Inorg. Chem. **2009**, *48*, 2899−2907

Inorganic Chemistry
Article

Coupling Reactions of Functionalized Zintl Ions $[E_9Cd(C_6H_5)]^{3-}$ (E = Sn, Pb) with Tributyltinhydride: Synthesis and Isolation of $\{Sn_9CdSn[(CH_2)_3CH_3]_3\}^{3-}$

Binbin Zhou, Mark S. Denning, Thomas A. D. Chapman, and Jose M. Goicoechea*

Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.

Received August 4, 2008

Reaction of ethylenediamine solutions of K_4E_9 (E = Sn, Pb) with diphenylcadmium yielded the $Cd(C_6H_5)$-functionalized Zintl ions, *closo*-$[E_9Cd(C_6H_5)]^{3-}$ (E = Sn (**1**); Pb (**2**)). Solution reactivity studies of **1** with tributyltinhydride in pyridine revealed that the cluster is capable of undergoing a coupling reaction to yield the tributyltin-functionalized cluster, *closo*-$\{Sn_9CdSn[(CH_2)_3CH_3]_3\}^{3-}$ (**3**). In-situ monitoring of this reaction by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy reveals the formation of the tributyltin functionalized cluster anion in addition to free benzene. Species **1**−**3** were characterized in the solid-state as $[K(2,2,2\text{-crypt})]^+$ salts by single crystal X-ray diffraction and elemental analysis, while the presence of all three cluster anions in solution was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and electrospray mass-spectrometry.

Introduction

The coordination chemistry of deltahedral group 14 Zintl ions, $[E_9]^{x-}$ (E = Si, Ge, Sn, Pb; $x = 2-4$), has advanced enormously over the course of the last 20 years.[1] Early reactivity studies on nine-atom tin and lead clusters with transition metal organometallics such as $LM(CO)_3$ (M = Cr, Mo, W; L = mesitylene, cycloheptatriene or toluene) were the first to report the isolation of functionalized cluster anions, the *closo*- species $[E_9M(CO)_3]^{4-}$ (E = Sn, Pb; M = Cr, Mo, W).[2] Later studies revealed that this research could be extended to late- and post-transition metal species as well, resulting in the characterization of a series of related functionalized clusters.[3,4] In the majority of these species, the nine-atom clusters are found to adopt a monocapped square antiprismatic geometry and coordinate to the metal centers through the available square face of the antiprism in η^4 mode. Analysis of this bonding mode shows that such $[E_9]^{4-}$ clusters act as formal six electron donors to metal centers, not unlike closely related carborane systems,[5] and can therefore be considered as benzene or cyclopentadienyl ligand analogues.

Coterminous with the aforementioned research, reactivity studies employing main-group organometallic nucleophiles as reagents toward nine atom germanium clusters were also conducted. These studies gave rise to a series of functionalized cluster species exhibiting *exo*-bonded main-group substituents such as $[Ge_9{-}Nu]^{3-}$, $[Nu{-}Ge_9{-}Nu]^{2-}$ and $[Nu{-}Ge_9{-}Ge_9{-}Nu]^{4-}$.[6] For all of these species bonding to the *exo*-substituents can be discussed as two-center two-electron bonds where each functional group is attached to a single germanium vertex. Very recently these studies have been extended to the heavier elements of group 14 and have resulted in the isolation of the first examples of organically functionalized tin Zintl ions.[7]

Also worth highlighting is the variety of interesting novel cluster geometries which have become available following research into the reactivity of deltahedral Zintl ions toward d^{10} transition metal reagents with one or more labile ligands.

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* To whom correspondence should be addressed. E-mail: jose.goicoechea@chem.ox.ac.uk.

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10.1021/ic8022826 CCC: $40.75

The resulting cluster species have been found to exhibit interstitial metal atoms,[8−13] or a combination of interstitial and functionalized surface metal atoms.[3,14,15] In all of these species, interstitial d^{10} metals play a crucial role in stabilizing higher overall cluster nuclearities despite the fact that they fail to contribute any electrons to the cluster bonding electron count.

The varied outcomes of the reactivity studies described above are evidence of the polyfaceted solution reactivity of deltahedral group 14 Zintl ions. Our research with such anions is currently focused on exploring the reactivity of these nine-atom clusters toward a series of organometallic reagents at the post-transition metal/main-group divide. The aim of these studies is to determine whether additional coordination modes are available for these fascinating cluster species and to probe the reactivity of such clusters toward a variety of substrates in solution. The differences highlighted above between the different substitutional modes of electrophilic (e.g., $M(CO)_3$) and nucleophilic (e.g $SnMe_3^-$) reagents, led us to hypothesize that additional coordination modes might become available when employing heavy group 12 and group 13 organometallic reagents. Herein, we report the results of a series of such studies carried out when employing diphenylcadmium ($CdPh_2$) as a reagent which yielded the functionalized clusters *closo*-$[E_9Cd(C_6H_5)]^{3-}$ (E = Sn (**1**); Pb (**2**)). Also reported are a series of solution reactivity studies on these functionalized cluster systems which reveal that they are capable of undergoing coupling reactions with reagents such as tributyltinhydride (HSn^nBu_3) making the replacement of substituents bound to the metal cluster core a possibility. These studies have yielded the novel *closo*-cluster $\{Sn_9CdSn[(CH_2)_3CH_3]_3\}^{3-}$ (**3**).

Experimental Section

General Synthetic Methods. All manipulations were carried out under an inert atmosphere using standard Schlenk-line or glovebox techniques. The intermetallic precursors, K_4E_9 (E = Sn, Pb), were synthesized according to previously reported synthetic procedures from stoichiometric mixtures of the elements (K: 99.95%, Aldrich; Sn: 99.8%, Strem, Pb: 99.99%, Strem) heated to 900 °C for 72 h in sealed niobium containers.[16] To avoid the oxidation of the niobium vessels at such high temperatures they were jacketed in flame-sealed silica ampoules under vacuum prior to heating. Pyridine (99.9%, Rathburn Chemicals, Ltd.) and ethylenediamine (99%, Aldrich) were distilled over CaH_2 and sodium metal, respectively, while *N*,*N*-dimethylformamide (99.9%, Rathburn Chemicals, Ltd.) and toluene (99.9%. Rathburn Chemicals, Ltd.) were used after purification through an MBraun MB SPS-800 solvent system. d_5-Pyridine (99.5%, Cambridge Isotope Laboratories, Inc.) was dried over CaH_2 and vacuum distilled. All solvents were stored in gastight ampoules under argon. 2, 2, 2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; ≥ 99%, Merck) and tributyltinhydride (97%, Aldrich) were used as received. Diphenylcadmium was prepared according to a modified literature procedure and stored in the dark in a glovebox under a nitrogen atmosphere.[17]

$[K(2,2,2\text{-crypt})]_3[Sn_9Cd(C_6H_5)]\cdot en$. In a typical experiment, 0.163 mmol (200 mg) of K_4Sn_9 precursor, 0.587 mmol (221 mg) of 2,2,2-crypt and 0.165 mmol (44 mg) of $CdPh_2$ were weighed out into a Schlenk tube in a glovebox. The reaction vessel was transferred to a Schlenk-line where approximately 2 mL of dry ethylenediamine were added yielding a dark reddish-brown reaction mixture. The reaction was allowed to stir for 1 h at room temperature and subsequently filtered to give an intensely colored dark red solution. Thin dark brown plate-like crystals of the compound were obtained by layering the ethylenediamine solution with dry toluene and leaving it to stand for several days (55% crystalline yield). Anal. Calcd for $C_{62}H_{121}CdK_3N_8O_{18}Sn_9$: C, 29.02; H, 4.76; N, 4.37. Found: C, 29.00; H, 4.83; N, 4.32. ^1H NMR (300.17 MHz, d_5-pyridine): δ (ppm) 8.86 (dd, $^3J_{ortho\text{-}meta} = 7.5$ Hz, $^4J_{ortho\text{-}para} = 1.4$ Hz, $^3J_{Cd-H} = 36$ Hz, 2H, *o*-C_6H_5), 7.55 (dd, $^3J_{meta-para} = 7.5$ Hz, $^4J_{Cd-H} = 6$ Hz, 2H, *m*-C_6H_5), 7.15 (tt, 1H, *p*-C_6H_5), 3.40 (s, 36H, 2,2,2-crypt), 3.33 (t, $^3J_{H-H} = 6$ Hz, 36H, 2,2,2-crypt), 2.32 (t, 36H, 2,2,2-crypt). ^{13}C NMR (75.49 MHz, d_5-pyridine): δ ppm 137.9 (s, *o*-C_6H_5), 127.5 (s, *m*-C_6H_5), 123.1 (s, *p*-C_6H_5), 73.2 (s, 2,2,2-crypt), 70.0 (s, 2,2,2-crypt), 55.63 (s, 2,2,2-crypt). ES-MS: *m/z* 1258.0 $[Sn_9Cd(C_6H_5)]^-$, 1673.2 $\{[K(2,2,2\text{-crypt})][Sn_9Cd(C_6H_5)]\}^-$, 2089.4 $\{[K(2,2,2\text{-crypt})]_2[Sn_9Cd(C_6H_5)]\}^-$.

$[K(2,2,2\text{-crypt})]_6[Pb_9Cd(C_6H_5)]_2\cdot 2en\cdot tol$. K_4Pb_9 (300 mg, 0.148 mmol), $CdPh_2$ (40 mg, 0.150 mmol), and 2,2,2-crypt (200 mg, 0.531 mmol) were dissolved in ethylenediamine (2 mL) under an inert atmosphere and allowed to stir for 1 h, after which the resulting dark brown solution was filtered and the filtrate layered with toluene to allow for crystallization. Large black rod-like crystals suitable for single-crystal X-ray diffraction were obtained after 3 days (47% crystalline yield). Anal. Calcd for $C_{131}H_{250}Cd_2K_6N_{16}O_{36}Pb_{18}$: C, 23.07; H, 3.70; N, 3.29. Found: C, 22.95; H, 3.67; N, 3.28. ^1H NMR (300.17 MHz, d_5-pyridine): δ (ppm) 9.38 (dd, $^3J_{ortho\text{-}meta} =$ 7.5 Hz, $^4J_{ortho\text{-}para} = 1.8$ Hz, $^3J_{Cd-H} = 33$ Hz, 2H, *o*-C_6H_5), 7.98 (dd, $^3J_{meta-para} = 7.5$ Hz, $^4J_{Cd-H} = 5$ Hz, 2H, *m*-C_6H_5), 7.36 (tt, 1H, *p*-C_6H_5), 3.41 (s, 36H, 2,2,2-crypt), 3.34 (t, $^3J_{H-H} = 5$ Hz, 36H, 2,2,2-crypt), 2.34 (t, 36H, 2,2,2-crypt). ^{13}C NMR (75.49 MHz, d_5-pyridine): δ (ppm) 134.6 (s, *o*-C_6H_5), 129.7 (s, *m*-C_6H_5), 122.7 (s, *p*-C_6H_5), 71.56 (s, 2,2,2-crypt), 68.70 (s, 2,2,2-crypt), 54.80 (s, 2,2,2-crypt). ES- MS: *m/z* 2054.4 $[Pb_9Cd(C_6H_5)]^-$, 2470.3 $\{[K(2,2,2\text{-crypt})][Pb_9Cd(C_6H_5)]\}^-$.

$[K(2,2,2\text{-crypt})]_6[Sn_9CdSn(^nBu)_3]_2\cdot 6tol\cdot py$. $[K(2,2,2\text{-crypt})]_3[Sn_9Cd(C_6H_5)]\cdot en$ (70 mg, 0.027 mmol) was dissolved in d_5-pyridine (1 mL) in a Youngs resealable NMR tube yielding a reddish brown solution to which HSn^nBu_3 (7 μL, 0.026 mmol) was added. The reaction mixture was shaken and left to stand for 1 h. After the reaction had come to completion the solution was reduced to dryness in vacuo and redissolved in pyridine yielding a yellowish-brown solution. The solution was filtered and layered with toluene to allow for crystallization. Orange-brown plate-like rectangular

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Table 1. Selected X-ray Data Collection and Refinement Parameters for [K(2,2,2-crypt)]$_3$[**1**]$_{0.8}$[Sn$_9$]$_{0.2}$·en, [K(2,2,2-crypt)]$_6$[**2**]$_2$·2en·tol, [K(2,2,2-crypt)]$_6$[**3**]$_2$·6tol·py

compound	[K(2,2,2-crypt)]$_3$[**1**]$_{0.8}$[Sn$_9$]$_{0.2}$·en	[K(2,2,2-crypt)]$_6$[**2**]$_2$·2en·tol	[K(2,2,2-crypt)]$_6$[**3**]$_2$·6tol·py
fw	2551.56	6814.29	6066.70
space group, Z	$P\bar{1}$, 2	$P\bar{1}$, 2	$P\bar{1}$, 2
a (Å)	15.2071(1)	15.8896(1)	15.5506(1)
b (Å)	15.4662(1)	22.6342(1)	28.2557(2)
c (Å)	21.4652(2)	27.7421(2)	28.9528(2)
α (deg)	91.0976(4)	88.0220(3)	78.8039(2)
β (deg)	95.6698(4)	74.9160(2)	75.0316(2)
γ (deg)	113.5806(4)	89.5042(2)	76.5925(3)
V (Å^3)	4594.79(6)	9627.90(10)	11832.37(14)
ρ_{calc} (g·cm^{-3})	1.844	2.351	1.703
radiation, λ (Å), temp (K)	Mo Kα, 0.71073, 150		
μ (cm^{-1})	2.822	16.078	2.409
reflections collected	31323	62371	100829
independent reflections	16029	33535	53966
R(int)	0.0241	0.0485	0.0540
R1/wR2, [a] $I \geq 2\sigma_I$ (%)	3.31/7.30	4.56/11.74	5.23/12.78
R1/wR2, [a] all data (%)	4.53/7.64	6.60/12.48	10.01/15.19

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma w(F_o{}^2)^2\}^{1/2}$; $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = [(F_o)^2 + 2(F_c)^2]/3$ and the A and B values are 0.0234 and 13.83 for [K(2,2,2-crypt)]$_3$[**1**]$_{0.8}$[Sn$_9$]$_{0.2}$·en, 0.0784 and 0.00 for [K(2,2,2-crypt)]$_6$[**2**]$_2$·2en·tol, and 0.0648 and 13.55 for [K(2,2,2-crypt)]$_6$[**3**]$_2$·6tol·py.

crystals suitable for single-crystal X-ray diffraction were obtained after 1 day (48% crystalline yield). Anal. Calcd for $C_{179}H_{323}Cd_2K_6N_{13}O_{36}Sn_{20}$: C, 35.42; H, 5.37; N, 3.00. Found: C, 35.44; H, 5.26; N, 3.16. ^{1}H NMR (300.17 MHz, d$_5$-pyridine): δ (ppm) 3.43 (s, 12H, 2,2,2-crypt), 3.36 (t, $^3J_{H-H}$ = 6 Hz, 12H, 2,2,2-crypt), 2.37 (m, 2H, H$_\beta$), 2.35 (t, 12H, 2,2,2-crypt), 1.74 (tq, $^3J_{\beta\text{-}\gamma}$ = 7.5 Hz, $^3J_{\gamma\text{-}\delta}$ = 7.5 Hz, 2H, H$_\gamma$), 1.44 (m, $^3J_{\alpha\text{-}\beta}$ = 7.5 Hz, 2H, H$_\alpha$), 1.08 (t, 3H, H$_\delta$). ^{13}C NMR (75.49 MHz, d$_5$-pyridine): δ (ppm) 71.0 (s, 2,2,2-crypt), 68.2 (s, 2,2,2-crypt), 54.5 (s, 2,2,2-crypt), 32.9 (s, ^{n}Bu), 29.5 (s, ^{n}Bu), 17.7 (s, ^{n}Bu), 15.1 (s, ^{n}Bu). ES+ MS: m/z 3131.0 $\{[K(2,2,2\text{-crypt})]_4[Sn_9CdSn(^nBu)_3]\}^+$.

Structure Determination. Single crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer equipped an Oxford Cryosystems low-temperature device. The crystals were selected under Paratone-N oil, mounted on micromount loops and positioned in the cold stream of the diffractometer. Data were collected at 150 K using graphite monochromated Mo Kα radiation; equivalent reflections were merged, and the images were processed with the DENZO and SCALEPACK programs.[18] Corrections for Lorentz-polarization effects and absorption were performed, and the structures were solved by direct methods and refined on F^2 using the SHELX-97 package.[19] Because of the large number of unique non-hydrogen atoms present in the asymmetric units of [K(2,2,2-crypt)]$_6$[Pb$_9$Cd(C$_6$H$_5$)]$_2$·2en·tol and [K(2,2,2-crypt)]$_6$[Sn$_9$CdSn(^{n}Bu)$_3$]$_2$·6tol·py, these species were refined on F^2 using SHELXH, a special version of SHELXL for the refinement of very large structures.[19] Details of selected data collections and refinement parameters are given in Table 1.

Electrospray Mass-Spectrometry. Positive and negative ion mode electrospray mass spectra were recorded from DMF solutions (10- 20 μM) on a Micromass LCT Time of Flight mass spectrometer with a Z-spray source (150 °C source temperature, 200 °C desolvation temperature, 2.2 kV capillary voltage, and 20 V cone voltage).

NMR. ^{13}C{^{1}H} and ^{1}H NMR spectra were recorded at room temperature in d$_5$-pyridine using a Varian Mercury VX300 spectrometer (^{1}H 300 MHz). ^{13}C{^{1}H} spectra were referenced to d$_5$-pyridine (δ 123.87) and ^{1}H NMR were referenced to the most upfield of residual protic solvent resonances (pyridine δ 7.22).

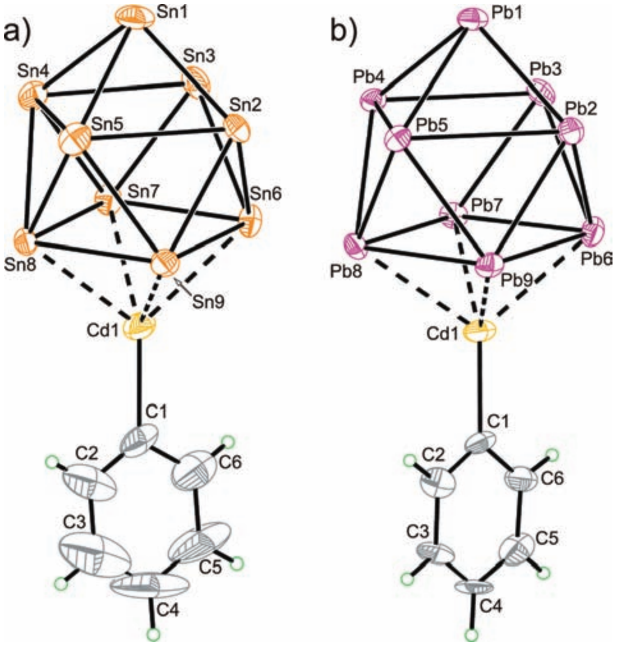

Figure 1. Thermal ellipsoid plots of (a) cluster **1** and (b) one of the two crystallographically distinct cluster anions present in [K(2,2,2-crypt)]$_6$[Pb$_9$Cd(C$_6$H$_5$)]$_2$·2en·tol (**2a**). Anisotropic displacement ellipsoids pictured at 50% probability level.

Results and Discussion

$[E_9Cd(C_6H_5)]^{3-}$ (E = Sn (1); Pb (2)). Reaction of ethylenediamine solutions of K$_4$E$_9$ (E = Sn, Pb) and 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) with diphenylcadmium in a 1:1 stoichiometric ratio (K$_4$E$_9$/CdPh$_2$) yielded the novel CdPh functionalized clusters, *closo*-[E$_9$Cd(C$_6$H$_5$)]$^{3-}$ (E = Sn (**1**); Pb (**2**); Figure 1), the first examples of cadmium functionalized Zintl ions. These reactions are analogous to those observed for group 14 Zintl ions with Zn(C$_6$H$_5$)$_2$,[4] and proceed via the reduction of one of the M−C bonds of the post-transition metal

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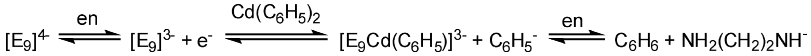
Scheme 1. Synthesis of *closo*-$[E_9Cd(C_6H_5)]^{3-}$ (E = Sn, Pb)



$$[E_9]^{4-} \xrightleftharpoons{\text{en}} [E_9]^{3-} + e^- \xrightleftharpoons{Cd(C_6H_5)_2} [E_9Cd(C_6H_5)]^{3-} + C_6H_5^- \xrightleftharpoons{\text{en}} C_6H_6 + NH_2(CH_2)_2NH^-$$

organometallic reagent by the free solvated electrons present in ethylenediamine solutions of $[E_9]^{4-}$.[1,6c] This results in the generation of the CdPh moiety and the $C_6H_5^-$ anion, the latter of which quickly abstracts a proton from the ethylenediamine solvent yielding benzene and an amide as pictured in Scheme 1. In situ monitoring of the crude reaction mixtures by ^1H NMR spectroscopy reveals the immediate generation of a singlet peak corresponding to free benzene, in addition to three separate multiplet resonances in the aromatic region arising from the protons of the coordinated CdPh fragments. Crystallization of the $[K(2,2,2\text{-crypt})]^+$ salts of clusters **1** and **2** in $[K(2,2,2\text{-crypt})]_3[Sn_9Cd(C_6H_5)]\cdot$en and $[K(2,2,2\text{-crypt})]_6[Pb_9Cd(C_6H_5)]_2\cdot 2en\cdot$tol, respectively, can be readily achieved by carefully layering the filtered ethylenediamine solutions with toluene.

Clusters **1** and **2** are best described as nine-atom deltahedral Zintl ions with monocapped square-antiprismatic geometries and pseudo-C_{4v} symmetry coordinated to $Cd(C_6H_5)$ moieties via the available square faces of the monocapped antiprisms. The overall cluster geometry of the $[E_9M]$ cluster cores is that of a bicapped square antiprism with the cadmium metal center occupying one of the capping vertices of the cluster. This bonding mode is entirely analogous to that observed for the aforementioned *closo*-$[E_9M(CO)_3]^{4-}$ (E = Sn, Pb; M = Cr, Mo, W) and *closo*-$[E_9Zn(C_6H_5)]^{3-}$ (E = Si, Ge, Sn, Pb) clusters and can be rationalized employing a delocalized bonding model.[2,4] A Wade/Mingos analysis of these species shows that the clusters have the correct electron count to be considered *closo*-deltahedra.[20] Each group 14 element contributes three orbitals and two electrons to cluster bonding and the CdPh fragment (isolobal with BH^+) contributes three orbitals and one electron, making the total electron count for such a species $(9 \times 2) + 1 + 3 = 22$ cluster bonding electrons. This is in accordance with what would be expected for a *closo*- ten vertex cluster ($n+1$ cluster bonding electron pairs, 22 electrons).

Bonding between $[\eta^4\text{-}E_9]^{4-}$ clusters and transition metal centers has been previously discussed in the literature.[1,4] Theoretical calculations have shown that the clusters can behave in an isolobal manner to more conventional organometallic ligands such as the cyclopentadienyl anion and that they can act as formal six electron donors to metals when coordinated in η^4-mode, in an analogous fashion to what is observed for η^5-Cp^-. A frontier orbital analysis reveals three fully occupied orbitals corresponding to the C_{4v} configuration of $[E_9]^{4-}$ which possess the correct symmetry to interact via a σ and two π interactions with three empty orbitals (an sp_z hybrid and the degenerate p_x, p_y pair) on the cadmium metal center. From a coordination chemistry viewpoint, this signifies that the electron count at the cadmium metal center is 18 electrons, 6 from the $[E_9]^{4-}$ cluster, 11 from the Cd^+ metal center, and one from the phenyl substituent. This bonding analysis implies that the reported *closo*-$[E_9Cd(C_6H_5)]^{3-}$ clusters are isoelectronic with the hypothetical species (η^5-Cp)CdPh, which has yet to be isolated because of the relative instability of such organometallic complexes. The dearth of structurally characterized base-free cyclopentadienyl- or alkylcyclopentadienyl-cadmium organometallics is largely due to the high air-, moisture-, and light-sensitivity of such complexes.[21] However, such an absence may also be attributed to the greater main-group character of the cadmium metal center, which makes base-free closed-shell organometallic complexes exhibiting an 18-electron count highly unusual.[22] This is largely due to the fact that cadmium and mercury exhibit a lesser tendency to engage in π-bonding compared to zinc. Further support for this argument can be found in the fact that species such as the η^1,η^5-bis(pentamethylcyclopentadienyl)zinc are known and have been structurally characterized by single crystal X-ray diffraction.[23] Furthermore, while there are no structurally characterized η^5-cyclopentadienyl or alkylcyclopentadienyl complexes of cadmium, the number of analogous zinc complexes is far greater.[24]

The crystalline phase from which **1** was structurally characterized exhibits compositional crystallographic disorder at the cluster site with two different anions, $[Sn_9Cd(C_6H_5)]^{3-}$ and $[Sn_9]^{3-}$, occupying the same position in a 4:1 ratio. The chemical formula of the crystalline phase can therefore best be formulated as $[K(2,2,2\text{-crypt})]_3[Sn_9Cd(C_6H_5)]_{0.8}[Sn_9]_{0.2}\cdot$en (see Supporting Information). Cluster **2** was structurally characterized as a $[K(2,2,2\text{-crypt})]^+$ salt in $[K(2,2,2\text{-crypt})]_6[Pb_9Cd(C_6H_5)]_2\cdot 2en\cdot$tol and contains two crystallographically unique cluster anions in the asymmetric unit. Both clusters **1** and **2** are largely isostructural and adopt bicapped square antiprismatic geometries for the $[E_9Cd]$ cluster cores, with the cadmium atoms occupying capping vertices. Because of the disorder present at the cluster site of **1** we cannot accurately discuss tin−tin bond distances. Pb−Pb bond lengths vary between 3.0479(6)−3.4410(6) Å and 3.0488(6)−3.4055(6) Å for the two unique cluster anions of **2**. A complete list of bond distances is listed in Table 2 following the numbering scheme employed in Figure 1. These distances are comparable to those observed for the analogous zinc compound *closo*-$[Pb_9ZnPh]^{3-}$ which varied between 3.0447(6)−3.4078(5) Å.[4]

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Table 2. Selected Bond Lengths for the Two Crystallographically Unique Clusters in $[K(2,2,2\text{-crypt})]_6[Pb_9Cd(C_6H_5)]_2\cdot 2en\cdot tol$, **2a** and **2b**.

bond[a]	**2a**	**2b**
E1−E2	3.0515(6)	3.0841(6)
E1−E3	3.0753(6)	3.0554(6)
E1−E4	3.0724(5)	3.0488(6)
E1−E5	3.0813(6)	3.0673(6)
E2−E3	3.4410(6)	3.3106(5)
E2−E5	3.4120(6)	3.3328(6)
E2−E6	3.0491(6)	3.0882(6)
E2−E9	3.0798(6)	3.0731(6)
E3−E4	3.3223(6)	3.3536(6)
E3−E6	3.0697(6)	3.0705(6)
E3−E7	3.0715(6)	3.0592(6)
E4−E5	3.3002(5)	3.3866(6)
E4−E7	3.1141(6)	3.0665(6)
E4−E8	3.0743(6)	3.0631(6)
E5−E8	3.0695(5)	3.0807(6)
E5−E9	3.0479(6)	3.0620(6)
E6−E7	3.3220(5)	3.3045(5)
E6−E9	3.3910(6)	3.3266(6)
E7−E8	3.2489(5)	3.4055(6)
E8−E9	3.3028(5)	3.3462(5)
Cd1−E6	2.9337(9)	2.9751(10)
Cd1−E7	2.9872(9)	2.9559(9)
Cd1−E8	3.0045(9)	2.9544(10)
Cd1−E9	2.9520(9)	2.9772(9)
Cd1−C1	2.183(11)	2.192(10)

[a] Element numbering scheme as employed in Figure 1.

The Pb−Cd bonds between the atoms comprising the square face of the Pb_9 monocapped square antiprism and the capping cadmium atom vary narrowly within the range 2.9337(9)−3.0045(9) Å and 2.9544(10)−2.9772(9) Å for **2**. As expected, these values are longer than the corresponding Zn−Pb bonds in $[Pb_9ZnPh]^{3-}$ compound by anywhere between 0.14 and 0.17 Å because of the larger atomic radius of cadmium, which is approximately 0.2 Å larger than that of zinc according to tables of both empirical and calculated atomic radii.[25] The Cd−Ph bond lengths are 2.234(9) Å for cluster **1** and 2.183(11) and 2.191(10) Å for **2**. These values are longer than the Zn−Ph distance in $[E_9Zn\text{-}Ph]^{3-}$ by approximately 0.2 Å and compare well with other reported Cd−Ar bonds which range between 2.1 Å to 2.2 Å.[26]

Characterization of clusters **1** and **2** in solution was carried out by means of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Analytically pure crystalline samples were dissolved in d^5-pyridine and analyzed by ^1H NMR spectroscopy revealing three multiplet resonances at 8.86, 7.55, and 7.15 ppm for **1** and 9.38, 7.98, and 7.36 ppm for **2**, corresponding to the *ortho*-, *meta*-, and *para*-protons, respectively (Figure 2).

The *ortho*- and *meta*- aromatic multiplet resonances for clusters **1** and **2** exhibit overlapping $^{113/111}Cd$ satellites. These satellites are much lower in intensity than the parent resonances because of the low natural abundance of the $^{113/111}Cd$ isotopes (^{111}Cd: $I = 1/2$, natural abundance = 12.8%, $\gamma = -5.6983 \times 10^7$ rad T^{-1} s^{-1}; ^{113}Cd: $I = 1/2$, natural abundance = 12.2%, $\gamma = -5.9609 \times 10^7$ rad T^{-1} s^{-1}),[27] and exhibit coupling constants of 36 and 6 Hz for the *ortho*- and *meta*-protons of **1**, respectively, and of 33 and 5 Hz for the *ortho*- and *meta*-protons of **2**, respectively. To confirm that these satellites were correctly assigned as such the ^1H NMR spectra of samples **1** and **2** were also run at a higher field on a Varian Unity 500 MHz (^1H 500 MHz) spectrometer and the J_{Cd-H} coupling constants found to be independent of field strength.

The $^{13}C\{^1H\}$ NMR spectra of the functionalized clusters displayed three resonances in the aromatic region, corresponding to the *ortho*-, *meta*-, and *para*-carbon environments of the η^1-bonded phenyl rings. All attempts to observe the *ipso*-carbon resonances proved unsuccessful because of the inherent weakness of such resonances and limitations on sample concentration. For cluster **1** resonances were observed at 137.9, 127.5, and 123.1 ppm for the *ortho*-, *meta*-, and *para*- hydrogen environments, respectively. Very similar chemical shifts were observed for **2** with aromatic resonances occurring at 134.6, 129.7, and 122.7 ppm.

Further confirmation of the presence of the clusters in solution was obtained by negative ion mode electrospray mass-spectrometry of DMF solutions clusters **1** and **2**. All peaks appear as distinct mass envelopes because of the wealth of Cd, Sn, and Pb isotopes which allows for the unequivocal assignment of cluster-based signals. As is often the case with the negative ion-mode electrospray mass-spectra of anionic Zintl ions, the clusters are observed with reduced charges as a result of the oxidation of the parent clusters during the ionization process. Furthermore, there is also evidence of extensive ion pairing between anions and the cryptated potassium cations, $[K(2,2,2\text{-crypt})]^+$. As a result, the spectra of **1** and **2** both reveal mass envelopes corresponding to $[E_9Cd(C_6H_5)]^-$ (Figures 3; m/z = 1258.0 and 2054.4 for **1** and **2**, respectively), and peaks corresponding to the ion-paired species $\{[K(2,2,2\text{-crypt})][E_9Cd(C_6H_5)]\}^-$ (Figures 3; m/z = 1673.2 and 2470.3 for **1** and **2**, respectively). The spectrum of cluster **1** also reveals a peak corresponding to the $\{[K(2,2,2\text{-crypt})]_2[Sn_9Cd(C_6H_5)]\}^-$ ion pair at m/z = 2089.4; however, no such species was observed in the spectrum of the heavier lead analogue. The data from the positive mode yielded no clear mass envelopes corresponding to Zintl ion containing species.

The aforementioned results detail an accessible route to organocadmium functionalized Zintl ions, the first examples of such species isolated to date and close relatives of analogous zinc counterparts, $[E_9Zn(C_6H_5)]^{3-}$ (E = Si, Ge,

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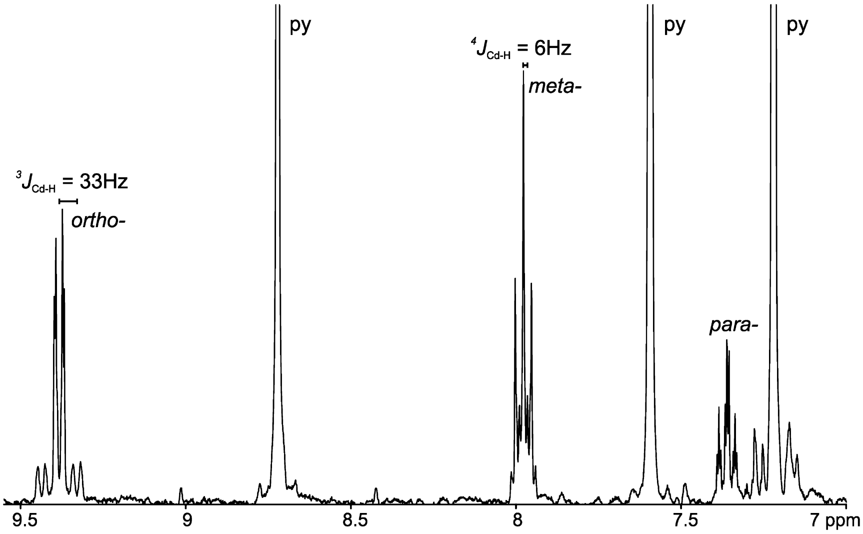

Figure 2. Aromatic region of ^{1}H NMR spectrum of **2** in d^5-pyridine. Data were recorded at 298 K at 300.17 MHz.

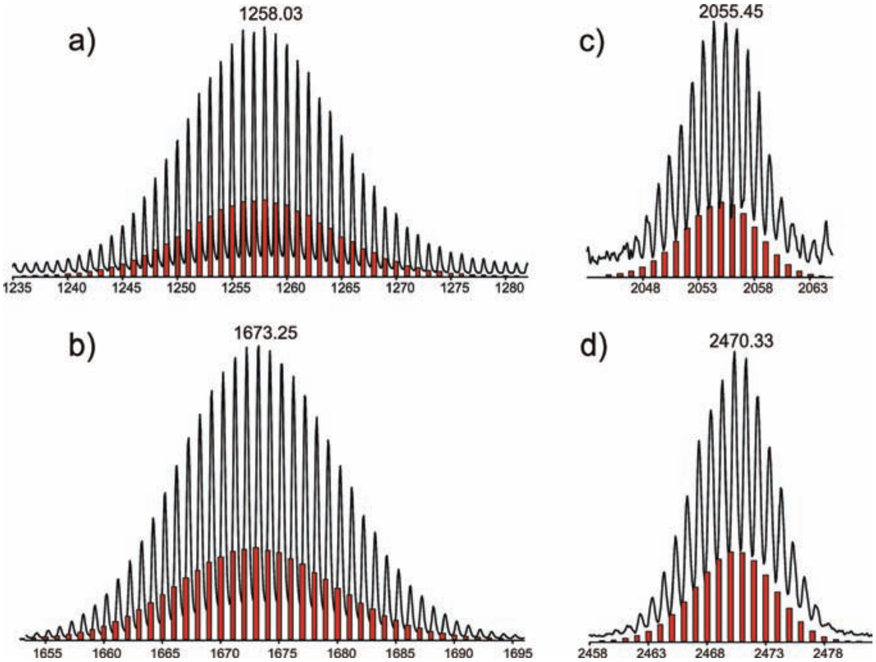

Figure 3. Selected negative ion-mode electrospray mass-spectrometry peaks from DMF solutions containing **1** and **2**. Mass envelopes correspond to (a) $[Sn_9Cd(C_6H_5)]^-$, (b) $\{[K(2,2,2\text{-crypt})][Sn_9Cd(C_6H_5)]\}^-$, (c) $[Pb_9Cd(C_6H_5)]^-$, and (d) $\{[K(2,2,2\text{-crypt})][Pb_9Cd(C_6H_5)]\}^-$. Recorded experimental data are given in black with calculated isotopic distributions in red.

Sn, Pb).[4] Furthermore, the stability of such anions in ethylenediamine, DMF, and pyridine solutions has been confirmed by multielement NMR measurements and electrospray mass-spectrometric studies opening up the potential for further solution reactivity studies to be carried out at the CdPh functionality.

$[Sn_9Cd(Sn[(CH_2)_3CH_3]_3)]^{3-}$ (3). The relative stability and high crystalline yields obtained for clusters **1** and **2** prompted us to explore their solution reactivity toward HSn^nBu_3 with the aim of reductively cleaving the remaining Cd−C bonds in the clusters and potentially yielding higher nuclearity species. The presence of the phenyl substituent associated with the cadmium metal center allows for the in situ monitoring of reactions via NMR spectroscopy yielding a great degree of information regarding the behavior of such species in solution. The choice of an organotin hydride was made as they are well-established radical reducing agents because of the relatively weak (BDE(^{n}Bu$_3$SnH) = 74 ± 2 kcal/mol)[28] non-ionic bond between tin and hydrogen which has been found to cleave homolytically.[29] The outcome of these reactions yielded the novel functionalized cluster $[Sn_9Cd(Sn[(CH_2)_3CH_3]_3)]^{3-}$ (**3**).

In a typical experiment, a crystalline sample of $[Sn_9Cd(C_6H_5)]^{3-}$ was dissolved in d$_5$-pyridine in an airtight NMR tube and a ^{1}H NMR recorded to corroborate the analytical purity of the sample. One equivalent of HSn^nBu_3 was added to the NMR tube, and the reaction followed by ^{1}H NMR. In situ monitoring of the reaction reveals the

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formation of free benzene arising from the coupling of H with the phenyl substituent. The disappearance of the multiplet resonances in the aromatic region of the spectrum, corresponding to the η^1-bonded phenyl rings in clusters **1**, is indicative of the completion of the reaction. Upon completion the ^{1}H NMR spectra of the crude reaction mixtures exhibit four intense multiplet resonances in the aliphatic regions corresponding the four different proton environments of the alkyl chains of the tributyltin functionalized cluster anions $[Sn_9Cd(Sn[(CH_2)_3CH_3]_3)]^{3-}$. Analogous reactions employing $[K(2,2,2\text{-crypt})]_6[Pb_9Cd(C_6H_5)]_2 \cdot 2en \cdot tol$ as a precursor exhibited closely related spectroscopic behavior hinting at the possibility of a tributyltin-functionalized $[CdPb_9]$ analogue, $[Pb_9Cd(Sn[(CH_2)_3CH_3]_3)]^{3-}$ (**4**); however, to date, we have been unable to characterize this species crystallographically.

The mechanism by which the coupling reaction between **1** and $HSnBu_3$ takes place is not yet fully understood. Both radical and concerted hydrogen transfer mechanisms are possible. Radical coupling reactions involving organotinhydrides typically require the presence of a radical initiator such as azobisisobutyronitrile (AIBN), thermal or photochemical activation to generate the initial radical species.[29,30] As no initiator was required for the reactions to take place, we believe that if the reaction proceeds via a radical mechanism it may be initiated by the presence of trace amounts of phenyl radical anion in solution resulting from the room temperature homolytic dissociation of $[E_9CdPh]^{3-}$ to yield $[CdE_9]^{3-}$ and $Ph^{\bullet}$. This is consistent with thermodynamic data reflecting the weak nature of the Cd−C bond (BDE: 139 kJ/mol; 33 kcal/mol),[31] a factor which is manifested in the photosensitivity of many organocadmium species such as the diphenylcadmium precursor.[17] Traces of $Ph^{\bullet}$ would immediately react with HSn^nBu_3 via an "S_N2" mechanism to yield benzene and the tributyltin radical, which would then initiate the radical chain reaction.[29,30] Similarly the presence of trace amounts of radical $[E_9]^{3-}$ (E = Sn, Pb) cluster anions in the crystalline precursors could also feasibly initiate the radical reaction, although this initiation step seems less likely as the bulk composition of starting materials were corroborated by elemental analysis. Either species would readily initiate the radical reaction and allow for the propagation steps to continue. All attempts to establish which species may act as an initiator for the first step of the radical coupling reaction proved unsuccessful because of the low concentrations of such species and the rates with which the reactions take place. Both the initiation and propagation steps must proceed extremely rapidly as no spectroscopic evidence for the HSn^nBu_3 hydride resonance was observed in the ^{1}H NMR spectrum, even at low temperatures. This resonance is typically encountered at 4.95 ppm in d_5-pyridine. NMR samples were prepared in an inert atmosphere glovebox and by the time the sample was taken out of the glovebox and transferred to the spectrometer no evidence of tributyltinhydride was observed in the NMR spectra. Furthermore, there is also no spectroscopic evidence of resonances corresponding to other possible radical coupling products between $H^{\bullet}$ and other radical species as the ^{1}H spectra fail to exhibit any evidence of cadmium-hydride adducts or of dihydrogen.

An alternative mechanism involving the association of both reagents in solution followed by hydrogen transfer from the tributyltinhydride to the phenyl substituent on **2** is also viable. The reaction of metal−hydrogen bonds in organometallic main-group hydrides with alkali metal organometallics has been frequently employed in the past to yield alkali metal complexes of *p*-block organometallics such as $[Ph_3SnLi(pmedta)]$ (pmedta = $MeN(CH_2CH_2NMe_2)_2$).[32,33] These reactions appear to proceed via non-radical mechanisms and could well be the route by which **3** is obtained, particularly considering that no radical cross-coupling products such as biphenyl were observed in the reaction mixtures of **1** and HSn^nBu_3. We are currently conducting a series of studies investigating the reactivity of these and other related functionalized clusters toward a series of main-group hydrides under a variety of reaction conditions.

Reduction of a d_5-pyridine solution of **1** and HSn^nBu_3 to dryness under vacuum affords a solid of the $[K(2,2,2\text{-crypt})]^+$ salt of cluster **3**. To our knowledge this is the first example of such a coupling reaction involving functionalized Zintl ions and only the second type of ligand substitution reactions reported for Zintl ions to date.[3] Furthermore, cluster **3** represents a rare example of a structurally characterized molecular complex exhibiting a Sn−Cd bond, of which only one other species has been previously reported in the literature.[34]

X-ray quality crystals of anion **3** (Figure 4) can be grown by layering pyridine solutions with toluene, yielding large plate-like crystals of $[K(2,2,2\text{-crypt})]_6[Sn_9CdSn(^nBu)_3]_2 \cdot 6tol \cdot py$. There are two largely identical crystallographically unique clusters in the asymmetric unit of this crystalline phase (**3a** and **3b**). For both anions the structure of the cluster core can once again be described as a bicapped square antiprism in which the cadmium metal center occupies one of the capping vertices. The cadmium metal completes its coordination sphere by binding to a Sn^nBu_3 moiety, with the $Cd-Sn^nBu_3$ bond perpendicular to the capped η^4 face of the E_9 cluster. Cluster bond distances vary between 2.9232(5) to 3.2520(5) Å, and 2.9206(6) to 3.2695(6) Å for **3a** and **3b**, respectively. Such bond distances are in good agreement with those observed for cluster **1** (2.9056(8)−3.2443(7) Å) and for analogous functionalized Zintl ions such as $[Sn_9Zn(C_6H_5)]^{3-}$ (2.9156(3)−3.2275(3) Å) or $[Sn_9M(CO)_3]^{3-}$ (2.9344(7)−3.2038(4) Å).[4,2b]

Bonding distances between the capping cadmium metal center and the η^4-face of the nine-atom tin clusters vary

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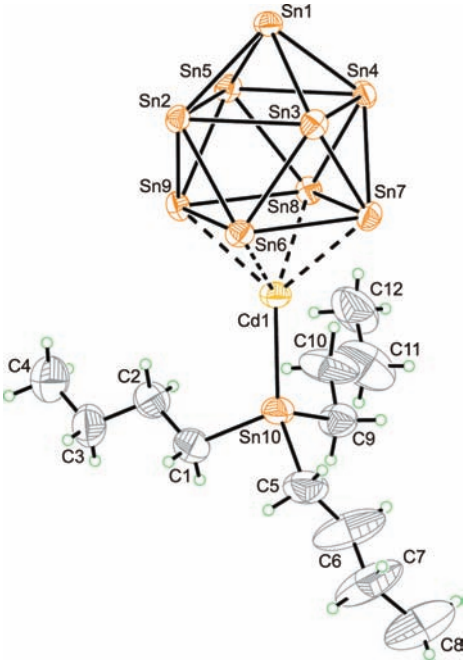

Figure 4. Thermal ellipsoid plot of one of the two crystallographically distinct anions in $[K(2,2,2\text{-crypt})]_6[Sn_9CdSn(^nBu)_3]_2 \cdot 6tol \cdot py$ (**3a**). Anisotropic displacement ellipsoids pictured at 50% probability level.

Table 3. Selected Bond Lengths for the Two Crystallographically Unique Clusters in $[K(2,2,2\text{-crypt})]_6[Sn_9CdSn(^nBu)_3]_2 \cdot 6tol \cdot py$, **3a** and **3b**

bond[a]	**3a**	**3b**
Sn1−Sn2	2.9546(6)	2.9521(6)
Sn1−Sn3	2.9466(6)	2.9472(6)
Sn1−Sn4	2.9418(6)	2.9456(6)
Sn1−Sn5	2.9236(6)	2.9255(7)
Sn2−Sn3	3.1757(6)	3.1692(6)
Sn2−Sn5	3.2520(5)	3.2695(6)
Sn2−Sn6	2.9397(6)	2.9424(6)
Sn2−Sn9	2.9591(6)	2.9528(6)
Sn3−Sn4	3.2328(6)	3.2243(6)
Sn3−Sn6	2.9570(6)	2.9584(6)
Sn3−Sn7	2.9563(6)	2.9625(6)
Sn4−Sn5	3.1795(6)	3.2068(6)
Sn4−Sn7	2.9519(6)	2.9427(6)
Sn4−Sn8	2.9459(6)	2.9487(6)
Sn5−Sn8	2.9321(6)	2.9270(6)
Sn5−Sn9	2.9232(6)	2.9206(6)
Sn6−Sn7	3.1496(6)	3.1368(6)
Sn6−Sn9	3.1806(6)	3.1677(6)
Sn7−Sn8	3.1835(6)	3.1722(6)
Sn8−Sn9	3.1773(6)	3.1794(6)
Cd1−Sn6	2.9220(7)	2.9296(7)
Cd1−Sn7	2.9504(7)	2.9416(7)
Cd1−Sn8	2.9354(6)	2.9149(6)
Cd1−Sn9	2.9251(6)	2.9074(7)
Cd1−Sn10	2.7337(7)	2.7218(7)

[a] Element numbering scheme as employed in Figure 4.

narrowly between 2.9220(7)−2.9504(7) Å, and 2.9074(7)−2.9416(7) Å for clusters **3a** and **3b**, respectively. A complete list of cluster bond distances is provided in Table 3. These distances are very similar to those observed for cluster **1** (2.9197(10)−2.9568(8) Å) and significantly longer (0.2 Å) than the Cd−Sn distance for the σ-bond between the cadmium metal center and the tributyltin moiety, 2.7337(7) and 2.7218(7) Å for clusters **3a** and **3b**, respectively. These latter bonds are in turn only slightly longer than that observed for the only other structurally characterized molecular species containing a cadmium−tin bond, $\{MeSi[SiMe_2N(p\text{-}Tol)]_3Sn\}_2Cd$, which exhibits a Cd−Sn bond distance of 2.6758(1) Å.[34]

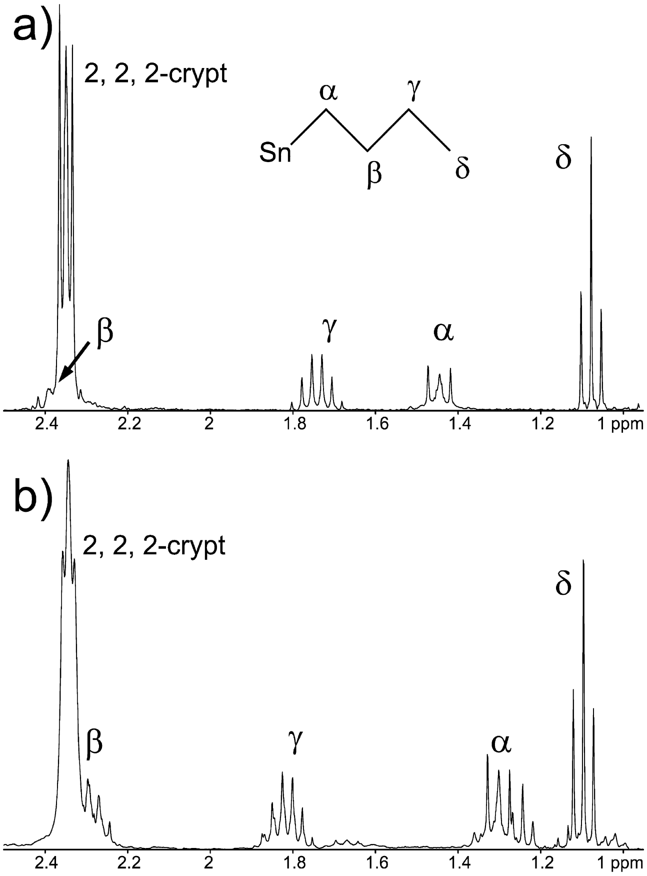

Figure 5. Aliphatic regions of ^1H NMR spectra for (a) $[Sn_9CdSn^nBu_3]^{3-}$ and (b) The crude reaction mixture of **2** and $HSiBu_3$ collected in d^5-pyridine. Data were recorded at 298 K at 300.17 MHz.

Attempts to grow crystals of $[K(2, 2, 2\text{-crypt})]^+$ salts of the lead analogue $[Pb_9CdSn(^nBu)_3]^{3-}$ proved unsuccessful because of the well-established long-term instability of related lead clusters in pyridine. The only crystals obtained were thin purple plate-like crystals of the 4, 4′-bipyridyl radical anion which results from the reduction of the pyridine solvent.[35] These crystals were found accompanied by metallic precipitates of elemental lead, a common product resulting from the uncontrolled oxidation of $[Pb_9]^{4-}$ in solution.

The ^1H NMR spectrum of a d_5-pyridine solution of analytically pure crystals of **3** reveals four distinct multiplet resonances at 2.37, 1.74, 1.44, and 1.08 ppm, corresponding to the four proton environments of the tributyltin moiety (Figure 5a). These resonances were also observed as the most intense peaks present in the aliphatic region of the ^1H NMR spectrum of the crude reaction mixture from which crystals containing **3** were obtained, giving a good indication of the relatively "clean" nature of the reaction. One of the multiplets is largely obscured by the resonance at 2.35 ppm corresponding to one of the 2, 2, 2-crypt proton environments; however, the remaining three multiplets at 1.74, 1.44, and

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(35) (a) Denning, M. S.; Irwin, M.; Goicoechea, J. M. *Inorg. Chem.* **2008**, *47*, 6118. (b) Goicoechea, J. M.; Hull, M. K.; Sevov, S. C. *J. Am. Chem. Soc.* **2007**, *129*, 7885.

1.08 ppm are found to integrate in a 2:2:3 ratio, respectively. Instrumental limitations prevented full resolution of the coupling between the four different proton environments because of the similar magnitude of the coupling constants. The resonance corresponding to the δ-hydrogen atoms of the aliphatic chains appears as a triplet at 1.08 ppm with a $^3J_{\gamma\text{-}\delta} = 7.5$ Hz. The resonance corresponding to the protons in the γ-position is centered at 1.74 ppm and appears as a sextet (an overlapping triplet of quartets) because of the similarity between $^3J_{\gamma\text{-}\delta}$ and $^3J_{\beta\text{-}\gamma}$. The obscured multiplet at 2.37 ppm corresponds to the β-hydrogen atoms while the pseudo-triplet at 1.44 ppm is assigned as arising from the α-protons. Assignment of the proton resonances was further confirmed by a 2D COSY experiment which highlighted the coupling between the distinct proton environments (see Supporting Information).

The ^{1}H NMR of the crude reaction mixture which we believe to contain $[Pb_9CdSn(^nBu)_3]^{3-}$ reveals an almost identical spectrum with four multiplet resonances at 2.30, 1.82, 1.30, and 1.10 ppm which would correspond to the β-, γ-, α-, and δ-proton environments, respectively (Figure 5b). The multiplicities are identical to those observed for cluster **3** with the exception that the multiplet arising from the β-hydrogen atoms is more visible and appears as a quintet (two overlapping triplets of triplets) which only moderately overlaps with 2, 2, 2-crypt resonance at 2.34 ppm.

In addition to the resonances arising from the 2, 2, 2-crypt carbon atoms, the $^{13}C\{^1H\}$ NMR spectra of species **3** and **4** reveal four resonances at 32.9, 29.5, 17.7, and 15.1 ppm and 35.0, 30.3, 19.2, and 15.2 ppm, respectively. These correspond to the four different chemical environments of the carbon atoms of the tributyltin functionalities. Despite our inability to grow suitable X-ray quality single crystals of cluster **4**, comparison of the NMR spectra of clusters **3** and **4** demonstrates that species **4** may also be available in solution as a result of the coupling of tributyltinhydride and cluster **2**.

Attempts to record the negative-ion mode electrospray mass-spectra of clusters **3** and **4** were hindered by the relative instability of the trialkyltin functionalities during the ionization process.[36] The mass-spectra of DMF solutions containing the tributyltin functionalized cluster anions reveal peaks corresponding to extensive fragmentation of the molecular ion, such as $[E_9CdSn(^nBu)]^-$, but no conclusive evidence of the $[E_9CdSn(^nBu)_3]^{3-}$ clusters. As a comparative test we also attempted to record the negative ion mode mass-spectrum for tributyltinhydride and were similarly unable to observe the molecular ion peak under standard ionization conditions. In the positive ion mode spectra we observe mass envelopes which correspond to ion pairs of the clusters with four $[K(2,2,2\text{-crypt}]^+$ cations, albeit at such high molecular weights there are limitations to the accuracy of the instrument and these peaks are off by several *m/z* units. The $\{[K(2,2,2\text{-crypt})]_4[Sn_9CdSn(^nBu)_3]^{3-}\}^+$ ion was observed at 3131.0 (predicted 3133.2) and the analogous lead species, $\{[K(2,2,2\text{-crypt})]_4[Sn_9PbSn(^nBu)_3]^{3-}\}^+$, observed at 3924.4 (predicted 3929.6). Despite the relative inaccuracy of measurements at such high *m/z* values, we believe that these data, in addition to the multinuclear NMR data discussed above, support the existence of cluster **4** in solution.

Conclusions

The three clusters reported in this manuscript provide further evidence of the growing number of possibilities arising from solution reactivity studies of deltahedral Zintl ions. Over the course of the last 20 years the coordination chemistry of these species in solution has advanced at a considerable rate. Clusters **1** and **2** provide further evidence of the ability of nine atom group 14 Zintl anions to act as six electron donor ligands to transition metal centers thus expanding the analogies between functionalized Zintl ions and half-sandwich metallocenes. The isolation of cluster **3** demonstrates that species which were traditionally perceived to be far too reductive for chemical transformations in solution are now beginning to show potential as “inert” ligands. The coupling reaction reported in this manuscript demonstrates that the clusters can be witnesses to chemical transformations occurring at the sites of coordinated metals, opening up the possibility of using group 14 Zintl ions as organometallic ligand systems. The electronic influence of these clusters on coordinated metal atoms is far from understood, and a great deal of additional basic research is needed if we are to develop a clearer picture of the behavior of such anions in solution. At present we are currently involved in a series of further studies probing the reactivity of post-transition metal functionalized Zintl ions toward a variety of small molecule substrates in solution with the aim of gaining further insight into the behavior of such species in solution.

Acknowledgment. We thank the EPSRC (EP/F00186X/1, PDRA MSD), the University of Oxford (studentship B.Z.) and the Royal Society of Chemistry for financial support of this research. We also thank Steve Boyer (London Metropolitan University) for the elemental analyses and the University of Oxford for access to Chemical Crystallography facilities. Special acknowledgement is also given to Dr. Simon Aldridge (Oxford) for helpful discussions, Dr. Amber Thompson (Oxford) for help with crystallography, and Professor Slavi Sevov (Notre Dame) for valuable support and advice.

Supporting Information Available: X-ray crystallographic file in CIF format (**1**−**3**), a diagrammatic representation detailing the disorder present at the cluster site for $[K(2,2,2\text{-crypt})]_3$-$[\mathbf{1}]_{0.8}[Sn_9]_{0.2}\cdot$en and 2D-COSY NMR data for a d_5-pyridine solution of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8022826

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