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Syntheses and Characterization of Tin(II) Complexes Containing 10-π-Electron Ring Systems

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Abstract: The compounds $[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{SnCl}$ (**1**) and $\{[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{Sn}\}[\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ZrCl_2}(\mu\text{-}\mathrm{Cl_3})\mathrm{ZrCl_2}(\eta^5\text{-}\mathrm{C_5H_5})]$ (**2**) in which $[(i\text{-Pr})_2\mathrm{ATI}]$ = *N*-isopropyl-2-(isopropylamino)troponimine have been prepared and characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies and X-ray crystallography. Compounds **1** and **2** feature heterobicyclic $\mathrm{C_7N_2Sn}$ ring systems with basically three- and two-coordinate tin atoms, respectively. Solid state structures of **1** and **2** show weak Sn···Cl interactions. The ^{119}Sn NMR signal of **2** appears at a significantly lower field compared to that of **1**. This is consistent with the reduction in coordination number at the Sn center of **2**. The ^{1}H NMR data also provide evidence for the formation of a more symmetric solution species with the removal of $\mathrm{Cl^-}$ from **1**. X-ray structural features of $\mathrm{C_7N_2Sn}$ moiety in $[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{SnCl}$ and the $\{[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{Sn}\}^+$ cation are very similar. The Sn−N bond distances of $\{[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{Sn}\}^+$ cation are not indicative of any significant Sn−N multiple bonding. The π-electrons of the $\mathrm{C_7N_2Sn}$ ring system, therefore, appears to be mostly delocalized over nitrogen and carbon atoms.

Introduction

Divalent derivatives of tin have attracted much interest in recent years.[1−6] The simplest of these involves a coordination number of 2 at the tin center. Syntheses and in some cases the X-ray crystal structures of several such compounds have been reported in the literature. These include $[(\mathrm{Me_3Si})_2\mathrm{N}]_2\mathrm{Sn}$,[7,8] $(\mathrm{Me_3Si})_2\mathrm{NSnN(SiMe_3)C_6H_{10}(SiMe_3)NSnN(SiMe_3)_2}$,[9] $\mathrm{Me_2Si[N\text{-}(}t\text{-}\mathrm{Bu})]_2\mathrm{Sn}$,[10] $(4\text{-Me-}2,6\text{-}t\text{-}\mathrm{Bu_2C_6H_2O})_2\mathrm{Sn}$,[11] $(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2S})_2\mathrm{Sn}$,[12] $4\text{-Me-}2,6\text{-}t\text{-}\mathrm{Bu_2C_6H_2OSnN(SiMe_3)_2}$,[13] $[2,4,6\text{-}(\mathrm{CF_3})_3\mathrm{C_6H_2}]_2\mathrm{Sn}$,[14] $[\mathrm{CH_2(SiMe_3)_2C}]_2\mathrm{Sn}$,[15] and $(2,4,6\text{-}t\text{-}\mathrm{Bu_3C_6H_2})_2\mathrm{Sn}$.[16] In general, very bulky ligands are required to stabilize these species in the monomeric state. In the absence of steric protection, they often form aggregates leading to dimers, oligomers, or polymers (e.g., $[(t\text{-BuO})_2\mathrm{Sn}]_2$, $[(2,4,6\text{-}i\text{-}\mathrm{Pr_3C_6H_2S})_2\mathrm{Sn}]_3$, or $[(\mathrm{EtO})_2\mathrm{Sn}]_n$).[3]

In contrast to these neutral molecules, cationic Sn(II) complexes have received little attention.[3,4,17,18] Majority of the well-characterized species of this type concerns compound with cyclopentadienyl ligands (e.g., $\{[(\mathrm{CH_3})_5\mathrm{C_5}]\mathrm{Sn}\}[\mathrm{BF_4}]$,[19,20] $\{[t\text{-}\mathrm{BuC_5H_4}]\mathrm{Sn}\}[\mathrm{BF_4}]$,[21] or $\{[(\mathrm{CH_3})_5\mathrm{C_5}]\mathrm{Sn}(2,2'\text{-bipy})\}[\mathrm{CF_3SO_3}]$.[22,23] To our knowledge, stable, two-coordinate cationic tin species have not been described in the literature. As a part of a comprehensive study of *N*-alkyl-2-(alkylamino)troponiminate ($[(\mathrm{R})_2\mathrm{ATI}]^-$) derivatives of main group elements, we have examined the chemistry of low-valent tin complexes.[24] We were particularly interested in investigating the role the two nitrogen donors of $[(\mathrm{R})_2\mathrm{ATI}]^-$ may play in stabilizing a Sn(II) species in the monomeric form.

Here we describe the use of a diisopropyl version of the aminotroponiminate ligand ($[(i\text{-Pr})_2\mathrm{ATI}]^-$) to isolate a novel two-coordinate tin(II) cation. This molecule, $\{[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{Sn}\}[(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{ZrCl_2}(\mu\text{-}\mathrm{Cl_3})\mathrm{ZrCl_2}(\eta^5\text{-}\mathrm{C_5H_5})]$, features an interesting 10-π-electron heterobicyclic $\mathrm{C_7N_2Sn}$ ring system[25] and a chloro-bridged zirconate anion. The synthesis and X-ray crystal structure of the precursor tin(II) chloro species $[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{SnCl}$ are also reported.

Experimental Section

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres single-station drybox equipped with a −25 °C refrigerator. Solvents were distilled from conventional drying agents and degassed twice prior to use.[26] Glassware was oven-dried at 150 °C overnight. $[(i\text{-Pr})_2\mathrm{ATI}]\mathrm{H}$ was prepared according to the previously reported

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method.[24] n-BuLi (1.6 M solution in hexane), (η^5-C_5H_5)$ZrCl_3$, and $SnCl_2$ were obtained from commercial sources and used as received. The ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded at 25 °C on a Bruker MSL-300 spectrometer (^{1}H, 300.15 MHz; ^{13}C, 75.47 MHz; ^{119}Sn, 111.82 MHz) or Nicolet NT-200 spectrometer (^{1}H, 200.06 MHz; ^{13}C, 50.31 MHz), unless otherwise noted. Chemical shifts for ^{1}H NMR spectra are relative to internal Me_4Si. The ^{13}C and ^{119}Sn NMR spectra were run with ^{1}H decoupling, and the chemical shifts are reported in ppm vs Me_4Si and Me_4Sn (external), respectively. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. Elemental analyses were performed by the Texas Analytical Laboratories, Inc., Houston, TX, or at the University of Texas at Arlington using a Perkin Elmer 2400 CHN analyzer.

Synthesis of [(*i*-Pr)$_2$ATI]SnCl (1). A diethyl ether solution (30 mL) of [(*i*-Pr)$_2$ATI]H (327 mg, 1.6 mmol) was treated with *n*-BuLi (1 mL, 1.6 M hexane solution) at 0 °C. It was stirred for 1 h and slowly added to $SnCl_2$ (303 mg, 1.6 mmol) in diethyl ether (20 mL) at 0 °C. The mixture immediately became cloudy. It was stirred overnight at room temperature. The resulting reddish solution was filtered through a bed of Celite, and the volatile materials were removed from the filtrate under reduced pressure to obtain **1** as a red solid (89% yield, 507 mg). Recrystallization from toluene−hexane at −20 °C gave orange-yellow crystals of **1**: 98−99.5 °C; ^{1}H NMR (C_6D_6) δ 1.18 (d, 6H, $J = 6.4$ Hz, CH_3), 1.45 (d, 6H, $J = 6.4$ Hz, CH_3), 3.74 (septet, 2H, $J = 6.4$ Hz, $CH(CH_3)_2$, 6.29 (t, 1H, $J = 9.2$ Hz, H_5), 6.34 (d, 2H, $J = 11.4$ Hz, $H_{3,7}$), 6.81 (dd, 2H, $J = 11.4$, 9.2 Hz, $H_{4,6}$); ^{13}C{^{1}H} NMR (C_6D_6) δ 24.17 (CH_3) 24.76 (CH_3), 49.84 ($CHMe_2$), 115.48 (C_5), 120.83 ($C_{3,7}$), 135.68 ($C_{4,6}$), 162.85 ($C_{2,8}$); ^{1}H NMR ($CDCl_3$) δ 1.56 (d, 6H, $J = 6.3$ Hz, CH_3), 1.63 (d, 6H, $J = 6.3$ Hz, CH_3), 4.32 (septet, 2H, $J = 6.3$ Hz, $CH(CH_3)_2$), 6.60 (t, 1H, $J = 9.2$ Hz, H_5), 6.80 (d, 2H, $J = 11.2$ Hz, $H_{3,7}$), 7.22 (dd, 2H, $J = 11.2$, 9.2 Hz, $H_{4,6}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 24.63 (br, CH_3), 49.63 ($CHMe_2$), 115.41 (C_5), 121.43 ($C_{3,7}$), 135.69 ($C_{4,6}$), 162.64 ($C_{2,8}$); ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ −68. Anal. Calcd for $C_{13}H_{19}N_2ClSn$: C, 43.68; H, 5.36; N, 7.84. Found: C, 43.64; H, 5.03; N, 7.27

Synthesis of {[(*i*-Pr)$_2$ATI]Sn}[(η^5-C_5H_5)$_2$$Zr_2Cl_7$] (2). [(*i*-Pr)$_2$ATI]-SnCl (75 mg, 0.21 mmol) and (η^5-C_5H_5)$ZrCl_3$ (110 mg, 0.42 mmol) were mixed in methylene chloride (15 mL) at room temperature. The mixture slowly became yellow. It was stirred overnight and filtered through a bed of Celite. The filtrate was collected, and the volatile materials were removed under reduced pressure to obtain a yellow solid (180 mg). This solid was recrystallized from a methylene chloride−hexane solution at −20 °C to obtain pale yellows crystals of **2**. At the melting point, the color slowly changed to reddish brown and the crystal started to melt at 172 °C. For **2**: ^{1}H NMR (CD_2Cl_2) 1.62 (d, 12H, $J = 6.2$ Hz, CH_3), 4.44 (septet, 2H, $J = 6.2$ Hz, $CHMe_2$), 6.65 (s, 5H, CH), 6.90 (t, 1H, $J = 9.3$ Hz, H_5), 7.04 (d, 2H, $J = 11.4$ Hz, $H_{3,7}$), 7.48 (dd, 2H, $J = 11.4$, 9.3 Hz, $H_{4,6}$); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 25.2 (CH_3), 50.34 ($CHMe_2$), 117.24 (C_5), 121.12, 124.81, 136.51 ($C_{4,6}$), 163.27 ($C_{2,8}$); ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ 734. Anal. Calcd for $C_{23}H_{29}N_2Cl_7SnZr{\cdot}6.5CH_2Cl_2$: C, 25.69; H, 3.07; N, 2.03. Found: 25.34; H, 3.27; N, 2.69.

X-ray Structure Determination. A suitable crystal covered with a layer of hydrocarbon oil was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream.[27] Data collections were carried out at −90 °C on a Siemens P4 diffractometer equipped with a LT-2A device for low-temperature work and graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters of [(*i*-Pr)$_2$ATI]SnCl and {[(*i*-Pr)$_2$ATI]Sn}[(η^5-C_5H_5)$ZrCl_2$-(μ-Cl_3)$ZrCl_2$(η^5-C_5H_5)] were determined by least-squares refinement of 28 and 50 reflections, respectively. Three standard reflections were measured every 97 data points to check for crystal deterioration and/or misalignment. No significant deterioration in intensity was observed. Data were corrected for Lorentz, polarization, and absorption (using ψ scans) effects. Structures were solved by direct methods followed by successive cycles of full-matrix least-squares refinement of F^2 and difference Fourier analysis. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at calculated positions. They were treated as riding atoms with isotropic displacement parameters fixed 1.2 or 1.5 times the value refined for the respective host atom. Software programs and the sources of scattering factors are contained in the SHELXTL (PC version 5 based on SHELXL-93) software package provided by the Siemens Analytical X-ray Instruments, Inc.[28] Some details of data collection and refinements are given in Table 1. Selected bond distances and angles are given in Table 2. Further details of the crystal structures are presented in the supporting information.

Table 1. Crystal Data and Summary of Data Collection and Refinement

	1	**2**·2(CH_2Cl_2)
formula	$C_{13}H_{19}ClN_2Sn$	$C_{25}H_{33}Cl_{11}N_2SnZr_2$
fw	357.44	1052.61
space group	*Cc*	$P\bar{1}$
a, Å	9.3375(11)	10.6747(9)
b, Å	16.7926(10)	13.0375(12)
c, Å	10.3931(7)	13.7710(12)
α, deg	90	91.711(7)
β, deg	116.160(7)	102.535(6)
γ, deg	90	96.652(7)
V, Å^3	1462.7(2)	1855.3(3)
Z	4	2
T, K	183(2)	183(2)
λ (Mo, Kα), Å	0.71073	0.71073
density (calc), g/cm^3	1.623	1.884
absorpn coeff, mm^{-1}	1.911	2.033
*R*1, wR2 [$I > 2\sigma(I)$][a]	0.0205, 0.0523	0.0244, 0.0557
*R*1, wR2 [all data][a]	0.0207, 0.0524	0.0308, 0.0591

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	[(*i*-Pr)$_2$ATI]SnCl	{[(*i*-Pr)$_2$ATI]Sn}$^+$
Sn−N1	2.164(5)	2.153(3)
Sn−N9	2.164(5)	2.142(3)
N1−C2	1.332(7)	1.335(5)
N9−C8	1.331(7)	1.341(5)
Sn−Cl	2.542(2)	
C2−C8	1.488(7)	1.474(6)
C2−C3	1.419(8)	1.413(6)
C3−C4	1.380(8)	1.382(7)
C4−C5	1.384(8)	1.374(8)
C5−C6	1.388(10)	1.374(8)
C6−C7	1.376(8)	1.383(7)
C7−C8	1.424(7)	1.417(6)
N1−Sn−N9	73.9(2)	74.48(12)
Sn−N1−C2	118.2(4)	117.7(3)
Sn−N9−C8	118.2(4)	117.9(3)
N1−Sn−Cl	92.44(13)	
N9−Sn−Cl	94.13(12)	

Results and Discussion

The treatment of [(*i*-Pr)$_2$ATI]Li with $SnCl_2$ in a 1:1 molar ratio in Et_2O afforded [(*i*-Pr)$_2$ATI]SnCl (**1**) as an orange solid in excellent yield (Scheme 1). Compound **1** has good solubility in solvents such as THF, Et_2O, C_6H_6, and CH_2Cl_2 and was characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopies and by X-ray diffraction. ^{1}H and ^{13}C NMR data indicate a fairly symmetric solution structure for the seven-membered ring. For example, the ring protons appear as three well-separated multiplets which correspond to H(5), H(3,7), and H(4,6). The ^{13}C NMR spectrum displayed four resonances for the ring carbons. The ^{13}C NMR signals due to C(2,8) appear at about 10 ppm downfield from the corresponding signal in the free ligand [(*i*-Pr)$_2$ATI]H (δ 151.98).[24] Similar chemical shift difference was observed between the aluminum derivative [(*i*-Pr)$_2$ATI]$AlMe_2$ or [(*i*-Pr)$_2$ATI]AlH_2 and the free ligand.[24] Interestingly, methyls of the isopropyl substituents appear as two sets of doublets in the ^{1}H NMR spectrum, suggesting two different environments for the CH_3 moieties. This is perhaps

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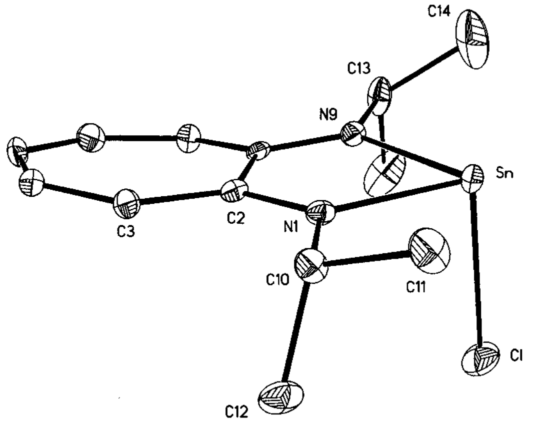
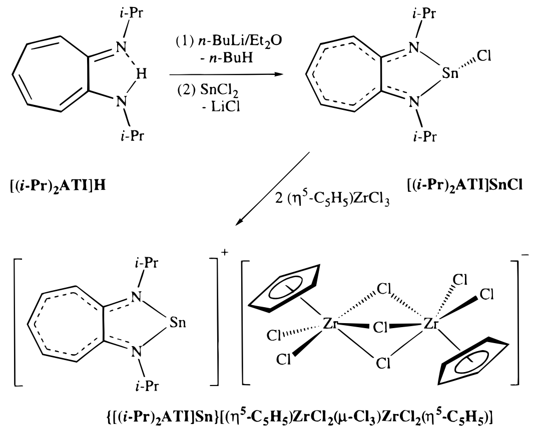


Figure 1. Structure and atom numbering scheme for [(*i*-Pr)$_2$ATI]SnCl (**1**).

Scheme 1



due to the asymmetry caused by the Cl group on the Sn atom. The separation between the two signals was somewhat larger in C_6D_6 (0.27 ppm) compared to that in $CDCl_3$ (0.07 ppm). Similarly, they appear as two signals in the ^{13}C NMR spectrum taken in C_6D_6. However, in $CDCl_3$, the methyl groups appear as a single peak. The ^{119}Sn{^{1}H} NMR spectrum of [(*i*-Pr)$_2$ATI]SnCl (**1**) exhibited a broad signal at −68 ppm.

X-ray crystal structure of **1** and the atom numbering scheme is shown in Figure 1. The tin center adopts a pyramidal geometry which is fairly common in Sn(II) chemistry. The Sn−Cl distance is 2.542(2) Å. In addition, there is a very long, intermolecular Sn···Cl interaction of 3.558 Å. This separation is much longer than the typical Sn−Cl distances (e.g., 2.542(2) Å of **1**, 2.485(3) Å of [$H_2B(Pz)_2$]SnCl (where Pz = pyrazolyl),[29] 2.629(1) Å of [HB(3,5-$(CH_3)_2Pz)_3$]SnCl,[30] or 2.68 Å of [C_5H_5]-SnCl)[31] but falls within the sum of the van der Waals radii of Sn and Cl (3.97 Å).[3] This weak interaction leads to a polymeric chain structure illustrated in Figure 2 with Cl−Sn···Cl angle of 172.3°. The bicyclic C_7N_2Sn ring system shows a minor twist along the Sn···C5 axis (mean deviation from plane = 0.056 Å; the largest displacement from the plane = 0.11 Å). The angle between the SnN_2C_2 and C_7 ring is 6.4°. Two Sn−N distances (2.164(5) Å) and N−C$_{\text{ring}}$ distances (1.332(7) and 1.331(7) Å) are identical. These Sn−N bond lengths of **1** are significantly shorter than those of three-coordinate [$H_2B(Pz)_2$]-SnCl (2.243(7), 2.302(8) Å)[29] but longer than the Sn−N distances of *trans*-[$(Me_3Si)_2NSn(\mu\text{-}Cl)$]$_2$ (2.069(3) Å).[32] For comparison, two-coordinate tin species such as [$(Me_3Si)_2N$]$_2$Sn have much shorter Sn−N bond distances (2.096(1), 2.088(6) Å).[7] The N−Sn−N angle of 73.9(2)° in **1** can be compared with 104.7(2)° of [$(Me_3Si)_2N$]$_2$Sn[7], 73.2° of Me_2Si-[N(*t*-Bu)]$_2$Sn,[6,33] and 80.7(3)° of [$H_2B(Pz)_2$]SnCl.[29] There is no interaction between the Sn atoms of neighboring molecules (closest Sn···Sn separation is about 5.29 Å).

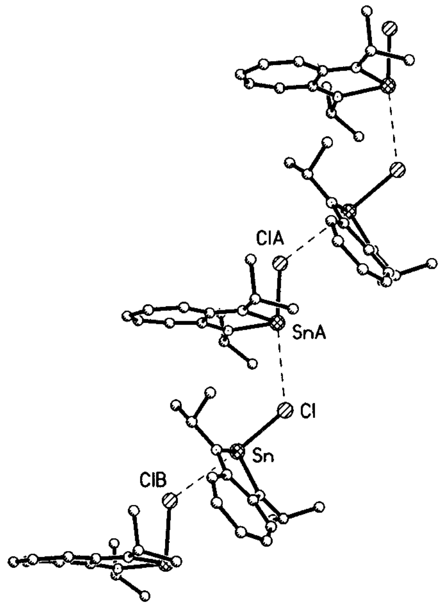


Figure 2. Solid state packing diagram of **1** showing weak Sn···Cl interactions.

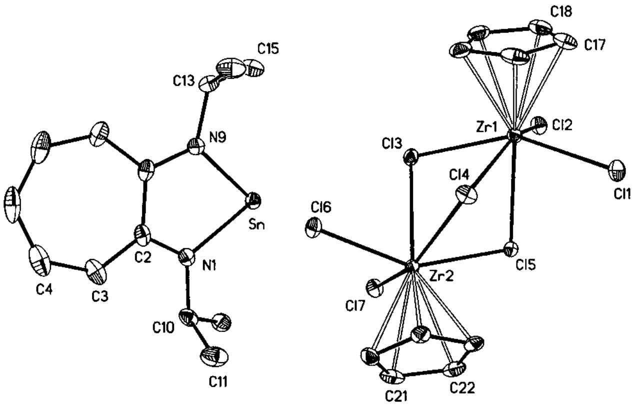


Figure 3. Structure and atom numbering scheme for {[(*i*-Pr)$_2$ATI]-Sn}[(η^5-C$_5$H$_5$)ZrCl$_2$(μ-Cl$_3$)ZrCl$_2$(η^5-C$_5$H$_5$)] (**2**).

The treatment of [(*i*-Pr)$_2$ATI]SnCl with 2 equiv of (η^5-C$_5$H$_5$)ZrCl$_3$ in CH_2Cl_2 led to the cationic Sn(II) species {[(*i*-Pr)$_2$ATI]Sn}[(η^5-C$_5$H$_5$)ZrCl$_2$(μ-Cl$_3$)ZrCl$_2$(η^5-C$_5$H$_5$)] (**2**) (Scheme 1). The (η^5-C$_5$H$_5$)ZrCl$_3$ serves as a chloride-abstracting agent in this reaction. Compound **2** is an air and moisture sensitive yellow solid which shows moderate solubility in $CHCl_3$ or CH_2Cl_2 but considerably less solubility (compared to **1**) in hydrocarbon solvents such as toluene.

The stucture of **2** in the solid state was determined by X-ray crystallography (Figure 3). It crystallizes in the triclinic $P\bar{1}$ space group with two molecules of CH_2Cl_2 in the asymmetric unit. Compound **2** consists of the cationic {[(*i*-Pr)$_2$ATI]Sn}$^+$ moiety and the chloride bridge [(η^5-C$_5$H$_5$)ZrCl$_2$(μ-Cl$_3$)ZrCl$_2$-(η^5-C$_5$H$_5$)]$^-$ anion. The Sn−N distances in the cation are 2.153(3) and 2.142(3) Å. In addition to these two bonds, there are two weak interactions between the tin atom of the cation and

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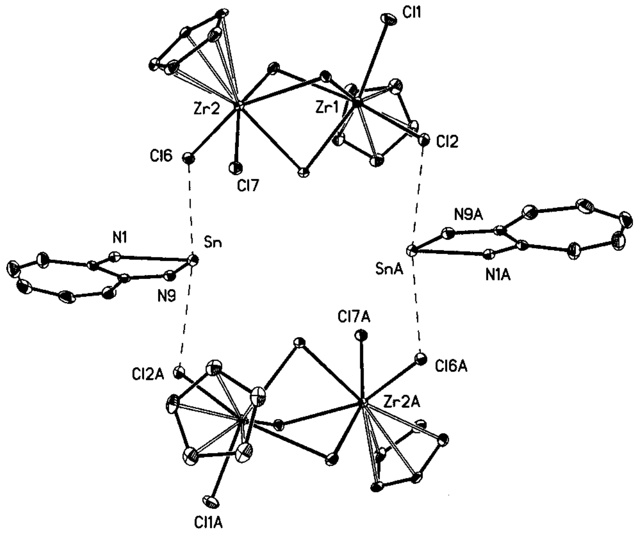

Figure 4. Diagram of **2** showing weak Sn···Cl interactions (isopropyl groups have been omitted for clarity).

terminal chloride atoms (Cl6 and Cl2A) of the $[(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl_3)ZrCl_2(\eta^5\text{-}C_5H_5)]^-$ anions. This gives rise to a dimeric structure shown in Figure 4. The Cl6···Sn···Cl2A angle is 166.1°. These Sn···Cl separations of 2.979 and 3.070 Å are still considerably long compared to the typical Sn−Cl single bond distance of 2.39 Å.[3] However, they have an effect on the corresponding Zr−Cl bond distances. For example, The Zr1−Cl2 and Zr2−Cl6 terminal bond distances are 2.4945(10) and 2.4958(10) Å, respectively. The chlorides with no such contacts have slightly shorter bond distances (Zr1−Cl1 = 2.4438(11) Å and Zr2−Cl7 = 2.4400(10) Å).[34]

Interestingly, the key structural parameters of the cationic $\{[(i\text{-Pr})_2ATI]Sn\}^+$ moiety is not very different from the neutral $[(i\text{-Pr})_2ATI]SnCl$ (see Table 2). For example, the average Sn−N distances of **1** and **2** are 2.164 and 2.147 Å, respectively. The N−Sn−N angles, of **1** and **2** (73.9(2) and 74.48(12)°) are almost identical. This 74.48(12)° bond angle in **2** is among some of the smallest X−Sn−X angles observed in Sn(II) chemistry. Typically, X−Sn−X angles in two-coordinate tin compounds range from 73 to 105°.[3,6]

The most notable differences between **1** and **2** were observed in the solution NMR data. The $^{119}Sn\{^1H\}$ NMR resonance of **2** appears at 734 ppm. This is a considerable downfield shift relative to that of **1**. This shift to a lower frequency upon chloride abstraction from **1** is consistent with the reduction in the coordination number at the tin center.[32,35] In fact, the ^{119}Sn chemical shift of **2** is very close to the values observed for two-coordinate Sn(II) amides such as $[(Me_3Si)_2N]_2Sn$ (759 ppm),[36] $(Me_3Si)_2NSnN(SiMe_3)C_6H_{10}(SiMe_3)NSnN(SiMe_3)_2$ (694 ppm),[9] and $Me_2Si[N(t\text{-Bu})]_2Sn$ (638 ppm).[36]

The resonance corresponding to the methyl groups of **2** appear as a doublet in the ^1H NMR spectrum. In contrast, compound **1** displayed two sets of doublets. This may also indicate the removal of Cl from the tin center leading to a less crowded and more symmetric environment. The signal due to protons of the C_5H_5 group of the zirconate anion appears at 6.65 ppm. The solvent, CH_2Cl_2, was difficult to remove completely from the solid samples of **2**. This is apparent from the ^1H NMR spectrum of **2** which often exhibits a signal at 5.33 ppm corresponding to methylene chloride protons.

Zirconium ions of the anionic $[(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl_3)ZrCl_2(\eta^5\text{-}C_5H_5)]^-$ adopt a pseudooctahedral geometry. The Zr−Cl(terminal) bond distances (2.440(1)−2.496(1) Å) are much shorter than the Zr−Cl(bridging) separations (2.552(1)−2.742(1) Å). They can be compared to the Zr−Cl(terminal) 2.419(3) Å and Zr−Cl(bridging) (2.518(3)−2.728(3) Å) distances of $[(\eta^5\text{-}C_5H_5)ZrCl_3]_n$[37] or to the Zr−Cl(terminal) (2.385(1), 2.402(1)) and Zr−Cl(bridging) (2.587(1), 2.589(1)) values of $[(\eta^5\text{-}C_5Me_5)ZrCl_3]_2$.[38]

One of the interesting features of $[(i\text{-Pr})_2ATI]SnCl$ and $\{[(i\text{-Pr})_2ATI]Sn\}^+$ is the planar, bicyclic 10-π-electron ring system. In contrast to the chloro adduct **1**, the Sn atom in $\{[(i\text{-Pr})_2ATI]Sn\}^+$ cation has an empty out-of-plane p-orbital which is capable of interacting with the π-electron system. This would lead to a shortening of the Sn−N distances relative to those of **1**. However, a comparison of structural data between $[(i\text{-Pr})_2ATI]SnCl$ and $\{[(i\text{-Pr})_2ATI]Sn\}^+$ did not reveal any significant evidence to support an increase in Sn−N bond order, thus suggesting the presence of a relatively localized π-system in **2**. This may perhaps be a consequence of relatively large size difference between the two bonding atoms. We are currently exploring the chemistry of the lighter elements of group 14 which might show more delocalized 10-π-electron systems.

Summary and Conclusion

Compounds $[(i\text{-Pr})_2ATI]SnCl$ (**1**) and $\{[(i\text{-Pr})_2ATI]Sn\}[(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl_3)ZrCl_2(\eta^5\text{-}C_5H_5)]$ (**2**) have been prepared and characterized by NMR spectroscopy and X-ray crystallography. Compounds **1** and **2** feature tin-containing heterobicyclic C_7N_2Sn ring systems. The solid state structure of **1** shows a three-coordinate, pyramidal Sn center. There is also a nonbonded Sn···Cl interactions between the Sn of **1** and the Cl atom of a neighboring molecule forming a polymeric chain. The Sn atom in **2** is basically two coordinate. However, there are two weak Sn···Cl interactions between the tin atom of the cation and two of the terminal Cl atoms of the $[(\eta^5\text{-}C_5H_5)ZrCl_2(\mu\text{-}Cl_3)ZrCl_2(\eta^5\text{-}C_5H_5)]^-$ anions. These contacts are shorter than that observed in **1**. The ^{119}Sn NMR signal of **2** appears at a significantly lower field compared to that of **1**, which is consistent with the reduction in coordination number at the Sn center. The ^{119}Sn NMR chemical shift value of **2** is very close to those observed for two-coordinate tin amides. The ^1H NMR data also provide evidence for the formation of a more symmetric solution species. The Sn−N distances of **1** and **2** are in the range typical for a Sn−N single bond (2.15 Å).[3] X-ray structural parameters of the C_7N_2Sn rings in $[(i\text{-Pr})_2ATI]SnCl$ and the cationic $\{[(i\text{-Pr})_2ATI]Sn\}^+$ moiety are very similar. The π-electrons of the C_7N_2Sn ring system, therefore, appear to be mostly delocalized over nitrogen and carbon atoms.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and complete bond distances and angles for **1** and **2** and a Figure showing the asymmetric unit of **2** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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