ORGANOMETALLICS

Low-Coordinate Tin and Lead Cations

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Supporting Information

ABSTRACT: A series of low-coordinate tin and lead cationic complexes have been synthesized using the bulky β -diketiminate ligand [{N(2,6-¹Pr₂C₆H₃)C(Me)}₂CH]⁻ (BDI) to stabilize the metal center. Two different routes to [(BDI)Sn]⁺-[X]⁻ and [(BDI)Pb]⁺[X]⁻ were explored (X = B(C₆F₅)₄, AlCl₄, MeB(C₆F₅)₃): abstraction of the chloride with a Lewis acid from (BDI)SnCl and (BDI)PbCl and abstraction of a methyl group with a borane from (BDI)SnMe and (BDI)PbMe. The crystal structures of the tin and lead cations were determined; in both, solvent molecules were found to coordinate to the metal center. In the case of [(BDI)Pb]⁺-[B(C₆F₅)₄]⁻, a dichloromethane molecule was found. Density functional theory (DFT) calculations showed that this could be due to crystal packing. In the case of [(BDI)Sn]⁺[MeB-(C₆F₅)₃]⁻, an ether molecule was coordinated to the tin metal center. DFT calculations revealed a significant energy gain for the



center. DFT calculations revealed a significant energy gain for the coordinated ether as opposed to the free molecules.

INTRODUCTION

The coordination chemistry of the heavier group 14 metals is diverse, with coordination numbers from 2 to 11 and even 12 reported for lead compounds.¹⁻⁷ With regard to the lower coordinate complexes of tin and lead, bulky terphenyl groups have been successfully utilized to generate several two-coordinate complexes,^{2,8} as well as a "quasi-one-coordinate" lead cation.9 However, it should be noted that, in the solid state of this lead cation complex, a nearby toluene molecule interacts with the lead center in an η^2 fashion. This result reflects the difficulty of isolating low-coordinate lead complexes. Outside of the growing number of diaryllead complexes, many of the formally two-coordinate lead complexes are rarely two-coordinate in the solid state,¹⁰ with $Pb(N(SiMe_3)_2)_2$ a very rare example of a PbN₂ two-coordinate lead compound.¹ The solid-state structure of most other "two-coordinate" PbN₂ complexes show inter- and intramolecular interactions between the metal center and nearby lone pairs,^{10,11} agostic interactions between Pb and a hydrogen atom (C-H or B-H), 8,12 or the complex exists as a dimer in which the metal center interacts intermolecularly with another ligand.^{13,14} Two-coordinate tin complexes are much more common than two-coordinate lead complexes,^{1,2,15–17} and there are many examples of stable two-coordinate tin complexes in the solid state.^{18–21} However, low-coordinate Sn(II) cations are rare, with only one two-coordinate tin cation reported, albeit stabilized by long-distance interactions with a triflate anion.²²

The chemistry of group 14 β -diketiminate complexes has recently been investigated by our group and others, ^{23–30} and the

bulky β -diketiminate ligand [{N(2,6-ⁱPr₂C₆H₃)C(Me)}₂CH]⁻ (BDI) has been shown to be able to stabilize several unusual complexes of germanium, tin, and lead. In this work, we have expanded the chemistry of these systems and have generated formally two-coordinate lead and tin cations using the bulky BDI ligand to stabilize the metal center. Two different routes were utilized for these group 14 metal cations: abstraction of chloride from the corresponding BDI-metal chloride complexes, ((BDI)-PbCl (1) and (BDI)SnCl (2)) and abstraction of a methyl group from the corresponding BDI-metal alkyl complexes, ((BDI)Pb-Me (3) and (BDI)SnMe (4)).

RESULTS AND DISCUSSION

Treatment of lead chloride 1 with Li[B(C₆F₅)₄] results in immediate formation of [(BDI)Pb][B(C₆F₅)₄] (5; eq 1). The ¹H NMR spectrum of **5** in CD₂Cl₂ reveals one environment for the N-aryl substituents, including a septet integrating to 4 protons at δ 2.74 ppm and two doublets integrating to 12 protons each at δ 1.26 and 1.21 ppm. These data indicate a symmetrically substituted, possibly two-coordinate, metal center. The ¹⁹F NMR spectrum shows three fluorine resonances, indicative of a noncoordinating [B(C₆F₅)₄]⁻ anion. A ²⁰⁷Pb NMR spectroscopic signal for this complex was not found, presumably due to fast relaxation of the lead nucleus. Complex **5** is not soluble in aliphatic or aromatic solvents such as hexane, toluene, and benzene; however, it is soluble in more polar solvents such as

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dichloromethane and will decompose in ethereal solvents such as diethyl ether and THF.

$$\begin{array}{c} Ar \\ \searrow N \\ N \\ Ar \\ Ar \\ Cl \\ M = Pb \\ \mathbf{2}, M = Sn \end{array} \xrightarrow{Ar} \begin{array}{c} Ar \\ \square \oplus [B(C_6F_5)_4] \\ Ar \\ Ar \\ \square \oplus [B(C_6F_5)_4] \\ Ar \\ \square \oplus [B(C_6F_5)$$

Crystals suitable for analysis by single-crystal X-ray diffraction experiments were obtained by slowly diffusing pentane into a

Table 1. Selected Bond Lengths ((Å) and Angles (deg) for
Lead Cation 5 and Tin Cation 9	

	5	9
M-N(1)	2.242(4)	2.1346(17)
M-N(2)	2.228(4)	2.1479(17)
$Pb \cdots Cl(1)$	3.213(4)	
Sn-O		2.3872(17)
N(1)-M-N(2)	84.24(15)	86.61(7)
N(1)-Sn-O		94.50(7)
N(2)-Sn-O		90.57(6)
C(30) - O - C(32)		108.3(3)
C(30)-O-Sn		125.65(18)
C(32)-O-Sn		123.6(2)
M-NCCCN plane	0.478(7)	0.474(3)

concentrated dichloromethane solution of **5** at -30 °C. Table 1 gives selected bond lengths and angles, and Table 2 gives data collection parameters. The solid-state structure of **5** (Figure 1) reveals a formally two-coordinate metal center; however, a dichloromethane molecule was found with partial occupancy (64%) to give a long-range lead—chlorine interaction (Pb-Cl(1) = 3.213(4) Å). In addition, a long-range interaction between lead and one fluorine from the $[B(C_6F_5)_4]$ anion is observed (Pb-F = 3.319(4) Å). The Pb-N bond distances of



Figure 1. Lead cation **5** with H atoms omitted (except for those on the dichloromethane molecule). BDI C atoms and three C_6F_5 rings are minimized for clarity.

Table 2. Crystallographic Data for Lead Cation 5 and Tin Cation 9

	5 ^{<i>a</i>}	9^b
chem formula	$C_{28}H_{41}Pb \cdot 0.64CH_2Cl_2, C_{24}BF_{20}$ (C_5H_{12} or CH_2Cl_2)	C ₅₂ H ₅₄ BF ₁₅ N ₂ OSn
formula wt	1430.40	1137.47
temp (K)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073
cryst size (mm ³)	0.25 imes 0.11 imes 0.06	0.20 imes 0.14 imes 0.14
cryst syst	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No.19)
a (Å)	17.7961(4)	14.4223(1)
b (Å)	18.4707(3)	18.4966(2)
c (Å)	22.4317(4)	19.3560(2)
α (deg)	90	90
β (deg)	126.654(1)	90
γ (deg)	90	90
$V(Å^3)$	5915.4(2)	5163.47(9)
Z	4	4
$\rho_{\rm c} ({\rm Mg}~{\rm m}^{-3})$	1.53	1.46
abs coeff (mm ⁻¹)	3.01	0.59
heta range for data collecn (deg)	3.45-27.10	3.46-27.49
no. of measd/indep rflns (R(int))	92 559/13 031 (0.077)	84679/11803 (0.059)
no. of rflns with $I > 2\sigma(I)$	10117	10 942
no. of data/restraints/params	13 031/0/723	11 803/1/652
goodness of fit on F^2	1.017	1.009
final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.056, wR2 = 0.122	R1 = 0.029, wR2 = 0.062
R indices (all data)	R1 = 0.081, $wR2 = 0.132$	R1 = 0.034, wR2 = 0.064
largest diff peak, hole (e Å ³)	$1.64, -1.11$ (close to CH_2Cl_2)	0.26, -0.41

^{*a*} The site occupancy factors of the dichloromethane solvate was freely refined (giving a total occupancy of 64%). The unit cell contains a highly disordered solvent molecule that was treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.^{32 *b*} One of the C–C bond lengths in the ether ligand was restrained to give a more chemically reasonable value; there is possible unresolved disorder in one of the C₆F₅ rings.

2.242(4) and 2.228(4) Å (average 2.24 Å) are slightly shorter than those reported for (BDI)PbOTf (average 2.27 Å)³¹ and significantly shorter than for (BDI)PbCl (average 2.29 Å),²⁴ indicating a more electropositive metal center. The N(1)–Pb–N(2) bond angle of 84.24(15)° is wider than that reported for other (BDI)Pb complexes.^{23–25,31} Interestingly, the lead is displaced from the N(1)–C(1)–C(2)–C(3)–N(2) plane by 0.478(7) Å. Although this deviation is significantly less than those for three-coordinate (BDI)Pb complexes such as (BDI)PbCl and (BDI)PbOTf (0.683 and 0.964 Å, respectively), it is similar to that for the carbonate complex (BDI)PbOCO₂iPr (0.420 Å), in which the metal center is coordinated to two or more oxygen atoms in addition to the BDI ligand.²⁵

The asymmetric environment in the solid state is in contrast to what is observed in the solution phase. This could either be due to a true planar environment around the Pb-N(1)-C(1)-C(2)-C(3)-N(2) ring in solution or a rapid inversion in which the lead center essentially flips from one side of the N(1)-C(1)-C(2)-C(3)-N(2) plane to the other; thus, we are observing average spectra in solution. This latter type of structure could be caused by coordination to dichloromethane; however, we were not able to gain any further spectroscopic evidence for this hypothesis. Although dichloromethane complexes are known, ^{33,34} including those of heavier elements,³⁵ the solution-state behavior of these complexes is variable and the coordinated dichloromethane molecule is not always observed by ¹H NMR spectroscopy, due to its lability. In addition, solid-state packing can also contribute to the observation of a coordinated dichloromethane molecule in the solid state.

In order to ascertain whether interaction with the dichloromethane was due to solid-phase packing, we performed density



Figure 2. View of the optimized geometry for $(BDI)Pb^+ \cdot DCM$ and the lead-centered lone pair (HOMO-11) for $(BDI)Pb^+$.

functional theory (DFT) calculations on the lead cation. Geometry optimization and frequency calculations were performed on both the free cation (BDI)Pb⁺ as well as the dichloromethane solvated cation $(BDI)Pb^+ \cdot DCM$; however, the anion was omitted from all calculations. In both cases, the experimental solid-state geometric coordinates were used as the initial geometry. All calculations were implemented in Gaussian 03.³⁶ Two different levels of theory were used: B3LYP DFT and LanL2DZ pseudopotentials (and basis set) on all atoms as well as B3LYP DFT and LanL2DZ pseudopotentials on Pb with 6-31G* on the other atoms. The former level of theory was performed in order to make comparisons with our previously published results on other "(BDI)Pb" compounds.²⁴ Both levels of calculations showed that the optimized geometry for the metal center lies in the N(1)-C(1)-C(2)-C(3)-N(2) plane (Figure 2). In addition, although the experimental solid-state geometry was used as the starting geometry in these calculations, the dichloromethane solvate changed its position relative to the lead center in the optimized geometry of the solvated molecule, $(BDI)Pb^+ \cdot DCM$, resulting in the dichloromethane molecule lying outside the Pb-Cl van der Waals radii. This result indicates that the metal center is indeed two-coordinate in the gas phase. Although there is a slight stabilization of -3 kcal mol⁻¹ for a lead cation in close proximity to a dichloromethane molecule in $(BDI)Pb^+ \cdot DCM$,³⁷ this stabilization is not due to any direct bonding between the lead center and the solvent. The lone pair resulting from these calculations is found at HOMO-11; it is almost spherical and occupies the space opposite the β -diketiminate ligand (Figure 2). The s character in this lone pair is 94.09% (or 94.74% with the higher level of theory) and is greater than that for the three-coordinate lead chloride complex 1 (91.79%) or (BDI)PbI (92.96%) with p orbital contribution decreasing accordingly (Table 3).²⁴ Although studies have shown a correlation between increasing s orbital contribution with the decreasing hardness of the coordinated ligand,^{38,39} our results could be simply due to the change in coordination number at the lead center.

Similar to the case for the lead system, treatment of tin chloride **2** with Li[B(C₆F₅)₄] results in the formation of [(BDI)Sn][B(C₆F₅)₄] (**6**; eq 1). This complex has solubility properties similar to those of the lead system, with the added benefit of being stable in ethereal solvents (diethyl ether and THF). Although we were unable to obtain crystals suitable for an X-ray diffraction study, the ¹H NMR spectrum reveals one environment for the N-aryl substituents, and thus is consistent with a symmetrically substituted metal center. A ¹¹⁹Sn NMR signal is observed at δ 197.0 ppm, which is significantly downfield from that of tin chloride **2** (δ –224 ppm).⁴⁰ Unfortunately, despite repeated attempts, we were unable to obtain satisfactory microanalysis for this compound. Addition of AlCl₃ to tin

	Table 3.	NBO Ana	lvsis of Lead	Cations	(BDI)I	Pb^+ and ((BDI)Pb	$^{+} \cdot DCM$
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compound	natural electron configuration	lone pair NBO on M	lone pair occupancy		
	LanL2DZ on Ev	very Atom			
(BDI)Pb ⁺	Pb: 6s (1.87), 6p (0.64)	s [94.09%], p 0.06 [5.91%]	1.979		
$(BDI)Pb^+ \cdot (DCM)$	Pb: 6s (1.87), 6p (0.65)	s [94.00%], p 0.06 [6.00%]	1.979		
LanL2DZ on Pb, 6-31G* on N, C, H					
(BDI)Pb ⁺	Pb: 6s (1.89, 6p (0.69), 7p (0.01)	s [94.74%], p 0.06 [5.26%]	1.986		
$(BDI)Pb^+ \cdot (DCM)$	Pb: 6s (1.91), 6p (0.66), 7p (0.01)	s [95.57%], p 0.05 [4.43%]	1.986		

chloride **2** also results in the abstraction of chloride from the tin (eq 2); similar to the case for **6**, only one environment for the N-aryl substituents is observed by ¹H NMR spectroscopy. In addition, one sharp ²⁷Al resonance was observed at δ 99.7 ppm, and a ¹¹⁹Sn NMR resonance was observed at δ –626.7 ppm. This chemical shift is significantly more upfield from other reported (BDI)Sn signals and could potentially indicate that the AlCl₄ anion is coordinated to the metal center. However, we have been unable to gain any further evidence for this hypothesis.⁴⁰ As with **6**, we were unable to grow X-ray-quality crystals of complex 7; however, in this case, the composition was confirmed by combustion analysis.

$$\begin{array}{c}
\stackrel{\text{Ar}}{\longrightarrow} \stackrel{\text{Ar}}{\rightarrow$$

The second route utilized to generate group 14 cations was abstraction of a methyl group from (BDI)PbMe or (BDI)SnMe using $B(C_6F_5)_3$ (eq 3). This proved successful with both the lead and tin systems, with complete conversion observed when the reactions were monitored by ¹H NMR spectroscopy. Although we were unable to obtain X-ray-quality crystals for $[(BDI)Pb][MeB(C_6F_5)_3]$ (8), the ¹H and ¹³C NMR spectra are almost identical with those obtained for 5, with only one environment observed for the isopropyl groups on the N-aryl substituent. The ¹H NMR spectrum also revealed a resonance at δ 0.45 ppm, corresponding to the CH₃ protons on the borate anion, and the ¹⁹F NMR spectrum revealed only three fluorine environments, with a $\Delta\delta(m,p)$ value of 2.6, which is indicative of a noncoordinating anion.⁴¹

$$Ar \rightarrow [MeB(C_6F_5)_3] \rightarrow N \rightarrow M$$

$$Ar Me = Pb, Sn$$

$$Ar = 2,6-iPr_2-C_6H_3$$

$$Ar = Sn$$

$$Ar = Sn$$

$$Ar = Pb$$

$$Ar = Pb$$

$$Ar = Pb$$

$$Ar = Pb$$

$$Ar = Sn$$

$$Ar = Pb$$

$$Ar = Pb$$

$$Ar = Sn$$

$$Ar = Sn$$

$$Ar = Pb$$

$$Ar = Sn$$

Addition of $B(C_6F_5)_3$ to (BDI)SnMe results in immediate abstraction of the methyl group to form $[(BDI)Sn][MeB(C_6F_5)_3]$ (9; eq 3). Similar to the case for the other Sn cations, this compound is soluble and stable in polar solvents such as dichloromethane, diethyl ether, and THF. As with the other cationic complexes, only one N-aryl environment is observed in the ¹H NMR spectrum. A resonance corresponding to the CH₃ protons on the borate anion was observed at δ 0.46 ppm. Attempts at growing X-ray-quality crystals in noncoordinating solvent systems were unsuccessful. However, crystals suitable for an X-ray diffraction study were grown by slowly cooling a concentrated diethyl ether solution to -30 °C (Figure 3). The solid-state structure has a diethyl ether molecule bound to the tin metal center (Sn-O = 2.3872(17) Å). The tin center is displaced from the N(1)-C(1)-C(2)-C(3)-N(2) plane by 0.473 Å, which is smaller than that of (BDI)SnCl $(0.658 \text{ Å})^{40}$ and (BDI)SnMe $(0.807 \text{ Å})^{42}$ as well as (BDI)SnOTf $(0.605 \text{ Å})^{40}$ but larger than that of (BDI)SnN(SiMe₃)₂ (0.361 Å).⁴² The Sn-N bond distances of 2.1342(17) and 2.1480(17) Å are shorter than those of (BDI)SnCl (2.185 and 2.180 Å) and (BDI)SnMe (2.209 and 2.218 Å) but very similar to those of (BDI)SnOTf (2.139 and 2.142 Å), therefore indicating a more electropositive metal center. The ¹¹⁹Sn NMR resonance of this etherate complex was found at δ –139.50 ppm.



Figure 3. Tin cation 9 with H atoms omitted, BDI C atoms minimized, and $[MeB(C_6F_5)]^-$ omitted for clarity.



Figure 4. View of the tin-centered lone pair (HOMO-9) for (BDI)Sn⁺ (left) and (BDI)Sn⁺ \cdot OEt₂ (right).

The ¹H NMR spectrum of the etherate crystals revealed a significant shift in the resonances corresponding to the ether molecule as well as the BDI ligand, indicating that diethyl ether is indeed coordinated to the tin metal center in solution; however, only one N-aryl environment is observed. This is presumably due to the lability of the coordinated ether; thus, an average structure is observed by ¹H NMR spectroscopy. DFT was used to calculate the ground-state energies of both the solvated tin cation and the solvent-free molecule. In contrast to $(BDI)Pb^+ \cdot DCM$, the diethyl ether molecule remains coordinated to the metal center in $(BDI)Sn^+ \cdot OEt_2$, and the calculated bond lengths and bond angles are generally within 4% of those in the solid-state structure of 9. The only significant difference is a slight elongation of the Sn-O bond by 4.1%, and the Sn metal center only deviates from the N(1)-C(1)-C(2)-C(3)-N(2) plane by 0.376 Å. The etherate complex (BDI)Sn⁺ \cdot OEt₂ is 6.1 kcal mol⁻¹ more stable than the free cation (BDI)Sn⁺ and ether alone.³⁷ When the unsolvated cation (BDI)Sn⁺ was considered, the lone pair was observed in the HOMO-9 molecular orbital; the lone pair of the tin etherate complex $(BDI)Sn^+ \cdot OEt_2$ was also found at HOMO-9 (Figure 4). The amount of s character in the lone pair for (BDI)Sn⁺ is 90.52% and for (BDI)Sn⁺ \cdot OEt₂ is 88.64%, whereas the amount of s character for (BDI)SnCl is 86.09% (Table 4).²⁴ The decrease in s character corresponds with a decrease in the population of the 5s orbital (1.81, 1.79, and 1.75, respectively). These trends are potentially consistent with the strength of the metal-ligand interaction-the stronger the interac-

compound	natural electron configuration	lone pair NBO on M	lone pair occupancy		
	LanL2DZ on I	Every Atom			
(BDI)Sn ⁺	Sn: 5s (1.81), 5p (0.72)	s [90.52%], p 0.10 [9.48%]	1.973		
$(BDI)Sn^+ \cdot OEt_2$	Sn: 5s (1.77), 5p (0.72), 6p (0.01)	s [88.64%], p 0.13 [11.36%]	1.963		
LanL2DZ on Sn, 6-31G* on N, C, H					
(BDI)Sn ⁺	Sn: 5s (1.83), 5p (0.76)	s [91.32%], p 0.10 [8.68%]	1.981		
$(BDI)Sn^+ \cdot OEt_2$	Sn: 5s (1.81), 5p (0.76), 6p (0.01)	s [90.10%], p 0.11 [9.90%]	1.978		

Table 4. NBO Analysis of Tin Cations (BDI)Sn⁺ and (BDI)Sn⁺ \cdot OEt₂

tion, the more s/p mixing is observed in the lone pair. Thus, as two-coordinate $(BDI)Sn^+$ does not possess any additional metal-ligand interaction, its lone pair has the highest relative percentage of s character.

CONCLUSIONS

We have synthesized a series of rare low-coordinate lead and tin cations. In solution, most of the cations appear as symmetrical, potentially two-coordinate species; however, in the solid state, both tin and lead are coordinated to solvent molecules. DFT calculations have revealed that the solvated complexes (BDI)Pb⁺·DCM and (BDI)Sn⁺·OEt₂ are slightly more stable than the free cations (BDI)Pb⁺ and (BDI)Sn⁺; however, in the case of (BDI)Pb⁺·DCM, the stabilization observed is minimal and is not due to a Cl–Pb interaction.

EXPERIMENTAL SECTION

All manipulations were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk techniques or in an inert-atmosphere glovebox. Solvents were dried from the appropriate drying agent, distilled, degassed, and stored over 4 Å sieves. The ¹H, ¹³C, ¹⁹F, ²⁷Al, ¹¹⁹Sn, and ²⁰⁷Pb NMR spectra were recorded on Varian 400, 500, and 600 MHz spectrometers which were equipped with X{¹H} broadband-observe probes. The ¹H and ¹³C NMR spectroscopy chemical shifts are given relative to residual solvent peaks, the ¹⁹F signals were externally referenced to CFCl₃, the ²⁷Al signals were externally referenced to SnMe₄, and the ²⁰⁷Pb signals were externally referenced to SnMe₄, and the ²⁰⁷Pb signals were externally referenced to PbMe₄. The data for the X-ray structures were collected at 173 K on a Nonius Kappa CCD diffractometer (λ (Mo K α) = 0.71073 Å) and refined using the SHELXL-97 software package.⁴³ (BDI)PbCl, (BDI)SnCl, (BDI)PbMe, and (BDI)SnMe were prepared via known literature procedures.^{24,31,40,42}

 $[CH{(CH_3)_2CN-2,6-Pr_2C_6H_3}_2Pb]^+[B(C_6F_5)_4]^-$ (5). Compound 1 (150 mg, 0.22 mmol) was dissolved in \sim 10 mL of toluene and cooled to -78 °C. To this solution was added 10 mL of a toluene solution of $Li[B(C_6F_5)_4]$ (200 mg, 0.29 mmol), dropwise. The mixture was stirred for 30 min and warmed to room temperature, after which the toluene was removed in vacuo and dichloromethane was added. The bright red-orange solution was filtered and then concentrated. Crystals were grown at -30 $^\circ\text{C}$ by slow diffusion of pentane into a concentrated dichloromethane solution of the compound. Yield: 95 mg (33.1%). ¹H NMR (500 MHz, CD₂Cl₂, $30 \,^{\circ}\text{C}$): δ 7.42 (m, 6H, H_{arvl}), 5.46 (s, 1H, middle CH), 2.74 (sept, 4H, J = 6.9 Hz, CHMe₂), 2.00 (s, 6H, NCMe), 1.26 (d, 12H, J = 6.8 Hz, CHMe₂), 1.21 (d, 12H, J = 6.8 Hz, CHMe₂). ¹³C NMR (100.5 MHz, CD₂Cl₂, 30 °C): δ 171.7 (NCMe), 144.2, 142.2, 130.0, 128.8, 123.9, 114.5 (C_{aryl}), 91.8 (middle CH), 27.9, 27.4 (CHMe2), 23.3, 22.4 (CHMe2), 21.5 (NCMe). ¹⁹F NMR (375.9 MHz, CD₂Cl₂, 30 °C): δ –133.1 (d, 6F, o-F), -163.8 (t, 3F, p-F), -167.7 (td, 6F, m-F). IR (KBr, Nujol): 1644.57 (s), 1261.30 (s), 1089.65 (br), 1021.09 (br), 800.81 (s), 722.87 (s) cm⁻¹. Anal. Calcd for C53H41N2F20BPb: C, 48.81; H, 3.15; N, 2.15. Found: C, 49.30; H, 3.47; N, 1.92.

[CH{(CH₃)₂CN-2,6⁻ⁱPr₂C₆H₃]₂Sn]⁺[B(C₆F₅)₄]⁻ (6). Compound 2 (100 mg, 0.17 mmol) was dissolved in ~10 mL of dichloromethane in a Schlenk tube and cooled to -78 °C. Li[B(C₆F₅)₄] (117 mg, 0.17 mmol) was mixed with 10 mL of dichloromethane in another Schlenk tube and added dropwise to the cold solution of compound 2. The mixture was stirred for 2 h before it was warmed to room temperature. The pale yellow solution was filtered and then concentrated to encourage crystallization. Yield: 87 mg (42.0%). ¹H NMR (500 MHz, CD₂Cl₂, 30 °C): δ 7.36 (m, 6H, H_{aryl}), 5.88 (s, 1H, CH), 2.97 (sept, 4H, *J* = 6.7 Hz, CHMe₂), 2.03 (s, 6H, NCMe), 1.25 (d, 12H, *J* = 6.8 Hz, CHMe₂), 1.23 (d, 12H, *J* = 6.8 Hz, CHMe₂). ¹³C NMR (100.5 MHz, CD₂Cl₂, 30 °C): δ 168.5 (NCMe), 143.5, 138.2, 128.9, 125.0 (C_{aryl}), 105.7 (middle CH), 28.6 (CHMe₂), 26.1, 24.1 (CHMe₂), 23.5 (NCMe). ¹¹⁹Sn NMR (223.6 MHz, CD₂Cl₂, 30 °C): δ 197.0. IR (KBr, Nujol): 1642.05 (s), 1511.13 (s), 1259.16 (m), 1167.82 (m), 978.33 (m), 798.67 (s), 773.24 (s), 755.10 (s), 694.10 (s), 659.01 (s) cm⁻¹.

[CH{(CH₃)₂CN-2,6⁻Pr₂C₆H₃)₂Sn]⁺[AlCl₄]⁻ (7). A 10 mL dichloromethane solution of AlCl₃ (47 mg, 0.35 mmol) was added dropwise to a 10 mL dichloromethane solution of compound 2 (200 mg, 0.35 mmol) at -78 °C. The mixture was stirred for 2 h before it was warmed to room temperature. The pale yellow solution was filtered and then concentrated to encourage crystallization. Yield: 82 mg (33%). ¹H NMR (500 MHz, CD₂Cl₂, 30 °C): δ 7.43 (m, 6H, H_{aryl}), 5.95 (s, 1H, CH), 2.83 (sept, 4H, *J* = 6.5 Hz, CHMe₂), 2.21 (s, 6H, NCM*e*), 1.30 (d, 12H, *J* = 6.7 Hz, CHMe₂), 1.28 (d, 12H, *J* = 6.7 Hz, CHMe₂). ¹³C NMR (100.5 MHz, CD₂Cl₂, 30 °C): δ 159.3 (NCMe), 140.6, 139.0, 123.6, 121.3 (C_{aryl}), 92.1 (middle CH), 26.4 (CHMe₂), 22.3, 21.2 (CHMe₂), 18.5 (NCM*e*). ¹¹⁹Sn NMR (149.0 MHz, C₆D₆, 20 °C): δ -626.7. ²⁷Al NMR (104.1 MHz, C₆D₆, 20 °C): δ 99.69 ppm. Anal. Calcd for C₂₉H₄₁N₂Cl₄AlSn: C, 49.24; H, 5.80; N, 3.96. Found: C, 49.35; H, 5.96; N, 3.92.

 $[CH{(CH_3)_2CN-2,6^{-i}Pr_2C_6H_3}_2Pb]^+[B(Me)(C_6F_5)_3]^-(8)$. $B(C_6F_5)_3$ (80 mg, 0.15 mmol) was mixed with 10 mL of dichloromethane and added dropwise to a -10 °C dichloromethane solution of compound 3 (100 mg, 0.15 mmol). The bright orange-red solution was stirred for 30 min; then the dichloromethane was removed in vacuo and the compound dissolved in the minimum amount of diethyl ether at -30 °C to encourage crystallization. Yield: 120 mg (66.7%). ¹H NMR (400 MHz, CD_2Cl_2 , 30 °C): δ 7.43 (m, 6H, H_{aryl}), 5.50 (s, 1H, CH), 2.77 (sept, 4H, J = 6.8 Hz, CHMe₂), 2.02 (s, 6H, NCMe), 1.27 (d, 12H, J = 6.8 Hz, CHMe₂), 1.22 (d, 12H, J = 6.9 Hz, CHMe₂), 0.45 (s, 1H, Me). $^{13}{\rm C}\,{\rm NMR}\,(100.5\,{\rm MHz},{\rm CD}_2{\rm Cl}_2,30\,^{\circ}{\rm C})$: δ 167.5 (NCMe), 142.9, 137.4, 129.5, 125.1 (C_{arvl}), 115.9 (middle CH), 28.0 (CHMe₂), 26.6 (CHMe₂), 26.3 (NCMe), 23.0 (Ar₃BMe). ¹⁹F NMR (375.9 MHz, CD₂Cl₂, 30 °C): δ -132.9 (d, 6F, o-F), -165.2 (t, 3F, p-F), -167.8 (td, 6F, m-F). IR (KBr, Nujol): 1641.18 (s), 1510.62 (s), 1261.00 (s), 1087.11 (br), 1019.90 (br), 799.79 (s) cm⁻¹. Anal. Calcd for C₄₈H₄₄N₂F₁₅BPb: C, 50.04; H, 3.82; N, 2.43. Found: C, 50.13; H, 3.77; N, 2.36.

 $[CH{(CH_3)_2CN-2,6^{-i}Pr_2C_6H_3}_2Sn]^+[B(Me)(C_6F_5)_3]^-(9).$ A 10 mL dichloromethane solution of B(C₆F₅)₃ (186 mg, 0.35 mmol) was added dropwise to a 10 mL dichloromethane solution of compound 4 (200 mg, 0.35 mmol) at -10 °C. The solution was stirred for 2 h; then the mixture was filtered and the dichloromethane removed in vacuo. A pale yellow solid was isolated. Yield: 130 mg (37.5%). ¹H NMR (500 MHz, CD₂Cl₂,

20 °C): δ 7.38 (m, 6H, H_{aryl}), 6.16 (s, 1H, CH), 2.71 (sept, 4H, *J* = 6.8 Hz, CHMe₂), 2.12 (s, 6H, NCMe), 1.31 (d, 12H, *J* = 6.8 Hz, CHMe₂), 1.15 (d, 12H, *J* = 6.9 Hz, CHMe₂), 0.46 (s, 3H, Me). ¹³C NMR (100.5 MHz, CD₂Cl₂, 20 °C): δ 170.1 (NCMe), 142.9, 136.8, 129.9, 128.9, 125.3 (C_{aryl}), 108.9 (middle CH), 28.6 (CHMe₂), 26.1, 24.1 (CHMe₂), 23.0 (NCMe), 21.1 (Ar₃BMe). ¹⁹F NMR (375.9 MHz, CD₂Cl₂, 30 °C): δ -133.05, -165.32, -167.90. ¹¹⁹Sn NMR (223.6 MHz, CD₂Cl₂, 30 °C): δ -139.50. IR (KBr, Nujol): 1957.41 (s), 1642.55 (m), 1595.40 (m), 1510.57 (s), 1268.11 (m), 1168.34 (br), 1022.08 (m), 952.04 (br), 848.95 (br), 801.10 (s), 753.43 (s), 694.09 (s) cm⁻¹. Anal. Calcd for C₄₈H₄₄N₂F₁₅BSn: C, 54.21; H, 4.14; N, 2.64. Found: C, 54.30; H, 4.23; N, 2.56.

ASSOCIATED CONTENT

Supporting Information. Tables giving Cartesian coordinates of the optimized structures of $(BDI)Pb^+$, $(BDI)Pb^+$. DCM, $(BDI)Sn^+$, $(BDI)Sn^+$. OEt₂, text giving the complete ref 35, and CIF files and figures giving crystallographic data and ORTEP diagrams for complexes 5 and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

- (1) Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. J. Chem. Soc., Chem. Commun. **1983**, 639–641.
- (2) Simons, R. S.; Pu, L. H.; Olmstead, M. M.; Power, P. P. Organometallics 1997, 16, 1920–1925.
- (3) Cramer, R. E.; Mitchell, K. A.; Hirazumi, A. Y.; Smith, S. L. J. Chem. Soc., Dalton Trans. 1994, 563–569.
- (4) Tsubomura, T.; Ito, M.; Sakai, K. Inorg. Chim. Acta 1999, 284, 149–157.
- (5) Liu, L. K.; Lin, C. S.; Young, D. S.; Shyu, W. J.; Ueng, C. H. Chem. Commun. 1996, 1255–1256.
- (6) Pu, L.; Twamley, B.; Power, P. P. Organometallics 2000, 19, 2874-2881.
- (7) Hino, S.; Olmstead, M. M.; Phillips, A. D.; Wright, R. J.; Power,
 P. P. *Inorg. Chem.* 2004, 43, 7346–7352.
- (8) Sturmann, M.; Weidenbruch, M.; Klinkhammer, K. W.; Lissner, F.; Marsmann, H. Organometallics **1998**, *17*, 4425–4428.
- (9) Hino, S.; Brynda, M.; Phillips, A. D.; Power, P. P. Angew. Chem., Int. Ed. **2004**, 43, 2655–2658.
- (10) Brooker, S.; Buijink, J. K.; Edelmann, F. T. Organometallics 1991, 10, 25–26.
- (11) Sturmann, M.; Saak, W.; Weidenbruch, M. Z. Anorg. Allg. Chem. 1999, 625, 705–706.
- (12) Izod, K.; McFarlane, W.; Wills, C.; Clegg, W.; Harrington, R. W. Organometallics **2008**, *27*, 4386–4394.
- (13) Charmant, J. P. H.; Haddow, M. F.; Hahn, F. E.; Heitmann, D.; Frohlich, R.; Mansell, S. M.; Russell, C. A.; Wass, D. F. *Dalton Trans.* **2008**, 6055–6059.
- (14) Hahn, F. E.; Heitmann, D.; Pape, T. Eur. J. Inorg. Chem. 2008, 1039-1041.
- (15) Zhong, H.; Zeng, X. R.; Yang, X. M.; Luo, Q. Y. Acta Crystallogr., Sect. E 2007, 63, M1566–U1169.

- (16) Weidenbruch, M.; Schlaefke, J.; Schafer, A.; Peters, K.; Vonschnering H. G.; Marsmann, H. Angew. Chem, Int. Ed. Engl. **1994**, 33, 1846–1848.
- (17) Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H.
 J. Am. Chem. Soc. 1991, 113, 7785–7787.
- (18) Jimenez-Perez, V. M.; Munoz-Flores, B. M.; Roesky, H. W.; Schulz, T.; Pal, A.; Beck, T.; Yang, Z.; Stalke, D.; Santillan, R.; Witt, M. *Eur. J. Inorg. Chem.* **2008**, 2238–2243.
- (19) Westerhausen, M.; Gruel, J.; Hausen, H. D.; Schwarz, W. Z. Anorg. Allg. Chem. 1996, 622, 1295–1305.
- (20) Braunschweig, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J. M. Angew. Chem., Int. Ed. Engl. **1994**, 33, 1156–1158.
- (21) Chorley, R. W.; Hitchcock, P. B.; Lappert, M. F.; Leung, W. P.; Power, P. P.; Olmstead, M. M. *Inorg. Chim. Acta* **1992**, *198*, 203–209.
 - (22) Ayers, A. E.; Dias, H. V. R. Inorg. Chem. 2002, 41, 3259-3268.
- (23) Fulton, J. R.; Hitchcock, P. B.; Johnstone, N. C.; Tam, E. C. Y. Dalton Trans. 2007, 3360–3362.
- (24) Chen, M.; Fulton, J. R.; Hitchcock, P. B.; Johnstone, N. C.; Lappert, M. F.; Protchenko, A. V. *Dalton Trans.* **2007**, 2770–2778.
- (25) Tam, E. C. Y.; Johnstone, N. C.; Ferro, L.; Hitchcock, P. B.; Fulton, J. R. *Inorg. Chem.* **2009**, *48*, 8971–8976.
- (26) Yao, S. L.; Brym, M.; Merz, K.; Driess, M. Organometallics 2008, 27, 3601–3607.
- (27) Jana, A.; Sarish, S. P.; Roesky, H. W.; Schulzke, C.; Samuel, P. P. Chem. Commun. 2010, 46, 707–709.
- (28) Wang, W. Y.; Inoue, S.; Yao, S. L.; Driess, M. Chem. Commun. 2009, 2661–2663.
- (29) Pineda, L. W.; Jancik, V.; Colunga-Valladares, J. F.; Roesky, H. W.; Hofmeister, A.; Magull, J. Organometallics **2006**, 25, 2381–2383.
- (30) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. Angew. Chem., Int. Ed. **2006**, 45, 2602–2605.
- (31) Jana, A.; Sarish, S. P.; Roesky, H. W.; Schulzke, C.; Doring, A.; John, M. Organometallics **2009**, *28*, 2563–2567.
 - (32) Spek, A. L. J. Appl. Crystallogr. 2003, 36, 7–13.
- (33) Burger, P.; Bergman, R. G. J. Am. Chem. Soc. 1993, 115, 10462– 10463.
- (34) Taw, F. L.; Mellows, H.; White, P. S.; Hollander, F. J.; Bergman,
- R. G.; Brookhart, M.; Heinekey, D. M. J. Am. Chem. Soc. 2002, 124, 5100–5108.
- (35) Bryan, J. C.; Kavallieratos, K.; Sachleben, R. A. Inorg. Chem. 2000, 39, 1568–1572.
- (36) Frisch, M. J., et al. *Gaussian 03, Revision C.02;* Gaussian, Inc., Wallingford, CT, 2004.
- (37) This value has not been corrected for basis set superposition error.(38) Akibo-Betts, G.; Barran, P. E.; Puskar, L.; Duncombe, B.; Cox,
- H.; Stace, A. J. J. Am. Chem. Soc. 2002, 124, 9257-9264.
- (39) Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W. Inorg. Chem. 1998, 37, 1853–1857.
- (40) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. Organometallics **2001**, 20, 1190–1194.
- (41) Horton, A. D.; DeWith, J.; vanderLinden, A. J.; vandeWeg, H. Organometallics 1996, 15, 2672–2674.
- (42) Jana, A.; Roesky, H. W.; Schulzke, C.; Doring, A.; Back, T.; Pal, A.; Herbst-Irmer, R. *Inorg. Chem.* **2009**, *48*, 193–197.
- (43) Sheldrick, G. M. Acta Crystallogr., Sect. A 2008, 64, 112-122.