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Transition-Metal-Stabilized Heavy Tetraphospholide Anions

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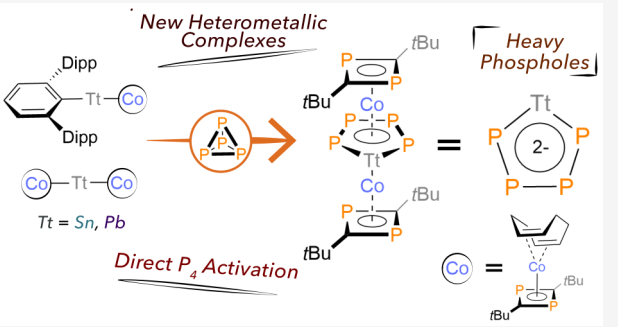
ABSTRACT: Phosphorus analogues of the ubiquitous cyclopentadienyl (Cp) are a rich and diverse family of compounds, which have found widespread use as ligands in organometallic complexes. By contrast, phospholes incorporating heavier group 14 elements (Si, Ge, Sn, and Pb) are hardly known. Here, we demonstrate the isolation of the first metal complexes featuring heavy cyclopentadienyl anions SnP_4^{2-} and PbP_4^{2-}. The complexes $[(\eta^4\text{-}t\mathrm{Bu}_2\mathrm{C}_2\mathrm{P}_2)_2\mathrm{Co}_2(\mu,\eta^5{:}\eta^5\text{-}\mathrm{P}_4\mathrm{Tt})]$ [Tt = Sn (**6**), Pb (**7**)] are formed by reaction of white phosphorus (P_4) with cyclooctadiene cobalt complexes $[\mathrm{Ar'TtCo}(\eta^4\text{-}\mathrm{P}_2\mathrm{C}_2t\mathrm{Bu}_2)(\eta^4\text{-COD})]$ [Tt = Sn (**2**), Pb (**3**), Ar′ = C_6H_3-2,6{C_6H_3-2,6-iPr$_2$}$_2$, COD = cycloocta-1,5-diene] and $\mathrm{Tt}\{\mathrm{Co}(\eta^4\text{-}\mathrm{P}_2\mathrm{C}_2t\mathrm{Bu}_2)(\mathrm{COD})\}_2$ [Tt = Sn (**4**), Pb (**5**)]. While the SnP_4^{2-} complex **6** was isolated as a pure and stable compound, compound **7** eliminated Pb(0) below room temperature to afford $[(\eta^4\text{-}t\mathrm{Bu}_2\mathrm{C}_2\mathrm{P}_2)_2\mathrm{Co}_2(\mu,\eta^4{:}\eta^4\text{-}\mathrm{P}_4)]$ (**8**), which is a rare example of a tripledecker complex with a P_4^{2-} middle deck. The electronic structures of **6**–**8** are analyzed using theoretical methods including an analysis of intrinsic bond orbitals and magnetic response theory. Thereby, the aromatic nature of P_5^- and SnP_4^{2-} was confirmed, while for P_4^{2-}, a specific type of symmetry-induced weak paramagnetism was found that is distinct from conventional antiaromatic species.



INTRODUCTION

The diagonal relationship between phosphorus and carbon in the periodic table has inspired the development of a wealth of phosphorus analogues of classical hydrocarbons.[1] Among this family of low-coordinate phosphorus compounds, phospholes take a prominent position due to their relationship to cyclopentadienes.[2] The sophisticated chemistry of phospholes and the corresponding phospholide anions developed over the last decades has inspired numerous applications in supramolecular chemistry, homogeneous catalysis, and molecular electronics, e.g., in organic light-emitting diodes (OLEDs).[3−5]

The synthesis of the pentaphospholide anion, P_5^- (**A**, Figure 1), by Baudler and co-workers was a seminal achievement in phosphole chemistry.[6] Phospholide **A** is the pure phosphorus analogue of the ubiquitous cyclopentadienyl anion, Cp^- (Cp = C_5H_5). The synthesis of **A** is achieved by reacting white phosphorus (P_4) with sodium in diglyme or with lithium phosphide in THF. It is noteworthy that the tetraphospholide anion, P_4CH^-, was observed by Baudler in the same reaction mixture but it was not isolated. The crystallographic characterization of the tetraphospholide anion P_4CMes^{*-} (**B**) was subsequently reported by Ionkin and co-workers.[7] This anion was isolated as the cesium salt Cs[P_4CMes*] in a low yield by fractional crystallization from a three-component reaction involving $P(SiMe_3)_3$, CsF, and Mes*C(O)Cl (Mes* = 2,4,6-tBu$_3$-C_6H_2).

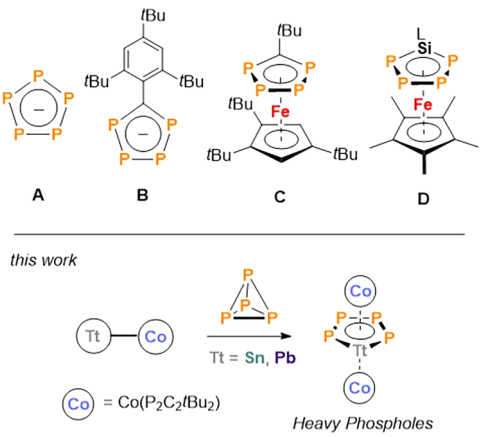


Figure 1. Previous examples of penta- and tetraphospholides (**A**–**D**, L = PhC(NtBu)$_2$) and schematic strategy for the synthesis of heavy phospholes reported in this work.

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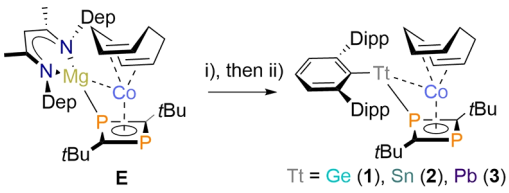
Similarly to Cp, the transition metal coordination chemistry of mono-, di-, tri-, and pentaphospholides is well developed. Notable examples are the pentaphosphaferrocenes $[(C_5R_5)Fe(\eta^5-P_5)]$ (R = H, Me), which are outstanding synthons for the assembly of giant supramolecular fullerene analogues.[4] However, there appears to be only a single example of a tetraphosphole complex in the literature (compound **C**, Figure 1).[8,9] Tin- and lead-containing aromatic compounds are still scarce.[10] Although heavier group 14 element analogues of the cyclopentadienyl anion, i.e., siloles, germoles, and stannoles, are of interest owing to their photophysical properties arising from $\sigma^*-\pi^*$ interactions,[10f,g,i] analogues of such systems that additionally incorporate a heavier group 15 element such as phosphorus are exceedingly rare. The recently reported compound **D** is a solitary example for a tetraphosphasilole complex.[11] Phospholes containing Ge, Sn, or Pb appear to be unknown.

A recent work from our group has successfully utilized the reaction of white phosphorus (P_4) with heterobimetallic complexes to prepare unusual polyphosphorus compounds.[12,13] Using this strategy, we have now synthesized the heavy tetraphospholide anions SnP_4^{2-} and PbP_4^{2-}. These hitherto unknown π-aromatic molecules are stabilized by the coordination to two cobalt atoms in the triple-decker sandwich compounds $[(\eta^4\text{-}tBu_2C_2P_2)_2Co_2(\mu,\eta^5:\eta^5-P_4Tt)]$ [Tt = Sn (**6**), Pb (**7**)]. We describe the structural and spectroscopic characterization of these complexes and analyze the electronic structure of the P_4Tt^{2-} ligands with quantum chemical methods.

RESULTS AND DISCUSSION

Our study commenced with the preparation of the bimetallic tetrel cobaltate complexes $[Ar'TtCo(\eta^4\text{-}P_2C_2tBu_2)(\eta^4\text{-COD})]$ [Tt = Ge (**1**), Sn (**2**), Pb (**3**)] used as precursors to our target complexes. Compound **1**–**3** were prepared by reacting the recently reported magnesium cobaltate salt $[(^{Dep}nacnac)MgCo(\eta^4P_2C_2tBu_2)(\eta^4\text{-COD})]$ (**E**, $^{Dep}nacnac$ = $CH(DepNCMe)_2$, Dep = 2,6-Et_2-C_6H_3) with terphenyl tetrel halides, $[Ar'Tt(\mu\text{-}X)]_2$ (Tt = Ge, X = Cl; Sn, Pb, X = Br) (Scheme 1). Low temperatures (−80 °C) are required for clean formation of the germanium compound **1**, while for tin and lead, the reactions are selective at ambient temperature. Addition of either Li($^{Dep}nacnac$) or Li(acac) (acac = acetyl acetonate) to the reaction mixtures is necessary during workup to convert $[(^{Dep}nacnac)MgX]$ into the *n*-hexane soluble complexes $[Mg(^{Dep}nacnac)_2]$ or $[Mg(^{Dep}nacnac)(acac)]$. Using this procedure, it is possible to isolate **1**–**3** in moderate yields as a dark green crystalline powder from concentrated *n*-hexane solutions.

Scheme 1. Synthesis of Compounds 1–3[a]



[a]Reagents and conditions: (i) +0.5 $[Ar'TtX]_2$ (Tt = Ge, X = Cl; Sn, Pb, X = Br; Ar′ = 2,6-$Dipp_2$-C_6H_3, Dipp = 2,6-iPr_2−C_6H_3), toluene, −78 °C to r.t., 12 h; (ii) + Li($^{Dep}nacnac$)/−Mg($^{Dep}nacnac$)$_2$, −LiX, toluene/THF, −78 °C to r.t. ($^{Dep}nacnac$ = $CH(DepNCMe)_2$, Dep = 2,6-Et_2-C_6H_3), 12 h.

The molecular structures of **1**–**3** were determined by single-crystal X-ray diffraction. Since all three structures share the same motif, only the molecular structure of **2** is displayed in Figure 2, while those of **1** and **3** are shown in the Supporting Information (SI) (Figures S1 and S3). The cobalt atoms feature η^4-coordinated 1,5-cyclooctadiene and 1,3-diphosphacyclobutadiene ligands, while the tetrel atom (Ge, Sn, or Pb) is in a *pseudo*-two-coordinate environment by terphenyl-substituent and one of the P atoms of the diphosphacyclobutadiene ligand. The Tt-P bond lengths in **1**–**3** (2.3946(8) Å, 2.6442(7) Å, 2.7402(10) Å, respectively) are similar to those of tertiary phosphine adducts of tetrelylenes.[14] The Tt-Co distances in **1**–**3** (Ge−Co 2.8434(6) Å, Sn−Co 2.9534(5) Å, Pb−Co: 3.0318(6) Å) are longer than the sum of their covalent radii ($\sum r_{GeCo}$ 2.70 Å, $\sum r_{SnCo}$ 2.89 Å, $\sum r_{PbCo}$ 2.96 Å).[15] These parameters suggest the absence of a covalent metal−metal bond, which is in line with quantum chemical calculations (*vide infra*). By contrast, the previously reported, related cluster compound $(Ar'SnCo)_2$ features strong covalent Sn−Co bonds, which even have partial multiple bond character.[12] The P−C bonds of the diphosphacyclobutadiene ligands are in a close range. It thus appears that the coordination of the tetrel element only has a minor influence on the ligand structure (see SI for a more detailed discussion).

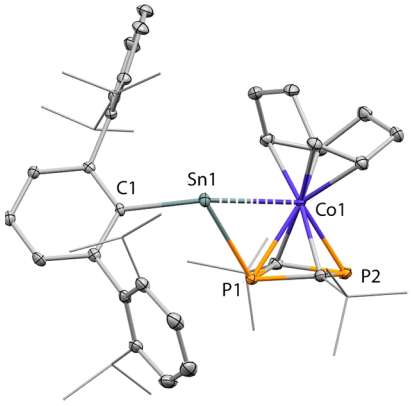


Figure 2. Molecular structure of **2**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted and the *t*Bu and *i*Pr groups drawn in the wire frame model for clarity. Selected bond lengths (Å) and angles (deg): Sn1−Co1 2.9534(5), Sn1−P1 2.6442(7), Sn1−C1 2.252(3), Co1−P1 2.3472(8), Co1−P2 2.2833(8), C1−Sn1−Co1 128.08(6), C1−Sn1−P1 102.17(7).

It is noteworthy that although the Tt-Co and Tt-P distances for **1**-**3** increase down the group, the bond angles are approximately the same (C1−Tt−Co1 127°−129°, C1−Tt−P1 102°−103°). As a consequence of the relatively short atomic radius of germanium, the terphenyl substituent and the $Co(P_2C_2tBu_2)(COD)$ unit in **1** are very close to each other resulting in a restricted rotation of the terphenyl ligand around the Tt-P/Tt-C bonds as evidenced by variable temperature (VT) NMR experiments. At room temperature, the NMR spectra of **1** show inequivalence in the ^1H and ^{13}C signals for the COD ligand and the *t*Bu groups in agreement with the molecular structure (see SI, Figures S9−15, for details). The ^1H NMR spectra for **2** and **3** are far simpler, showing only six signals for the COD ligand and one singlet for the *t*Bu moiety,

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indicating a C_s symmetry on the NMR time scale. At lower temperatures, the ^{1}H NMR signals of **2** and **3** resemble that of **1**. The VT NMR spectrum of **1** at higher temperatures shows only signals corresponding to several decomposition products (at T > 60 °C) but not signals corresponding to a C_s symmetric **1**. In contrast, **2** and **3** show no appreciable decomposition up to 110 °C.

The $^{31}P\{^1H\}$ NMR spectra for **1**−**3** are in agreement with the molecular structures. In each case, two doublet signals are observed. Coordination of the P atom to the tetrel center results in a high-field shift of the $^{31}P\{^1H\}$ NMR signals (δ = −43.5, −62.3, and −56.1 ppm for **1**, **2**, and **3**, respectively; see SI) with respect to the signal for the uncoordinated P atom (δ = 57.4, 59.1, and 59.5 ppm for **1**, **2**, and **3**, respectively). In the case of **2** and **3**, Sn and Pb satellites are present for the signals of the Tt-coordinated P atom ($^1J_{SnP}$ = 1050 Hz, and $^1J_{PbP}$ = 1192 Hz, respectively, see Figures S17 and S25). The corresponding ^{119}Sn and ^{207}Pb NMR signals were observed at 298 K as broad doublets at 1899.7 ppm for **2** (Figure S18) and at 8592 ppm for **3** (Figure S26) and could be unambiguously assigned via the scalar coupling values ($^1J_{PSn}$ = 1053 Hz and $^1J_{PPb}$ = 1200 Hz). At lower temperature (233 K), a significant broadening of the ^{119}Sn NMR signal of **2** was observed (Figure S19), while the ^{207}Pb NMR signal of **3** could not be detected anymore.

Intrinsic bond orbital (IBO), natural bond orbital (NBO) and atoms in molecules (AIM) analyses of DFT calculated electron densities were employed to analyze the bonding situation in **1**−**3**.[16,17] The IBO analyses show the expected bond-like localized molecular orbitals. In addition, substantial π-bonding interactions are apparent between the cobalt atom and the π-orbitals of the diphosphacyclobutadiene ligand, which should result in a significant amount of charge transfer (see SI for a more detailed discussion and graphical representations of relevant IBOs). Additionally, there is a delocalized IBO between the tetrel, coordinating phosphorus and cobalt centers, but with low contributions from Co (**1**: Ge (24%) Co (8%) P (59%), **2**: Sn (14%) Co (10%) P (59%), **3**: Pb (13%) Co (10%) P (59%)). The Wiberg bond indices for Ge−Co, Sn−Co, and Pb−Co linkages in **1**−**3** (0.20, 0.15 and 0.13, respectively) are lower than expected for a covalent bond. In line with the results from DFT, the AIM analysis shows bond critical points (BCPs) between cobalt and phosphorus as well as the tetrel atoms and phosphorus (see Figure 3 and SI). However, no BCPs were found between the tetrel atoms and the cobalt center. All these results indicate the presence of only a weak interaction between Tt and Co.

It was also possible to synthesize the homoleptic tin(II) complex Sn[Co(η^4-P_2C_2tBu$_2$)(COD)]$_2$ (**4**) by reacting **E** with commercially available Sn(acac)$_2$ (Figure 4). Single-crystal X-ray diffraction on **4** revealed that the tin atom is coordinated by the two P atoms of the diphosphacyclobutadiene ligands with Sn−P distances (Sn1−P1 2.6490(10), Sn1−P2 2.6484(10) Å) similar to **2** and a P−Sn−P angle of 102.17(7)°. Similar to the structures of **1**−**3** discussed above, the Sn−Co distances (Sn1−Co2 2.9682(6) and Sn1−Co2 2.9649(7) Å) suggest that there is only a weak interaction between the cobalt atom and tin. The $^{31}P\{^1H\}$ NMR spectrum for **4** is comparable to that of **2**, showing two doublet signals (δ = 77.2 and −83.3 ppm, $^2J_{PP}$ = 17.4 Hz). The high-field shifted signal can be assigned to the P atoms coordinated to tin due to the observation of ^{119}Sn satellites ($^1J_{SnP}$ = 1067 Hz; see Figure S32).

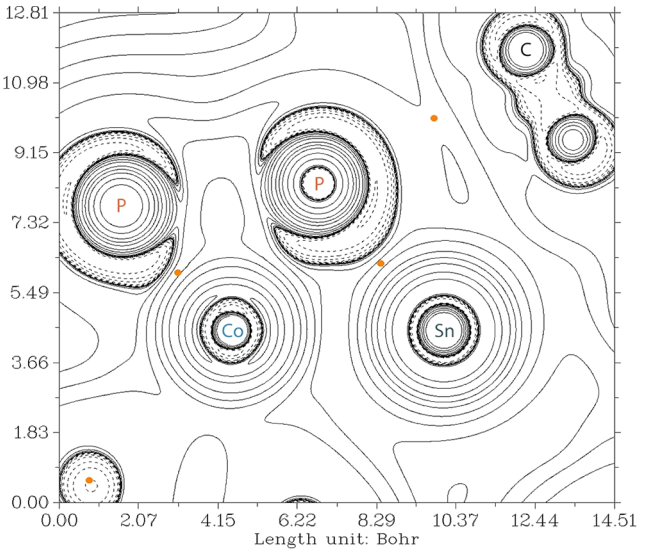

Figure 3. Laplacian contour plot in the P1, P2, Co1, Sn1 plane of **2**; bond critical points are shown as orange dots.

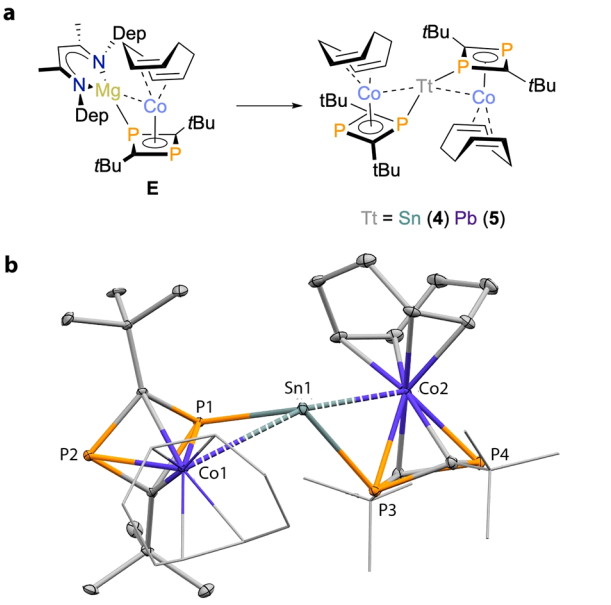

Figure 4. (a) Synthesis of compounds **4** and **5**; reagents and conditions: Tt = Sn: +Sn(acac)$_2$ (0.5 equiv)/−Mg(^{Dep}nacnac)(acac), toluene, r.t., 12 h; Tt = Pb: +Pb(acac)$_2$ (0.5 equiv)/−Mg(^{Dep}nacnac)-(acac), toluene, −30 °C to r.t., 16 h; (b) molecular structure of **4**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted and two *t*Bu groups and the COD ligand drawn in the wire frame model for clarity. Selected bond lengths (Å) and angles (deg): Sn1−Co1 2.9682(6), Sn1−Co2 2.9649(7), Sn1−P1 2.6490(10), Sn1−P3 2.6484(10), Co1−Sn1−Co2 149.374(19), P1−Sn1−P3 100.24(3).

$^{31}P\{^1H\}$ NMR analysis of the related reaction of **E** (two equiv) with Pb(acac)$_2$ indicates the formation of analogous dimetalloplumbylene, Pb[Co(η^4-P_2C_2tBu$_2$)(η^4-COD)]$_2$ (**5**, see Figure S36). Two doublet signals (δ = −65.9 and 74.1 ppm) are detected of which the high-field shifted signal possesses Pb satellites ($^1J_{PbP}$ = 1004 Hz, $^2J_{PP}$ = 19 Hz). Unfortunately, it was not possible to isolate **5** due to the low thermal stability of the compound. Any isolation attempt resulted in the deposition of a black precipitate (presumably metallic lead).

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Having compounds **1**−**4** in hand, we studied their reactivity toward P_4 to ascertain whether they can be used as precursors to novel polyphosphorus compounds. Reactions between **1** and P_4 were unsuccessful. While no reaction occurs at ambient temperature, heating to 55 °C affords an intractable mixture of products according to $^{31}P\{^1H\}$ NMR spectra (see Figure S15). By contrast, reactions of **2** or **4** with P_4 at elevated temperatures afford the dark red, crystalline compound $[(tBu_2C_2P_2)_2Co_2(\mu,\eta^5{:}\eta^5\text{-}SnP_4)]$ (**6**) in each case (Figure 5a).[18] When using **2**, separation of **6** from the unknown

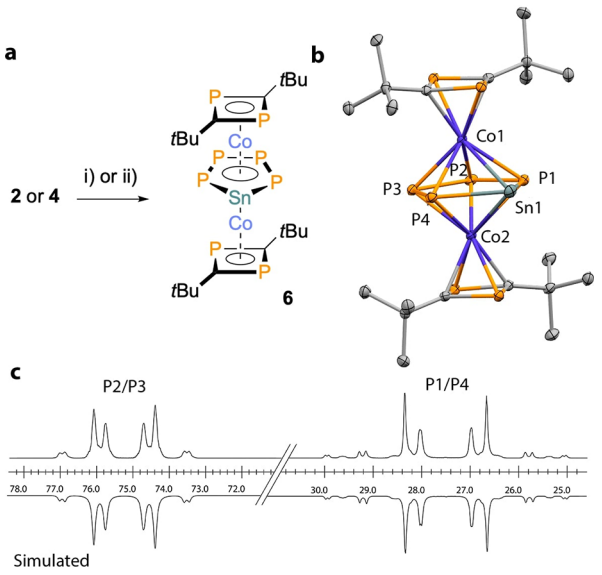


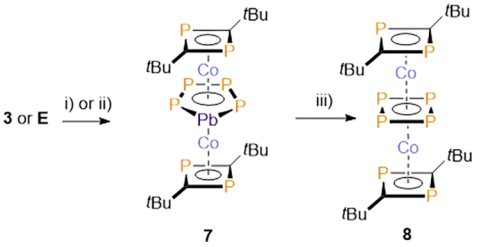
Figure 5. (a) Synthesis of compound **6** via **2** or **4**. Reagents and conditions: (i) **2** (1 equiv), $+P_4$ (1.4 equiv)/−COD, "−Ar′P", THF, 65 °C, 16 h; (ii) **4** (1 equiv), $+P_4$ (1.2 equiv)/−COD, toluene, 55 °C, 16 h, toluene, r.t., 16 h; (b) molecular structure of **6**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Sn1−P1 2.5198(8), Sn1−P4 2.5375(9), P1−P2 2.1101(12), P2−P3 2.2296(11), P3−P4 2.1104(12), Co1−Co2 3.050, P1−Sn1−P4 88.17(3), Sn1−P1−P2 118.23(4), P1−P2−P3 107.96(5), P2−P3−P4 107.60(5), P3−P4−Sn1 118.02(4); (c) sections of the measured (upward) and simulated (downward) $^{31}P\{^1H\}$ NMR spectrum of **6**.

terphenyl containing byproducts proved difficult. Fortunately, the reaction of **4** with P_4 forms **6** selectively at ambient temperature, with 1,5-cyclooctadiene being the only byproduct, making isolation facile and allowing the crystallographic characterization of **6** by single-crystal X-ray diffraction (Figure 5b). The crystallographic analysis reveals the formation of a triple decker complex of two $(\eta^4\text{-}P_2C_2tBu_2)Co$ units and a planar *cyclo*-SnP_4 middle deck, for which a pronounced alternation of the P−P bond lengths is observed. The P−P bonds adjacent to the Sn atom (P1−P2 2.1101(12) and P3−P4 2.094(4) Å) approach the range for a P=P double bond.[19] The P2−P3 bond length (2.2296(11) Å) suggests the presence of a single bond. The bond lengths between phosphorus and tin (av. P−Sn 2.52865(9) Å) are comparable to the single bonds found in diphosphastannylenes.[20]

The $^{31}P\{^1H\}$ spectrum of **6** shows one singlet and two multiplets with an integral ratio of 4:2:2. The singlet at δ = 67.1 ppm can be assigned to the P atoms within the $P_2C_2tBu_2$ rings. One of the two multiplet signals (δ = 29.6 and 77.0 ppm), the high-field shifted signal shows coupling to $^{117/119}Sn$, allowing for its definitive assignment to the P atoms adjacent to the Sn atom (P1 and P4). Simulation of the $^{31}P\{^1H\}$ spectrum by an iterative fitting procedure gave a $^1J_{PP}$ coupling constant of −434.7 Hz for the P1−P2/P3−P4 pairs, whereas the $^1J_{PP}$ coupling for P2−P3 (magnetically not equivalent) was −289.0 Hz (see Figures S39−S41, Figure 5c). A ^{119}Sn NMR spectrum of **6** shows a broad triplet at δ = 339.7 ppm with a $^1J_{SnP}$ coupling constant of 797 Hz, which is in agreement with the simulated $^{31}P\{^1H\}$ NMR spectrum (see Figures 5c and S41 and Table S1). The line broadening of the ^{119}Sn NMR is likely due to interactions with the quadrupolar ^{59}Co nuclei.[21]

It is noteworthy that the analogous lead compound $[(tBu_2C_2P_2)_2Co_2(\mu,\eta^5{:}\eta^5\text{−}PbP_4)]$ (**7**) is formed by reacting **3** with P_4 (Scheme 2). In solution, **7** shows a similar $^{31}P\{^1H\}$ NMR spectrum as **6** (see the SI for details). However, in contrast to **6**, **7** is unstable at ambient temperature, depositing lead metal and affording a new species, which was identified as $[Co_2(P_2C_2tBu_2)_2(\mu,\eta^4{:}\eta^4\text{−}P_4)]$ (**8**).

Scheme 2. Synthesis of Compounds 7 and 8[a]



[a]Reagents and conditions: (i) **3** (1 equiv), $+P_4$ (1 equiv)/−COD, $-P_4Ar'_2$, −"Ar′P", toluene, 55 °C, 16 h; (ii) **E** (2 equiv), $+Pb(acac)_2$ (1 equiv), P_4 (1 equiv)/−Mg(^{Dep}nacnac)(acac) (2 equiv), −COD (2 equiv), toluene, −30 °C to r.t., 16 h; (iii) −Pb, toluene, storage at r.t.

Since no intermediates en route to **6** or **7** were detected by ^{31}P NMR spectroscopy, any mechanistic proposal remains speculative at this point. However, in principle, two distinct scenarios are plausible (i) an initial oxidative addition of P_4 to the group 14 atom (tin or lead) followed by substitution of the cod ligand on cobalt or (ii) the substitution of the cod ligand by P_4, which would be followed by an insertion of tin(II) or lead(II) into a P−P bond of the resulting tetraphosphido ligand (see SI, Schemes S1 and S2).[13,22]

While the isolation of **7** and **8** as pure compounds has so far not been possible, their identity was firmly established by singe-crystal X-ray analysis and multinuclear NMR spectroscopy (*vide infra*). Additionally, the resonances for the terphenyl−P_4 butterfly compound $^{Dipp}Ar_2P_4$ were observed, confirming the fate of the terphenyl ligand attached to the lead center (see Figure S46).[23] Note that these resonances are not present in the $^{31}P\{^1H\}$ NMR spectra for the reaction of **2** with P_4; in this case, the fate of the terphenyl substituent remains presently unclear. It should be noted that the one-pot reaction of **E**, $Pb(acac)_2$, and P_4 also forms **7**, as observed in the $^{31}P\{^1H\}$ NMR spectrum, but only small amounts of crystalline material could be isolated, which were contaminated with Mg(^{Dep}nacnac)(acac).

Similar to complex **6**, the molecular structure of **7** (Figure S6) features a triple-decker structure with a planar *cyclo*-PbP_4 middle deck. The bond lengths are similar to those observed for **6**, with two short P−P bonds adjacent to the Pb atom (P1−P2 2.1104(12) and P3−P4 2.083(4) Å), and a longer P2−P3 bond in the typical range for P−P single bonds. The P−Pb

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distances (av. P−Pb 2.625(3) Å) are in the typical range expected for P−Pb single bonds.[20] The $^{31}P\{^{1}H\}$ NMR spectrum for **7** is in line with the molecular structure, showing a singlet at δ = 67.9 ppm and multiplet signals at δ = 18.5 and 64.9 ppm (Figure S50).

The molecular structure of **8** (Figure 6) shows the same η^4-1,3-diphosphacyclobutadiene cobalt moieties as observed in **6**

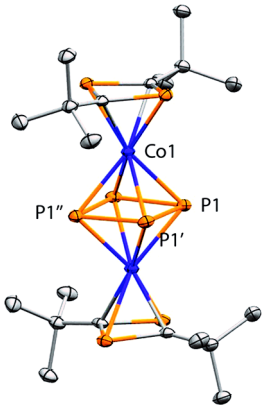

Figure 6. Molecular structure of **8**, with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−P1′ 2.2411(7), Co1−P1 2.3015(6), Co1−Co2 3.377, P1−P1′−P1″ 89.981(1).

and **7**, while the middle deck of the triple-decker structure is a square planar tetraphosphorus ring with equal P−P bond lengths (2.2411(7) Å) and P−P−P bond angles of 90°. The P−P bond length is longer than that found in Cs_2P_4 (2.146(1)/2.1484(9) Å), which also possesses a square planar *cyclo*-P_4 ring.[24] Triple-decker sandwich complexes with a *cyclo*-P_4 middle deck have rarely been reported. To our knowledge, the only other examples are $[(Cp^RFe)_2(\mu,\eta^4{:}\eta^4{-}P_4)]$[25] and $[(Cp^RCo)_2(\mu,\eta^4{:}\eta^4{-}P_4)]^{2+}$ (Cp^R = 1,2,4-tBu$_3$-C_5H_2).[26] Notably, the structure of the iron complex is distinct, featuring a highly distorted, "kite-like" P_4 ring.[25] Tripledecker sandwich complexes with a middle deck composed of two separate P_2 units are much more common, such as in $[(Cp''Co)_2(\mu,\eta^2{:}\eta^2{-}P_2)_2]$ (Cp′′ = 1,3-$(Me_3Si)_2C_5H_3$).[27,28]

The presence of a triple-decker structure for **8** in solution is confirmed by the $^{31}P\{^{1}H\}$ NMR spectrum, which shows a broad singlet at δ = 80.8 ppm for the P_2C_2tBu$_2$ ring and a quintet at δ = 302.6 ppm corresponding to the *cyclo*-P_4 middle deck. The splitting pattern of the latter signal indicates that the P_4 ring is coupled with the P atoms within the phosphacyclobutadiene rings. Due to the broadness of the singlet for the P_2C_2tBu$_2$ ring, the $^2J_{PP}$ coupling is not resolved. An iterative fit of the $^{31}P\{^{1}H\}$ NMR spectrum gave a $^2J_{PP}$ coupling constant of 10.6 Hz (see the SI for details). The low field signal is in a similar range to Cs_2P_4 (δ = 330.3 ppm) and vastly different from that of $[(Cp''Co)_2(\mu,\eta^2{:}\eta^2{-}P_2)_2]$ (δ = −36.3) showing two dumbbell P_2 units. The ^{31}P NMR spectroscopic data hence indicate that the P_4 ring of **8** remains intact in solution.

In order to gain insight into the electronic structures of the planar polyphosphorus ligands, quantum chemical calculations were performed on the free P_4^{2-}, P_5^-, and TtP_4^{2-} (Tt = Sn, Pb) anions and complexes **6**−**8** in the gas phase to analyze their electronic properties. The geometry optimization (TPSS-D3BJ/def2-SVP) of the lone dianionic tetraphosphametallole ring, TtP_4^{2-} gives a planar structure with almost identical P−P bond lengths. To analyze the degree of aromaticity or antiaromaticity, we have undertaken calculations of magnetic response properties. NICS(0) (nucleus independent chemical shifts) calculations indicate that the free molecules P_4Sn^{2-} (−16.0) and PbP_4^{2-} (−15.2) are aromatic. It is apparent that the introduction of the Co moieties in **6** and **7** greatly enhances the aromaticity of the TtP_4 ring. These findings compare well to what was found for the all phosphorus titanocene, $[Ti(\eta^5{-}P_5)_2]$ (−36.8) and P_5^- (**A**, Figure 1, −15.4,).[29] This trend continues for the P_4 ring within **8** (−3.5) and P_4^{2-} (4.0). Analogous results are obtained when calculating the NICS(1) values (see SI for further details). In addition, we have calculated total molecular currents for P_4^{2-}, P_5^-, and SnP_4^{2-} (at TPSS/def2-TZVP level of theory). According to the magnetic criterium for aromaticity, aromatic molecules maintain a strongly diamagnetic response and antiaromatic molecules maintain a strongly paramagnetic response.[29] For a homogeneous magnetic field of strength 1 T perpendicular to the molecular plane, we find total molecular currents of −6.6, 18.9, and 20.2 nA/T for P_4^{2-}, P_5^-, and SnP_4^{2-}, respectively. For comparison, molecular currents of 12.0 and −20.0 nA/T were calculated for benzene and cyclobutadiene (in D_{6h} and D_{2h} symmetry, respectively) at the same level of theory. This suggests that P_5^- and P_4Sn^{2-} are aromatic species, while P_4^{2-} is nonaromatic or antiaromatic at best.[30] Indeed, the paramagnetic response in P_4^{2-} does not emerge from the π system alone but from magnetic $\pi \rightarrow \sigma^*$ (virtual) excitations (see SI for further details).[31]

To investigate how the aromaticity of the $[TtP_4]^{2-}$ is affected by coordination to the cobalt atoms, we have performed a fragment orbital interaction analysis with AMS (formerly known as ADF), and also closely inspected the Kohn−Sham molecular orbitals of **6** and **7** (see SI for details). The two highest occupied π orbitals of $[SnP_4]^{2-}$ are nondegenerate and strongly interact with the empty p_x and p_y orbitals on the cobalt atoms perpendicular to the Co−Co axis. In the complex, the two relevant π orbitals of the $[TtP_4]^{2-}$ ring (the donor orbitals) become almost degenerate. An interesting consequence of this energetic approximation of the π orbitals is that the P−P distances ring become more different in the complex in comparison with the free $[TtP_4]^{2-}$ species.

These results are corroborated by IBO analyses (TPSS D3BJ/def2-SVP level) of the lone dianionic tetraphosphametallole ring, P_4Tt^{2-}, which show a delocalized π-system involving the Tt, P1/P3, P2/P4 centers. Figure 7 depicts the multicentered IBOs of SnP_4^{2-} and shows the typical interaction of an aromatic π-system with transition

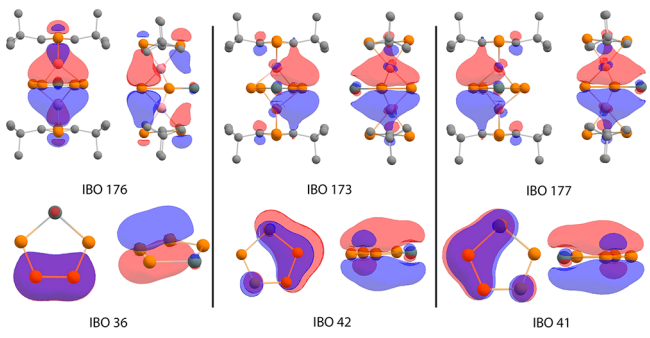

Figure 7. Selected IBOs for compound **6** (above) and the corresponding orbitals for SnP_4^{2-} (below, TPSS-D3BJ/def2-SVP, contour value = 0.03); each IBO is shown from two different perspectives.

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metal atoms. The bonding situation of **7** (Figures S74 and S75) and **8** appears to be similar, except the bonding orbitals appear to be more delocalized for **8** (see Figure S76).

CONCLUSION

We have synthesized the first metal complexes of the heavy tetraphospholide anions, $SnP_4^{2-}$and PbP_4^{2-}. These ligands are of fundamental interest as group 14 analogues of the well-known P_5^- anion. A substantial aromatic character was deduced for P_5^- and SnP_4^{2-} using quantum chemical calculations. The observation of SnP_4^{2-} and PbP_4^{2-} is a milestone in the chemistry of phospholides, while it also bodes well for the preparation of further elusive group 14/group 15 element anions.[32] A rich organometallic chemistry is anticipated for these anions, which may offer access to further unusual compounds as shown by the preparation of the phosphorus-rich triple-decker complex **8**. More generally, our work also demonstrates that the activation of P_4 by heterobimetallic complexes has a high utility for the preparation of previously inaccessible (poly-)phosphorus species. We are continuing to explore these avenues.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08754.

Full experimental details, X-ray crystallographic data, NMR and UV−vis data, computational details (PDF)

Accession Codes

CCDC 2096444−2096451 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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