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

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Supporting Information

ABSTRACT: $[Ar'SnCo]_2$ (**1**, Ar′ = C_6H_3-2,6{C_6H_3-2,6-$^iPr_2$}$_2$), a rare metal−metal bonded cobalt−tin cluster with low-coordinate tin atoms, was prepared by the reaction of $[K(thf)_{0.2}][Co(1,5\text{-cod})_2]$ (cod = 1,5-cyclooctadiene) with $[Ar'Sn(\mu\text{-Cl})]_2$. 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 $[Ar'_2Sn_2Co_2P_4]$ (**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 $R_2Sn = SnR_2$ (R = CH{$SiMe_3$}$_2$) by Lappert and co-workers in 1976.[2] Distannyne Ar′SnSnAr′ (Ar′ = C_6H_3-2,6(C_6H_3-2,6-$^iPr_2$)$_2$), one of the first heavier group 14 element alkyne analogues, was described in 2002.[3] Moreover, homo- and heterometallic Zintl ions,[4] metalloid cages $[SnR]_n$,[5] and metalloid clusters $[Sn_nR_m]$ ($n > m$)[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 coligands.

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 $[K(thf)_{0.2}][Co(\eta^4\text{-cod})_2]$ (**D**, cod = 1,5-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 $[Ar'SnCo]_2$ 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 $[Ar'_2Sn_2Co_2P_4]$ (**2**), which is the first molecular cluster composed of tin, cobalt and phosphorus atoms.

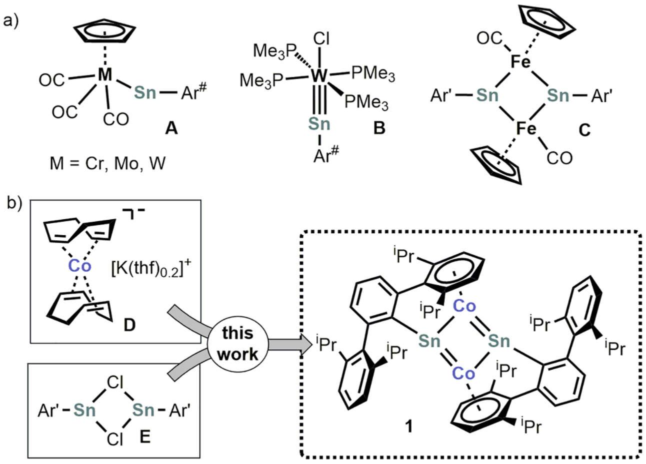

Figure 1. (a) Selected metallostannylene and stannylidyne complexes ($Ar^\#$ = C_6H_3-2,6(C_6H_2-2,4,6-Me_3)$_2$); (b) synthesis of Co_2Sn_2 compound **1**, reagents and byproducts: $[Ar'Sn(\mu\text{-Cl})]_2$ + $3[K(thf)_{0.2}][Co(\eta^4\text{-cod})_2]$/−2KCl, −4 cod; conditions: toluene, −30 °C → r.t., 20 h.

$[Ar'SnCo]_2$ (**1**) was obtained by reacting $[K(thf)_{0.2}][Co(\eta^4\text{-cod})_2]$ (**D**) with $[Ar'Sn(\mu\text{-Cl})]_2$ (**E**) in toluene (Figure 1b). An excess of cobaltate **D** (three equiv. per $[Ar'Sn(\mu\text{-Cl})]_2$ 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 ($\sum r_{cov}$ = 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 $[^tBu_3SnSn^tBu_3]$ (2.894(1) Å),[13] $[(PhCH_2)_3SnSn(CH_2Ph)_3]$ (2.823(1) Å)[13] and $[(o\text{-Tol})_3SnSn(o\text{-Tol})_3]$ (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 [Ar′CoCoAr′] (1.764(2) Å),[15]

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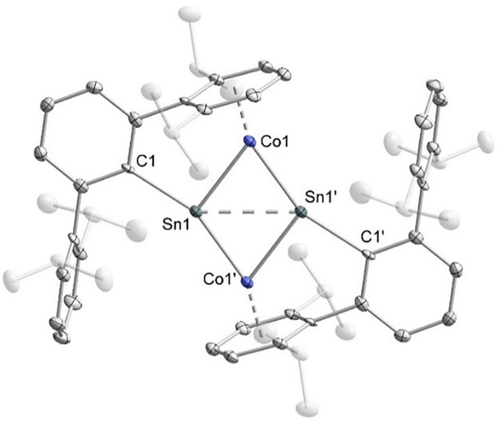

Figure 2. Displacement ellipsoid (40%) drawing of the centrosymmetric complex **1**. The cocrystallized *n*-hexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Sn1−Sn1′ 2.8700(5), Sn1−Co1 2.5365(5), Sn1−Co1′ 2.4071(6), Sn1−C1 2.174(3), 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).

[(nacnac)Co(η^6-C_7H_8)] (1.747(2), nacnac = HC{C(Me)N-(2,6-$Me_2C_6H_3$)}$_2$)[16] and [(η^6-C_7H_8)CoAr*] (1.659(1) Å, Ar* = C_6H-2,6(C_6H_2-2,4,6-$^iPr_3$)$_2$-3,5-$^iPr_2$).[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-π^* 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 *RE*CoSn stannides (*RE* = rare earth metal),[20,21] However, the Co_2Sn_2 units in *RE*CoSn (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 $[Co@Sn_9]^{5-}$ and $[Co_2@Sn_{17}]^{5-}$ with Co^- anions encapsulated into Sn_9 cages.[22] A bridging μ-η^1:η^6 coordination mode of the terphenyl ligand was observed for the doubly reduced distannyne [K_2Ar′SnSnAr′] and the digermyne silver complexes [AgAr′GeGeAr′][SbF_6] and [Ag_2Ar′GeGe(F)Ar′][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′** (^{i}Pr 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 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[25] 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(stannylidyne) complex seems to be more important than resonance structure II describing a distannyne dicobalt complex.

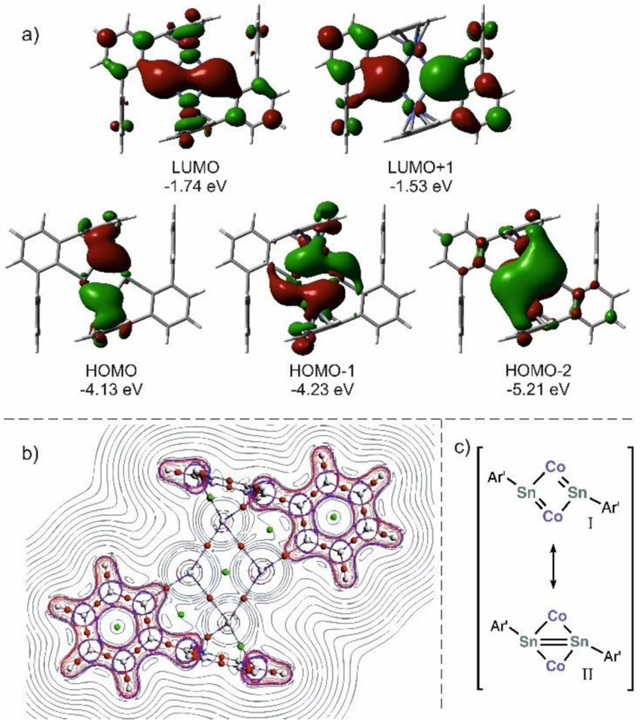

Figure 3. (a) Selected molecular orbitals of **1′** which describe the most significant interactions within the Co_2Sn_2 core; (b) AIM (Bader) analysis (bond critical points: red, ring critical points green); (c) proposed Lewis resonance structures of **1** based on DFT calculations.

The ^{119}Sn Mössbauer spectrum of solid **1** recorded at 6 K (Figure S9 (SI)) shows a single quadrupole doublet. The isomer shift of **1** (δ = 2.14(1) mm s^{-1}) is slightly lower than that of β-Sn (δ = 2.6 mm s^{-1}) and comparable to those of stannides and intermetallic tin compounds, e.g. DyCoSn (δ = 1.80 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 $SnCo_{4/4}$ coordination and a small electric quadrupole splitting parameter of ΔE_Q = 0.55 mm s^{-1}.[21] The electric quadrupole splitting is drastically larger for the Co_2Sn_2 core in **1** (ΔE_Q = 2.86(1) mm s^{-1}). This indicates a highly anisotropic charge distribution analogous to that of the related distannyne [Ar′SnSnAr′] (δ = 2.658(2) mm s^{-1}; ΔE_Q = 2.995(2) 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 [$Ar'_2Sn_2Co_2P_4$] (**2**) as a well-defined, crystalline species in up to 76% isolated yield

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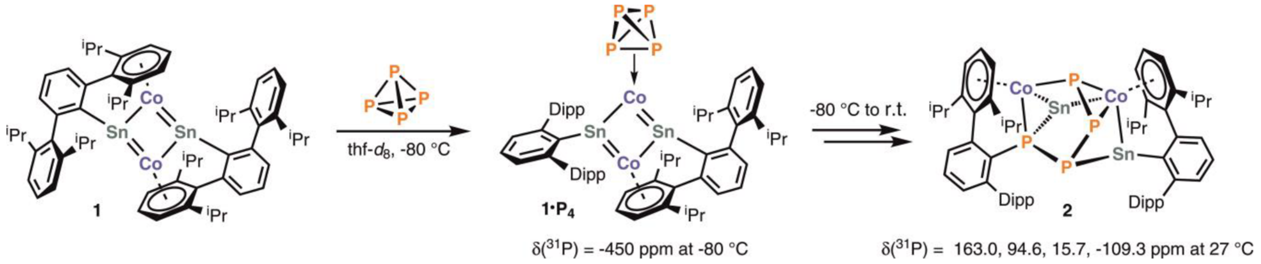
Scheme 1. Proposed Pathway of Formation of 2 Involving the Coordination of P_4 to 1 and Subsequent Insertion into the Cluster Framework



(Scheme 1). $^{31}P\{^1H\}$ NMR monitoring of the reaction in thf-d_8 (Figure S11, Supporting Information) revealed the formation of an intermediate **1·P$_4$** at −80 °C with a broad singlet at −450 ppm. We presume that **1·P$_4$** is a highly fluxional η^2-P_4 complex analogous to coinage metal complexes reported by Krossing, Russell, and Scheer.[28] Intermediate **1·P$_4$** is converted to **2** on warming the reaction solution to >0 °C. Minor unidentified species with resonances at +180, +15, −44, and −157 ppm arising at −20 °C may presumably represent further intermediates en route to **2**. These resonances disappear upon warming to room temperature. The primary phospane Ar′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 phosphaalkyne with a terphenyl allyl stannylene.[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) Å are slightly longer than those in **1**. The P−P bond distances ranging from 2.2005(8) to 2.1621(8) Å are typical for single bonds ($\sum r_{cov}$ = 2.22 Å).[12] As expected, the Co−P bonds of the terminal P atoms coordinating to Co1 (Co1−P1 2.1864(6) and Co1−P4 2.2289(7) Å) are shorter than those of the side-on coordinated P−P bond coordinating to Co2 (Co2−P3 2.3350(6) and Co2−P4 2.3501(6) Å). The Co−Sn distances (Co1−Sn1 2.7380(4) Å, Co2−Sn1 2.8263(4), and Co2−Sn2 2.6500(4) Å) are significantly longer than in **1**, while the Sn1−P2 and Sn2−P1 distances (2.6587(6) Å and 2.5716(6) Å, respectively) compare well with Sn−P single bonds reported for other tin−phosphorus cage compounds.[32] 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) Å are much smaller than the sum of van der Waals radii ($\sum r_{vdW}$ = 4.02 Å).[33]

The $^{31}P\{^1H\}$ NMR spectrum of **2** shows four multiplets with an integral ratio of 1:1:1:1 (Figure 4b) with additional coupling to $^{117/119}$Sn. The spectrum was successfully simulated by an iterative fitting procedure (see the SI). The $^1J_{PP}$ 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 $^{117/119}$Sn satellites at P2 and P4 ($^1J_{P2Sn1}$ = 579 Hz, $^1J_{P1Sn2}$ = 1482 Hz). Direct bonding to quadrupolar ^{59}Co nuclei can considerably affect the line width of ^{31}P NMR resonances depending on the $^1J_{PCo}$ 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 Hz), P3 ($\Delta\nu_{1/2}$ = 54 Hz) and P4 ($\Delta\nu_{1/2}$ = 121 Hz).

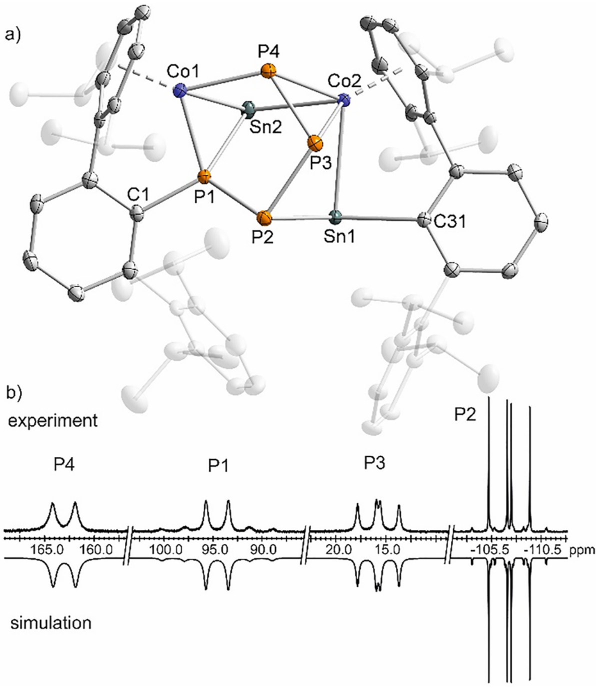


Figure 4. (a) Displacement ellipsoid (40%) drawing of the $Co_2Sn_2P_4$ cluster **2**. The cocrystallized cyclohexane solvent molecule and the hydrogen atoms are not shown for clarity. Selected bond lengths [Å] and angles [deg]: Sn1−Co2 2.8263(4), Sn2−Co1 2.7380(4), Sn2−Co2 2.6500(4), Sn1−P2 2.6587(6), 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) $^{31}P\{^1H\}$ NMR spectra of compound **2** in thf-d_8.

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 δ = 2.58(1) mm s^{-1} and δ = 2.94(1) mm s^{-1}. These isomer shifts are comparable to those of other organotin(II) compounds[36] and metalloid tin clusters.[37] Both signals show similar quadrupole splittings of ΔE_Q = 1.41(1) and 1.43(1) 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 $[K(thf)_{0.2}][Co(1,5\text{-}cod)_2]$ (**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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(18) A ^{119}Sn NMR signal was not detected for **1** in the range of −4200 to +4200 ppm. This is probably due to the unsymmetric electron environment at the tin atoms in **1**, which leads to fast relaxation through the anisotropy of the chemical shift tensor. The $^1J_{SnCo}$ coupling to the two adjacent ^{57}Co nuclei ($I = -7/2$) may additionally cause considerable broadening of the signal rendering it unobservable above the baseline. It seems noteworthy that the ^{119}Sn resonance of the distannyne [Ar′SnSnAr′] could also not be detected despite extensive efforts (see refs 3a and 23a), but large differences were observed for the solid-state ^{119}Sn NMR data of [Ar′SnSnAr′] and the closely related species [Ar*SnSnAr*] ($Ar^* = C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}i\text{Pr}_3)_2$, see ref 27).

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