\text{Ar}'_2\text{Sn}_2\text{Co}_2\text{P}_4]$ (**2**), which is the first molecular cluster composed of tin, cobalt and phosphorus atoms.

$[\text{Ar}'\text{SnCo}]_2$ (**1**) was obtained by reacting $[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2]$ (**D**) with $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2]$ (**E**) in toluene

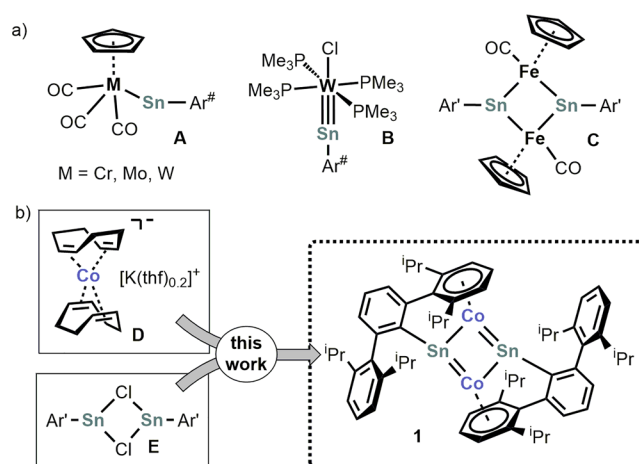


Figure 1. (a) Selected metallostannylene and stannylidyne complexes ($\text{Ar}' = \text{C}_6\text{H}_3-2,6\{\text{C}_6\text{H}_2-2,4,6\text{-Me}_3\}_2$); (b) synthesis of Co_2Sn_2 compound **1**, reagents and byproducts: $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2] + 3[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2] / -2\text{KCl}, -4 \text{cod}$; conditions: toluene, $-30^\circ\text{C} \rightarrow \text{r.t.}$, 20 h.

(Figure 1b). An excess of cobaltate **D** (three equiv. per $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2]$ dimer) is required to produce **1** in up to 42% isolated yield. Deep-green single crystals suitable for single-crystal XRD were obtained from *n*-hexane. The structure of **1** (Figure 2) shows a centrosymmetric, rhomboidal Co_2Sn_2 core with two distinct Co–Sn bond lengths. The Sn1–Co1 distance of 2.5365(5) Å resembles that predicted for a Co–Sn single bond ($\sum r_{\text{cov}} = 2.51$ Å), whereas the Sn1–Co1' bond length (2.4071(6) Å) is closer to that of a double bond (calculated covalent double bond radius 2.33 Å).¹² The Sn1–Sn1' distance (2.8700(5) Å) is similar to those of Sn–Sn single bonds in bulky hexaorganodistannanes such as $[\text{tBu}_3\text{SnSn}^t\text{Bu}_3]$ (2.894(1) Å),¹³ $[(\text{PhCH}_2)_3\text{SnSn}(\text{CH}_2\text{Ph})_3]$ (2.823(1) Å)¹³ and $[(o\text{-Tol})_3\text{SnSn}(o\text{-Tol})_3]$ (2.883(1) Å),¹⁴ but see DFT calculations below. The cobalt atoms are η^6 -coordinated by the flanking 2,6-diisopropylphenyl rings with a very short cobalt–centroid distance (1.560(1) Å), which suggests a particularly strong cobalt–arene interaction, cf. >0.1 Å shorter than the η^6 -arene interactions in $[\text{Ar}'\text{CoCoAr}']$ (1.764(2) Å),¹⁵

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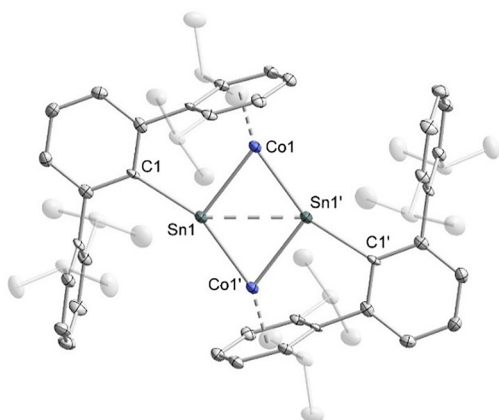


Figure 2. Displacement ellipsoid (40%) drawing of the centrosymmetric complex **1**. The cocrystallized *n*-hexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Sn1–Sn1' 2.8700(5), Sn1–Co1 2.5365(5), Sn1–Co1' 2.4071(6), Sn1–C1 2.174(3), Co–Dipp(c) 1.560(1), C1–Sn1–Sn1' 145.96(8), Co1–Sn1–Sn1' 52.43(1), Co1'–Sn1–Sn1' 56.64(1), Sn1'–Co1–Sn1 70.92(2), C1–Sn1–Co1 93.53(8), C1–Sn1–Co1' 157.38(8).

$[(\text{nacnac})\text{Co}(\eta^6\text{-C}_7\text{H}_8)]$ (1.747(2), $\text{nacnac} = \text{HC}\{\text{C}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_2$)¹⁶ and $[(\eta^6\text{-C}_7\text{H}_8)\text{CoAr}^*]$ (1.659(1) Å, $\text{Ar}^* = \text{C}_6\text{H}_2\text{-}2,6(\text{C}_6\text{H}_2\text{-}2,4,6\text{-iPr}_3)_2\text{-}3,5\text{-iPr}_2$).¹⁷ The average C–C bond length within the metal-coordinated aryl rings is nearly 0.025 Å longer than those in the noncoordinated rings. The existence of $d\text{-}\pi^*$ backbonding is also underlined by the substantial upfield shift of the aryl resonances of the coordinated Dipp groups (4.76 and 4.56 ppm) in the ¹H NMR spectrum.^{15,18}

Crystallographically characterized molecular cobalt–tin clusters are rare and the known organometallic cobalt–tin complexes contain cobalt carbonyl fragments and tetravalent tin atoms.¹⁹ The structure of **1** has a resemblance to those of ternary RECoSn stannides ($\text{RE} = \text{rare earth metal}$),^{20,21} However, the Co_2Sn_2 units in RECoSn (2.61 and 2.67 Å Co–Sn in DyCoSn) are condensed to a ladder-like motif and the units show an inverse tilt, i.e. the tin atoms show a maximum separation of 4.04 Å. Fässler and co-workers described endohedral Zintl cluster anions $[\text{Co}@\text{Sn}_9]^{5-}$ and $[\text{Co}_2@\text{Sn}_{17}]^{5-}$ with Co^- anions encapsulated into Sn_9 cages.²² A bridging $\mu\text{-}\eta^1\text{:}\eta^6$ coordination mode of the terphenyl ligand was observed for the doubly reduced distannyne $[\text{K}_2\text{Ar}'\text{SnSnAr}']$ and the digermene silver complexes $[\text{AgAr}'\text{GeGeAr}'][\text{SbF}_6]$ and $[\text{Ag}_2\text{Ar}'\text{GeGe}(\text{F})\text{Ar}'][\text{SbF}_6]$, where the K^+ and Ag^+ cations are coordinated by two flanking Dipp substituents.²³ Additionally, the bonding in **1** differs markedly since these structures have relatively long Ag–Ge and K–Sn distances and short, multiple Sn–Sn and Ge–Ge bonds.

Density functional theory (DFT) studies at the B3LYP-D3/def2-TZVP level on the truncated model compound **1'** (iPr substituted by H) support the presence of strong intermetallic interactions.²⁴ The HOMO and HOMO–2 (Figure 3a) and a natural bond orbital analysis (Figure S13, Supporting Information) illustrate the π -character of the shortened Sn1–Co1' bond. Several other occupied molecular orbitals (HOMO–1, HOMO–3, HOMO–5, HOMO–10, see Figure S12, Supporting Information) furthermore show σ -interactions between tin and cobalt. Notably, the occupied MOs do not

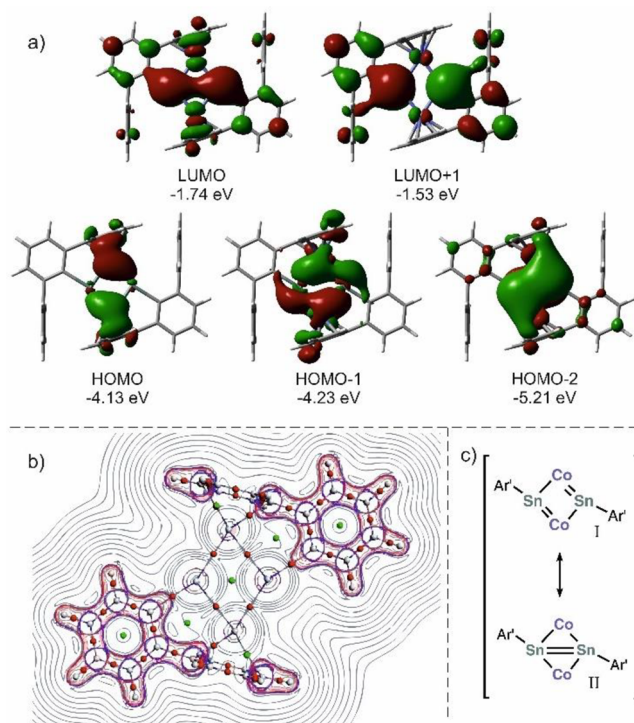
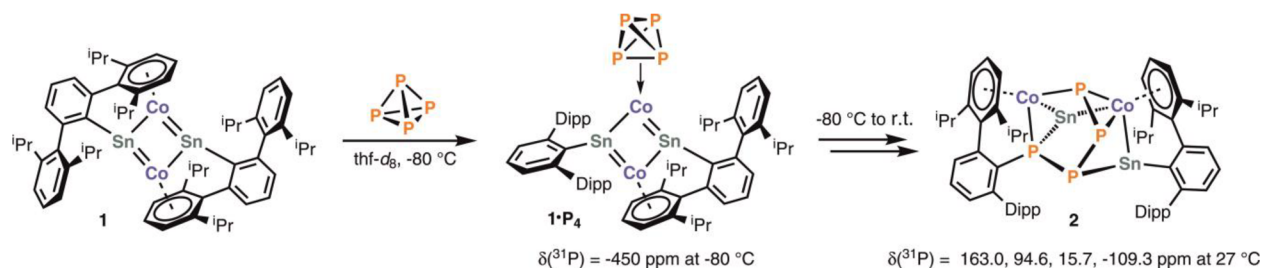


Figure 3. (a) Selected molecular orbitals of **1'** which describe the most significant interactions within the Co_2Sn_2 core; (b) AIM (Bader) analysis (bond critical points: red, ring critical points green); (c) proposed Lewis resonance structures of **1** based on DFT calculations.

show an interaction between the tin atoms. Sn–Sn bonding is only apparent in the LUMO. A Wiberg bond index (WBI) analysis gave values of 0.68 and 0.59 for the Sn1–Co1' and Sn1–Co1 bonds, respectively, and a WBI of 0.65 for the Sn–Sn interaction. An AIM analysis (Figure 3b) at the ZORA/OPBE/QZ4P level²⁵ showed no bond-critical point between the two tin atoms and revealed a ring critical point at the center of the four membered ring. Taken together, these calculations suggest that the covalent Sn–Sn interaction in **1** is quite weak. In terms of Lewis representations, resonance structure I in Figure 3c representing a bis(stannyldiyne) complex seems to be more important than resonance structure II describing a distannyne dicobalt complex.

The ¹¹⁹Sn Mössbauer spectrum of solid **1** recorded at 6 K (Figure S9 (SI)) shows a single quadrupole doublet. The isomer shift of **1** ($\delta = 2.14(1) \text{ mm s}^{-1}$) is slightly lower than that of $\beta\text{-Sn}$ ($\delta = 2.6 \text{ mm s}^{-1}$) and comparable to those of stannides and intermetallic tin compounds, e.g. DyCoSn ($\delta = 1.80 \text{ mm s}^{-1}$, 295 K data), showing Co_2Sn_2 units similar to those of **1**.^{21,26} Adjacent ladders in DyCoSn condense via further Co–Sn bonds, leading to a slightly distorted tetrahedral $\text{SnCo}_{4/4}$ coordination and a small electric quadrupole splitting parameter of $\Delta E_Q = 0.55 \text{ mm s}^{-1}$.²¹ The electric quadrupole splitting is drastically larger for the Co_2Sn_2 core in **1** ($\Delta E_Q = 2.86(1) \text{ mm s}^{-1}$). This indicates a highly anisotropic charge distribution analogous to that of the related distannyne $[\text{Ar}'\text{SnSnAr}']$ ($\delta = 2.658(2) \text{ mm s}^{-1}$; $\Delta E_Q = 2.995(2) \text{ mm s}^{-1}$).²⁷

While reactivity studies with small molecules such as O_2 and CO gave intractable products so far, **1** reacted readily with white phosphorus in toluene to afford $[\text{Ar}'_2\text{Sn}_2\text{Co}_2\text{P}_4]$ (**2**) as a well-defined, crystalline species in up to 76% isolated yield

Scheme 1. Proposed Pathway of Formation of **2** Involving the Coordination of P_4 to **1** and Subsequent Insertion into the Cluster Framework

(Scheme 1). $^{31}\text{P}\{^1\text{H}\}$ NMR monitoring of the reaction in $\text{thf-}d_8$ (Figure S11, Supporting Information) revealed the formation of an intermediate $1\cdot P_4$ at $-80 \text{ }^\circ\text{C}$ with a broad singlet at -450 ppm . We presume that $1\cdot P_4$ is a highly fluxional $\eta^2\text{-}P_4$ complex analogous to coinage metal complexes reported by Krossing, Russell, and Scheer.²⁸ Intermediate $1\cdot P_4$ is converted to **2** on warming the reaction solution to $>0 \text{ }^\circ\text{C}$. Minor unidentified species with resonances at $+180$, $+15$, -44 , and -157 ppm arising at $-20 \text{ }^\circ\text{C}$ may presumably represent further intermediates en route to **2**. These resonances disappear upon warming to room temperature. The primary phosphane $\text{Ar}'\text{PH}_2$ (-140 ppm) was detected as the only minor byproduct ($<3\%$ integral ratio).²⁹

Dark-brown crystals of **2** suitable for single-crystal XRD were obtained from cyclohexane. The molecular structure (Figure 4a) shows a P_4 chain resulting from the insertion of the white phosphorus molecule into the Co_2Sn_2 core of **1**. One of the terphenyl moieties migrated from tin to phosphorus, but both cobalt atoms retain the η^6 -coordination from flanking aryl rings as observed in the structure of **1**. Terphenyl migration from tin to phosphorus was previously observed by Wesemann and co-workers in the reaction of adamantyl phosphalkyne with a terphenyl allyl stannylenes.³⁰ Moreover, a similar terphenyl transfer from thallium to phosphorus was observed in the reaction of a dithallene with P_4 .³¹ The cobalt-centroid distances of $1.585(1)$ and $1.612(1) \text{ \AA}$ are slightly longer than those in **1**. The P-P bond distances ranging from $2.2005(8)$ to $2.1621(8) \text{ \AA}$ are typical for single bonds ($\sum r_{\text{cov}} = 2.22 \text{ \AA}$).¹² As expected, the Co-P bonds of the terminal P atoms coordinating to Co1 ($\text{Co1-P1 } 2.1864(6)$ and $\text{Co1-P4 } 2.2289(7) \text{ \AA}$) are shorter than those of the side-on coordinated P-P bond coordinating to Co2 ($\text{Co2-P3 } 2.3350(6)$ and $\text{Co2-P4 } 2.3501(6) \text{ \AA}$). The Co-Sn distances ($\text{Co1-Sn1 } 2.7380(4) \text{ \AA}$, $\text{Co2-Sn1 } 2.8263(4)$, and $\text{Co2-Sn2 } 2.6500(4) \text{ \AA}$) are significantly longer than in **1**, while the Sn1-P2 and Sn2-P1 distances ($2.6587(6) \text{ \AA}$ and $2.5716(6) \text{ \AA}$, respectively) compare well with Sn-P single bonds reported for other tin-phosphorus cage compounds.³² Weak interactions between $\text{Sn1}\cdots\text{P3}$ and $\text{Sn2}\cdots\text{P4}$ are also apparent, since the corresponding Sn-P distances of $2.8519(6)$ and $2.9277(6) \text{ \AA}$ are much smaller than the sum of van der Waals radii ($\sum r_{\text{vdW}} = 4.02 \text{ \AA}$).³³

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** shows four multiplets with an integral ratio of $1:1:1:1$ (Figure 4b) with additional coupling to $^{117/119}\text{Sn}$. The spectrum was successfully simulated by an iterative fitting procedure (see the SI). The $^1J_{\text{PP}}$ coupling constants range from -303 to -370 Hz .³⁴ The proximity of P1 and P2 to adjacent tin atoms is confirmed by the observation of $^{117/119}\text{Sn}$ satellites at P2 and P4 ($^1J_{\text{P2Sn1}} = 579 \text{ Hz}$, $^1J_{\text{P1Sn2}} = 1482 \text{ Hz}$). Direct bonding to quadrupolar ^{59}Co nuclei can

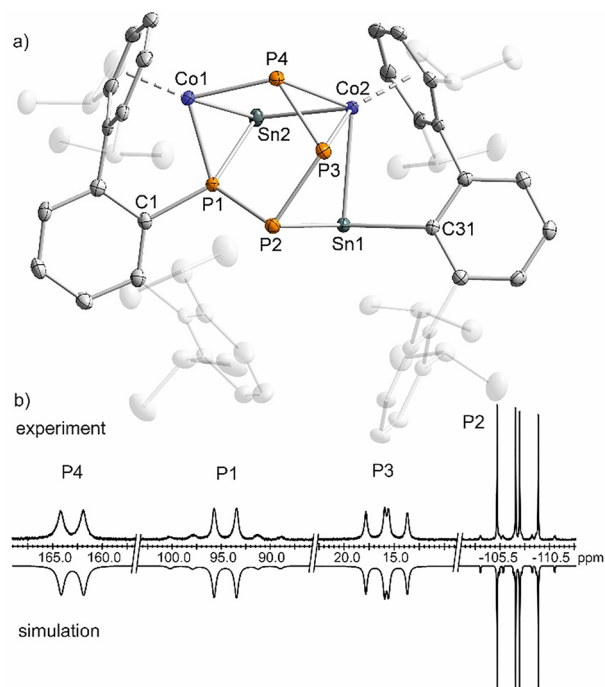


Figure 4. (a) Displacement ellipsoid (40%) drawing of the $\text{Co}_2\text{Sn}_2\text{P}_4$ cluster **2**. The cocrystallized cyclohexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: $\text{Sn1-Co2 } 2.8263(4)$, $\text{Sn2-Co1 } 2.7380(4)$, $\text{Sn2-Co2 } 2.6500(4)$, $\text{Sn1-P2 } 2.6587(6)$, $\text{Sn2-P1 } 2.5716(6)$, $\text{Sn1}\cdots\text{P3 } 2.9277(6)$, $\text{Sn2}\cdots\text{P4 } 2.8519(6)$, $\text{Sn1-C31 } 2.279(2)$, $\text{Co1-P1 } 2.1864(6)$, $\text{Co1-P4 } 2.2289(7)$, $\text{Co2-P3 } 2.3350(6)$, $\text{Co2-P4 } 2.3501(6)$, $\text{P1-P2 } 2.2005(8)$, $\text{P2-P3 } 2.1809(8)$, $\text{P3-P4 } 2.1621(8)$, $\text{P1-C1 } 1.843(2)$, $\text{Co1-Dipp(c) } 1.585(1)$, $\text{Co2-Dipp(c) } 1.612(1)$, $\text{P1-P2-P3 } 93.40(3)$, $\text{P2-P3-P4 } 109.79(3)$, $\text{P1-P2-P3-P4 } 16.27(3)$. (b) Measured (upward) and simulated (downward) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compound **2** in $\text{thf-}d_8$.

considerably affect the line width of ^{31}P NMR resonances depending on the $^1J_{\text{PCo}}$ coupling constant and the longitudinal relaxation time.³⁵ Provided that there is a direct correlation of the signal width to the number of bound Co atoms, the broadened multiplets can be assigned to P1 ($\Delta\nu_{1/2} = 77 \text{ Hz}$), P3 ($\Delta\nu_{1/2} = 54 \text{ Hz}$) and P4 ($\Delta\nu_{1/2} = 121 \text{ Hz}$).

In agreement with the two different Sn sites in the solid-state structure, the ^{119}Sn Mössbauer spectrum of **2** (Figure S10, Supporting Information) was well reproduced with two doublets in a $1:1$ ratio with isomer shifts of $\delta = 2.58(1) \text{ mm s}^{-1}$ and $\delta = 2.94(1) \text{ mm s}^{-1}$. These isomer shifts are comparable to those of other organotin(II) compounds³⁶ and metalloid tin clusters.³⁷ Both signals show similar quadrupole splittings of $\Delta E_Q = 1.41(1)$ and $1.43(1) \text{ mm s}^{-1}$,

respectively, reflecting the noncubic site symmetries. Similar quadrupole splittings for organotin compounds with an asymmetric environment are reported in the literature.^{37a}

In conclusion, we successfully used the anionic cobaltate salt $[K(thf)_{0.2}][Co(1,5-cod)_2]$ (**D**) as a Co^- source for the synthesis of the unique Co_2Sn_2 cluster **1**. The synthesis of **1** illustrates a promising avenue to new bimetallic species with strong intermetallic bonding. The application of this synthetic strategy to a range of other metalate anions and metal halides available across the periodic table may lead to a rich family of new heterobimetallic clusters, which may have an interesting and rich reaction chemistry as illustrated by the synthesis of the ternary cluster **2** from **1** and white phosphorus. Further reactivity studies of **1** and investigations of the synthesis of further d-block/p-block element clusters are in hand.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b08517.

Full details of the synthesis and characterization of **1** and **2**, X-ray structural, spectroscopic and computational data (PDF)

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Notes

The authors declare no competing financial interest.

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