

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

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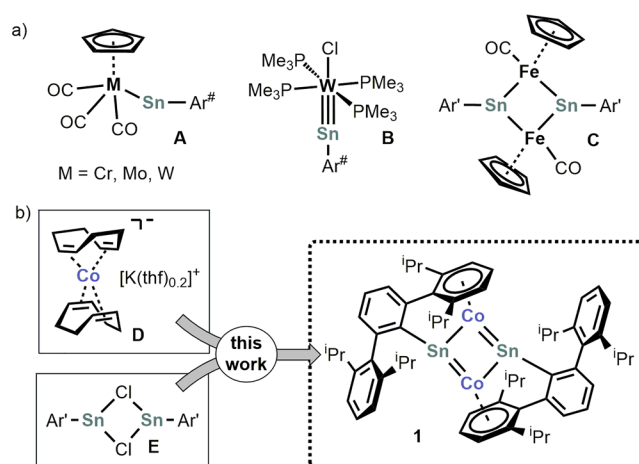
### Supporting Information

**ABSTRACT:**  $[\text{Ar}'\text{SnCo}]_2$  (**1**,  $\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6\{\text{C}_6\text{H}_3\text{-}2,6\text{-iPr}_2\}_2$ ), 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  $\text{Ar}'\text{SnSnAr}'$  ( $\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6\{\text{C}_6\text{H}_3\text{-}2,6\text{-iPr}_2\}_2$ ), 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 metallostanlylenes 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

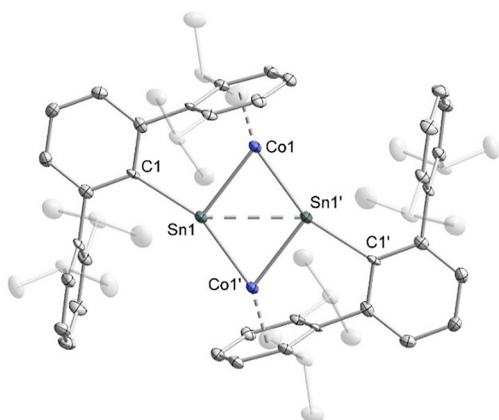


**Figure 1.** (a) Selected metallostanlylene and stannylidyne complexes ( $\text{Ar}' = \text{C}_6\text{H}_3\text{-}2,6\{\text{C}_6\text{H}_2\text{-}2,4,6\text{-Me}_3\}_2$ ); (b) synthesis of  $\text{Co}_2\text{Sn}_2$  compound **1**, reagents and byproducts:  $[\text{Ar}'\text{Sn}(\mu\text{-Cl})_2]_2 + 3[\text{K}(\text{thf})_{0.2}][\text{Co}(\eta^4\text{-cod})_2]^- - 2\text{KCl}, -4 \text{cod}$ ; 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>

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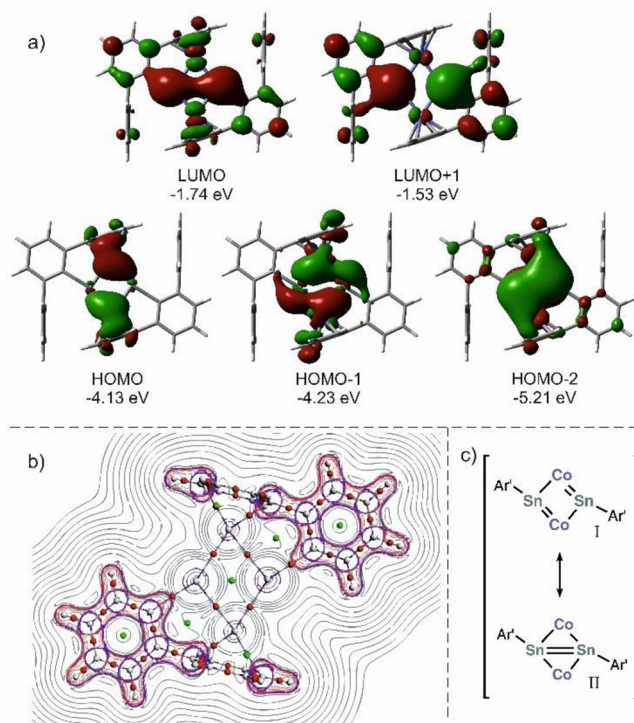


**Figure 2.** Displacement ellipsoid (40%) drawing of the centrosymmetric complex **1**. The cocrystallized *n*-hexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Sn1–Sn1' 2.8700(5), Sn1–Co1 2.5365(5), Sn1–Co1' 2.4071(6), Sn1–C1 2.174(3), 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),  $\text{nacnac} = \text{HC}\{\text{C}(\text{Me})\text{N}(2,6\text{-Me}_2\text{C}_6\text{H}_3)\}_2$ )<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

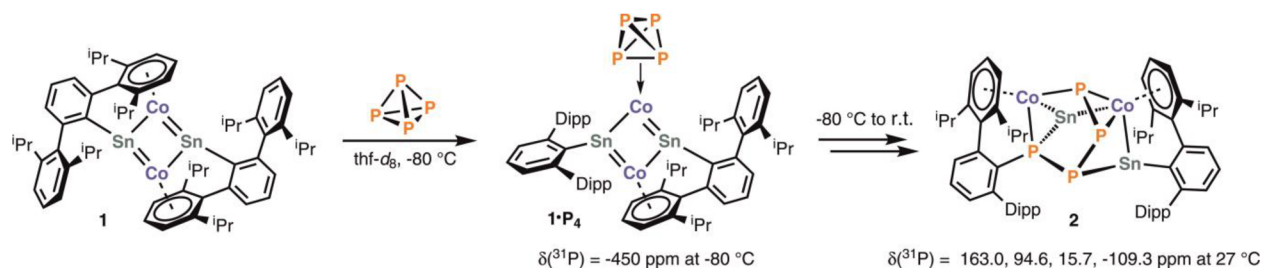


**Figure 3.** (a) Selected molecular orbitals of **1'** which describe the most significant interactions within the  $\text{Co}_2\text{Sn}_2$  core; (b) AIM (Bader) analysis (bond critical points: red, ring critical points green); (c) proposed Lewis resonance structures of **1** based on DFT calculations.

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>

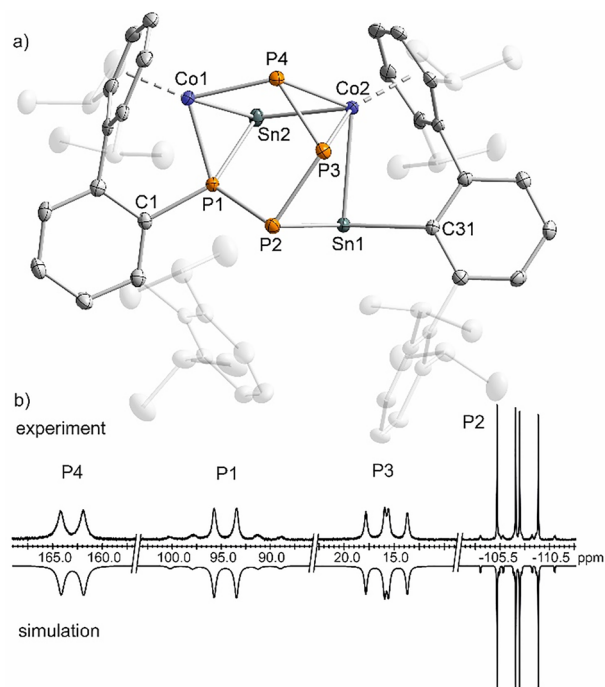
While reactivity studies with small molecules such as  $\text{O}_2$  and CO gave intractable products so far, **1** reacted readily with white phosphorus in toluene to afford  $[\text{Ar}'_2\text{Sn}_2\text{Co}_2\text{P}_4]$  (**2**) as a well-defined, crystalline species in up to 76% isolated yield

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  $\text{Co1}$  ( $\text{Co1-P1 } 2.1864(6)$  and  $\text{Co1-P4 } 2.2289(7) \text{ \AA}$ ) are shorter than those of the side-on coordinated  $\text{P-P}$  bond coordinating to  $\text{Co2}$  ( $\text{Co2-P3 } 2.3350(6)$  and  $\text{Co2-P4 } 2.3501(6) \text{ \AA}$ ). The  $\text{Co-Sn}$  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  $\text{Sn1-P2}$  and  $\text{Sn2-P1}$  distances ( $2.6587(6) \text{ \AA}$  and  $2.5716(6) \text{ \AA}$ , respectively) compare well with  $\text{Sn-P}$  single bonds reported for other tin-phosphorus cage compounds.<sup>32</sup> Weak interactions between  $\text{Sn1}\cdots\text{P3}$  and  $\text{Sn2}\cdots\text{P4}$  are also apparent, since the corresponding  $\text{Sn-P}$  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 [ $^\circ$ ]:  $\text{Sn1-Co2 } 2.8263(4)$ ,  $\text{Sn2-Co1 } 2.7380(4)$ ,  $\text{Sn2-Co2 } 2.6500(4)$ ,  $\text{Sn1-P2 } 2.6587(6)$ ,  $\text{Sn2-P1 } 2.5716(6)$ ,  $\text{Sn1}\cdots\text{P3 } 2.9277(6)$ ,  $\text{Sn2}\cdots\text{P4 } 2.8519(6)$ ,  $\text{Sn1-C31 } 2.279(2)$ ,  $\text{Co1-P1 } 2.1864(6)$ ,  $\text{Co1-P4 } 2.2289(7)$ ,  $\text{Co2-P3 } 2.3350(6)$ ,  $\text{Co2-P4 } 2.3501(6)$ ,  $\text{P1-P2 } 2.2005(8)$ ,  $\text{P2-P3 } 2.1809(8)$ ,  $\text{P3-P4 } 2.1621(8)$ ,  $\text{P1-C1 } 1.843(2)$ ,  $\text{Co1-Dipp(c) } 1.585(1)$ ,  $\text{Co2-Dipp(c) } 1.612(1)$ ,  $\text{P1-P2-P3 } 93.40(3)$ ,  $\text{P2-P3-P4 } 109.79(3)$ ,  $\text{P1-P2-P3-P4 } 16.27(3)$ . (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  $^{31}\text{P}$  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  $[\text{K}(\text{thf})_{0.2}][\text{Co}(1,5\text{-cod})_2]$  (**D**) as a  $\text{Co}^-$  source for the synthesis of the unique  $\text{Co}_2\text{Sn}_2$  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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