Flexible coordination of the carboxylate ligand in tin(II) amides and a 1,3-diaza-2,4-distannacyclobutanediyl†

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Received 27th March 2007, Accepted 8th May 2007
First published as an Advance Article on the web 23rd May 2007
DOI: 10.1039/b704588c

A series of tin(II) amido complexes possessing *m*-terphenyl carboxylate ligands have been prepared. These complexes, namely $[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_2Ph_3)]_2$, $[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_3Mes_2)]_2$, and $[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_2Mes_2Me)]_2$ [Mes = 2,4,6-trimethylphenyl], are the first structurally characterized examples of tin(II) carboxylate complexes exhibiting discrete $Sn_2O_4C_2$ heterocyclic cores. Initial reactivity studies led to the isolation of a 1,3-diaza-2,4-distannacyclobutanediyl, $[(Mes_2C_6H_3CO_2)Sn(\mu\text{-}NSiMe_3)]_2$. This molecule possesses a Sn_2N_2 heterocyclic core and it was crystallised as both the CH_2Cl_2 and Et_2O solvates. Although the tin atoms in this molecule have a formal oxidation state of 3+, preliminary computational studies on this molecule suggest that it is best described as a ground state singlet. Finally, the X-ray crystal structure of $(CH_2Cl)(Cl)Sn[N(SiMe_3)_2]_2$, the product of oxidative addition of CH_2Cl_2 to $Sn[N(SiMe_3)_2]_2$, is also presented herein.

Introduction

The variety of bonding modes available to carboxylate anions (Fig. 1), coupled with their ability to readily shift from one mode to another, makes them one of the most versatile known ligand classes for main group and transition metal complexes.[1] Another important ligand class is the *m*-terphenyl substituent,[2] which can enforce low coordination numbers at a metal centre thus often leading to unprecedented bonding[3] and/or reactivity[4] at that centre. We[5,6] and others[7] have previously shown that when the carboxylate functional group is placed within the *m*-terphenyl pocket, unusual metal coordination motifs are readily accessible. Herein we present the preparation of a series of tin(II) carboxylate complexes and the results of initial reactivity studies of these complexes.

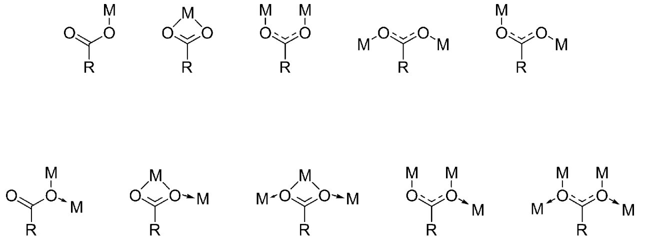

Fig. 1 Common bonding modes for carboxylate ligands.

Stannylenes (:SnR_2) were first isolated[8] more than a decade before the analogous carbenes[9] (:CR_2) and several stannylene derivatives are commercially available. We note that some aspects of stannylene chemistry have been less explored than carbene chemistry, likely due at least in part to the significant commercial interest in *N*-heterocyclic carbene chemistry *vis-á-vis* catalyst applications.[10] Our previous studies of the reactions of carbenes with simple reagents[11] prompted us to explore similar reactions with stannylenes. This investigation was further motivated by observation that although tin(II) carboxylates have long been studied,[12] and are implicated in a variety of catalytic processes,[13] commercial resins,[14] and even food safety,[15] structural data are relatively rare and composed mainly, though not exclusively,[15,16] of oxalate[17] and acetate[12b,18] complexes. This is in contrast to Sn(IV) carboxylate complexes, which are extremely well characterized.[19]

Results and discussion

Treatment of *m*-terphenyl carboxylic acids **1–3** with bis[bis(trimethylsilyl)amido] tin(II), $Sn[N(SiMe_3)_2]_2$, in anhydrous CH_2Cl_2 gives the Sn(II) carboxylate complexes **4–6** with concomitant loss of hexamethyldisilazane (Scheme 1). ^1H and ^{13}C NMR studies on the isolated products are consistent with the presence of *two* trimethylsilyl groups per *m*-terphenyl substituent.

Compounds **4–6** crystallise readily, and X-ray crystallographic studies reveal that the bulky carboxylate anion acts as a bridging bidentate ligand connecting two tricoordinate tin(II) atoms. This is in contrast to isoelectronic amidinate complexes, which exhibit a chelating rather than a bridging coordination mode.[20] The tin atoms in **4–6** exhibit the trigonal pyramidal geometry typical of divalent tin,[21] causing the resultant $Sn_2O_4C_2$ heterocyclic eight-membered cores to adopt a chair conformation (Fig. 2). The core structures of compounds **4–6** have not, to the best of our knowledge, been previously reported for tin(II) carboxylate complexes. The core structure is, however, reminiscent of

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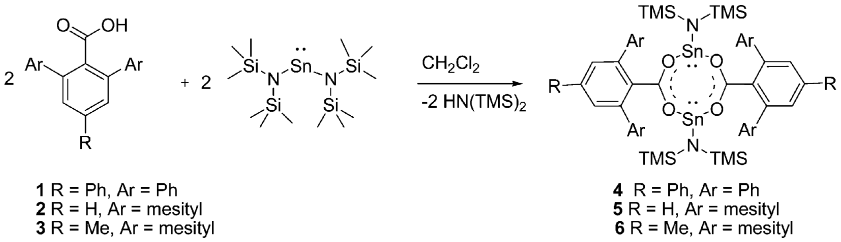
† CCDC reference numbers 618666–618671. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704588c



Scheme 1 Synthesis of tin(II) carboxylate complexes **4–6**.

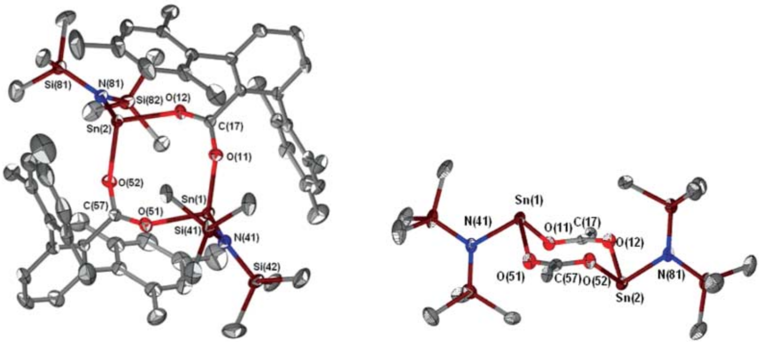


Fig. 2 Structure of $[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_3Mes_2)]_2$ **5** (left) and its heterocyclic core, which is common to **4–6** (right). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and CH_2Cl_2 solvent of crystallisation have been removed for clarity.

bis(trimethylsilyl)amido tin(II) triflate $[\{Sn(NR_2)(\mu\text{-}\eta^2\text{-}OTf)_2\}]$[22] in which the central core is a tin-containing eight-membered heterocyclic ring. The triflate derivative, in the solid-state, is a coordination polymer with extensive Sn · · · O interactions between adjacent eight-membered rings. In contrast, compounds **4–6** are discrete entities, and significant *intermolecular* interactions are likely precluded due to the large size of the *m*-terphenyl carboxylate ligands.

Although the somewhat greater steric demands of the 2,4,6-trimethylphenyl substituent in **5** and **6** compared to the phenyl substituent in **4** do not appear to have much impact on the solid state structural parameters of the $Sn_2O_4C_2$ heterocyclic core (Table 1), this does not hold true for their behaviour in solution. While routine ^1H and ^{13}C NMR spectroscopic studies revealed the expected signals for complexes **4–6**, the ^{119}Sn NMR studies were not as straightforward. The two 2,4,6-trimethylphenyl-substituted *m*-terphenyl derivatives each exhibited a single peak in the ^{119}Sn NMR spectrum, at δ 74 or 76 ppm for **5** and **6** respectively, but under identical conditions, no signal was observed in the ^{119}Sn NMR spectrum of **4**. Variable temperature studies to temperatures as low as −85 °C were inconclusive.

We note here that care must be taken during the preparation of **4–6** to ensure that a large excess of $Sn[N(SiMe_3)_2]_2$ is not used in the reaction. In the absence of other reagents such as the carboxylic acids **1–3**, $Sn[N(SiMe_3)_2]_2$ will react with the CH_2Cl_2 solvent to give the insertion product $(CH_2Cl)(Cl)Sn[N(SiMe_3)_2]_2$ **7**. In a single experiment where an excess of $Sn[N(SiMe_3)_2]_2$ was used, **7** was identified spectroscopically[23] in the reaction mixture, and its presence subsequently confirmed by single-crystal X-ray diffraction studies (Fig. 3). On the other hand, once **4–6** were formed, they did not appear to react with solvent, and in fact a molecule of CH_2Cl_2 was incorporated as a solvent of crystallisation in each case.

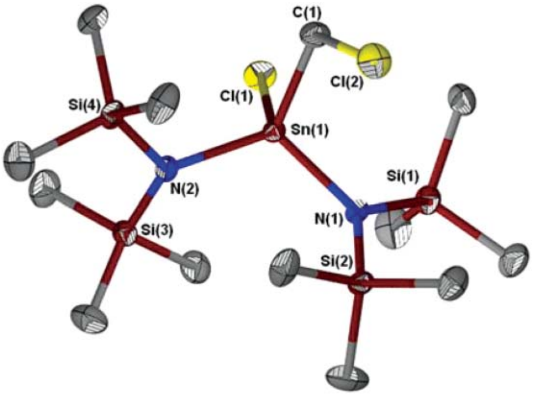


Fig. 3 Structure of $(CH_2Cl)(Cl)Sn[N(SiMe_3)_2]_2$ **7**. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been removed for clarity. Selected bond lengths (Å): Sn(1)–N(1) 2.0318(16); Sn(1)–N(2) 2.0270(17); Sn(1)–C(1) 2.160(2); Sn(1)–Cl(1) 2.3689(5); C(1)–Cl(2) 1.782(2). Selected bond angles (°): N(1)–Sn(1)–N(2) 116.50(7); N(1)–Sn(1)–Cl(1) 108.49(5); N(1)–Sn(1)–C(1) 109.66(8); N(2)–Sn(1)–C(1) 117.81(8); N(2)–Sn(1)–Cl(1) 102.34(5); Cl(1)–Sn(1)–C(1) 99.94(6).

To probe the reactivity of the *m*-terphenyl tin(II) carboxylate complexes, we attempted to remove an amido ligand from **5** through a protonolysis reaction. Studies have shown that $B(C_6F_5)_3{\cdot}H_2O$ is an excellent Brønsted acid, with a pK_a of 8.4 in acetonitrile.[24] This strong acid exhibits novel reactivity in main group chemistry, and was successfully used in the preparation of the first monoalumoxane complex.[25] We expected similar reactivity of $B(C_6F_5)_3{\cdot}H_2O$ with **5**. However, the reaction afforded compound **8**. On isolation, the crystalline product **8** exhibited a ^1H NMR spectrum consisting of a singlet with an integration corresponding to nine hydrogens at δ 0.11 ppm and the anticipated

Table 1 Selected structural data (bond lengths/Å, bond angles/°) for tin(II) carboxylate complexes **4–6**

4 (Ar = R = Ph)		**5** (Ar = 2,4,6-trimethylphenyl, R = H)		**6** (Ar = 2,4,6-trimethylphenyl, R = Me)	
Sn(1)–O(1)	2.243(2)	Sn(1)–O(11)	2.2175(16)	Sn(1)–O(1)	2.240(4)
		Sn(1)–O(51)	2.2194(18)		
Sn(1)–O(2)	2.199(2)	Sn(2)–O(12)	2.2222(17)	Sn(1)–O(2)	2.208(4)
		Sn(2)–O(52)	2.2407(16)		
O(1)–C(1)	1.262(3)	O(11)–C(17)	1.267(3)	O(1)–C(1)	1.257(7)
		O(12)–C(17)	1.264(3)		
O(2)–C(1)	1.259(4)	O(51)–C(57)	1.258(3)	O(2)–C(1)	1.259(7)
		O(52)–C(57)	1.263(3)		
Sn(1)–N(1)	2.072(2)	Sn(1)–N(41)	2.090(2)	Sn(1)–N(1)	2.093(5)
		Sn(2)–N(81)	2.087(2)		
Si(1)–N(1)	1.734(3)	Si(41)–N(41)	1.738(2)	Si(1)–N(1)	1.729(5)
		Si(42)–N(41)	1.733(2)		
Si(2)–N(2)	1.727(3)	Si(81)–N(81)	1.735(2)	Si(2)–N(2)	1.737(5)
		Si(82)–N(81)	1.742(2)		
Sn(1)···Sn(1)	4.397	Sn(1)···Sn(2)	4.411	Sn(1)···Sn(1)	4.557
O(1)–Sn(1)–O(2)	96.63(8)	O(11)–Sn(1)–O(51)	100.44(7)	O(1)–Sn(1)–O(2)	98.15(15)
		O(12)–Sn(2)–O(52)	99.91(6)		
N(1)–Sn(1)–O(1)	90.97(9)	N(41)–Sn(1)–O(11)	90.63(7)	N(1)–Sn(1)–O(1)	91.53(17)
		N(41)–Sn(1)–O(51)	89.79(8)		
N(1)–Sn(1)–O(2)	90.08(9)	N(81)–Sn(2)–O(12)	91.90(7)	N(1)–Sn(1)–O(2)	89.53(17)
		N(81)–Sn(2)–O(52)	90.42(7)		
Si(1)–N(1)–Si(2)	122.61(15)	Si(41)–N(41)–Si(42)	121.48(12)	Si(1)–N(1)–Si(2)	120.3(3)
Si(1)–N(1)–Sn(1)	113.18(13)	Si(41)–N(41)–Sn(1)	123.94(11)	Si(1)–N(1)–Sn(1)	116.1(3)
Si(2)–N(1)–Sn(1)	123.93(14)	Si(42)–N(41)–Sn(1)	114.58(12)	Si(2)–N(1)–Sn(1)	123.3(3)
		Si(81)–N(81)–Si(82)	120.14(12)		
		Si(81)–N(81)–Sn(2)	115.14(12)		
		Si(82)–N(81)–Sn(2)	124.72(11)		

peaks for an *m*-terphenyl ligand at δ 2.01 and 2.27 ppm. The upfield shift was assigned to a single trimethylsilyl group.

Curiously, as with compound **4**, no signal was observed in the *solution* state ^{119}Sn NMR studies on **8**, nor were variable temperature experiments conclusive. *Solid* state ^{119}Sn NMR studies were performed on samples of **8** and gave broad isotropic peaks at δ −108 and −121 ppm. Unfortunately these studies were hampered by the extreme air and moisture sensitivity of the compound.

In order to obtain the atom connectivity of the molecule we performed crystallographic studies and found that the isolated compound was a 1,3-diaza-2,4-distannacyclobutanediyl **8**·CH_2Cl_2 (Fig. 4), formed through an unknown mechanism. This molecule is structurally similar to that described in a recent report by Lappert, specifically $\{[ClSn(\mu\text{-}NSiMe_3)]_2\}_\infty$ **9**.[26] Lappert's group also reported a rational, although nonetheless curious, synthetic procedure for the preparation of **9** in high yield, which we followed for subsequent preparations of **8**. Specifically, compound **5** was treated with two equivalents of AgOCN in Et_2O, to give **8** (Scheme 2). The carbodiimide by-product $Me_3SiN{=}C{=}NSiMe_3$ was identified in the IR spectrum of the crude reaction mixture,

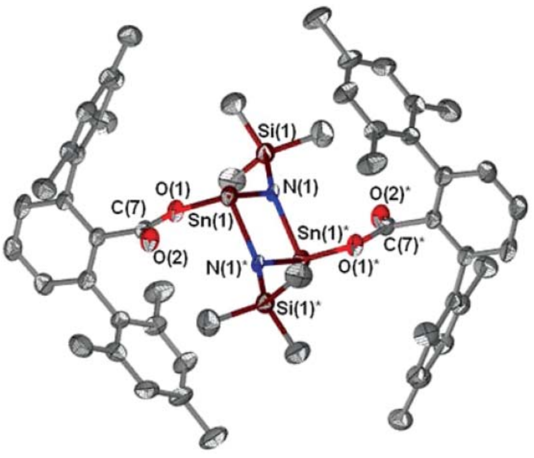
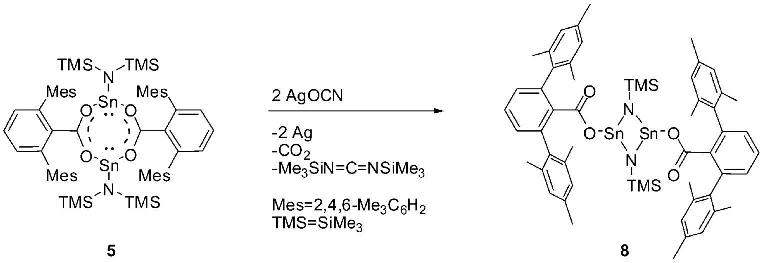


Fig. 4 Structure of $[(Mes_2C_6H_3CO_2)Sn(\mu\text{-}NSiMe_3)]_2$ **8**·CH_2Cl_2. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms and solvent of crystallisation have been removed for clarity.



5

8

Scheme 2 Rational synthesis of $[(Mes_2C_6H_3CO_2)Sn(\mu\text{-}NSiMe_3)]_2$ **8**.

and metallic silver precipitated. In the course of these experiments we also crystallographically characterised **8**·Et_2O. Elemental analyses on the bulk materials are in accord with the results obtained by crystallography.

The structural parameters of the two solvates (Table 2) are comparable. Neither **8**·CH_2Cl_2 nor **8**·Et_2O showed any significant contact between the tin atoms and the solvent of crystallisation. The carboxylate coordination was found to be terminal monodentate, with an Sn–O bond length of 2.149(3) Å in **8**·CH_2Cl_2 or 2.169(2) Å in **8**·Et_2O. The somewhat longer formally non-bonded Sn · · · O distances of 2.628(3) and 2.573(2) Å, respectively, are close enough to suggest possible intramolecular carboxylate shifting in solution. The nitrogen atoms in **8** are almost trigonal planar, with $\sum N = 355.73°$ (**8**·CH_2Cl_2) or 354.11° (**8**·Et_2O). As in **4–6**, the tin atoms show trigonal pyramidal geometry, however the N–Sn–N and N–Sn–O angles in **8**, which range from 75.94(9) to 93.17(8)°, are much more acute than they are in **5**. The Sn · · · Sn separation of 3.3896(5) Å in **8**·CH_2Cl_2 or 3.404(4) Å in **8**·Et_2O, suggests no transannular bonding. The N–Si bond lengths of 1.677(3) Å (**8**·CH_2Cl_2) or 1.674(2) Å (**8**·Et_2O) are significantly shorter than those in **4–6**, while the N–Sn bond lengths are slightly longer, ranging from 2.116(3) to 2.198(2) Å. These structural parameters are similar to those in the related compound $\{[ClSn(\mu\text{-}NSiMe_3)]_2\}_\infty$ **9**.[26]

Extended intermolecular Sn · · · Cl coordination in **9** gives rise to infinite one-dimensional chains in the solid state, however these interactions are disrupted in solution, leading to a dramatic solvent dependence in the reported solution state ^{119}Sn NMR data, with chemical shifts ranging from δ −83 [PhMe/C_6D_6] to −285 [$(Me_2N)_3PO$/PhMe/C_6D_6] ppm.[26] These values are all significany upfield from the isotropic solid state chemical shift of **9** at δ −17 ppm. This effect is exacerbated by the ability of the more polar solvents to act as donors to the electron-deficient tin centre. The isotropic solid state chemical shifts of **8** (−108 and −121 ppm) are most similar to the solution state chemical shift of **9** in CD_2Cl_2. This is not surprising because in both cases the predominant species should be disctrete Sn_2N_2 heterocycles. In the case of $\{[ClSn(\mu\text{-}NSiMe_3)]_2\}_\infty$ **9**, the CD_2Cl_2 breaks the intermolecular Sn–Cl bonds but does not form tin–solvent interactions. For **8**, the bulky *m*-terphenyl substituent prevents both inter- and intramolecular interactions at tin.

Table 2 Selected structural data (bond lengths/Å, bond angles/°) for **8**·CH_2Cl_2 and **8**·Et_2O[a]

8·CH_2Cl_2		**8**·Et_2O	
Sn(1)–N(1)	2.194(3)	Sn(1)–N(1)	2.198(2)
Sn(1)–N(1)*	2.116(3)	Sn(1)–N(1)*	2.119(2)
Sn(1)–O(1)	2.149(3)	Sn(1)–O(1)	2.169(2)
Sn(1) · · · O(2)	2.628(3)	Sn(1) · · · O(2)	2.573(2)
N(1)–Si(1)	1.677(3)	N(1)–Si(1)	1.674(2)
O(1)–C(7)	1.286(5)	O(1)–C(7)	1.286(4)
O(2)–C(7)	1.231(5)	O(2)–C(7)	1.234(4)
Sn(1) · · · Sn(1)*	3.3896(5)	Sn(1) · · · Sn(1)*	3.404(4)
N(1)–Sn(1)–N(1)*	76.28(11)	N(1)–Sn(1)–N(1)*	75.94(9)
O(1)–Sn(1)–N(1)*	92.72(11)	O(1)–Sn(1)–N(1)*	93.17(8)
O(1)–Sn(1)–N(1)	81.98(10)	O(1)–Sn(1)–N(1)	81.77(8)
Sn(1)–N(1)–Sn(1)*	103.72(11)	Sn(1)–N(1)–Sn(1)*	104.06(9)
Sn(1)–N(1)–Si(1)	123.99(15)	Sn(1)–N(1)–Si(1)	123.05(12)
Sn(1)*–N(1)–Si(1)	128.02(16)	Sn(1)*–N(1)–Si(1)	127.00(12)

[a] Symmetry transformations used to generate equivalent atoms: * −x,−y,−z + 1.

Only one other heavy (*i.e.*, Si, Ge, Sn, Pb) Group 14/15 heterocycle analogous to **8** and **9** has been reported to date, namely $[(2,6\text{-}Dipp_2C_6H_3)C_6H_2Ge(\mu\text{-}NSiMe_3)]_2$ (Dipp = 2,6-diisopropylphenyl) **10**.[27] Molecule **10**, in our opinion, is dramatically different from either **8** or **9**, and this is likely because of the following two reasons. First, **10** possesses a strong and somewhat inflexible Ge–C bond whereas the tin derivatives have flexible carboxylate and chloride counterions, *i.e.*, good leaving groups. Secondly, both the size and electronegativity of tin are significantly different from those of the germanium analogue. For these reasons, marked differences in bonding should be anticipated between that observed for **8** and **9** and that observed for **10**.

Using a simple fragment analysis, compound **8** can be viewed as a dimer of the tin iminyl radical, $[(Mes_2C_6H_3CO_2)Sn(NSiMe_3)]^\bullet$, for which persistent examples of dicoordinate tin aminal radicals are, to our knowledge, unknown. This model offers several attractive features, and also, perhaps, provides insight into new synthetic directions. First of all, the tin–nitrogen bonds in both complexes **8** and **9** are quite long, and indeed these are longer than in the starting materials. This again is quite surprising since one would anticipate that an imide–tin bond would be shorter than a tin–amide bond. Secondly, this model avoids the invocation of the peculiar oxidation state three for tin. Indeed, the Mössbauer spectra obtained by Lappert clearly suggests that there is nothing particularly unusual for the tin center in **9**.[26] In our opinion, and indeed this is reflected by an assessment of the products formed in the reaction, the nitrogen fragment, which enters the ring to help satisfy its valency, is the primary reaction centre. In the initial report of **9**, the authors concluded that the Sn_2N_2 ring behaved like a typical diamagnetic material with a 6-π electron 4-centre core (pseudo-aromatic).[26] This is in contrast to the germanium analogue **10**[27,28] and other isoelectronic heterocycles including P_2C_2,[29] B_2P_2,[30] and E_2N_2 (E = S, Se, Te)[31] which have been shown through extensive experimental and theoretical studies to have varying degrees of biradical character.[32] As we mentioned above, we are reluctant to directly compare our results, and those for compound **9**, with the germanium analogue **10**. We note that the experimental data for **8** (sharp NMR resonances, the lack of an unusual absorption in the visible spectrum, and absence of an EPR signal) is more consistent with the ground state singlet **9** than the apparent biradical **10**.

In order to shed light on the bonding observed in the unusual compound **8**, we performed DFT calculations (B3LYP/LANL2DZ) using Gaussian 98[33] on a model compound of **8**, namely $[HCO_2Sn(\mu\text{-}NSiMe_3)]_2$. The results of this study, although not comprehensive, have provided some insight into the bonding (Fig. 5) and broadly parallel those obtained for **9**.[26] Both the singlet and the triplet states of $[HCO_2Sn(\mu\text{-}NSiMe_3)]_2$ were optimized and the singlet was found to be by 54 kJ mol^{-1} more stable than the triplet, which is consistent with the value of 76 kJ mol^{-1} reported by Lappert for compound **9**.[26] The calculated singlet–triplet gap is small and alters its sign with the deformation of molecular structure: from 68 kJ mol^{-1} for the singlet-optimized geometry to −10 kJ mol^{-1} for the triplet-optimized geometry.

It is tempting to suggest that a standard four-centred six-π electron system is at play in **8**, but this clearly oversimplifies the situation given the well-recognized poor 5p–π 2p–π overlap

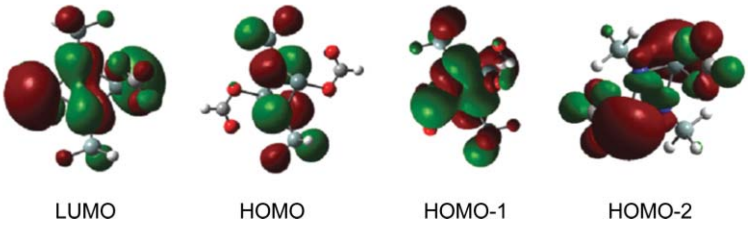


Fig. 5 Frontier molecular orbitals of $[HCO_2Sn(\mu\text{-}NSiMe_3)]_2$ calculated for its crystallographic geometry.

that would be required between the tin and nitrogen atoms.[34] The planarity of the Sn_2N_2 core could be taken as evidence for π-electron delocalisation within the ring, but the low inversion barrier for nitrogen as well as the steric strain imparted by the bulky ligands can easily enforce planarity. The presence of a silyl group on the nitrogen further complicates matters, as this substituent is known to engage in negative hyperconjugation with four-centre six π-electron systems (π*–σ* overlap), thereby lowering the energy of the LUMO.[35] This effect is likely to be at least partially responsible for the remarkably short N–Si bond observed in both **8** and **9**. We note that the HOMO is located primarily on the nitrogen atoms, and this is reminiscent of the bonding structure suggested for the Nieke-type biradicals, where the HOMO is primarily based on the most electronegative element, specifically carbon *versus* phosphorus. In our case, the HOMO is primarily based on the two nitrogen sites, that is to say the HOMO is based primarily on the most electronegative element within the ring. In light of these results, further theoretical and experimental work is required before a definitive statement can be made about the nature of the bonding in compound **8**, and indeed in many other main group biradicaloid complexes as well.[32]

Conclusions

In conclusion, we have presented a series of tin complexes that illustrate the versatility of the *m*-terphenyl carboxylate ligand in low-valent main group chemistry. In one case, the carboxylate acts as a bridging bidentate ligand and in the other case is an extra-annular ligand stabilising an unusual tin–nitrogen heterocycle. The complexes **4–6** exhibit a chair-like $Sn_2O_4C_2$ core which is a previously unknown structural motif for tin(II) compounds. Loss of [$SiMe_3$] and rearrangement of the carboxylate-bridged eight-membered dimer gives an amido-bridged four-membered heterocyclic molecule **8** possessing a formally trivalent tin centre. The experimental and calculated properties of this Sn_2N_2 compound agree with those reported for $\{[ClSn(\mu\text{-}NSiMe_3)]_2\}_\infty$ **9**[26] and also suggest that AgOCN oxidation is a general route to such molecules. By incorporating a *m*-terphenyl ligand, we were able to isolate the Sn_2N_2 core free from *inter*-molecular interactions, a feature that should be very useful for future studies of this unusual system.

Experimental

General experimental

A nitrogen-atmosphere MBraun UL-99–245 dry box and standard Schlenk techniques on a double manifold vacuum line were used in the manipulation of air and moisture sensitive compounds. Solution-state NMR spectra were recorded in 5 mm tubes at Simon Fraser University on Bruker AMX 400 or 600 MHz spectrometers or Varian AS 400 or 500 MHz spectrometers, or at Dalhousie University by Dr Mike Lumsden on a Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from $SiMe_4$ (^1H and ^{13}C), or $SnMe_4$ (^{119}Sn). ^1H and ^{13}C spectra are calibrated to the residual signal of the solvent. ^{119}Sn spectra are calibrated to the external $SnMe_4$ standard. Solid-state ^{119}Sn NMR spectra were recorded at the University of Alberta on a Bruker Avance 500 NMR spectrometer, operating at a frequency of 186.6 MHz for ^{119}Sn with ramped CP/MAS (cross-polarization, with magic angle spinning) and TPPM (two-pulse phase modulated) decoupling. The MAS frequencies were 6 and 11 kHz, the contact time was 7 ms, the recycle delay was 3 s and up to 29168 transients were co-added.

Infrared spectra were obtained using a Bomem MB spectrometer with the % transmittance values reported in cm^{-1}. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Elemental analyses were obtained at Simon Fraser University by Mr M. K. Yang on a Carlo Erba Model 1106 CHN analyzer. Anhydrous solvents were obtained from an MBraun Solvent Purification system, or were purchased from Aldrich and used without further purification. $Sn[N(SiMe_3)_2]_2$ was purchased from Strem and used as received. All other reagents and solvents were purchased from commercial sources and used without further purification, except deuterated solvents for NMR experiments, which were dried over P_2O_5 and distilled prior to use.

Synthetic procedures

2,4,6-Triphenylbenzoic acid (1). Prepared according to a variation of literature procedures.[36] Under an inert atmosphere, *n*-BuLi (20 mL, 1.6 M in hexanes) was added dropwise to a suspension of 2,4,6-triphenylbromobenzene (10.0 g, 26.0 mmol) in *ca.* 100 mL anhydrous Et_2O. The mixture was allowed to stir for 3.5 h and then CO_2 was bubbled through the solution for 1.5 h. The reaction was quenched with H_2O and dilute (*ca.* 1 M) HCl, then extracted with Et_2O. The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under vacuum to give a yellow powder that was recrystallized from CH_2Cl_2. Slow evaporation of the CH_2Cl_2 solution resulted in a white powder. Yield: 6.07 g (67%), mp = 259–260 °C (lit.,[36] 253–255 °C). ^1H NMR (CD_2Cl_2, 499.768 MHz) δ 7.70 (d, J = 7 Hz, 2H), 7.66 (s, 2H), 7.40–7.51 (m, 13H). IR (Nujol mull) ν 1696 (vs), 1597 (m), 1575 (w), 1561 (w), 1493 (m), 1445 (m), 1399 (w), 1293 (s), 1133 (w), 1076 (w), 886 (w), 777 (s), 765 (m), 699 (vs).

2,6-Bis(2,4,6-trimethylphenyl)benzoic acid[37] (2). Prepared according to the same procedure as **1**, beginning with 2,6-bis(2,4, 6-trimethylphenyl)iodobenzene (5.0 g, 11.4 mmol). The crude product was recrystallized from Et_2O to give a white powder. Yield: 3.17 g (78%), mp = 292–295 °C. ^1H NMR ($CDCl_3$, 400.136 MHz) δ 7.47 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2 H), 6.97 (s, 4H), 2.36 (s, 6 H), 1.99 (s, 12 H). $^{13}C\{^1H\}$ ($CDCl_3$, 125.680 MHz) δ 136.7, 128.5, 128.0, 31.2, 20.6 (quaternary carbons not observed). IR (Nujol mull) ν 3208 (br), 1733 (vs), 1705 (s), 1611 (m), 1577 (m), 1365 (s), 1216 (vs), 1127 (m), 844 (m), 820 (m), 799 (m), 791 (m), 688 (m). Anal. calcd for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 83.41; H, 7.57%.

4-Methyl-2,6-bis(2,4,6-trimethylphenyl)benzoic acid (3). Prepared according to the same procedure as **1**, beginning with 4-methyl-2,6-bis(2,4,6-trimethylphenyl) iodobenzene (3.00 g, 6.61 mmol). The crude product was recrystallized from hexanes to give a white powder. Yield = 0.90 g (37%), mp = 257–259 °C. ^1H NMR (C_6D_6, 499.767 MHz) δ 6.86 (s, 4H), 6.73 (s, 2H), 2.20 (s, 12H), 2.19 (s, 6H), 2.03 (s, 3H). $^{13}C\{^1H\}$ ($CDCl_3$, 125.679 MHz) δ 169.5, 140.4, 139.6, 137.0, 136.9, 136.5, 130.0, 129.2, 127.9, 21.4, 20.7, 20.6. IR (Nujol mull) ν 3208 (br), 1731 (vs), 1699 (m), 1613 (m), 1597 (w), 1573 (w), 1224 (vs), 1186 (m), 1160 (m), 1110 (s), 864 (m), 844 (s), 831 (m), 768 (m). Anal. calcd for $C_{26}H_{28}O_2$: C, 83.83; H, 7.58. Found: C, 83.67; H, 7.49%.

$[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_2Ph_3)]_2$ (4). Under an inert atmosphere, a solution of $Sn[N(SiMe_3)_2]_2$ (1.38 g, 3.14 mmol) in 5 mL anhydrous CH_2Cl_2 was added dropwise to a stirring suspension of 2,4,6-triphenylbenzoic acid **1** (1.00 g, 2.85 mmol). After 1.5 h, the solution was decanted from a brown precipitate that was recrystallized from warm hexanes to give colourless crystals. Yield = 0.59 g (32%), mp = 242–247 °C (decomp.). ^1H NMR (CD_2Cl_2, 499.767 MHz) δ 7.69 (d, J = 7.6 Hz, 2H), 7.57 (s, 2H), 7.39–7.49 (m, 13H), 0.00 (s, 18H). ^{13}C NMR$\{^1H\}$ (CD_2Cl_2, 125.678 MHz) δ 141.0, 139.9, 129.2, 128.9, 128.8, 127.9, 127.7, 127.2, 5.3 (quaternary carbons not observed). IR (Nujol mull) ν 3083 (w), 3058 (w), 3034 (w), 1595 (s), 1583 (m), 1567 (vs), 1544 (vs), 1503 (s), 1496 (s), 1439 (s), 1346 (m), 1262 (m), 1252 (m), 1241 (s), 1194 (w), 1150 (m), 1073 (w), 1056 (w), 1030 (w), 936 (vs), 869 (vs), 849 (s), 833 (s), 790 (m), 778 (m), 759 (s), 740 (w), 698 (s), 687 (m), 670 (m). Anal. calcd for $C_{64}H_{90}N_2O_4Si_4Sn_2$: C, 59.08; H, 6.97; N, 2.15. Found: C, 58.91; H, 5.43; N, 2.41%.

$[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_3Mes_2)]_2$ (5). Under an inert atmosphere, a solution of $Sn[N(SiMe_3)_2]_2$ (1.35 g, 3.07 mmol) in 5 mL anhydrous CH_2Cl_2 was added dropwise to a stirring suspension of 2,6-bis(2,4,6-trimethylphenyl)benzoic acid **2** (1.00 g, 2.79 mmol) in 15 mL anhydrous CH_2Cl_2. Over the course of 5.5 h, the solution faded from bright orange to very pale yellow. It was then concentrated under vacuum and cooled to −30 °C to give colourless crystals. Yield = 1.47 g (83%) mp = 168–169 °C. ^1H NMR (C_6D_6, 499.767 MHz) δ 6.92 (d, J = 7 Hz, 2H), 6.89 (s, 4H), 6.87 (br, 1H), 2.27 (s, 6H), 2.17 (s, 12H), 0.09 (s, 18H). $^{13}C\{^1H\}$ (CD_2Cl_2, 125.678 MHz) δ 137.2, 136.8, 128.6, 128.0, 21.0, 20.8, 2.32 (quaternary carbons not observed). ^{119}Sn (C_6D_6, 223.867 MHz) δ 74.43. IR (Nujol mull) ν 1613 (m), 1580 (m), 1538 (vs), 1442 (s), 1257 (m), 1245 (s), 1183 (w), 1146 (w), 1065 (w), 1033 (w), 926 (vs), 866 (vs), 849 (vs), 833 (s), 790 (m), 780 (m), 755 (m), 740 (m), 710 (w), 699 (w), 670 (m). Anal. calcd for $C_{62}H_{86}N_2O_4Si_4Sn_2$: C, 58.49; H, 6.81; N, 2.20. Found C, 57.99; H, 6.63; N, 2.27%.

$[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_2Mes_2Me)]_2$ (6). Prepared according to the same procedure as **7**, beginning with 4-methyl-2,6-bis(2,4,6-trimethylphenyl)benzoic acid **3** (0.45 g, 1.21 mmol). Yield = 0.47 g (60%), mp = 151–155 °C. ^1H NMR (C_6D_6, 499.767 MHz) δ 6.85 (s, 4H), 6.69 (s, 2H), 2.21 (s, 12H), 2.20 (s, 6H), 1.98 (s, 3H), 0.00 (s, 18H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.678 MHz) δ 137.8, 137.6, 136.6, 136.4, 136.2, 129.2, 128.8, 127.9, 21.3, 21.0, 20.8, 5.2. ^{119}Sn (C_6D_6, 223.867 MHz) δ 75.86. IR (Nujol mull) ν 1715 (w), 1612 (m), 1597 (m), 1573 (m), 1536 (vs), 1486 (m), 1246 (s), 1164 (w), 1121 (w), 1102 (w), 1033 (w), 921 (s), 865 (vs), 849 (vs), 834 (s), 790 (m), 757 (w), 709 (w), 669 (m), 608 (s). Anal. calcd for $C_{64}H_{90}N_2O_4Si_4Sn_2$: C, 59.08; H, 6.97; N, 2.15. Found: C, 58.78; H, 6.68; N, 2.01%.

$[(Mes_2C_6H_3CO_2)Sn(\mu\text{-}NSiMe_3)]_2$ (8). Under an inert atmosphere, silver cyanate (0.12 g, 0.80 mmol) was added to a solution of $[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_3Mes_2)]_2$ **5** (0.46 g, 0.36 mmol) in 15 mL anhydrous Et_2O. The beige suspension was stirred overnight in the dark, then filtered through glass wool and Celite and cooled to −30 °C to give colourless crystals. Yield = 0.23 g (57%), mp = 170 °C (decomp.). ^1H NMR (CD_2Cl_2, 500.132 MHz) δ 7.48 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 6.83 (s, 4H), 2.27 (s, 6 H), 2.01 (s, 12 H), 0.11 (s, 9H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.772 MHz) δ 138.0, 137.2, 136.9, 136.6, 128.9, 127.7, 127.5, 20.9, 20.1, 1.6. ^{119}Sn (186.6 MHz, CP/MAS) δ −100. IR (Nujol mull) ν 2729 (w), 1715 (w), 1610 (m), 1588 (m), 1574 (s), 1556 (s), 1519 (s), 1484 (m), 1461 (vs), 1359 (vs), 1309 (w), 1259 (s), 1249 (s), 1180 (w), 1140 (m), 1101 (m), 1088 (m), 1060 (m), 1032 (m), 938 (w), 847 (vs), 810 (m), 785 (s), 771 (m), 752 (m), 737 (m), 709 (s), 667 (w). Anal. calcd for $C_{56}H_{68}N_2O_4Si_2Sn_2$: C, 59.69; H, 6.08; N, 2.49. Found: C, 59.90; H, 5.97; N, 2.67%.

Crystallographic studies

Data collection (compounds 4 and 6). Single crystals of **4** or **6** were mounted on a glass fibre. Data were collected at the temperature indicated in Table 3 on a Nonius Kappa-CCD diffractometer with COLLECT.[38] The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO.[39] The data were scaled using SCALEPACK.[39] The SHELXTL-NT V6.1 suite of programs[40] was used to solve the structure by direct methods. Subsequent difference Fourier transformations allowed the remaining atoms to be located. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective heavy atoms.

Data collection (compounds 5, 7, and 8·Et_2O). Single crystals of **5**, **7**, or **8**·Et_2O were coated with oil (Paratone 8277, Exxon), collected on top of the nylon fibre of a CryoLoopTM (diameter of the nylon fibre: 10 microns; loop diameter 0.2–0.3 mm; Hampton Research, USA) that had previously been attached using epoxy resin to a metallic pin. All measurements were made on a Nonius Kappa CCD 4-Circle Kappa FR540C diffractometer using monochromated Mo-K_α radiation (λ = 0.71073 Å) at the temperature indicated in Tables 3 (**5**) and 4 (**7**, and **8**·Et_2O). Cell parameters were initially retrieved using the COLLECT[38] software, and refined with the HKL DENZO and SCALEPACK software,[39] that was also used for data reduction. The structure

Table 3 Crystallographic data for compounds **4–6**

Compound name (no.)	$[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_2Ph_3)]_2$ (**4**)	$[(Me_3Si)_2NSn(\mu\text{-}O_2CC_6H_3Mes_2)]_2$ (**5**)	$[(Me_3Si)_2NSn(\mu\text{-}O_2\ CC_6H_2Mes_2Me)]_2$ (**6**)
Formula	$C_{64}H_{74}Cl_4N_2O_4Si_4Sn_2$	$C_{63}H_{88}Cl_2N_2O_4Si_4Sn_2$	$C_{66}H_{94}Cl_4N_2O_4Si_4Sn_2$
M	1426.79	1357.99	1470.97
T/K	150(2)	173(2)	150(2)
Colour	Colourless	Colourless	Colourless
Size/mm	0.125 × 0.20 × 0.225	0.25 × 0.25 × 0.25	0.125 × 0.30 × 0.40
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2/c$	$P\bar{1}$
a/Å	10.429(2)	17.2290(2)	11.8023(6)
b/Å	13.276(3)	19.5480(2)	12.5695(9)
c/Å	14.405(3)	20.4440(2)	14.2170(10)
α/°	104.92(3)	90	67.446(3)
β/°	110.62(3)	95.4530(6)	65.690(2)
γ/°	101.70(3)	90	76.473(3)
V/Å^3	1706.1(6)	6854.23(13)	1767.8(2)
Z	1	4	1
D_{calc}/Mg m^{-3}	1.389	1.316	1.382
μ/m^{-1}	1.004	0.920	0.971
$R_1{}^a$	0.0348	0.0368	0.0635
$wR_2{}^b$	0.0737	0.0716	0.1723
CCDC no.	618667	618668	618669

[a] $R_1 = [\sum\|F_o| - |F_c\|]/[\sum|F_o|]$ for $[F_o{}^2 > 2\sigma(F_o{}^2)]$. [b] $wR_2 = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

Table 4 Crystallographic data for **7**, **8**·CH_2Cl_2 and **8**·Et_2O

Compound name (no.)	$(CH_2Cl)(Cl)Sn[N(Si\ Me_3)_2]_2$ (**7**)	$[(Mes_2C_6H_3CO_2)Sn\ (\mu\text{-}NSiMe_3)]_2$ (**8**·CH_2Cl_2)	$[(Mes_2C_6H_3CO_2)Sn(\mu\text{-}NSiMe_3)]_2$ (**8**·Et_2O)
Formula	$C_{13}H_{38}Cl_2N_2Si_4Sn$	$C_{29}H_{36}Cl_2NO_2SiSn$	$C_{60}H_{78}N_2O_5Si_2Sn_2$
M	524.40	648.29	1200.80
T/K	173(2)	223(2)	173(2)
Colour	Colourless	Colourless	Colourless
Size/mm	0.15 × 0.20 × 0.20	0.2 × 0.45 × 0.45	0.20 × 0.20 × 0.25
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.55900(10)	10.5733(6)	10.8922(3)
b/Å	11.3010(2)	11.8229(6)	11.7957(3)
c/Å	14.9150(3)	13.8362(7)	12.3240(3)
α/°	105.9710(12)	67.2930(10)	77.2409(16)
β/°	96.8970(13)	79.9680(10)	75.5426(16)
γ/°	108.9690(14)	89.7190(10)	87.3334(17)
V/Å^3	1276.35(4)	1567.46(14)	1495.34(7)
Z	2	2	1
D_{calc}/Mg m^{-3}	1.365	1.374	1.333
μ/mm^{-1}	1.397	1.048	0.922
$R_1{}^a$	0.0247	0.0433	0.0427
$wR_2{}^b$	0.0562	0.1173	0.0920
CCDC no.	618666	618670	618671

[a] $R_1 = [\sum\|F_o| - |F_c\|]/[\sum|F_o|]$ for $[F_o{}^2 > 2\sigma(F_o{}^2)]$. [b] $wR_2 = \{[\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum w(F_o{}^2)^2]\}^{1/2}$.

was solved using direct methods using SIR-97[41] and refined by full-matrix least-squares method on F^2 with SHELXL97-2.[42] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom.

Data collection (compound 8·CH_2Cl_2). A single crystal of **8**·CH_2Cl_2 was mounted on a glass fibre and centred on a Siemens 1 K SMART/CCD diffractometer. Data were collected at the temperature indicated in Table 4 using Mo (K_α) radiation. Lorentz and polarization corrections were applied and data were corrected for absorption using redundant data and the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structures. Refinement was conducted using full-matrix least-squares calculations and SHELX-TL PC V 5.03. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as riding models and were updated after each refinement.

Acknowledgements

The authors thank Dr Hilary Jenkins (SMU) and Dr Michael Jennings (UWO) for collection of X-ray crystallographic data. Thanks also to Michelle Hauser and Sarah Khoo for their synthetic contributions. JACC and REW acknowledge support from the Canada Research Chairs Program and the Canadian

Foundation for Innovation, and the Natural Sciences and Engineeering Research Council of Canada.

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