Self-assembly using stannylplatinum(IV) halide complexes as ligands for organotin halides

Michael C. Janzen, Michael C. Jennings, and Richard J. Puddephatt

Abstract: The possibility of forming extended structures by self-association using transition metal halides as donors to organotin acceptors has been investigated. The stannylplatinum(IV) complex $[PtClMe_2(SnMe_2Cl)(bu_2bpy)]$ forms a 1:1 adduct $[PtClMe_2(SnMe_2Cl)(bu_2bpy)]\cdot Me_2SnCl_2$ with Me_2SnCl_2 in which the organoplatinum complex acts as a donor to the organotin halide. Similarly, $[PtClMe_2(SnMeCl_2)(bu_2bpy)]$ forms adducts $[PtClMe_2(SnMeCl_2)(bu_2bpy)]\cdot MeSnCl_3$ or $[PtClMe_2(SnMeCl_2)(bu_2bpy)]\cdot Me_2SnCl_2$, and $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]$ forms $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]\cdot Me_2SnCl_2$. Structure determinations on selected compounds show that the donor is the Pt-Cl group and the acceptor tin centre is 5-coordinate. In the similar bromo complex $[PtBrMe_2(SnMeBr_2)(bu_2bpy)]\cdot Me_2SnBr_2$ both the Pt-Br and PtSn-Br groups coordinate to the Me_2SnBr_2 acceptor with short (3.14 or 3.29 Å) and long (3.99 or 4.05 Å) contacts, respectively, so that the acceptor tin centre adopts distorted octahedral stereochemistry in the solid state and a folded polymeric structure is formed. Reaction of $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]$ with AgO_3SCF_3 yields the complex $[\{PtClMe_2(bu_2bpy)\}(\mu\text{-}SnCl_2)\{PtMe_2(bu_2bpy)O_3SCF_3\}]$, which is fluxional in solution.

Key words: platinum, tin, self-assembly, coordination chemistry, organometallics.

Résumé : On a étudié la possibilité de former des structures étendues par autoassociation en utilisant des halogénures de métaux de transition comme donneurs à des composés organostanniques agissant comme accepteurs. Le complexe stannylplatine(IV) $[PtClMe_2(SnMe_2Cl)(bu_2bpy)]$ et le Me_2SnCl_2 forment un adduit 1:1 $[PtClMe_2(SnMe_2Cl)(bu_2bpy)]\cdot Me_2SnCl_2$ dans le complexe organoplatine agit comme donneur pour l'halogénure d'organoétain. De la même manière, $[PtClMe_2(SnMeCl_2)(bu_2bpy)]$ forme les adduits $[PtClMe_2(SnMeCl_2)(bu_2bpy)]\cdot MeSnCl_3$ ou $[PtClMe_2(SnMeCl_2)\text{-}(bu_2bpy)]\cdot Me_2SnCl_2$ alors que $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]$ forme $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]\cdot Me_2SnCl_2$. Des déterminations de structure effectuées sur des composés choisis montrent que le donneur est le groupe Pt-Cl et que le centre étain accepteur est pentacoordiné. Dans le complexe bromé semblable $[PtBrMe_2(SnMeBr_2)(bu_2bpy)]\cdot Me_2SnBr_2$ les deux groupes Pt-Br et PtSn-Br se coordonnent à l'accepteur Me_2SnBr_2 avec des contacts respectivement courts (3,14 ou 3,29 Å) et longs (3,99 ou 4,05 Å) qui font que le centre étain accepteur adopte une stéréochimie octaédrique déformée à l'état solide et qu'il y a formation d'une structure polymérique repliée. La réaction du $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)]$ avec le AgO_3SCF_3 conduit à la formation du complexe $[\{PtClMe_2(bu_2bpy)\}_2(\mu\text{-}SnCl_2)\{PtMe_2(bu_2bpy)O_3SCF_3\}]$ qui, en solution, est en état de fluxion.

Mots clés : platine, étain, autoassemblage, chimie de coordination, organométalliques.

[Traduit par la Rédaction]

Introduction

The oxidative addition of the tin–halogen bond in organotin(IV) halides to transition-metal complexes is well established and provides an easy synthesis of stannylplatinum(IV) halides (1–7). For example, the oxidative addition of Me_3SnI to $[PtMe_2(bu_2bpy)]$ (**1**) (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) gives $[PtIMe_2(Me_3Sn)(bu_2bpy)]$ (1), which forms a complex $[PtIMe_2(SnMe_3)(bu_2bpy)]\cdot Me_3SnI$ by coordination of the Pt-I donor to the Me_3SnI acceptor, as shown in Scheme 1 (8). It was argued that the Pt-I group *trans* to Me_3Sn is polarized $Pt^{\delta+}\text{-}I^{\delta-}$, and as a result the iodide is a strong enough donor to form a complex with the weak acceptor Me_3SnI (9, 10). The platinum complex thus acts as a ligand for Me_3SnI through the Pt-I group.

Trimethyltin iodide is a tetrahedral monomer in the solid state, but many other organotin halides undergo self-association in the solid state (9–11). For example, Me_2SnCl_2 self-associates to form one-dimensional chains (Sn—Cl = 2.40(4) Å, Sn···Cl = 3.54(5) Å), and $MeSnCl_3$ also undergoes association by weak bridging through two of the three chlorine atoms (Sn—Cl = 2.283(2) Å, 2.318(1) Å; Sn···Cl = 3.714(2) Å) as illustrated in Chart 1 below (12, 13). The dimethyltin dihalides can also form adducts with one or two halide ions in which the tin centres adopt distorted trigonal bipyramidal or octahedral stereochemistry, respectively (Chart 1); they are stronger acceptors than the trimethyltin halides (14).

Based on the structures shown in Scheme 1 and Chart 1, it was considered possible that association between stannyl-

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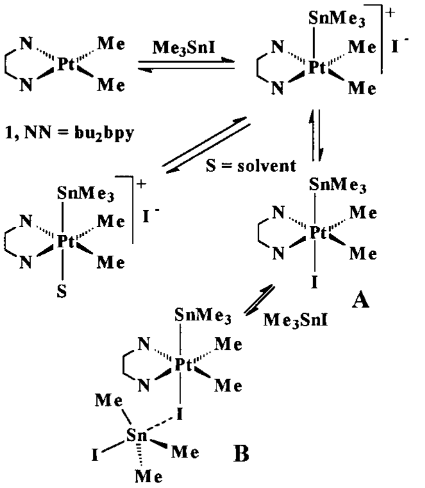
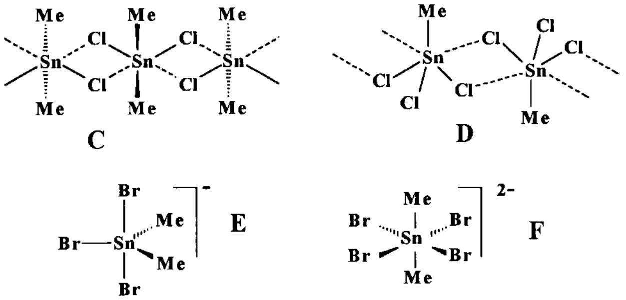
Scheme 1. S = solvent.



platinum(IV) complexes and excess Me_2SnX_2 (X= Cl, Br) or $MeSnCl_3$ could lead to new forms of supramolecular association through Pt-X···Sn and (or) PtSnX···Sn secondary bonding, and this paper reports the results of a systematic study of such systems.

Chart 1



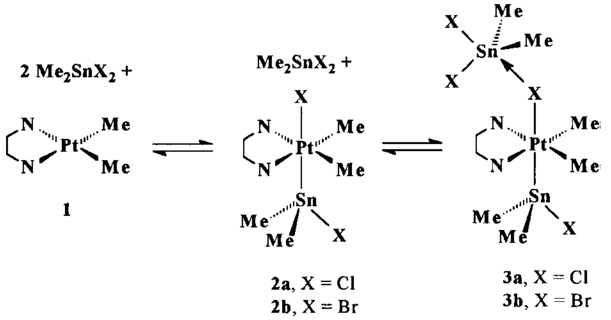
Results and discussion

Synthesis of the complexes

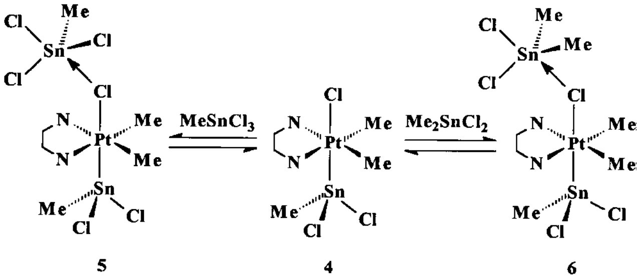
The reaction of complex **1** with Me_2SnX_2 gave the corresponding products of *trans* oxidative addition $[PtXMe_2(SnMe_2X)(bu_2bpy)]$ (**2a**: X = Cl, **2b**: X = Br), and crystallization in the presence of excess Me_2SnX_2 allowed isolation of the corresponding complexes $[PtXMe_2(SnMe_2X)(bu_2bpy)]\cdot Me_2SnX_2$ (**3a**: X = Cl, 3b:, X = Br) (Scheme 2). Similarly, reaction of **1** with $MeSnCl_3$ gave $[PtClMe_2(SnMeCl_2)(bu_2bpy)]$ (**4**), which could be crystallized with either $MeSnCl_3$ or Me_2SnCl_2 to give the complexes $[PtClMe_2(SnMeCl_2)(bu_2bpy)]\cdot MeSnCl_3$ (**5**) or $[PtClMe_2(SnMeCl_2)(bu_2bpy)]\cdot Me_2SnCl_2$ (**6**), respectively (Scheme 3). It was not possible to crystallize **2a** with $MeSnCl_3$, since a reaction occurred to give **4** with displacement of Me_2SnCl_2 from platinum.

In a similar way, crystallization of the μ-stannylene complex $[(\mu\text{-}SnCl_2)\{PtClMe_2(bu_2bpy)\}_2]$ (**7**) (2) with excess Me_2SnCl_2 yielded air-stable, colorless crystals of the complex $[(\mu\text{-}SnCl_2)\{PtClMe_2(bu_2bpy)\}_2]\cdot Me_2SnCl_2$ (**8**), as shown in Scheme 4. Although complex **7** contains two Pt-Cl groups that could act as ligands, it was not possible to crystallize a potential 1:2 complex $[(\mu\text{-}SnCl_2)\{PtClMe_2(bu_2bpy)\}_2]\cdot 2Me_2SnCl_2$.

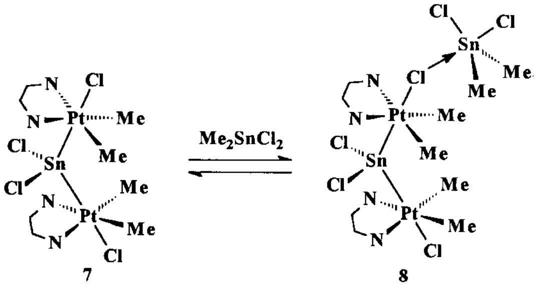
Scheme 2. NN = bu_2bpy.



Scheme 3. NN = bu_2bpy.



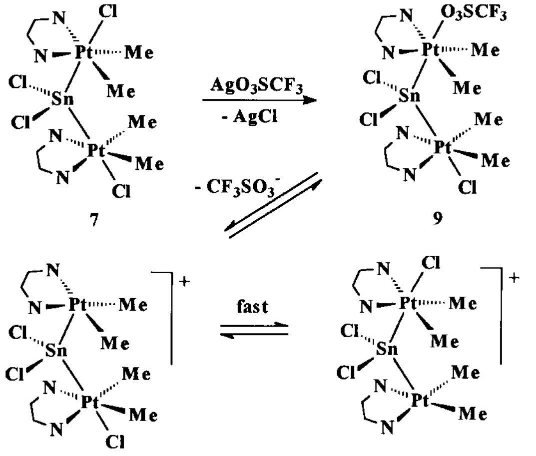
Scheme 4. NN = bu_2bpy.



In each case the adduct formation was reversible and the complexes existed in solution mainly in dissociated form at room temperature. For example, the ^1H NMR spectrum of **3a** at room temperature contained peaks assigned to the complex **2a** and free Me_2SnCl_2 (δ(MeSn) = 1.14, ^2J(SnMe) = 69 Hx) only, indicating effectively complete dissociation in solution. However, at lower temperatures there is an increase in the magnitude of the coupling constant ^2J(SnMe) for the Me_2SnCl_2 resonance (75 Hz at –2°C, 80 Hz at –67°C) indicating reversible coordination to the Me_2SnCl_2 that is more favorable at lower temperatures (8). At no temperature were separate signals for free and complexed Me_2SnCl_2 observed, indicating that exchange between free and complexed forms was rapid and making it difficult to determine the association constant. The adducts clearly must be characterized in the solid state by X-ray structure determinations, since the easy exchange, involving reversible addition of Me_2SnCl_2, makes solution characterization difficult.

One extreme formulation of the adducts is as complexes of 16-electron platinum(IV) complexes (15) with $[SnMe_xX_{5-x}]^-$ anions, and we have attempted to isolate further examples of

Scheme 5. NN = bu$_2$bpy.



the 16-electron complexes. In one case, a pure compound was isolated, but it could not be crystallized for structural characterization. Thus reaction of **7** with 1 equiv of silver triflate gave the corresponding triflate derivative [(μ-SnCl$_2$){PtClMe$_2$(bu$_2$bpy)}{Pt(O$_3$SCF$_3$)Me$_2$(bu$_2$bpy)}] (**9**) (Scheme 5). The ^{1}H NMR spectrum of **9** at room temperature contained only three aromatic bu$_2$bpy peaks, one *tert*-butyl peak, and one Pt-Me resonance. All peaks were broad, indicating fluxionality such that the two platinum centres become effectively equivalent through chloride for triflate exchange. At –80°C the ^{1}H NMR spectrum is very complex, indicating the presence of several complexes in equilibrium. In the solid state, the structure could be as shown in Scheme 5 but it could also be polymeric with intermolecular PtCl···Pt coordination and free triflate ions. The exchange in solution indicates very easy dissociation of triflate is possible, with subsequent chloride exchange giving effective twofold symmetry.

Structural chemistry

Complexes **5**, **6**, and **8** exist in the solid state as 1:1 complexes, as shown in Figs. 1–3, and relevant bond parameters are listed in Table 1. In each case, the chloride atom of the Pt-Cl group acts as a donor to the acceptor MeSnCl$_3$ in **5** or Me$_2$SnCl$_2$ in **6** or **8**, so that the organotin chloride has distorted trigonal bipyramidal stereochemistry. These structures therefore complement that found previously for a trimethyltin halide acceptor in [PtIMe$_2$(Me$_3$Sn)(bu$_2$bpy)]·Me$_3$SnI (Scheme 1) (8). The Pt—Sn bond lengths appear not to be greatly affected by adduct formation. For example, the Pt—Sn distances in complex **8** (2.5561(6) and 2.5479(6) Å) are similar to those in the parent complex **7** (2.5451(5) and 2.5386(6) Å),[2] and the distances in complexes **5** (2.5055(5) Å) and **6** (2.5011(6) Å) are similar to that in [PtClMe$_2$(SnCl$_2$Ph)(bu$_2$bpy)] (2.5186(6) Å) (2). They also fall in the range reported for other Pt—Sn bonded compounds (2.34–2.80 Å) (7).

Fig. 1. A view of the structure of complex **5**.

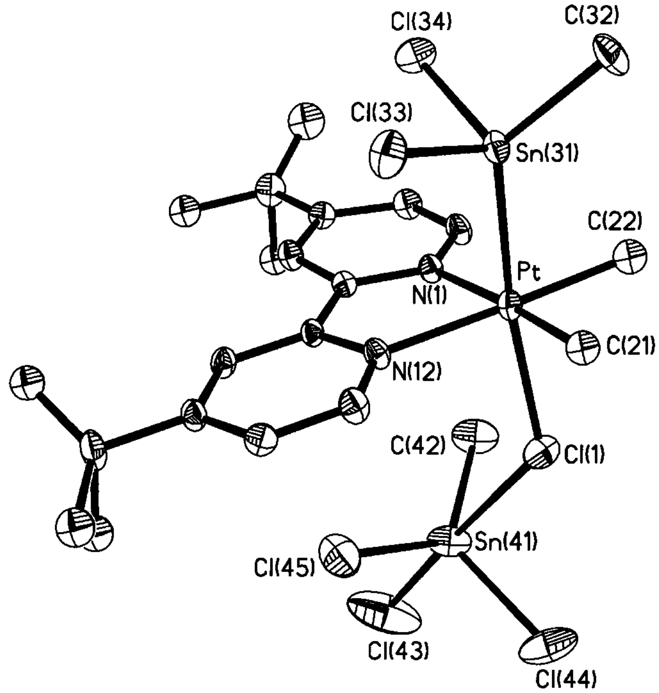
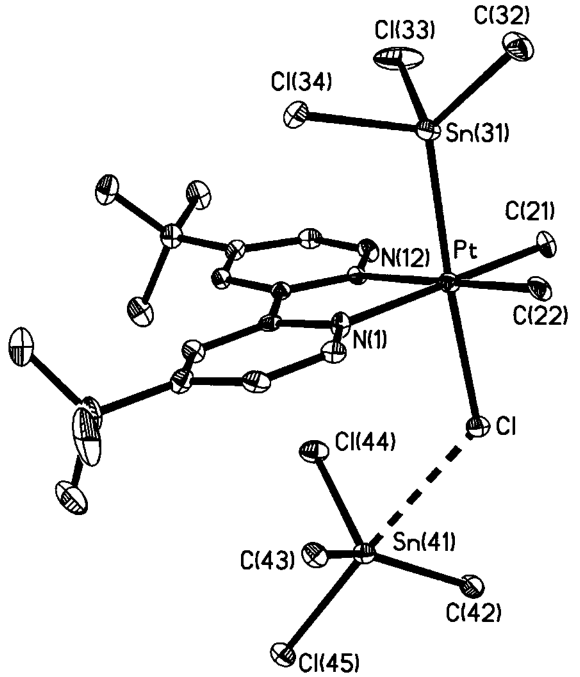


Fig. 2. A view of the structure of complex **6**.



The main point of interest is the nature of the bridging chloride in the adducts. There are two extreme formulations possible, namely as 18-electron platinum complexes with weak Pt-X···Sn bonding or as weak complexes between a

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[2] Supplementary data (tables of X-ray data for the complexes) may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 185200–185203 inclusive contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Fig. 3. A view of the structure of complex **8**.

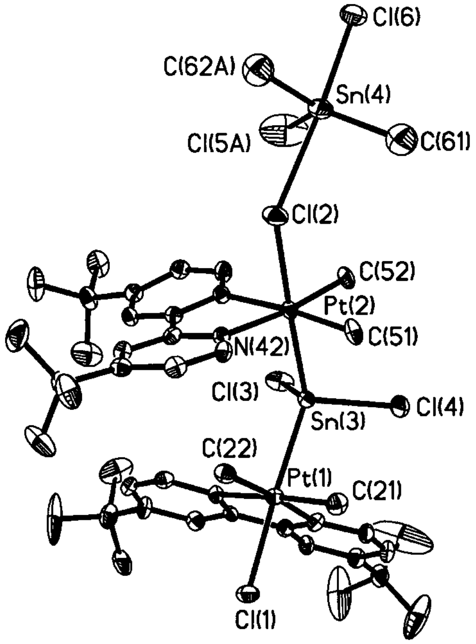


Table 1. Selected bond distances (Å) and angles (°) for complexes **5**, **6**, and **8**.

Complex	**5**	**6**	**8**·pentane
Pt—X	2.510(2)	2.480(2)	2.524(2) 2.466(2)
Pt—Sn	2.5011(6)	2.5055(5)	2.5561(6) 2.5479(6)
Sn—X	2.366(2) 2.357(2)	2.359(2) 2.352(2)	2.386(2) 2.384(2)
Sn—C	2.111(7)	2.099(6)	
Sn—X	2.365(3) 2.319(3) 2.311(3)	2.428(2) 2.342(2)	2.457(3) 2.313(7)
Sn—C	2.098(9)	2.109(6) 2.096(5)	2.14(2) 2.14(1)
Sn···X	2.813(2)	3.04	2.870(3)
Pt-X··*Sn*	132	130	129.0(1)
C-Sn-X	105.3(3) 103.1(3)	105.6(2) 103.7(2)	
X-Sn-X	102.35(8)	100.60(9)	97.1(1)
C-*Sn*-C		133.9(3)	126(1)
C-*Sn*-X_e	125.9(3) 123.4(4)	111.3(2) 108.8(2)	122.1(5) 110.5(8)
C-*Sn*-X_a	97.1(3)	99.4(2) 97.7(2)	95.2(4) 90(1)
X-*Sn*-X_e	106.6(1)		
X-*Sn*-X_a	97.1(2)	96.61(6)	95.5(4)
X··*Sn*-C	83.3(3)	83 78	87.2(4) 86(1)
X··*Sn*-X_a	177.3(2)	177	175.90(9)
X··*Sn*-X_e	84.83(9) 81.7(1)	86	86.0(4)

Note: Italicized *Sn* refers to the coordinated organotin compound, e = equatorial, a = axial.

16-electron platinum(IV) cation and the anionic tin halide complex $[Me_2SnCl_3]^-$ or $[MeSnCl_4]^-$. The first true 16-electron platinum(IV) complexes have been isolated recently (15). This issue is most readily addressed for complex **8**, since it contains Pt-Cl groups involved and not involved in coordination to tin, and axial Sn-Cl groups involved and not involved in coordination to platinum. The differences in bond lengths are *d*[Pt(2)Cl(2)] – *d*[Pt(1)Cl(1)] = 2.524(2) – 2.466(2) = 0.058 Å and *d*[Sn(4)Cl(2)] – *d*[Sn(4)Cl(6)] = 2.870(3) – 2.457(3) = 0.413 Å. It is clear that the formulation as 18-electron platinum complexes with weak Pt-X···Sn bonding is the correct one, based on this structural criterion, and it is also consistent with the solution properties discussed above. The Pt-Cl···Sn angles for the complexes fall in the narrow range 129–132° (Table 1).

The stereochemistry of the Cl···$SnMeCl_3$ unit of complex **5** is distorted trigonal bipyramidal with axial Cl.Sn-Cl and equatorial $SnMeCl_2$ groups. The equatorial substituents are displaced towards Cl(1) and away from Cl(43), as indicated by the angles Cl(1)Sn(41)C(42), Cl(1)Sn(41)Cl(44), Cl(1)Sn(41)Cl(45) = 83.3(3), 81.7(1), 84.8(1)° and Cl(43)Sn(41)C(42), Cl(43)Sn(41)Cl(44), Cl(43)Sn(41)Cl(45) = 97.1(3), 95.9(2), 97.0(2)°, respectively. The Sn—Cl bond distances follow the series bridging Sn—Cl (2.813(2) Å) >> axial Sn—Cl (2.365(3) Å) > equatorial Sn—Cl (2.319(3) Å, 2.311(3) Å). The Sn—Cl bond lengths in free $MeSnCl_3$ (2.283(2), 2.318(1) Å) are similar to the Sn—-Cl(equatorial) distances in **5**. The intermolecular Sn···ClSn bond distance in $MeSnCl_3$ (Chart 1, **D** (13)) is 3.714(2) Å and is significantly longer than the bridging Sn···Cl-Pt distance of 2.813(2) Å in complex **5**. There are no short intermolecular SnCl···Sn contacts involving the chloride ligands in the $PtSnMeCl_2$ and $MeSnCl_3$ groups in complex **5**. It is clear therefore that the Pt-Cl group is a stronger donor than the $SnMeCl_2$ group.

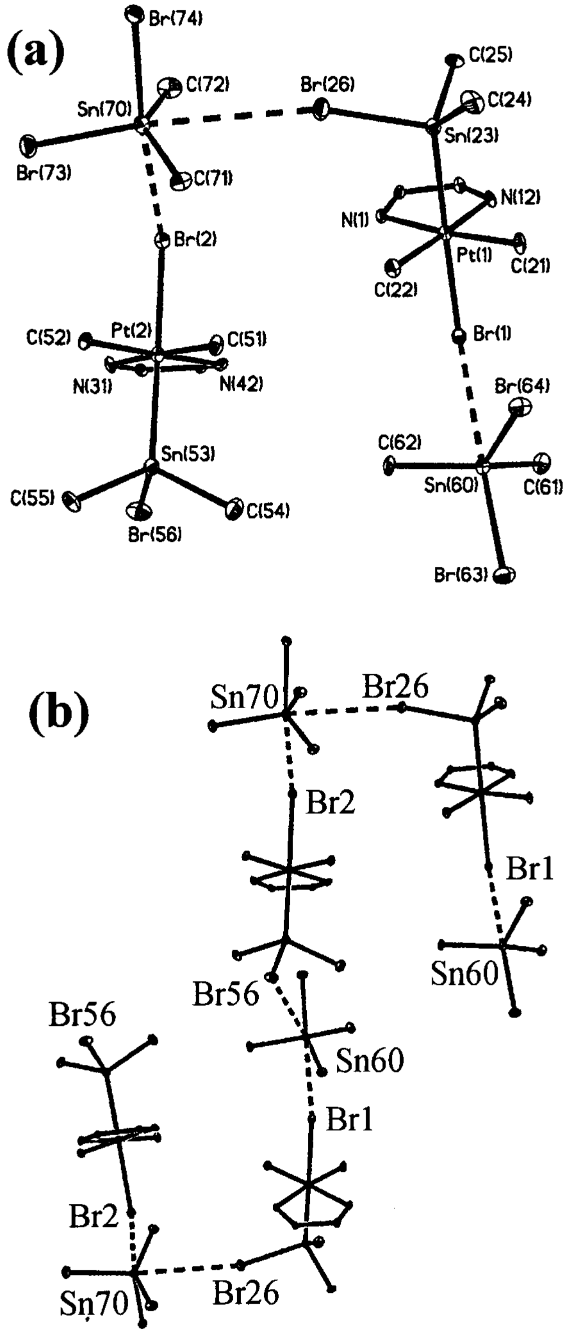
The Cl···$SnMe_2Cl_2$ units in complexes **6** and **8** have similar distorted trigonal bipyramidal stereochemistries at tin, with axial Cl···Sn-Cl and equatorial $SnMe_2Cl$ groups. The equatorial substituents are also displaced away from the terminal axial chloride and toward the more weakly bonding bridging chloride. For example, in **6** the angles Cl(45)Sn(41)C(42), Cl(45)Sn(41)C(43), and Cl(45)Sn(41)Cl(44) (99.4(2), 97.7(2), and 96.6(1)°, respectively) are all greater than 90°. The C-Sn-C angles for Me_2SnCl_2 in **6** (133.9(3)°) and **8** (126(1)°) are larger than the ideal angle of 120°, and the Cl···Sn-Cl bond angle (**6**, 177° (**6**), **8**, 175.90(9)° (**8**)) is close to linear in each complex. The order of the Sn—Cl bond lengths again follows the series: bridging chloride (3.04(1) Å (**6**), 2.870(3) Å (**8**)) >> axial chloride (2.457(3) Å (**6**), 2.428(2) Å (8)) > equatorial chloride (2.342(2) (**6**), 2.313(7) Å (**8**)). For comparison, the Sn—Cl distance in Me_2SnCl_2 is 2.40(4) Å and the intermolecular Sn···Cl distance is 3.54(5) Å (11). There are no short intermolecular SnCl···Sn contacts in complexes **6** and **8**, whereas such interactions in Me_2SnCl_2 give rise to the infinite chain structure **C** (Chart 1).

The structure of complex **3b** is of particular interest, and is shown in Fig. 4. Selected bond parameters are in Table 2. There are two independent molecules of $[PtBrMe_2(SnMe_2Br)(bu_2bpy)]$ and of Me_2SnBr_2 in the unit cell. The independent platinum complexes differ primarily by rotation about the Pt—Sn bond, and the independent Me_2SnBr_2 molecules differ mostly by rotation about the bridging PtBr···Sn bond, as shown in Fig. 4*a*. There is a clear PtBr···Sn secondary bond to each molecule of Me_2SnBr_2 with distances Br(1)···Sn(60) and Br(2)···Sn(70) of 3.14 and 3.29 Å. There are also longer contacts between the bromide atoms of the $PtSnMe_2Br$ groups and the Me_2SnBr_2 groups. These distances Br(26)···Sn(70) and Br(56)···Sn(60) are 3.99 and 4.05 Å, which is marginally longer than the sum of the van der Waals radii of Br and Sn of 3.95 Å (16). The orientation of the SnBr···Sn groups is such that the bromide is directed towards the tin atom and essentially bisects the C-Sn-C angle of the Me_2SnBr_2 acceptor molecule. This orientation, observed in both independent units, suggests that there is an attraction involved but it must be a very weak one. To place these distances in perspective, the covalent bond distances are Sn(23)—Br(26) = 2.533(1) and Sn(53)—Br(56) = 2.557(1) Å for the $PtSnMe_2Br$ groups and for the Me_2SnBr_2 molecules, pseudo-axial Sn(60)—Br(63) = 2.558(1), Sn(70)—Br(74) = 2.587(1) Å and pseudo-equatorial Sn(60)—Br(64) = 2.492(1), Sn(70)—Br(73) = 2.499(1) Å. The differences between primary and secondary Sn—Br distances is then approximately 0.64 Å for the pseudo-axial bonds and 1.52 Å for the pseudo-equatorial bonds, again emphasizing that the PtBr···Sn secondary bonds are strong relative to the PtSnBr···Sn interactions. In the solid state structure of Et_2SnBr_2, the difference between primary and secondary Sn—Br distances is 1.27 Å, about midway between the values for the stronger and weaker secondary interactions in **3b**.

Another criterion for the strength of the secondary bonding is based on the stereochemistry at tin in the Me_2SnBr_2 acceptor molecules. In trigonal bipyramidal $[SnMe_2Br_3]^-$ the C-Sn-C angle is 133.2(8)°, whereas in octahedral $[SnMe_2Br_4]^{2-}$ the angle is 180° (14). In **3b**, the C-Sn-C angles are 131.9(3)° and 137.4(4)° for the two independent Me_2SnBr_2 acceptor molecules, very similar to the angle in the trigonal bipyramidal model compound. The analogous angle in the Me_2SnCl_2 complex (**6**) is 133.9(3)°, again very similar to the average C-Sn-C angle in **3b**. These data also indicate that the secondary SnBr···Sn bonding must be very weak, since the stereochemistry at the acceptor molecule is not significantly affected by it. If both types of secondary bonds are included, the solid state structure can be considered as a folded polymer, as illustrated in Fig. 4*b*.

Overall, it is clear that the secondary bonds formed by dimethyltin dihalide or methyltin trihalide acceptors can lead to supramolecular association and even to polymer formation in the solid state. At present, though, it is not easy to predict or control the degree of association. The secondary X···Sn bonds are weak coordinate bonds, and they appear to have similar energies to hydrogen bonds, aryl–aryl secondary bonds, or aurophilic attractions that have been used more extensively in supramolecular chemistry for assembling complex organometallic structures (11, 17). There is therefore a clear potential for further expansion of this field of research.

Fig. 4. Views of the structure of complex **3b**: (*a*) the two independent units $[PtBrMe_2(SnMe_2Br)(bu_2bpy)]\cdot Me_2SnBr_2$; (*b*) part of the folded polymeric structure formed by secondary Br···Sn bonding. Only the inner atoms of the bu_2bpy ligands are shown for clarity.



Experimental

NMR spectra were recorded by using Varian Mercury 400 or Inova 600 MHz spectrometers. Chemical shifts are reported in ppm with respect to TMS (^1H) reference. Unless otherwise specified, all quoted couplings to tin are for the ^{119}Sn isotope only. $[PtMe_2(bu_2bpy)]$ (18) and $[(PtClMe_2bu_2bpy)_2(\mu\text{-}SnCl_2)]$ (2) were prepared according to the literature procedures.

$[PtClMe_2(SnMe_2Cl)(bu_2bpy)]\cdot Me_2SnCl_2$ (3a)

An NMR tube was charged with **1** (40 mg, 0.081 mmol), Me_2SnCl_2 (178 mg, 0.810 mmol), and CH_2Cl_2 (0.5 mL). After 5 min, pentane was slowly layered on top of the solution

Table 2. Selected bond distances (Å) and angles (°) for complex **3b**.

Pt(1)—Br(1)	2.675(1)	Pt(2)—Br(2)	2.706(1)
Pt(1)—Sn(23)	2.5332(7)	Pt(2)—Sn(53)	2.5465(7)
Sn(23)—Br(26)	2.533(1)	Sn(53)—Br(56)	2.557(1)
Sn(23)—C(24)	2.148(8)	Sn(53)—C(54)	2.135(8)
Sn(23)—C(25)	2.146(8)	Sn(53)—C(55)	2.130(7)
Sn(60)—Br(63)	2.558(1)	Sn(70)—Br(73)	2.499(1)
Sn(60)—Br(64)	2.492(1)	Sn(70)—Br(74)	2.587(1)
Sn(60)—C(61)	2.117(8)	Sn(70)—C(71)	2.115(8)
Sn(60)—C(62)	2.119(7)	Sn(70)—C(72)	2.105(9)
Sn(60)···Br(1)	3.29	Sn(70)···Br(2)	3.14
Br(56)···Sn(60)	4.05	Br(26)···Sn(70)	3.99
C(24)-Sn(23)-C(25)	111.8(4)	C(54)-Sn(53)-C(55)	113.9(4)
C(24)-Sn(23)-Br(26)	103.3(3)	C(54)-Sn(53)-Br(56)	100.6(3)
C(25)-Sn(23)-Br(26)	101.5(2)	C(55)-Sn(53)-Br(56)	102.9(2)
C(61)-Sn(60)-C(62)	131.9(3)	C(71)-Sn(70)-C(72)	137.4(4)
C(61)-Sn(60)-Br(63)	100.6(3)	C(71)-Sn(70)-Br(73)	107.6(2)
C(61)-Sn(60)-Br(64)	113.7(3)	C(71)-Sn(70)-Br(74)	98.4(3)
C(62)-Sn(60)-Br(63)	99.8(2)	C(72)-Sn(70)-Br(73)	110.3(3)
C(62)-Sn(60)-Br(64)	106.6(3)	C(72)-Sn(70)-Br(74)	95.4(3)
Br(63)-Sn(60)-Br(64)	96.60(4)	Br(73)-Sn(70)-Br(74)	97.27(4)
Br(1)···Sn(60)-Br(63)	178	Br(2)···Sn(70)-Br(73)	88
Br(1)···Sn(60)-Br(64)	85	Br(2)···Sn(70)-Br(74)	173
Br(56)···Sn(60)-Br(63)	84	Br(26)···Sn(70)-Br(73)	174
Br(56)···Sn(60)-Br(64)	177	Br(26)···Sn(70)-Br(74)	89
Sn(60)···Br(1)-Pt(1)	127	Sn(70)···Br(2)-Pt(2)	126
Sn(60)···Br(56)-Sn(53)	150	Sn(70)···Br(26)-Sn(23)	166

and the sample stored at –5°C. After several days colorless crystals suitable for X-ray crystallographic studies were formed. Yield 72%. ^{1}H NMR (CDCl$_3$) δ: 8.76 (d, 2H, $^{3}J_{\mathrm{H6H5}}$ = 6 Hz, $^{3}J_{\mathrm{PtH6}}$ = 16 Hz, H-6, 8.11 (d, 2H, $^{4}J_{\mathrm{H3H5}}$ = 1.5 Hz, H-3), 7.60 (dd, 2H, $^{3}J_{\mathrm{H5H6}}$ = 6 Hz, $^{4}J_{\mathrm{H5H3}}$ = 1.5 Hz, H-5), 1.43 (s, 18H, *t*-bu), 1.32 (s, 6H, $^{2}J_{\mathrm{PtMe}}$ = 55 Hz, Pt-Me), 1.18 (s, 6H, $^{2}J_{\mathrm{SnH}}$ = 68.5 Hz, free Me$_2$SnCl$_2$), 0.38 (br s, 6H, $^{2}J_{\mathrm{SnH}}$ = 50 Hz, Sn-Me). Anal. calcd. for $C_{24}H_{42}Cl_4N_2PtSn_2$ (%): C 30.90, H 4.54, N 3.00; found: C 30.77, H 4.46, N 2.94.

[PtBrMe$_2$(SnMe$_2$Br)(bu$_2$bpy)]·Me$_2$SnBr$_2$ (3b)

This was prepared similarly but using Me$_2$SnBr$_2$ in place of Me$_2$SnCl$_2$. Yield 74%. ^{1}H NMR (CDCl$_3$) δ: 8.78 (d, 2H, $^{3}J_{\mathrm{H6H5}}$ = 4.5 Hz, $^{3}J_{\mathrm{PtH6}}$ = 16 Hz, H-6), 8.11 (d, 2H, $^{4}J_{\mathrm{H3H5}}$ = 1 Hz, H-3), 7.60 (dd, 2H, $^{3}J_{\mathrm{H5H6}}$ = 4.5 Hz, $^{4}J_{\mathrm{H5H3}}$ = 1 Hz, H-5), 1.43 (s, 18H, *t*-bu), 1.42 (s, 6H, $^{2}J_{\mathrm{PtMe}}$ = 56 Hz, Pt-Me), 1.34 (s, 6H, $^{2}J_{\mathrm{SnH}}$ = 65 Hz, free Me$_2$SnBr$_2$), 0.46 (br s, 6H, $^{2}J_{\mathrm{SnH}}$ = 49 Hz, Sn-Me). Anal. calcd. for $C_{24}H_{42}Br_4N_2PtSn_2$ (%): C 25.95, H 3.81, N 2.62: found: C 26.05, H 3.89, N 2.63.

[PtClMe$_2$(SnMeCl$_2$)(bu$_2$bpy)]·MeSnCl$_3$ (5)

This was prepared similarly from **1** (40 mg, 0.081 mmol), MeSnCl$_3$ (195 mg, 0.810 mmol), and CH$_2$Cl$_2$ (0.5 mL). Yield 68%. ^{1}H NMR (CDCl$_3$) δ: 8.74 (d, 2H, $^{3}J_{\mathrm{H6H5}}$ = 6 Hz, $^{3}J_{\mathrm{PtH6}}$ = 15 Hz, H-6), 8.43 (d, 2H, $^{4}J_{\mathrm{H3H5}}$ = 2 Hz, H-3), 7.72 (dd, 2H, $^{3}J_{\mathrm{H5H6}}$ = 6 Hz, $^{4}J_{\mathrm{H5H3}}$ = 2 Hz, H-5), 1.67 (s, 6H, $^{2}J_{\mathrm{SnH}}$ = 99 Hz, free MeSnCl$_3$), 1.48 (s, 18H, *t*-bu), 1.45 (s, 6H, $^{2}J_{\mathrm{PtMe}}$ = 56 Hz, Pt-Me), 1.03 (s, 3H, $^{2}J_{\mathrm{SnH}}$ = 52 Hz, Sn-Me). Anal. calcd. for $C_{22}H_{36}Cl_6N_2PtSn_2$ (%): C 27.14, H 3.73, N 2.88; found: C 27.07, H 3.65, N 2.77.

[PtClMe$_2$(SnMeCl$_2$)(bu$_2$bpy)]·Me$_2$SnCl$_2$ (6)

This was prepared similarly from **1** (40 mg, 0.081 mmol), MeSnCl$_3$ (20 mg, 0.081 mmol), and CH$_2$Cl$_2$ (0.5 mL) followed by addition of Me$_2$SnCl$_2$ (89 mg, 0.405 mmol). Yield 77%. ^{1}H NMR (CDCl$_3$) δ: 8.74 (d, 2H, $^{3}J_{\mathrm{H6H5}}$ = 6 Hz, $^{3}J_{\mathrm{PtH6}}$ = 15 Hz, H-6), 8.43 (d, 2H, $^{4}J_{\mathrm{H3H5}}$ = 2 Hz, H-3), 7.72 (dd, 2H, $^{3}J_{\mathrm{H5H6}}$ = 6 Hz, $^{4}J_{\mathrm{H5H3}}$ = 2 Hz, H-5), 1.48 (s, 18H, *t*-bu), 1.45 (s, 6H, $^{2}J_{\mathrm{PtMe}}$ = 56 Hz, Pt-Me), 1.18 (s, 6H, $^{2}J_{\mathrm{SnH}}$ = 68 Hz, free Me$_2$SnCl$_2$), 1.03 (s, 3H, $^{2}J_{\mathrm{SnH}}$ = 52 Hz, Sn-Me). Anal. calcd. for $C_{23}H_{39}Cl_5N_2Pt$ (%): C 28.98, H 4.12, N 2.94; found: C 28.90, H 4.06, N 2.88.

[(PtClMe$_2$bu$_2$bpy)$_2$(μ-SnCl$_2$)]·Me$_2$SnCl$_2$ (8)

This was prepared similarly from complex **9** (45 mg, 0.035 mmol), Me$_2$SnCl$_2$ (38 mg, 0.175 mmol), and CH$_2$Cl$_2$ (0.5 mL). Yield 83%. ^{1}H NMR (CDCl$_3$) δ: 8.69 (d, 2H, $^{3}J_{\mathrm{H6H5}}$ = 6 Hz, $^{3}J_{\mathrm{PtH}}{}^{6}$ = 16 Hz, H-6), 8.07 (d, 2H, $^{4}J_{\mathrm{H3H5}}$ = 1 Hz, H-3), 7.55 (dd, 2H, $^{3}J_{\mathrm{H5H6}}$ = 6 Hz, $^{4}J_{\mathrm{H5H3}}$ = 1 Hz, H-5), 1.40 (s, 36H, *t*-bu), 1.36 (br s, 12H, $^{2}J_{\mathrm{PtMe}}$ = 59 Hz, Pt-Me), 1.18 (s, 6H, $^{2}J_{\mathrm{SnH}}$ = 68 Hz, free Me$_2$SnCl$_2$). Anal. calcd. for $C_{43}H_{66}Cl_6N_4Pt_2Sn_2$.pentane (%): C 36.67, H 5.11, N 3.64; found: C 36.75, H 5.18, N 3.70.

(PtClMe$_2$bu$_2$bpy)(μ-SnCl$_2$)(PtMe$_2$bu$_2$bpy)(CF$_3$SO$_3$) (9)

To a solution of **9** (100 mg, 0.078 mmol) in CH$_2$Cl$_2$ (10 mL) was added AgO$_3$SCF$_3$ (20 mg, 0.078 mmol), and the mixture was stirred for 30 min in the dark. The solution was filtered through dry celite to remove AgCl. Pentane (40 mL) was added to the filtrate to precipitate the product, which was isolated by filtration, washed with pentane, and dried in vacuo. Yield 88%. ^{1}H NMR (CDCl$_3$) δ: 8.55 (br d,

Table 3. Crystal data and experimental details.

Complex	**5**	**3b**	**6**	**8**·pentane
Empirical formula	$C_{22}H_{36}Cl_6N_2PtSn_2$	$C_{24}H_{42}Br_4N_2PtSn_2$	$C_{23}H_{39}C_{l5}N_2PtSn_2$	$C_{47}H_{78}C_{l6}N_4Pt_2Sn_2$
Formula weight	973.7	1110.71	953.28	1539.39
T (°C)	25(2)	–123(2)	–123(2)	21(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	12.1321(2)	23.8100(7)	12.5953(5)	18.7589(4)
b (/Å)	25.9092(5)	13.4608(3)	24.6511(6)	13.5089(3)
c (Å)	12.0843(2)	22.0228(6)	11.9861(5)	22.7772(5)
β (°)	118.490(1)	106.169(1)	118.111(2)	92.835(1)
V (Å^3)	3338.5(1)	6779.1(3)	3282.5(2)	5765.0(2)
Z	4	8	4	4
$D_{\text{calcd.}}$ (g cm^{-1})	1.937	2.177	1.929	1.774
Absorption coefficient μ (mm)	6.159	10.309	6.183	6.006
$F(000)$	1848	4144	1816	2984
R [$I > 2\sigma(I)$]^a				
R_1	0.0510	0.0471	0.0397	0.0576
wR_2	0.1444	0.0898	0.0634	0.1422

$^aR_1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$.

2H, $^3J_{H6H5}$ = 6 Hz, H-6), 8.07 (br s, 2H, H-3), 7.59 (d, 2H, $^3J_{H5H6}$ = 6 Hz, H-5), 1.38 (s, 36H, *t*-bu), 1.07 (br s, 12H, Pt-Me). Anal. calcd. for $C_{41}H_{60}Cl_3F_3N_4O_3Pt_2SSn$ (%): C 36.18, H 4.44, N 4.12; found: C 36.10, H 4.38, N 4.02.

X-ray structure determinations

Crystals were mounted on glass fibers. Data were collected by using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The SHEXTL 5.1 (G.M. Sheldrick, Madison, Wisc.) program was used to solve the structures by direct methods, followed by refinement by successive difference Fouriers. For complex **5** the *tert*-butyl groups were modeled as two half-occupancy isotropic groups. For **8** there was disorder at the $SnMe_2Cl_2$ acceptor, and atoms Cl(5) and C(62) were disordered across their two positions. This disorder was modeled as 50% of each atom type with the Sn—Cl (2.39 Å) and Sn—C (2.13 Å) distances being fixed. Crystal and refinement data are listed in Table 3.

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