

## Synthesis of a Cyclic $\text{Co}_2\text{Sn}_2$ Cluster Using a $\text{Co}^-$ Synthone

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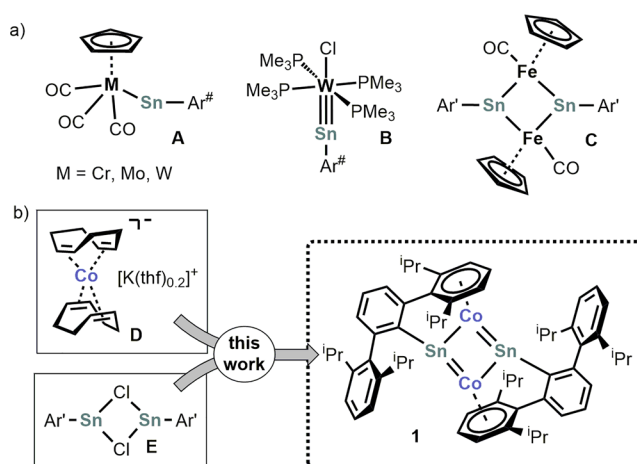
### S Supporting Information

**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  $\text{Co}_2\text{Sn}_2$  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.<sup>1</sup> 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.<sup>2</sup> Distannene  $\text{Ar}'\text{SnSnAr}'$  ( $\text{Ar}' = \text{C}_6\text{H}_3-2,6\{\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2\}_2$ ), one of the first heavier group 14 element alkyne analogues, was described in 2002.<sup>3</sup> Moreover, homo- and heterometallic Zintl ions,<sup>4</sup> metalloid cages  $[\text{SnR}]_n$ <sup>5</sup> and metalloid clusters  $[\text{Sn}_n\text{R}_m]$  ( $n > m$ )<sup>6</sup> have attracted significant attention. Various transition metal stannyl and stannylidene complexes were reported, while stannylidyne complexes and metallostannylenes are still scarce.<sup>1,7</sup> 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**,  $\text{cod} = 1,5\text{-cyclooctadiene}$ )<sup>8</sup> and many related alkene and polyarene metalates.<sup>9,10</sup> However, such anions were employed mainly in redox-neutral ligand exchange reactions.<sup>10,11</sup> We now show that anion **D** can be used to obtain the unusual  $[\text{Ar}'\text{SnCo}]_2$  cluster (**1**), which features a cyclic  $\text{Co}_2\text{Sn}_2$  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

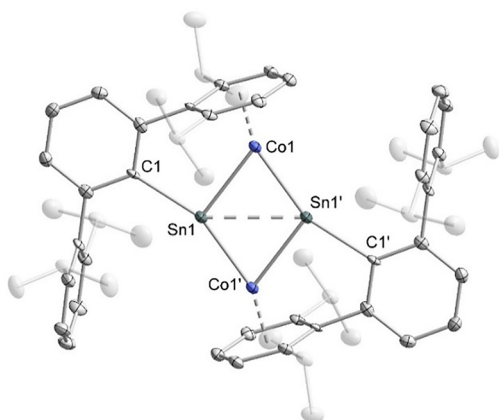


**Figure 1.** (a) Selected metallostannylene and stannylidyne complexes ( $\text{Ar}' = \text{C}_6\text{H}_3-2,6\{\text{C}_6\text{H}_2-2,4,6\text{-Me}_3\}_2$ ); (b) synthesis of  $\text{Co}_2\text{Sn}_2$  compound **1**, reagents and byproducts:  $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2] + 3[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2] / -2\text{KCl}, -4 \text{cod}$ ; 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  $\text{Co}_2\text{Sn}_2$  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).<sup>12</sup> The Sn1–Sn1' distance (2.8700(5) Å) is similar to those of Sn–Sn single bonds in bulky hexaorganodistannanes such as  $[\text{Bu}_3\text{SnSn}^t\text{Bu}_3]$  (2.894(1) Å),<sup>13</sup>  $[(\text{PhCH}_2)_3\text{SnSn}(\text{CH}_2\text{Ph})_3]$  (2.823(1) Å)<sup>13</sup> and  $[(o\text{-Tol})_3\text{SnSn}(o\text{-Tol})_3]$  (2.883(1) Å),<sup>14</sup> but see DFT calculations below. The cobalt atoms are  $\eta^6$ -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  $\eta^6$ -arene interactions in  $[\text{Ar}'\text{CoCoAr}']$  (1.764(2) Å),<sup>15</sup>

Received: August 8, 2018

Published: October 1, 2018

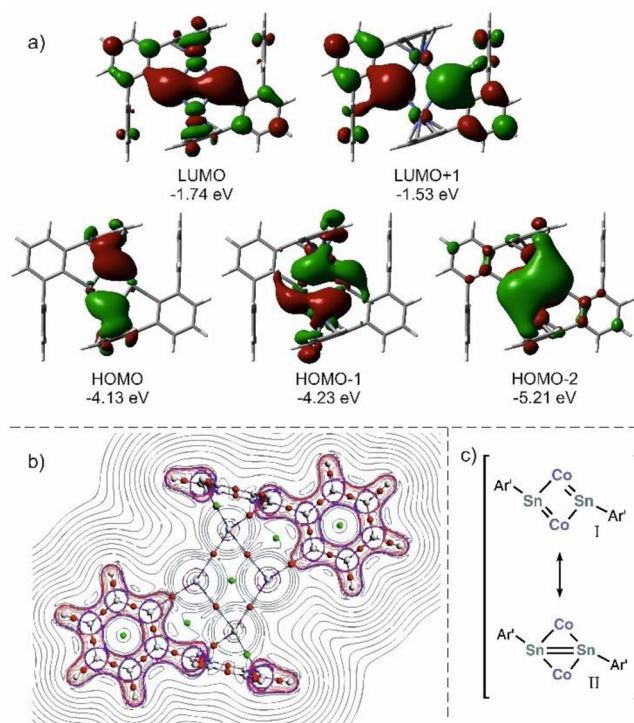


**Figure 2.** Displacement ellipsoid (40%) drawing of the centrosymmetric complex **1**. The cocrystallized *n*-hexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Sn1–Sn1' 2.8700(5), Sn1–Co1 2.5365(5), Sn1–Co1' 2.4071(6), Sn1–C1 2.174(3), 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),  $\text{nacnac} = \text{HC}\{\text{C}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_2$ )<sup>16</sup> and  $[(\eta^6\text{-C}_7\text{H}_8)\text{CoAr}^*]$  (1.659(1) Å,  $\text{Ar}^* = \text{C}_6\text{H}_2\text{-}2,6(\text{C}_6\text{H}_2\text{-}2,4,6\text{-iPr}_3)_2\text{-}3,5\text{-iPr}_2$ ).<sup>17</sup> 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 <sup>1</sup>H NMR spectrum.<sup>15,18</sup>

Crystallographically characterized molecular cobalt–tin clusters are rare and the known organometallic cobalt–tin complexes contain cobalt carbonyl fragments and tetravalent tin atoms.<sup>19</sup> The structure of **1** has a resemblance to those of ternary  $\text{RECoSn}$  stannides ( $\text{RE} = \text{rare earth metal}$ ),<sup>20,21</sup> However, the  $\text{Co}_2\text{Sn}_2$  units in  $\text{RECoSn}$  (2.61 and 2.67 Å Co–Sn in  $\text{DyCoSn}$ ) 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  $\text{Co}^-$  anions encapsulated into  $\text{Sn}_9$  cages.<sup>22</sup> 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  $\text{K}^+$  and  $\text{Ag}^+$  cations are coordinated by two flanking Dipp substituents.<sup>23</sup> 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.<sup>24</sup> The HOMO and HOMO–2 (Figure 3a) and a natural bond orbital analysis (Figure S13, Supporting Information) illustrate the  $\pi$ -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  $\sigma$ -interactions between tin and cobalt. Notably, the occupied MOs do not

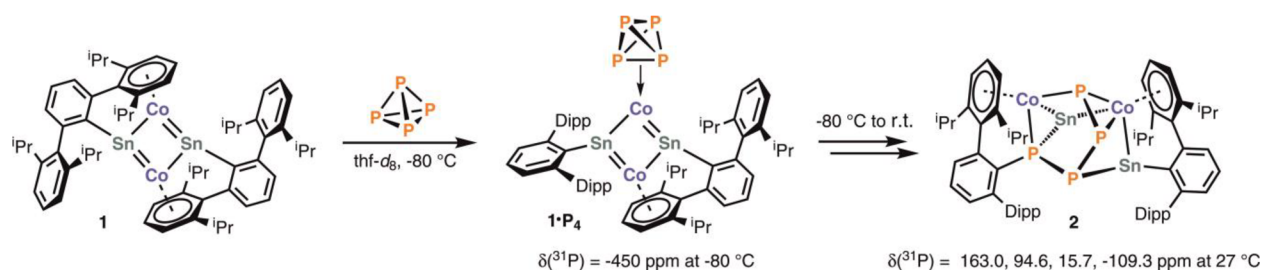


**Figure 3.** (a) Selected molecular orbitals of **1'** which describe the most significant interactions within the  $\text{Co}_2\text{Sn}_2$  core; (b) AIM (Bader) analysis (bond critical points: red, ring critical points green); (c) proposed Lewis resonance structures of **1** based on DFT calculations.

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 level<sup>25</sup> 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 <sup>119</sup>Sn 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.  $\text{DyCoSn}$  ( $\delta = 1.80 \text{ mm s}^{-1}$ , 295 K data), showing  $\text{Co}_2\text{Sn}_2$  units similar to those of **1**.<sup>21,26</sup> Adjacent ladders in  $\text{DyCoSn}$  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  $\Delta E_Q = 0.55 \text{ mm s}^{-1}$ .<sup>21</sup> The electric quadrupole splitting is drastically larger for the  $\text{Co}_2\text{Sn}_2$  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  $[\text{Ar}'\text{SnSnAr}']$  ( $\delta = 2.658(2) \text{ mm s}^{-1}$ ;  $\Delta E_Q = 2.995(2) \text{ mm s}^{-1}$ ).<sup>27</sup>

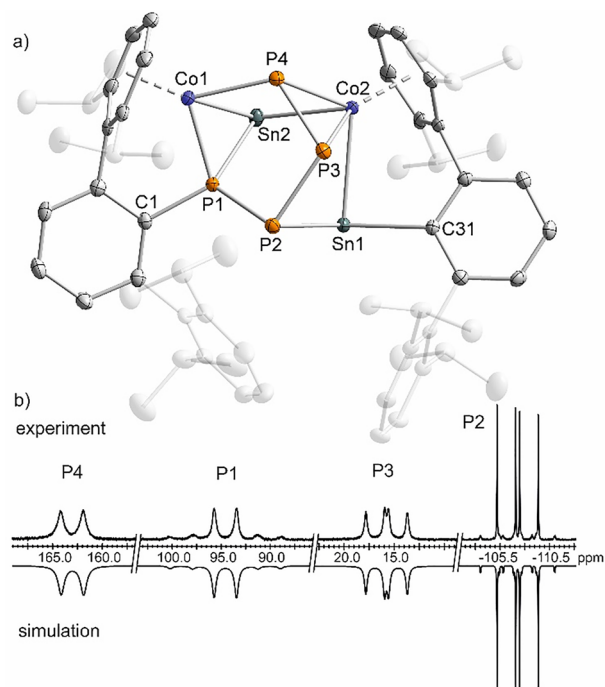
While reactivity studies with small molecules such as  $\text{O}_2$  and CO gave intractable products so far, **1** reacted readily with white phosphorus in toluene to afford  $[\text{Ar}'_2\text{Sn}_2\text{Co}_2\text{P}_4]$  (**2**) as a well-defined, crystalline species in up to 76% isolated yield

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  $-450 \text{ ppm}$ . 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.<sup>28</sup> 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  $-157 \text{ ppm}$  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  $\text{Ar}'\text{PH}_2$  ( $-140 \text{ ppm}$ ) was detected as the only minor byproduct ( $<3\%$  integral ratio).<sup>29</sup>

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  $\text{Co}_2\text{Sn}_2$  core of **1**. One of the terphenyl moieties migrated from tin to phosphorus, but both cobalt atoms retain the  $\eta^6$ -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.<sup>30</sup> Moreover, a similar terphenyl transfer from thallium to phosphorus was observed in the reaction of a dithallene with  $P_4$ .<sup>31</sup> The cobalt-centroid distances of  $1.585(1)$  and  $1.612(1) \text{ \AA}$  are slightly longer than those in **1**. The  $\text{P-P}$  bond distances ranging from  $2.2005(8)$  to  $2.1621(8) \text{ \AA}$  are typical for single bonds ( $\sum r_{\text{cov}} = 2.22 \text{ \AA}$ ).<sup>12</sup> As expected, the  $\text{Co-P}$  bonds of the terminal P atoms coordinating to Co1 (Co1-P1  $2.1864(6)$  and Co1-P4  $2.2289(7) \text{ \AA}$ ) are shorter than those of the side-on coordinated  $\text{P-P}$  bond coordinating to Co2 (Co2-P3  $2.3350(6)$  and Co2-P4  $2.3501(6) \text{ \AA}$ ). The  $\text{Co-Sn}$  distances (Co1-Sn1  $2.7380(4) \text{ \AA}$ , Co2-Sn1  $2.8263(4)$ , and 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.<sup>32</sup> Weak interactions between Sn1...P3 and Sn2...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 ( $\sum r_{\text{vdW}} = 4.02 \text{ \AA}$ ).<sup>33</sup>

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  $-370 \text{ Hz}$ .<sup>34</sup> 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  $^{59}\text{Co}$  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 [ $\text{\AA}$ ] and angles [ $^\circ$ ]: Sn1-Co2  $2.8263(4)$ , Sn2-Co1  $2.7380(4)$ , Sn2-Co2  $2.6500(4)$ , Sn1-P2  $2.6587(6)$ , Sn2-P1  $2.5716(6)$ , Sn1...P3  $2.9277(6)$ , Sn2...P4  $2.8519(6)$ , Sn1-C31  $2.279(2)$ , Co1-P1  $2.1864(6)$ , Co1-P4  $2.2289(7)$ , Co2-P3  $2.3350(6)$ , Co2-P4  $2.3501(6)$ , P1-P2  $2.2005(8)$ , P2-P3  $2.1809(8)$ , P3-P4  $2.1621(8)$ , P1-C1  $1.843(2)$ , Co1-Dipp(c)  $1.585(1)$ , Co2-Dipp(c)  $1.612(1)$ , P1-P2-P3  $93.40(3)$ , P2-P3-P4  $109.79(3)$ , 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  $^{31}\text{P}$  NMR resonances depending on the  $^1J_{\text{PCo}}$  coupling constant and the longitudinal relaxation time.<sup>35</sup> 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  $^{119}\text{Sn}$  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) compounds<sup>36</sup> and metalloid tin clusters.<sup>37</sup> 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.<sup>37a</sup>

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.

## ■ ACKNOWLEDGMENTS

We thank M.Sc. Florian Hastreiter and Prof. Dr. Ruth Gschwind for NMR spectroscopic measurements (all University of Regensburg). Financial support by the Stiftung der Deutschen Wirtschaft (sdw, doctoral fellowship to C.M.H.), the European Research Council (ERC CoG 772299), and the National Science Foundation (CHE-1565501) is gratefully acknowledged.

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