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Insights into the Intramolecular Donor Stabilisation of Organostannylene Palladium and Platinum Complexes: Syntheses, Structures and DFT Calculations**

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Dedicated to Professor Dainis Dakternieks on the occasion of his 65th birthday

Abstract: The syntheses of the transition metal complexes *cis*-[(4-*t*Bu-2,6-$\{P(O)(OiPr)_2\}_2C_6H_2SnCl)_2MX_2$] (**1**, M = Pd, X = Cl; **2**, M = Pd, X = Br; **3**, M = Pd, X = I; **4**, M = Pt, X = Cl), *cis*-[{2,6-$(Me_2NCH_2)_2C_6H_3SnCl\}_2MX_2$] (**5**, M = Pd, X = I; **6**, M = Pt, X = Cl), *trans*-[{2,6-$(Me_2NCH_2)_2C_6H_3SnI\}_2PtI_2$] (**7**) and *trans*-[(4-*t*Bu-2,6-$\{P(O)(OiPr)_2\}_2C_6H_2SnCl)PdI_2]_2$ (**8**) are reported. Also reported is the serendipitous formation of the unprecedented complexes *trans*-[(4-*t*Bu-2,6-$\{P(O)(OiPr)_2\}_2C_6H_2SnCl)_2Pt(SnCl_3)_2$] (**10**) and [(4-*t*Bu-2,6-$\{P(O)(OiPr)_2\}_2C_6H_2SnCl)_3Pt(SnCl_3)_2$] (**11**). The compounds were characterised by elemental analyses, ^{1}H, ^{13}C, ^{31}P, ^{119}Sn and ^{195}Pt NMR spectroscopy, single-crystal X-ray diffraction analysis, UV/Vis spectroscopy and, in the cases of compounds **1**, **3** and **4**, also by Mössbauer spectroscopy. All the compounds show the tin atoms in a distorted trigonal-bipyramidal environment. The Mössbauer spectra suggest the tin atoms to be present in the oxidation state III. The kinetic lability of the complexes was studied by redistribution reactions between compounds **1** and **3** as well as between **1** and *cis*-[{2,6-$(Me_2NCH_2)_2C_6H_3SnCl\}_2PdCl_2$]. DFT calculations provided insights into both the bonding situation of the compounds and the energy difference between the *cis* and *trans* isomers. The latter is influenced by the donor strength of the pincer-type ligands.

Keywords: density functional calculations · palladium · platinum · structure elucidation · tin · transition metals

Introduction

One important characteristic of tin(II) compounds is their lone electron pair,[1] which makes both inorganic as well as organically substituted tin compounds interesting ligands for Lewis acids such as transition metals.[2] The topic of transition metal complexes bearing Sn^{II}-based ligands has become an active area of research and a vast number of transition metal complexes containing stannylenes have been reported.[3–24] In the last few decades, complexes with palladium or platinum have gained considerable interest,[25–38] probably due to the fact that tin(II) chloride, as the simplest example of Sn^{II}-based ligands, is an important co-catalyst in various group-10 metal-catalysed reactions such as hydroformylation,[39] hydrogenation,[40] isomerisation[41] or hydrogen-mediated reductive coupling reactions.[42]

The synthesis of palladium or platinum complexes is usually accompanied by the insertion of stannylenes SnR_2 into metal chloride bonds providing complexes containing weakly coordinated $[SnR_2Cl]^-$ anions with a *trans* labilising effect although the importance and exact role of SnR_2 as a co-catalyst is still unclear.[43] Besides these, there are a few examples in which the stannylenes behave as a σ donor, as shown in **A**,[34,35] **B**,[28,29] **C**,[36] **D**[25] and **E**[44] (Scheme 1).

Most of these complexes contain stannylene ligands bearing bulky substituents, for example, $(Me_3Si)_2N$,[28,29]

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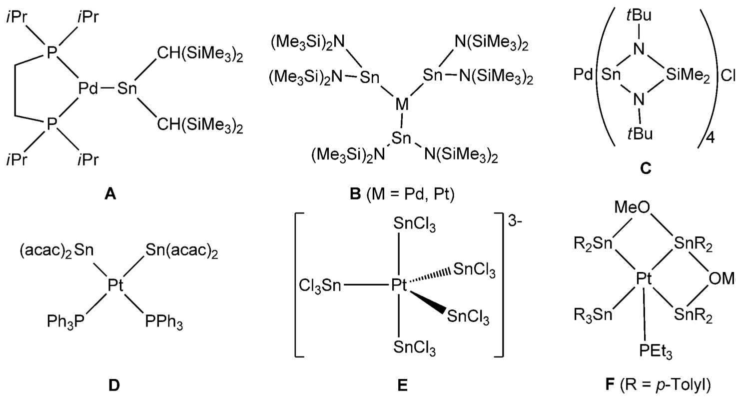
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203511. ORTEP drawings of **2** and **3**, ^{31}P and ^{119}Sn NMR spectra of the redistribution reactions, MO diagram of **4**, bond critical points for $[PtCl_2(SnClH)_2]$, ball-and-stick representation of the effect of the toluene solvate molecule on the pincer-ligand backbone (aromatic ring) in $\mathbf{4}\cdot 1.5\,C_7H_8$ and coordinates of calculated complexes.



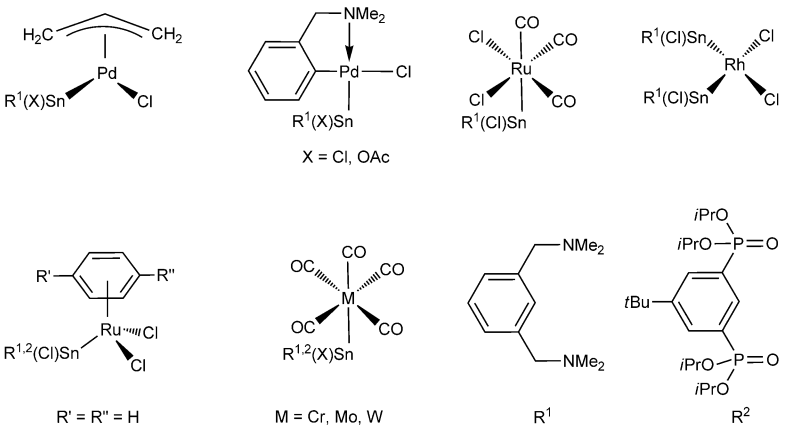
Scheme 1. Randomly selected examples of tin(II) complexes of palladium and platinum.

$(Me_3Si)_2CH$[33] and $Me_2Si(NtBu)_2$.[36] Recent studies have shown that anionic main-group element donors such as $(SnB_{11}H_{11})^-$ or $[MeSi\{SiMe_2N(aryl)\}_3Sn]^-$ are also able to bind various transition metals.[8,45]

A search of the Cambridge Crystallographic Data Base and the literature for tin-containing platinum complexes revealed that the majority of structures contain Sn/Pt ratios of 1:1[44d] and 2:1. There are only six compounds with a Sn/Pt ratio of 3:1,[25,30,46] seven compounds with a Sn/Pt ratio of 4:1[26,45a,b,l,47] and three compounds with a Sn/Pt ratio of 5:1.[44] Notably, with the exceptions of compound **F**[26] (Scheme 1) and $[\{Me_2Si(ArN)_2Sn\}_2Pt(SnCl_2NAr)_2SiMe_2]$,[45l] each of the platinum complexes mentioned above contains only one type of tin ligand.

In addition to the examples given in Scheme 1, we have shown that heteroleptic organostannylenes containing Y,C,Y-coordinating pincer-type ligands R^1 (Y = N) or R^2 (Y = O) are able to complex a variety transition metals (Scheme 2).[48]

The presence of N→Sn and O→Sn intramolecular coordination in the organochloridostannylenes $2,6\text{-}(Me_2NCH_2)_2\text{-}C_6H_3SnCl$ and $4\text{-}tBu\text{-}2,6\text{-}[P(O)(OiPr)_2]_2C_6H_2SnCl$, respectively, should increase the Lewis base capacity of these tin(II) compounds and we were interested in learning whether heteroleptic organostannylenes, like phosphane ligands, complex palladium and platinum halides as σ donors without inserting into the M–X bond. Herein we present a number of such complexes and investigate their structures in solution and in the solid state as well as their reactivity. We complemented the experimental work by performing DFT calculations to shed light on the chemical bonding in these complexes. We also report attempts to obtain complexes with higher nuclearity.



Scheme 2. Examples of transition-metal complexes with intramolecularly coordinated tin(II) compounds.

Results and Discussion

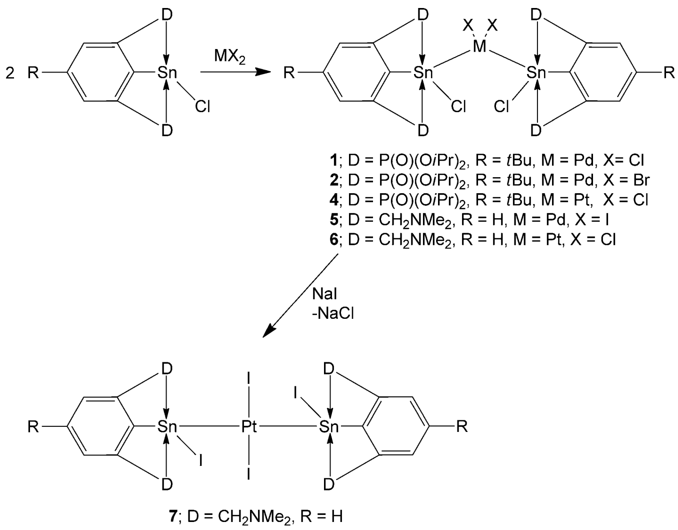
The reaction of the heteroleptic organostannylenes RSnCl ($R = 4\text{-}tBu\text{-}2,6\text{-}[P(O)(OiPr)_2]_2C_6H_2$, $2,6\text{-}(Me_2NCH_2)_2C_6H_3$) with palladium and platinum dihalides MX_2 (M = Pd, Pt; X = Cl, Br, I) provided the corresponding *cis* transition metal complexes **1**–**6** (Scheme 3) in good yields whereas, under the same conditions, no reaction was observed with nickel dihalides NiX_2 (X = Cl, Br). The reaction in THF of $4\text{-}tBu\text{-}2,6\text{-}[P(O)(OiPr)_2]_2C_6H_2SnCl$ with $[Ni(PPh_3)_2Cl_2]$ in a molar ratio of 2:1 gave, after heating the reaction mixture at reflux, metallic nickel and the organotin trichloride $4\text{-}tBu\text{-}2,6\text{-}[P(O)(OiPr)_2]_2C_6H_2SnCl_3$.

The reaction of the platinum dichloride complex **6** with sodium iodide provided the complex *trans*-$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3SnI\}_2PtI_2]$ (**7**) as a crystalline material (Scheme 3).

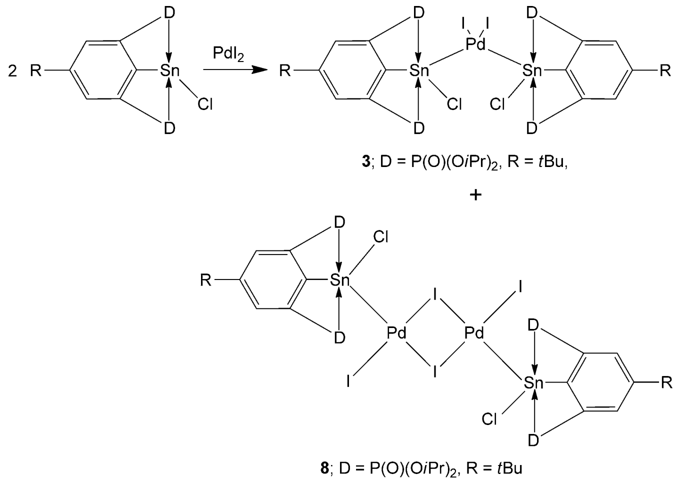
Notably, the reaction that gave compound **3** also provided the 1:1 complex *trans*-$[(4\text{-}tBu\text{-}2,6\text{-}\{P(O)(OiPr)_2\}_2C_6H_2SnCl)\text{-}PdI_2]_2$ (**8**) as a by–product (Scheme 4). Changing the stoichiometry of the reaction to 1:1, however, did not increase the yield of complex **8**.

Moreover, compounds **2** and **3** were also obtained by the reaction of 2 mol equiv of $4\text{-}tBu\text{-}2,6\text{-}[P(O)(OiPr)_2]_2C_6H_2SnX$ (X = Br, I) with $PdCl_2$, which indicates halogen exchange between the tin and palladium atoms (Scheme 5) with the latter preferring the softer halide anions bromide and iodide.

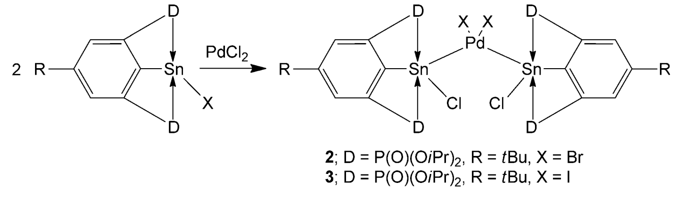
The complexes are yellow (**1**, **4**, **6**) or red (**2**, **3**, **5**, **7**) crystal-



Scheme 3. Synthesis of the *cis*-configured complexes **1**, **2** and **4**–**6** and the *trans*-configured complex **7**.



Scheme 4. Synthesis of the *cis*-configured complex **3** and the formation of the 1:1-complex *trans*-[(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$C$_6$H$_2$SnCl)PdI$_2$]$_2$ (**8**) as a byproduct.



Scheme 5. Alternative synthesis of complexes **2** and **3**.

line solids and are readily soluble in common organic solvents such as toluene, dichloromethane and THF, but poorly soluble in *n*-hexane. Complex **8** is a deep-red crystalline solid that is only poorly soluble in toluene but readily soluble in dichloromethane.

Single crystals of complexes **1**–**8** suitable for X-ray diffraction analysis, some as their benzene, toluene or chloroform solvates, **1**$\cdot C_6H_6$, **2**$\cdot C_7H_8$, **3**$\cdot C_7H_8$, **4**$\cdot 1.5\,C_7H_8$ and **7**$\cdot 2\,CHCl_3$, were obtained from solutions of the corresponding solvents.

The molecular structures of complexes **1**$\cdot C_6H_6$, **4**$\cdot 1.5\,C_7H_8$, **5**, **6**, **7**$\cdot 2\,CHCl_3$ and **8** are shown in Figures 1–6 and those of complexes **2**$\cdot C_7H_8$ and **3**$\cdot C_7H_8$ are given in the Supporting Information (see Figures S1 and S2). Selected interatomic distances and angles for complexes **1**–**7** are collected in Table 1 and Table 2, those of **8** are given in the caption to Figure 6.

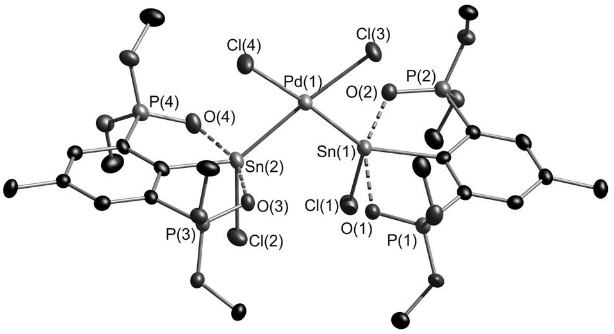


Figure 1. Molecular structure of **1**$\cdot C_6H_6$. Displacement ellipsoids are drawn at the 30 % probability level. The benzene solvate molecule and all methyl groups have been omitted for clarity.

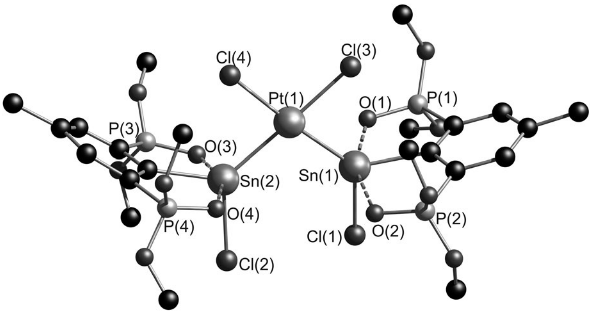


Figure 2. Standard ball-and-stick model of **4**$\cdot 1.5\,C_7H_8$. The toluene solvate molecules and all methyl groups have been omitted for clarity.

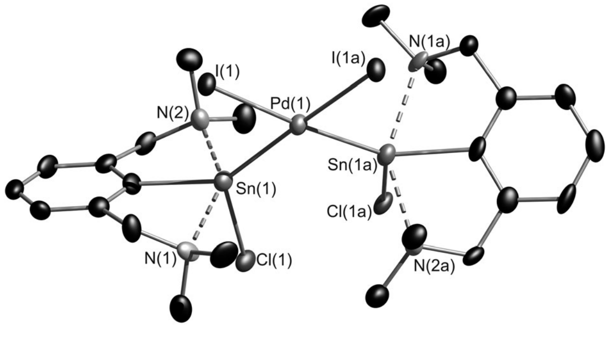


Figure 3. Molecular structure of **5**. Displacement ellipsoids are drawn at the 30 % probability level. Symmetry code: (a) x, y, $-z$.

Notably, the palladium and platinum atoms in compounds **1**–**6** adopt *cis* square-planar environments in which the orga-

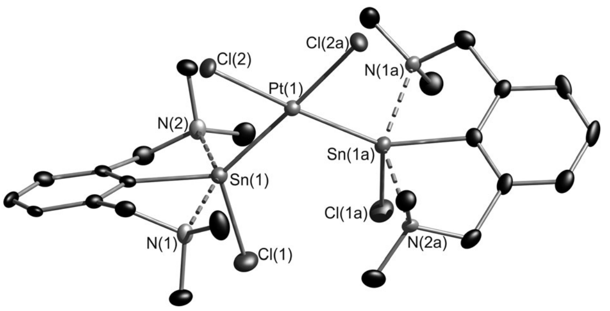


Figure 4. Molecular structure of **6**. Displacement ellipsoids are drawn at the 30 % probability level. Symmetry code: (a) *x*, *y*, −*z*.

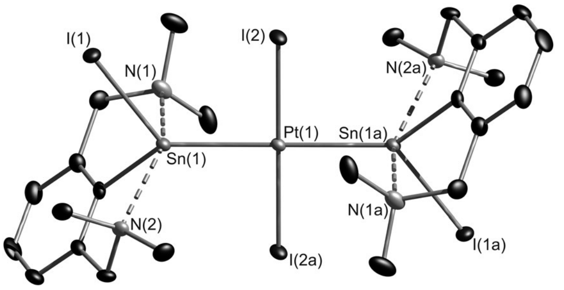


Figure 5. Molecular structure of **7**·2 $CHCl_3$. Displacement ellipsoids are drawn at the 30 % probability level. The chloroform solvate molecules have been omitted for clarity. Symmetry code: (a) −*x*, −*y*, −*z*.

nostannylene ligands coordinate the transition metal atoms through their lone electron pair. The Pd−Sn distances vary between 2.464(1) (Pd1−Sn2, **2**·C_7H_8) and 2.5138(9) Å (Pd1−Sn1, **5**) and the Pt−Sn distances vary between 2.469(1) (Pt1−Sn1, **4**·C_7H_8) and 2.4865(4) Å (**6**). These values are close to those reported for other tin-containing platinum and palladium complexes.[25,26,44,45l,46,47,49] Interestingly, the Pd−Sn distances are somewhat shorter than the distances given by Pyykkö and Atsumi for single Pd−Sn bonds (2.6 Å).[50]

The Sn(1) and Sn(2) atoms are pentacoordinated and each show a strongly distorted trigonal-bipyramidal environment with C(1)/C(11), X(1)/X(2) and M(1) (**1**, X = Cl, M = Pd; **2**, X = Br, M = Pd; **3**, X = I, M = Pd; **4**, X = Cl, M = Pt; **5**, X = I, M = Pd; **6**, X = Cl, M = Pt) occupying the equatorial positions and the oxygen and nitrogen atoms O(1) and O(2) (**1**–**4**), O(3) and O(4) (**1**, **2**, **4**), and N(1) and N(2) (**5**, **6**) occupying the axial positions. The distortion from the ideal geometry is especially manifested by the equatorial angles, which vary between 94.75(8) (C(1)-Sn(1)-Cl(1), **3**) and 138.6(1)° (C(1)-Sn(1)-Pt(1), **6**), and the axial angles, which vary between 147.8(2) (N(1)-Sn(1)-N(2), **5**) and 157.1(2)° (O(3)-Sn(2)-O(4), **2**). These two latter angles clearly result from ligand constraint, which appears to be more pronounced for the dimethylaminomethyl-substituted pincer-type ligand. The deviation of the equatorial angles from 120° is a result of the differences in the steric bulk of the halogen atoms, the metal atoms and the organic substituents. The platinum complex **4** shows the smallest C(1)-Sn(1)-M(1) angle of 126.9(3)°.

The Sn−O distances vary between 2.272(9) (Sn(1)−O(1), **4**) and 2.339(3) Å (Sn(2)−O(3), **1**), and the Sn−N distances between 2.437(7) (Sn(1)−N(1), **5**) and 2.534(7) Å (Sn(1)−N(2), **5**). The Sn−Cl distances vary between 2.380(1) (Sn(1)−Cl(1), **4**) and 2.493(3) Å (Sn(1)−Cl(1), **2**). The latter distance and that of 2.470(2) Å (**5**) are close to those of the parent organochloridostannylenes 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$$C_6H_2$SnCl (2.4708(8) Å)[51,52] and 2,6-(Me_2NCH_2)$_2$$C_6H_3$SnCl (2.488(3) Å).[53]

In complexes **1**–**6**, the organostannylenes RSnCl (R = 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$$C_6H_2$, 2,6-($Me_2NCH_2$)$_2$$C_6H_3$) are mutually *cis* coordinated with the Sn-M-Sn angles ranging between 96.37(2) (**1**) and 100.33(2)° (**6**). A rather interesting feature in the structures of complexes **1**–**6** is the intramolecular Sn···Sn distance, which ranges between 3.682(1) (**1**) and 3.837(1) Å (**5**) and which is shorter than twice the van der

Table 1. Selected bond lengths [Å] for compounds **1**–**7**.

	1·C_6H_6 M = Pd, X = Cl	**2**·C_7H_8 M = Pd, X = Br	**3**·C_7H_8 M = Pd, X = I	**4**·1.5 C_7H_8 M = Pt, X = Cl	**5** M = Pd, X = I	**6** M = Pt, X = Cl	**7**·2 $CHCl_3$ M = Pt, X = I
Sn(1)−C(1)	2.171(4)	2.145(10)	2.159(3)	2.172(13)	2.128(8)	2.115(5)	2.112(6)
Sn(1)−O(1)	2.304(3)	2.325(6)	2.326(2)	2.272(9)			
Sn(1)−O(2)	2.302(3)	2.302(6)	2.335(2)	2.295(8)			
Sn(1)−N(1)					2.437(7)	2.487(4)	2.467(5)
Sn(1)−N(2)					2.534(7)	2.439(4)	2.526(5)
Sn(1)−Cl(1)	2.390(1)	2.493(3)	2.398(1)	2.380(1)	2.470(2)	2.3828(15)	
Sn(1)−I(1)							2.7672(6)
Sn(1)−M(1)	2.4742(5)	2.474(1)	2.4945(3)	2.469(1)	2.5138(9)	2.4865(4)	2.5532(5)
Sn(2)−C(11)	2.175(4)	2.146(9)		2.186(14)			
Sn(2)−O(3)	2.339(3)	2.361(6)		2.318(9)			
Sn(2)−O(4)	2.314(3)	2.291(6)		2.316(8)			
Sn(2)−Cl(2)	2.391(1)	2.464(3)		2.388(4)			
Sn(2)−M(1)	2.4659(5)	2.464(1)		2.476(1)			
M(1)−X(1)					2.6581(9)		
M(1)−X(2)						2.391(1)	2.5837(4)
M(1)−X(3)	2.363(1)	2.474(2)	2.6545(3)	2.363(3)			
M(1)−X(4)	2.376(1)	2.481(2)		2.355(3)			

Table 2. Selected bond angles [°] for compounds **1**–**7**.

	1·C_6H_6 M=Pd X=Cl Y=Cl	**2**·C_7H_8 M=Pd X=Br Y=Cl	**3**·C_7H_8 M=Pd X=I Y=Cl	**4**·1.5 C_7H_8 M=Pt X=Cl Y=Cl	**5** M=Pd X=I Y=Cl	**6** M=Pt X=Cl Y=Cl	**7**·2 $CHCl_3$ M=Pt X=I Y=I
C(1)-Sn(1)-M(1)	134.67(9)	136.9(2)	135.95(8)	126.9(3)	137.5(2)	138.6(1)	138.2(2)
C(1)-Sn(1)-Y(1)	95.88(9)	95.6(2)	94.75(8)	101.1(3)	98.6(2)	98.74(14)	101.8(2)
M(1)-Sn(1)-Y(1)	129.14(3)	127.11(7)	129.30(2)	132.0(1)	123.90(5)	122.63(4)	119.72(2)
O(1)-Sn(1)-O(2)	156.65(9)	156.6(2)	156.89(7)	156.7(3)			
C(11)-Sn(2)-M(1)	137.76(9)	137.1(2)		128.5(3)			
C(11)-Sn(2)-Y(2)	94.7(1)	94.0(2)		102.7(3)			
M(1)-Sn(2)-Y(2)	127.43(3)	128.86(7)		128.8(1)			
O(3)-Sn(2)-O(4)	156.72(8)	157.1(2)		156.3(3)			
Sn(1)-M(1)-Sn(2)	96.37(2)	97.23(4)	98.55(2)	99.88(4)	99.49(4)	100.33(2)	180.0
Sn(1)-M(1)-X(3)	83.93(3)	84.36(5)	81.228(9)	83.13(9)			
Sn(2)-M(1)-X(4)	79.80(3)	79.33(4)		83.65(8)			
X(3)-M(1)-X(4)	99.64(4)	98.85(5)	98.99(2)	93.4(1)			
N(1)-Sn(1)-N(2)					147.8(2)	148.7(1)	148.2(2)
Sn(1)-M(1)-Y(1)					82.40(2)	82.53(3)	86.57(2)
Y(1)-M(1)-Y(1a)					96.02(4)	94.62(7)	180.0

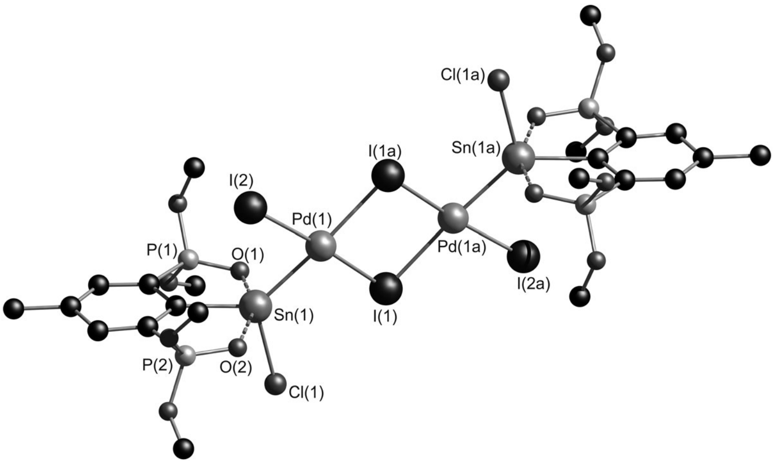


Figure 6. Standard ball-and-stick model of the molecular structure of **8**. All methyl groups have been omitted for clarity. Symmetry code: (a) $-x+1$, $-y$, $-z+2$. Selected interatomic distances [Å]: Sn(1)−Pd(1) 2.4804(15), Pd(1)−I(1) 2.5866(16), Pd(1)−I(2) 2.5829(16), Pd(1)−I(1a) 2.6867(15), Sn(1)−O(1) 2.312(9), Sn(1)−O(2) 2.272(8), Sn(1)−Cl(1) 2.419(4), Sn(1)−C(1) 2.147(15). Selected interatomic angles [°]: I(1)-Pd(1)-I(2) 175.41(6), Sn(1)-Pd(1)-I(1a) 175.82(7), I(1)-Pd(1)-I(1a) 88.99(5), Pd(1)-I(1)-Pd(1a) 91.01(5), O(1)-Sn(1)-O(2) 156.6(3), C(1)-Sn(1)-Cl(1) 102.3(4), C(1)-Sn(1)-Pd(1) 135.5(4), Cl(1)-Sn(1)-Pd(1) 121.62(10).

Waals radius of tin (2.20 Å).[54] DFT calculations (see below) suggest that these are bonding interactions.

The Mössbauer spectra of compounds **3** and **4** show isomer shifts (ISs) of 1.81 (quadrupole splitting, QS = 3.51 mm s^{-1}) and 1.70 mm s^{-1} (QS = 3.48 mm s^{-1}), respectively. These IS values are very unusual and lie out of the range generally observed for organotin(II) (2.10–3.00 mm s^{-1})[55] and organotin(IV) compounds (1.1–1.6 mm s^{-1}),[56] which suggests that the tin atoms in **3** and **4** have an oxidation state of III. This view is correct when considering mainly covalent bonds to the three more electronegative carbon, chlorine or iodine, and palladium atoms. It is also supported by the natural bond order (NBO) calculations (see below).

The Pt(1) atom in **7**·2 $CHCl_3$ exhibits a perfect square-planar environment with the Sn(1)/Sn(1a) and I(2)/I(2a) atoms being *trans* to each other. The I(1) and I(1a) atoms are also in a *trans* disposition. The Pt(1)−Sn(1) distance of 2.5532(5) Å is longer than the corresponding distances in the *cis*-configured complexes **4** (2.469(1) Å) and **6** (2.4865(4) Å). The same holds for the Sn(1)−N(1) and Sn(2)−N(2) distances of 2.467(5) and 2.526(5) Å, respectively, which are longer than the corresponding distances in **6**. From the data at hand, however, it is not evident whether these effects are exclusively the result of the *trans* configuration in complex **7**·2 $CHCl_3$ as the *cis*-configured complexes **4** and **6** contain chlorido instead of iodido substituents.

Complex **8** is a centrosymmetric *trans*-configured dimer containing non-symmetric μ-iodido bridges at Pd(1)−I(1) and Pd(1)−I(1a) distances of 2.587(2) and 2.687(2) Å, respectively. Notably, the Pd(1)−I(2) distance (2.583(2) Å) involving a non-bridging iodine atom is almost identical to the corresponding distance Pd(1)−I(1) involving a bridging iodine atom. The Sn(1) atom, as in compounds **1**–**4**, shows a distorted trigonal-bipyramidal environment with the interatomic distances and angles being close to those of **1**–**4**. In contrast to compounds **1**–**6**, but similarly to the iodido substituents at the tin atoms in **7**·2 $CHCl_3$, the chlorido substituents in **8** are mutually *trans* to each other.

The structures of complexes **1**–**6** are retained in solution. Thus, the ^{31}P NMR spectra of compounds **1**–**4** recorded in CD_2Cl_2[57] show, with respect to the parent organochlorido stannylene 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$C$_6$H$_2$SnCl ($\delta = 37.5$ ppm, $J(^{31}P,^{117/119}Sn) = 120$ Hz), low-frequency shifted singlet resonances falling in the narrow range of $\delta = 27.5$ (**1**, **4**) and 28.0 ppm (**3**). They are flanked by $^{117/119}$Sn satellites ranging between 126 Hz (unresolved) for the platinum dichlorido complex **4** and 184/192 Hz for the palladium diiodido complex **3**. Notably, there are also unresolved $^4J(^{31}P,^{117/119}Sn)$ couplings of 24 (**1**) and 27 Hz (**2**, **3**). Moreover, the spectrum of complex **4** also shows $J(^{31}P,^{195}Pt)$ satellites of 126 Hz that are superimposed on the $^{117/119}$Sn satellites giving rise to a total satellite-to-signal-to-satellite integral ratio of 24:52:24, which is close to the calculated ratio. The ^{119}Sn NMR spectra recorded in CD$_2$Cl$_2$ show triplet-of-triplet resonances at $\delta = -363$ ($J(^{119}Sn,^{31}P) = 186$, 24 Hz, $J(^{119}Sn,^{117}Sn) = 4490$ Hz, **1**), -321 ($J(^{119}Sn,^{31}P) = 178$, 27 Hz, $J(^{119}Sn,^{117}Sn) = 5640$ Hz, **2**) and -257 ppm ($J(^{119}Sn,^{31}P) = 192$, 27 Hz, $J(^{119}Sn,^{117}Sn) = 6480$ Hz, **3**) and a triplet resonance at $\delta = -483$ ppm ($J(^{119}Sn,^{31}P) = 130$ Hz, $^1J(^{119}Sn,^{195}Pt) = 28470$ Hz, $J(^{119}Sn,^{117}Sn) = 1500$ Hz, **4**), respectively, which is low-frequency shifted with respect to 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$C$_6$H$_2$SnCl ($\delta = -99$ ppm ($J(^{119}Sn,^{31}P) = 121$ Hz),[51] as well as singlet resonances at $\delta = -20$ ($J(^{119}Sn,^{117}Sn) = 3885$ Hz, **5**) and -254 ppm ($^1J(^{119}Sn,^{195}Pt) = 12640$ Hz, **6**), with the latter also being low-frequency shifted with respect to the parent organostannylene 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnCl ($\delta = 156$ ppm).[53] Notably, the resonances for the complexes **1**–**4** are more low-frequency shifted than those for complexes **5**, **6** and *cis*-[{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnCl}$_2$PdCl$_2$] ($\delta = -122$ ppm).[48g] This hints at a stronger intramolecular P=O→Sn coordination in **1**–**4** compared with the N→Sn interaction in **5** and **6**. A striking feature of the ^{119}Sn NMR spectra of complexes **1**–**3** and **5** is the observation of large $J(^{119}Sn,^{117}Sn)$ couplings in the range 3885 (**5**) and 6480 Hz (**3**). The magnitude of the coupling depends on both the nature of the intramolecularly coordinating donor atom (P=O→Sn in **1** versus N→Sn in **5**) and the halogen substituents at the palladium atom with the largest coupling observed for the palladium diiodide complex **3**. With caution we interpret these couplings as being composed of ^1J and ^2J with both showing the same sign.

The ^{195}Pt NMR spectrum of complex **4** shows a quintet resonance at $\delta = -4482$ ppm ($J(^{195}Pt,^{31}P) = 122$ Hz, $J(^{195}Pt,^{117/119}Sn) = 27190/28480$ Hz).

As in the chromium–pentacarbonyl complex [4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$C$_6$H$_2$(Cl)SnCr(CO)$_5$],[51,58] the ^{1}H NMR spectra of complexes **1**–**4** each show four doublet resonances for the isopropyloxy methyl protons. Exemplarily, the spectrum of a solution of complex **4** in [D$_8$]toluene was recorded at 80 °C. No coalescence phenomena were observed, which indicates high configurational stability of the tin atoms. As in the related complex [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$(H)SnW(CO)$_5$],[59] the ^{1}H NMR spectra of complexes **5** and **6** each exhibit two equally intense singlet resonances for the *N*-methyl protons and AB-type resonances for the methylene protons. These observations indicate the tin atoms in these compounds to be configurationally stable as well.

In solution, the intramolecular N→Sn coordination in compound **7** is kinetically labile on the ^{1}H NMR timescale. Thus, the ^{1}H NMR spectrum of **7** in CDCl$_3$ at room temperature shows single resonances for the NCH$_2$ ($\delta = 4.13$ ppm) and NCH$_3$ ($\delta = 2.88$ ppm) protons. No decoalescence phenomena were observed at 270 K. Measurements at lower temperature failed as a result of the rather poor solubility of compound **7**. The ^{119}Sn NMR spectrum of compound **7** shows a single resonance at $\delta = -80$ ppm, which is considerably high-frequency shifted compared with the *cis*-configured complex **6** ($\delta = -254$ ppm) it was synthesised from. The ^{31}P NMR spectrum of **8** recorded in CD$_2$Cl$_2$ shows two resonances at $\delta = 26.2$ ($J(^{31}P,^{117/119}Sn) = 186$ Hz, integral 2) and 26.3 ppm ($J(^{31}P,^{117/119}Sn) = 172$ Hz integral 1), which indicates that compound **8** disintegrates. This was not investigated further.

Redistribution reactions: The ^{31}P NMR spectrum (see Figure S3 in the Supporting Information) of a solution containing equimolar quantities of the palladium dichloride complex **1** and the palladium diiodide complex **3** in C$_6$D$_6$ shows four almost equally intense resonances at $\delta = 29.2$ (integral 29 %, $J(^{31}P,^{117/119}Sn) = 195$ Hz, **3**), 29.1 (integral 26 %, $J(^{31}P,^{119/117}Sn) = 204$ Hz, signal *a*), 29.0 (integral 24 %, $J(^{31}P,^{117/119}Sn) = 178$ Hz, signal *b*) and 28.8 ppm (integral 21 %, $J(^{31}P,^{117/119}Sn) = 182$ Hz, **1**). The ^{119}Sn NMR spectrum (see Figure S4 in the Supporting Information) of the same solution displays four triplet resonances at $\delta = -257$ (integral 33 %, $J(^{119/117}Sn,^{31}P) = 195$ Hz, **3**), -301 (integral 26 %, $J(^{119/117}Sn,^{31}P) = 205$ Hz, signal *c*), -327 (integral 22 %, $J(^{119/117}Sn,^{31}P) = 178$ Hz, signal *d*) and -365 ppm (integral 20 %, $J(^{119/117}Sn,^{31}P) = 205$ Hz, **1**). These spectra indicate halogen exchange between the palladium atoms and the in situ formation of the complex *cis*-[(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2$-C$_6$H$_2$SnCl)$_2$PdClI] with the signals *a*–*d* assigned to this latter complex.

The ^{31}P NMR spectrum of a solution of complex **1** in C$_6$D$_6$ to which had been added 2 mol equiv of triphenylphosphane shows broad resonances at $\delta = 37.8$ ($\nu_{1/2} = 143$ Hz, 4-*t*Bu-2,6-[P(O)(O-*i*Pr)$_2$]$_2$C$_6$H$_2$SnCl), 28.8 ($\nu_{1/2} = 220$ Hz, **1**) and -3.8 ppm ($\nu_{1/2} = 107$ Hz, Ph$_3$P).

The ^{31}P NMR spectrum of a solution of complex **1** in C$_6$D$_6$ to which had been added 2 mol equiv of 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$C$_6$H$_2$SnCl shows rather broad resonances with equal integrals at $\delta = 37.4$ ($\nu_{1/2} = 270$ Hz, 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2$C$_6$H$_2$SnCl) and $\delta = 28.8$ ppm ($\nu_{1/2} = 216$ Hz, **1**). The ^{119}Sn NMR spectrum of the same solution displays only one broad resonance at $\delta = -366$ ppm ($\nu_{1/2} = 520$ Hz). The spectra indicate kinetic lability of the Pd–Sn bond in complex **1** and suggest the possibility of replacing one organostannylene moiety by another one or by other ligands.

This idea was confirmed by recording time-dependent ^{31}P NMR spectra of a solution of equimolar amounts of complex **1** and *cis*-[{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$SnCl}$_2$PdCl$_2$] in CDCl$_3$. The spectrum recorded 1 h after the solution had been prepared displays a major sharp resonance at $\delta = 28.3$ ppm ($J(^{31}P,^{117/119}Sn) = 176$, 21 Hz, signal *e*). In addition, there is a minor intense signal (approx. 5 %) at $\delta = 27.8$ ppm belonging to residual amounts of complex **1**. The ^{119}Sn NMR spectrum of the same solution shows a singlet resonance *f* at $\delta = -125$ ppm ($J(^{119}Sn,^{117/119}Sn) = 3942$ Hz) and a triplet resonance *g* at $\delta = -335$ ppm ($J(^{119}Sn,^{31}P) = 174$ Hz, $J(^{119}Sn,^{117/119}Sn) = 3921$ Hz) with an integral ratio of 1:1. The signals *e*–*g* were assigned to the complex [{2,6-($Me_2NCH_2)_2C_6H_3$-SnCl}(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2C_6H_2$SnCl)PdCl$_2$] (**9**) containing two different organostannylene ligands. From the data at hand, however, it is not clear whether complex **9** has a *cis* or *trans* configuration. The ^{119}Sn NMR spectrum of this solution to which a further amount of *cis*-[{2,6-($Me_2NCH_2)_2C_6H_3$SnCl}$_2$PdCl$_2$] had been added shows, in addition to the resonances for **9**, a resonance at $\delta = -122$ ppm belonging to the former complex. Apparently the non-symmetrically substituted complex **9** is thermodynamically favoured over the symmetrically substituted complexes. However, so far, attempts to isolate complex **9** as an analytically pure material have failed.

Serendipitous formation of the penta- and hexanuclear complexes 10 and 11: In the complexes **1**–**8** discussed above, the heteroleptic organostannylene ligands act as σ donors towards the platinum atom. On the other hand, there are numerous platinum complexes that contain the $[SnCl_3]^-$ ligand as a result of the insertion of tin(II) chloride into Pt−Cl bonds.[44] These observations suggest that it should be possible to obtain platinum complexes containing both types of ligands at the same time.

The ^{31}P NMR spectrum of a solution (A) of compound **4** and tin(II) chloride (molar ratio of 1:2) in CD_2Cl_2 shows a major resonance at $\delta = 29.85$ ppm (integral approx. 58%) that is flanked by satellites of 87 Hz. The satellite-to-signal-to-satellite ratio of 14:30:14 indicates these satellites to be the superposition of $J(^{31}P,^{117/119}Sn)$ and $J(^{31}P,^{195}Pt)$ (calculated ratio: 25:50:25). In addition, there are six minor intense resonances at $\delta = 29.0$, 28.8, 28.4, 28.3, 27.6 and 27.0 ppm (total integral approx. 36%). The ^{119}Sn NMR spectrum of the same solution shows, even after extensive data acquisition (10240 scans), a rather noisy spectrum in which at least 10 resonances at $\delta = -48$, −67, −122, −150, −234, −336, −396, −484, −504 and −550 ppm were identified. The ^{31}P NMR spectrum of a clear deep-red solution (B) of compound **4** and $SnCl_2$ (molar ratio of 1:3) in C_6D_6 shows a single resonance at $\delta = 30.00$ ppm flanked by satellites of 87 Hz with the satellite-to-signal-to-satellite ratio as above. From this solution no ^{119}Sn NMR signals could be detected. So far, all attempts to obtain a pure compound from this solution have failed. However, from the many experiments with reaction mixtures containing platinum dichloride, tin dichloride and the organochloridostannylene 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2C_6H_2$-SnCl in a molar ratio of 1:2:2 or 1:3:2 we obtained, by crystal picking, small quantities of the novel complexes [(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2C_6H_2$SnCl)$_n$Pt(SnCl$_3$)$_2$] (**10**·2C_7H_8, $n = 2$; **11**·C_7H_8·0.5C_6H_{14}, $n = 3$) as red single crystals suitable for X-ray diffraction analysis. So far, attempts at obtaining these compounds by rational syntheses in bigger quantities have failed.

The molecular structure of complex **10**·2C_7H_8 is shown in Figure 7 and selected interatomic distances and angles are given in the caption. The Pt(1) atom in **10**·2C_7H_8 is four-coordinate and exhibits a slightly distorted square-planar environment with the Sn(1)/Sn(1a) and Sn(2)/Sn(2a) atoms mutually *trans* to each other. The deviation of the Sn(1)-Pt(1)-Sn(1a) and Sn(2)-Pt(1)-Sn(2a) angles from 180° might be the result of steric congestion and/or additional weak intramolecular Cl(2)⋯Sn(1) and Cl(1)⋯Sn(2) interactions at distances of 3.511(1) and 3.602(1) Å, respectively, which are shorter than the sum of the van der Waals radii[54] of tin (2.20 Å) and chlorine (1.70–1.90 Å). Thus, the Sn(1) atom is [5+1] coordinate and exhibits a distorted octahedral environment with the O(1), O(2), C(1) and Pt(1) atoms occupying the equatorial positions and the Cl(1) and Cl(2) atoms the axial positions, whereas the Sn(2) atom is [4+1] coordinate and exhibits a distorted trigonal-bipyramidal environment. The Cl(1) atom approaches the Sn(2) atom at the tetrahedral face defined by Pt(1), Cl(3) and Cl(4). Both the Pt(1)−Sn(1) (2.5460(6) Å) and Pt(1)−Sn(2) (2.5352(6) Å) distances are slightly longer than the Pt(1)−Sn(1) and Pt(1)−Sn(2) distances of 2.469(1) and 2.476(1) Å, respectively, in compound **4**. The other distances and the bond angles are rather similar to those in **4**.

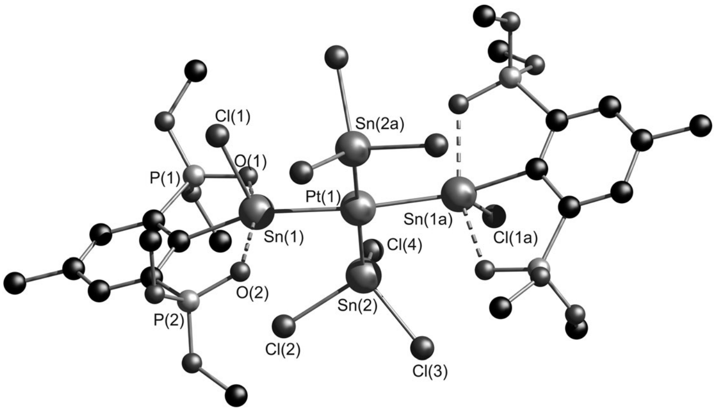


Figure 7. Standard ball-and-stick model of **10**·2C_7H_8. The toluene solvate molecules and all methyl groups have been omitted for clarity. Symmetry code: (a) $-x$, $-y$, z. Selected interatomic distances [Å]: Pt(1)−Sn(1) 2.5460(6), Pt(1)−Sn(2) 2.5352(6), Sn(1)−O(1) 2.303(7), Sn(1)−O(2) 2.278(7), Sn(1)−Cl(1) 2.392(3), Sn(1)−C(1) 2.171(7), Sn(2)−Cl(2) 2.378(3), Sn(2)−Cl(3) 2.340(4), Sn(2)−Cl(4) 2.338(4). Selected interatomic angles [°]: Sn(1)-Pt(1)-Sn(1a) 172.84(8), Sn(2)-Pt(1)-Sn(2a) 173.95(9), O(1)-Sn(1)-O(2) 155.5(2), C(1)-Sn(1)-Cl(1) 91.7(3), C(1)-Sn(1)-Pt(1) 157.4(2), Cl(1)-Sn(1)-Pt(1) 110.59(7).

The molecular structure of **11**·C_7H_8·0.5C_6H_{14} is shown in Figure 8 and selected interatomic distances and angles are given in Tables 3 and 4. The Pt(1) atom is pentacoordinated and exhibits a distorted trigonal-bipyramidal environment with the aryl-bound Sn(2) and Sn(3) atoms occupying the axial positions and the aryl-bound Sn(1) and the trichlorido-substituted Sn(4) and Sn(5) atoms occupying the equatorial positions. The distortion from ideal geometry is manifested by the equatorial Sn(1)-Pt(1)-Sn(5) (115.84(2)°), Sn(1)-Pt(1)-Sn(4) (127.95(2)°) and Sn(4)-Pt(1)-Sn(5) (116.19(2)°) angles, which deviate from 120°. The axial Sn(2)-Pt(1)-Sn(3) angle (178.06(2)°), however, is close to 180°. The Pt−Sn distances fall in the narrow range between 2.5597(5) (Pt(1)−Sn(2)) and 2.5801(5) Å (Pt(1)−Sn(5)). Interestingly, the longest distance is observed for an equatorially and not an axially located tin atom. This observation is in line with findings reported for $[NHEt_3]_3[Pt(SnCl_3)_5]$[44c] and $[PtCl(SMe_2)_3]_3[Pt(SnCl_3)_5]$[44b] and consistent with the theory for trigonal-bipyramidal d^8-configured transition metals according to which axial bonds should be shorter than equatorial ones.[60] The geometries around the tin atoms and the bond lengths and angles within the organostannylene moieties resemble those discussed for compound **10**·2 C_7H_8. As for the latter compound, the intramolecular Sn(2)···Cl(41) and Sn(3)···Cl(52) distances of 3.634 (1) and 3.623(1) Å, respectively, are shorter than the sum of the van der Waals radii[54] of tin and chlorine.

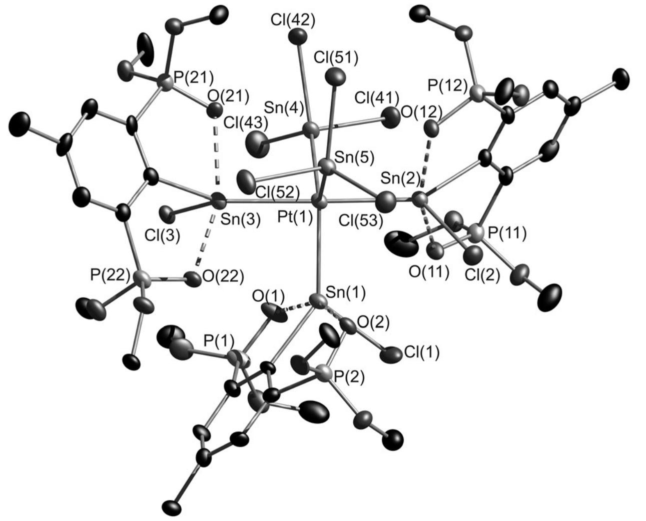


Figure 8. Molecular structure of **11**·C_7H_8·0.5 C_6H_{14}. Displacement ellipsoids are drawn at the 30 % probability level. The solvate molecules have been removed by the Squeeze routine of the program Platon.[61] The methyl groups have been omitted for clarity.

Table 3. Selected bond lengths [Å] for **11**·C_7H_8·0.5 C_6H_{14}.

Pt(1)−Sn(1)	2.5613(5)				
Pt(1)−Sn(2)	2.5597(5)				
Pt(1)−Sn(3)	2.5635(5)				
Pt(1)−Sn(4)	2.5806(5)				
Pt(1)−Sn(5)	2.5801(5)				
Sn(1)−C(1)	2.162(5)	Sn(2)−C(11)	2.170(5)	Sn(3)−C(21)	2.138(6)
Sn(1)−O(1)	2.318(4)	Sn(2)−O(11)	2.277(3)	Sn(3)−O(21)	2.342(4)
Sn(1)−O(2)	2.315(4)	Sn(2)−O(12)	2.317(3)	Sn(3)−O(22)	2.278(3)
Sn(1)−Cl(1)	2.441(4)	Sn(2)−Cl(2)	2.3787(17)	Sn(3)−Cl(3)	2.406(7)
Sn(1)−O(1Cl)	1.883(13)			Sn(3)−O(3Cl)	2.07(2)
Sn(4)−Cl(41)	2.4129(16)	Sn(5)−Cl(51)	2.4068(16)		
Sn(4)−Cl(42)	2.4082(16)	Sn(5)−Cl(52)	2.4307(16)		
Sn(4)−Cl(43)	2.3737(18)	Sn(5)−Cl(53)	2.3903(17)		

Table 4. Selected bond angles [°] for **11**·C_7H_8·0.5 C_6H_{14}.

Sn(1)-Pt(1)-Sn(2)	90.907(16)	Sn(2)-Pt(1)-Sn(4)	90.325(16)
Sn(1)-Pt(1)-Sn(3)	89.947(16)	Sn(2)-Pt(1)-Sn(5)	90.207(16)
Sn(1)-Pt(1)-Sn(4)	127.950(17)	Sn(3)-Pt(1)-Sn(4)	87.778(16)
Sn(1)-Pt(1)-Sn(5)	115.841(17)	Sn(3)-Pt(1)-Sn(5)	90.986(16)
Sn(2)-Pt(1)-Sn(3)	178.062(18)	Sn(4)-Pt(1)-Sn(5)	116.186(17)
O(1Cl)-Sn(1)-C(1)	97.3(6)		
O(2)-Sn(1)-O(1)	155.43(13)		
C(1)-Sn(1)-Cl(1)	94.4(2)		
C(1)-Sn(1)-Pt(1)	139.64(15)		
Cl(1)-Sn(1)-Pt(1)	125.82(16)		
O(11)-Sn(2)-O(12)	156.56(12)	O(3Cl)-Sn(3)-C(21)	97.8(7)
O(11)-Sn(2)-Cl(2)	90.87(11)	O(21)-Sn(3)-O(22)	156.73(13)
C(11)-Sn(2)-Pt(1)	143.67(15)	C(21)-Sn(3)-Cl(3)	92.8(3)
Cl(2)-Sn(2)-Pt(1)	120.28(4)	O(3Cl)-Sn(3)-Pt(1)	115.2(7)
		C(21)-Sn(3)-Pt(1)	146.04(15)
Cl(41)-Sn(4)-Cl(42)	91.10(6)	Cl(51)-Sn(5)-Cl(52)	94.27(6)
Cl(41)-Sn(4)-Cl(43)	94.10(6)	Cl(51)-Sn(5)-Cl(53)	95.45(6)
Cl(42)-Sn(4)-Cl(43)	97.07(7)	Cl(52)-Sn(5)-Cl(53)	96.35(6)
Cl(41)-Sn(4)-Pt(1)	113.75(4)	Cl(51)-Sn(5)-Pt(1)	127.30(4)
Cl(42)-Sn(4)-Pt(1)	130.72(5)	Cl(52)-Sn(5)-Pt(1)	111.59(4)
Cl(43)-Sn(4)-Pt(1)	121.10(5)	Cl(53)-Sn(5)-Pt(1)	124.39(4)

DFT calculations: To elucidate the bonding situation in complexes **1**–**7**, DFT calculations were performed. Turbomole[62] with the pure functional BP86[63] and the def2-TZVP basis set[64] was used for the geometry optimisation because this combination has already been employed for similar compounds.[65] The calculated data for all seven compounds are in good agreement with the experimental data (Tables 5 and 6). The energy differences between the *cis* and *trans* isomers have also been determined (Table 7). In the case of the O,C,O-coordinating pincer-type ligand-stabilised complexes **1**–**4**, DFT predicts the *cis* isomers to be considerably more stable than the *trans*-configured complexes, whereas for complexes **5**–**7** containing the N,C,N-coordinating pincer-type ligands, the energy difference between the *cis* and *trans* isomers is predicted to be rather small and at the limit of significance of the calculations. From these calculations it becomes understandable that, as shown in Scheme 2, *trans*-$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3SnI\}_2PtI_2]$ (**7**) could be obtained from the reaction of the platinum dichloride complex **6** with sodium iodide.

In further theoretical investigations, NBO calculations[66] were performed with the BP86/def2-TZVP combination in Gaussian 03[67] to gain an insight into the electronic structures of the complexes. The calculations reveal both the Sn−Pd and Sn−Pt bonds to be highly covalent with an almost equal contribution from each bonding partner. The two degenerate HOMO-90/91 MOs of the highly covalent Sn−Pt bonds in compound **4** are shown in Figure 9.

The Wiberg bond index for the Sn−M bond possesses values between 0.62 (**3**) and 0.72 (**4**), whereas the donor stabilisation of the pincer-type ligands is reflected by Wiberg bond indices of 0.19 (**1**–**3**) to 0.23 (**4**) for P=O donors and 0.16 (**5**, **7**) to 0.18 (**6**) for the nitrogen donors.

Table 5. Calculated bond lengths [Å] for compounds **1**–**7** (BP86/def2-TZVP).

	1 M=Pd X=Cl	**2** M=Pd X=Br	**3** M=Pd X=I	**4** M=Pt X=Cl	**5** M=Pd X=I	**6** M=Pt X=Cl	**7** M=Pt X=I
Sn(1)–C(1)	2.209	2.206	2.212	2.207	2.1255	2.155	2.165
Sn(1)–O(1)	2.400	2.384	2.381	2.389			
Sn(1)–O(2)	2.375	2.369	2.379	2.378			
Sn(1)–N(1)					2.557	2.630	2.640
Sn(1)–N(2)					2.622	2.532	2.563
Sn(1)–Cl(1)	2.417	2.430	2.424	2.417	2.467	2.440	2.821
Sn(1)–M(1)	2.521	2.532	2.550	2.525	2.559	2.533	2.617
M(1)–X(3)	2.392	2.524	2.693	2.394	2.694	2.392	2.642
M(1)–X(4)	2.398	2.529	2.690	2.404			

Table 6. Calculated bond angles [°] for compounds **1**–**7** (BP86/def2-TZVP).

	1 M=Pd X=Cl	**2** M=Pd X=Br	**3** M=Pd X=I	**4** M=Pt X=Cl	**5** M=Pd X=I	**6** M=Pt X=Cl	**7** M=Pt X=I
C(1)-Sn(1)-M(1)	131.3	132.8	134.5	129.7	141.0	138.5	136.5
C(1)-Sn(1)-Cl(1)	95.4	97.6	96.4	98.0	97.0	102.1	101.4
M(1)-Sn(1)-Cl(1)	133.2	129.5	129.2	132.2	121.7	119.1	121.9
O(1)-Sn(1)-O(2)	159.5	157.4	157.3	159.4			
N(1)-Sn(1)-N(2)					146.2	146.0	145.6
Sn(1)-M(1)-Sn(2)	100.6	101.0	99.2	100.6	104.0	106.5	180.0
X(3)-M(1)-X(4)	103.5	96.7	95.4	103.5	97.1	93.8	180.0

Most interestingly, the Wiberg bond indices for the Sn···Sn interactions in the *cis*-configured complexes **1**–**6**, which range between 0.09 (**4**) and 0.12 (**5**), show that these are bonding interactions and contribute to the stabilisation of the complexes. The corresponding MO that illustrates this interaction for the platinum complex **4** is shown in Figure 9. This is the HOMO-4 orbital, which can be described as a three-centre bonding interaction of the d_{xy} orbital of the platinum atom with two formal sp^2-hybridised orbitals of the tin atoms (following the NBO theory). A more detailed MO diagram is given in Figure S5 in the Supporting Information.

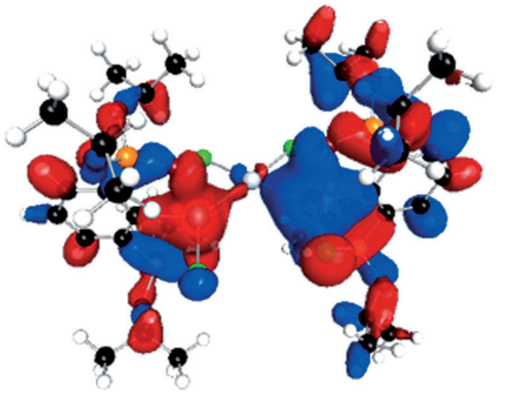
The molecular structures of the square-planar complexes **1**–**6** exhibit intramolecular Sn···X–M (X=Cl, Br, I; M=Pd, Pt) interactions ranging between 3.106(1) (Sn(2)····Cl(4), **1**) and 3.408(1) Å (Sn(1)···I(3), **5**), which are shorter than the sum of the van der Waals radii of the corresponding atoms. These distances are the result of the square-planar geometries of the complexes rather than of bonding interactions. This view is supported by an atoms-in-molecules (AIM) analysis performed on the model compound *cis*-[$PtCl_2(SnClH)_2$], which gave no bond critical point for the Sn···Cl–Pt interaction (see Figure S6 in the Supporting Information).

The NBO analysis of *cis*-configured compounds **1**–**6** revealed that the O→Sn charge transfer in compounds **1**–**4** is twice as big as the N→Sn charge transfer in compounds **5** and **6** (Table 7). When analysing the hypothetical *trans*-configured counterparts of complexes **1** and **4**, it appeared that the O,C,O-coordinating pincer-type ligands provide the same charge-transfer stabilisation as in the *cis*-configured complexes. This is in contrast to the behaviour of the N,C,N-coordinating pincer-type ligands, which display a higher donor strength in *trans* complexes than in the *cis* complexes (Table 7). Furthermore, the NBO analysis indicates a natural charge at the tin atoms ranging from +1.45 (**5**) to +1.54 (**4**) and from −0.73 (**5**) to −0.40 (**1**) at the platinum or palladium atoms, respectively. The NBO charges of the metal-

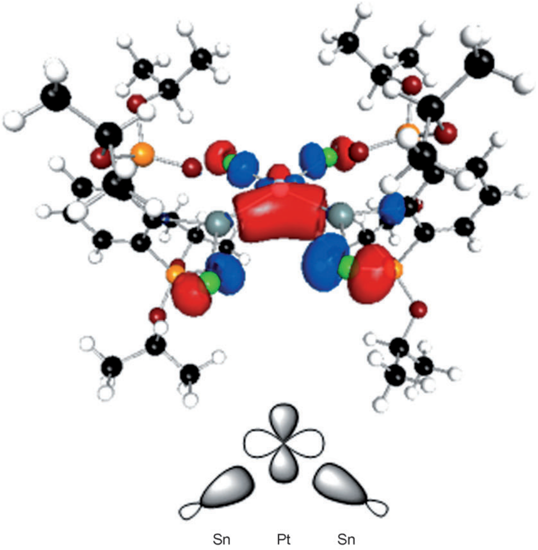
Table 7. Results of NBO calculations on complexes **1**–**7**.

Compound[a]	Energy[b] [kcal mol^{-1}]	Sn···Sn WBI[c]	Sn–M WBI[c]	Sn–O/N WBI[c]	Sn NBO charge	M NBO charge	M–Y NBO charge	Sn–X NBO charge	Charge transfer to Sn[d] [kcal mol^{-1}]
cis-[$(R^1SnCl)_2PdCl_2$] (**1**)	−6.0	0.107	0.65	0.19	+1.47	−0.40	−0.48	−0.49	50
cis-[$(R^1SnCl)_2PdBr_2$] (**2**)	−5.8	0.105	0.64	0.19	+1.47	−0.49	−0.42	−0.51	50
cis-[$(R^1SnCl)_2PdI_2$] (**3**)	−10.2	0.106	0.62	0.19	+1.45	−0.64	−0.31	−0.51	50
cis-[$(R^1SnCl)_2PtCl_2$] (**4**)	−10.5	0.092	0.72	0.23	+1.54	−0.47	−0.50	−0.50	60
cis-[$(R^2SnCl)_2PdI_2$] (**5**)	2.1	0.119	0.63	0.16	+1.45	−0.73	−0.27	−0.58	24
cis-[$(R^2SnCl)_2PtCl_2$] (**6**)	0.5	0.104	0.68	0.18	+1.45	−0.62	−0.41	−0.56	26
trans-[$(R^2SnI)_2PtI_2$] (**7**)	3.2	0.077	0.70	0.16	+1.35	−1.06	−0.16	−0.39	46

[a] R^1=4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2C_6H_2$, R^2=2,6-(Me_2NCH_2)$_2C_6H_3$. [b] Negative values indicate stabilisation of the *cis* over the *trans* isomer. [c] WBI=Wiberg bond index. [d] Per O/N donor group.



HOMO-90/91: Sn-Pt bond



HOMO-4: Sn···Sn interaction

Figure 9. Top: Two degenerate HOMO-90/91 orbitals showing the two Pt−Sn bonds with high covalent character. Bottom: HOMO-4 orbital showing the weak intramolecular Sn···Sn interaction.

bound halides and of the metals sum to approximately −1.5 to −1.3. This is due to the greater electronegativity of the platinum and palladium atoms compared with tin and electron transfer from both tin-containing units. Formally, one would expect a charge of −2 for the MX_2 unit, but the NBO charges represent not the formal charges but an impression of the charge distribution.[66] This is consistent with the interpretation of the Mössbauer data, on the basis of which the tin atoms were assigned the oxidation state III (in compounds **3** and **4**). In the *trans*-configured compound **7**, the situation is different due to a special delocalisation of the Sn−Pt−Sn bonding interaction, which results in a more negative charge at the platinum (−1.1) and tin (+1.35) atoms. A more detailed description will be the subject of further studies.

Conclusion

In this work we have shown that intramolecularly coordinated heteroleptic organostannylenes of the type RSnCl (R = 4-*t*Bu-2,6-$[P(O)(OiPr)_2]_2C_6H_2$, 2,6-$(Me_2NCH_2)_2C_6H_3$) behave as σ donors in Pd^{II} and Pt^{II} complexes and do not insert into the corresponding M−X bond. DFT calculations revealed the intramolecular P=O→Sn coordination to be considerably stronger than the N→Sn coordination and to favour the *cis*-configured complexes over the *trans* compounds. For the complexes containing the nitrogen-donor-stabilised organostannylenes, the differences between the *cis*- and *trans*-configured complexes are much smaller with the consequence that both representatives (**6**, **7**) could be isolated. The N,C,N-coordinating pincer-type ligands are stronger donors in the *trans*-configured complexes than in the *cis*-configured complexes.

The Sn···Sn interactions in the *cis*-configured complexes **1**–**6**, with distances shorter than twice the van der Waals radius of the tin atom, are bonding interactions and contribute to the stability of the complexes. This is of fundamental interest for understanding the chemical bonding in such complexes. Finally, the family of tin–platinum complexes has been extended by the first examples of complexes that contain both σ-bonded organostannylenes and trichloridostannyl ligands, with the latter originating from the insertion of $SnCl_2$ into the Pt−Cl bond.

Experimental Section

General: All solvents were dried and purified by standard procedures. All reactions were carried out under an atmosphere of dry nitrogen or argon. The metal dihalides $PtCl_2$, $PdCl_2$ and PdI_2 were purchased from Sigma–Aldrich. The organostannylenes 4-*t*Bu-2,6-$[P(O)(OiPr)_2]_2C_6H_2SnX$ (X = Cl, Br, I) and 2,6-$(Me_2NCH_2)_2C_6H_3SnCl$ were prepared according to literature procedures.[51–53] Bruker DPX-300, DRX-400 and Bruker Avance 500 spectrometers were used to record ^{1}H, ^{13}C, ^{31}P, ^{119}Sn and ^{195}Pt NMR spectra. NMR chemical shifts (δ) are given in ppm and are referenced to Me_4Si (^{1}H, ^{13}C), H_3PO_4 (85 %, ^{31}P), Me_4Sn (^{119}Sn) and 1.2 M $Na_2[PtCl_6]$ (^{195}Pt). The NMR spectra were recorded at room temperature. Mössbauer spectra were recorded in constant-acceleration mode on a home-made instrument designed and built by the Institut voor Kernen Stralingsfysica (IKS), Leuven. The isomer shifts are referenced to a source of $Ca^{119m}SnO_3$ from Amersham, UK, the samples being maintained at 90 ± 2 K. The data were treated with a least-squares iterative program, deconvoluting the spectrum into the sum of Lorentzians. IR spectra were measured on a Nicolet 5PC device as KBr discs. ESI mass spectra were recorded on a Thermoquest-Finnigan TSQ instrument with acetonitrile as the mobile phase. UV/Vis spectra were recorded on an Agilent Cary 60 UV/Vis spectrophotometer. The elemental analyses were performed on a LECO-CHNS-932 analyser.

Computational details: The calculations were performed with Turbomole[62] by using the BP86 pure functional[63] with the Ahlrichs def2-TZVP basis set,[64] which includes effective core potentials on tin and platinum. Tight conversion criteria were applied. Both stationary points were characterised by frequency analysis and show the correct number of negative eigenvalues (zero for a local minimum). Based on the geometry obtained by the PB86/def2-TZVP method, a NBO analysis was performed by using this method with NBO 5.0[66] as implemented in Gaussian 03.[67]

Synthesis of compounds 1–8, 10, and 11

cis-$[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PdCl_2}]$ (1): 4-*t*Bu-2,6-$[\mathrm{P(O)(O}i\mathrm{Pr)_2}]_2\mathrm{C_6H_2SnCl}$ (2.0 g, 3.25 mmol) was added to a suspension of $\mathrm{PdCl_2}$ (0.29 g, 1.62 mmol) in toluene (5 mL). After the reaction mixture had been stirred for 12 h, the solution was filtered and the toluene removed in vacuo. Recrystallisation from benzene yielded 1.2 g (53 %) of $[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PdCl_2}]\cdot\mathrm{C_6H_6}$ as yellow crystals that were suitable for X-ray diffraction analysis. The crystals were dried in vacuo for 2 h at 40 °C to remove the solvate.

M.p. 153 °C (decomp.); ^{1}H NMR (300.13 MHz, $\mathrm{C_6D_6}$): $\delta=8.04$ (d, ^3J(H,P) = 13.9 Hz, 4H; Ar-H), 5.55–5.43 (m, 4H; CH), 4.91–4.79 (m, 4H; CH), 1.51 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.20 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.14 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.04 (s, 18H; $\mathrm{CH_3}$), 0.92 ppm (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$); ^{13}C NMR (100.63 MHz, $\mathrm{CD_2Cl_2}$): $\delta=166.1$ (t, ^2J(C,P) = 21.4 Hz; C-1), 154.6 (t, ^3J(C,P) = 12.1 Hz; C-4), 132.0 (dd, ^2J(C,P) = 4.9 Hz, ^4J(C,P) = 13.6 Hz; C-3/5), 130.8 (dd, ^1J(C,P) = 184.7 Hz, ^3J(C,P) = 19.0 Hz; C-2/6), 74.9 (brs; CH), 74.2 (brs; CH), 35.7 (s; $C(\mathrm{CH_3})_3$), 31.4 (s; $\mathrm{C}(C\mathrm{H_3})_3$), 24.5–23.6 ppm (not resolved; $\mathrm{CH}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR (121.49 MHz, $\mathrm{CD_2Cl_2}$): $\delta=27.5$ ppm (J(P,Sn) = 24.5 Hz, J(P,Sn) = 178.2/170.4 Hz); ^{119}Sn{^{1}H} NMR (111.92 MHz, $\mathrm{CD_2Cl_2}$): $\delta=-363$ ppm (t, J(Sn,P) = 178 Hz, J(Sn,Sn) = 4490 Hz); IR (KBr): ν = 2978, 2934, 1385, 1178 (P=O), 1160 (P=O), 1094, 1002, 897, 560 cm^{-1}; UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}=390$ nm; elemental analysis calcd (%) for $\mathrm{C_{44}H_{78}Cl_4O_{12}P_4PdSn_2\cdot C_6H_6}$ (1486.71):C 40.39, H 5.69; found: C 39.3, H 5.6.

***cis*-$[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PdBr_2}]$ (2)**: 4-*t*Bu-2,6-$[\mathrm{P(O)(O}i\mathrm{Pr)_2}]_2\mathrm{C_6H_2SnCl}$ (665 mg, 1.08 mmol) was added to a suspension of $\mathrm{PdBr_2}$ (144 mg, 0.54 mmol) in toluene (5 mL). After the reaction mixture was stirred for 12 h, the solution was filtered. Crystallisation from toluene/*n*-hexane yielded orange crystals that were suitable for X-ray diffraction analysis. Recrystallisation from hexanes/$\mathrm{CH_2Cl_2}$ in air and drying in vacuo at 40 °C for 2 h gave 539 mg (66 %) of $[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PdBr_2}]$.

M.p. 165 °C (decomp.); ^{1}H NMR (300.13 MHz, $\mathrm{CD_2Cl_2}$): $\delta=8.00$ (d, ^3J(H,P) = 14.3 Hz, 4H; Ar-H), 5.08–4.93 (m, 4H; CH), 4.86–4.73 (m, 4H; CH), 1.44 (d, ^3J(H,H) = 5.9 Hz, 12H; $\mathrm{CH_3}$), 1.43 (d, ^3J(H,H) = 5.9 Hz, 12H; $\mathrm{CH_3}$), 1.40 (s, 18H; $\mathrm{CH_3}$), 1.21 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.16 ppm (d, ^3J(H,H) = 6.2 Hz; $\mathrm{CH_3}$); ^{13}C NMR (100.63 MHz, $\mathrm{CD_2Cl_2}$): $\delta=167.8$ (t, ^2J(C,P) = 21.4 Hz; C-1), 154.5 (t, ^3J(C,P) = 12.1 Hz; C-4), 131.9 (dd, ^2J(C,P) = 4.4 Hz, ^4J(C,P) = 14.1 Hz; C-3/5), 130.7 (dd, ^1J(C,P) = 184.7 Hz, ^3J(C,P) = 19.4 Hz; C-2/6), 74.9–74.8 (not resolved; CH), 74.1–74.0 (not resolved; CH), 35.7 (s; $C(\mathrm{CH_3})_3$), 31.4 (s; $\mathrm{C}(C\mathrm{H_3})_3$), 24.5–24.4 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 24.3–24.2 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 24.1–24.0 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 23.9–23.8 ppm (not resolved; $\mathrm{CH}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR (121.49 MHz, $\mathrm{CD_2Cl_2}$): $\delta=27.7$ ppm (J(P,Sn) = 26.7 Hz, J(P,Sn) = 181.6/174.9 Hz); ^{119}Sn{^{1}H} NMR (111.92 MHz, $\mathrm{CD_2Cl_2}$): $\delta=-321$ ppm (t, J(Sn,P) = 178 Hz, J(Sn,Sn) = 5640 Hz); IR (KBr): ν = 2977, 2930, 1384, 1177 (P=O), 1159 (P=O), 1120, 1094, 1000, 897, 558 cm^{-1}; UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}=410$ nm; elemental analysis calcd (%) for $\mathrm{C_{44}H_{78}Br_2Cl_2O_{12}P_4PdSn_2\cdot C_7H_8}$: C 38.53, H 5.45; found: C 38.1, H 5.1.

***cis*-$[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PdI_2}]$ (3) and *trans*-$[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})\mathrm{PdI_2}]_2$ (8)**: 4-*t*Bu-2,6-$[\mathrm{P(O)(O}i\mathrm{Pr)_2}]_2\mathrm{C_6H_2SnCl}$ (1.0 g, 1.62 mmol) was added to a suspension of $\mathrm{PdI_2}$ (0.29 g, 0.81 mmol) in toluene (5 mL). After the reaction mixture had been stirred for 12 h, the solution was filtered. Crystallisation from toluene/*n*-hexane yielded dark-red crystals that were suitable for X-ray diffraction analysis. Recrystallisation from hexanes/$\mathrm{CH_2Cl_2}$ in air and drying in vacuo at 40 °C for 2 h gave 442 mg (61 %) of **3**.

M.p. 170 °C (decomp.). ^{1}H NMR (300.13 MHz, $\mathrm{CD_2Cl_2}$): $\delta=8.01$ (d, ^3J(H,P) = 14.3 Hz, 4H; Ar-H), 5.09–4.94 (m, 4H; CH), 4.85–4.74 (m, 4H; CH), 1.43–1.41 (not resolved, 52H; $\mathrm{CH_3}$ + *t*Bu), 1.22 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.16 ppm (d, ^3J(H,H) = 5.9 Hz, 12H; $\mathrm{CH_3}$); ^{13}C NMR (100.63 MHz, $\mathrm{CD_2Cl_2}$): $\delta=170.6$ (t, ^2J(C,P) = 21.4 Hz; C-1), 154.3 (t, ^3J(C,P) = 12.6 Hz; C-4), 131.9 (dd, ^2J(C,P) = 4.4 Hz, ^4J(C,P) = 14.1 Hz; C-3/5), 130.5 (dd, ^1J(C,P) = 185.6 Hz, ^3J(C,P) = 18.5 Hz; C-2/6), 74.8–74.6 (m; CH), 74.0–73.9 (m; CH), 35.7 (s; $C(\mathrm{CH_3})_3$), 31.5 (s; $\mathrm{C}(C\mathrm{H_3})_3$), 24.5–24.4 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 24.3–24.2 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 23.9–23.8 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 23.9–23.8 ppm (not resolved; $\mathrm{CH}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR (121.49 MHz, $\mathrm{CD_2Cl_2}$): $\delta=28.0$ ppm (J(P,Sn) = 26.7 Hz, J(P,Sn) = 191.7/183.8 Hz); ^{119}Sn{^{1}H} NMR (111.92 MHz, $\mathrm{CD_2Cl_2}$, 22 °C, $\mathrm{Me_4Sn}$): $\delta=-257$ ppm (t, J(Sn,P) = 192 Hz, J(Sn,Sn) = 6480 Hz); IR (KBr): ν = 2976, 2932, 1384, 1177 (P=O), 1094, 999, 896, 848, 558 cm^{-1}; UV/Vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}=440$ nm; elemental analysis calcd (%) for $\mathrm{C_{44}H_{78}Cl_2I_2O_{12}P_4PdSn_2\cdot 2\,C_7H_8}$: C 39.23, H 5.34; found: C 38.7, H 5.1.

The residue that had been filtered off was extracted with dichloromethane. Addition of *n*-hexane to the extract gave compound **8** as deep-red crystals that were suitable for X-ray diffraction analysis.

M.p. >250 °C (decomp.); ^{1}H NMR (300.13 MHz, $\mathrm{CD_2Cl_2}$): $\delta=8.02$ (d, ^3J(H,P) = 14.3 Hz, 4H; Ar-H), 5.00 (m, 4H; CH), 4.75 (m, 4H; CH), 1.49 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH}C\mathrm{H}_3$), 1.41 (d, ^3J(H,H) = 7.0 Hz, $\mathrm{CH}C\mathrm{H}_3$), 1.40 (s, 18H; $\mathrm{CCH_3}$), 1.24 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH}C\mathrm{H}_3$), 1.13 ppm (d, ^3J(H,H) = 6.3 Hz, 12H; $\mathrm{CH}C\mathrm{H}_3$); ^{31}P{^{1}H} NMR (121.49 MHz, $\mathrm{CD_2Cl_2}$): $\delta=26.2$ (J(P,Sn) = 186 Hz, integral 3), 26.3 ppm (J(P,Sn) = 193 Hz, integral 1); no reasonable ^{119}Sn NMR spectrum was obtained; elemental analysis calcd (%) for $\mathrm{C_{44}H_{78}Cl_2I_4O_{12}P_4Pd_2Sn_2}$: C 27.08, H 4.03; found: C 26.8, H 4.0.

***cis*-$[(4\text{-}t\mathrm{Bu}\text{-}2,6\text{-}\{\mathrm{P(O)(O}i\mathrm{Pr)_2}\}_2\mathrm{C_6H_2SnCl})_2\mathrm{PtCl_2}]$ (4)**: 4-*t*Bu-2,6-$[\mathrm{P(O)(O}i\mathrm{Pr)_2}]_2\mathrm{C_6H_2SnCl}$ (1.055 g, 1.71 mmol) was added to a suspension of $\mathrm{PtCl_2}$ (228 mg, 0.85 mmol) in toluene (5 mL). After the reaction mixture had been stirred for 12 h, the solution was filtered. Recrystallisation from toluene/hexanes yielded yellow crystals of **4**·1.5 $\mathrm{C_7H_8}$ that were suitable for X-ray diffraction analysis. After drying in vacuo for 2 h at 40 °C 663 mg (52 %) of compound **4** were obtained.

M.p. 128 °C; ^{1}H NMR (300.13 MHz, $\mathrm{C_6D_6}$): $\delta=8.04$ (d, ^3J(H,P) = 14.3 Hz, 4H; Ar-H), 5.53–5.42 (m, 4H; CH), 4.87–4.73 (m, 4H; CH), 1.53 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.19 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.15 (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$), 1.04 (s, 18H; *t*Bu), 0.91 ppm (d, ^3J(H,H) = 6.2 Hz, 12H; $\mathrm{CH_3}$); ^{13}C NMR (100.61 MHz, $\mathrm{CD_2Cl_2}$): $\delta=163.9$ (t, ^2J(C,P) = 20.9 Hz; C-1), 154.6 (t, ^3J(C,P) = 12.1 Hz; C-4), 131.9 (dd, ^2J(C,P) = 4.9 Hz, ^4J(C,P) = 14.6 Hz; C-3/5), 131.5 (dd, ^1J(^{13}C,^{31}P) = 183.7 Hz, ^3J(C,P) = 18.5 Hz; C-2/6), 74.8–74.6 (m; CH), 74.1–73.9 (m; CH), 35.6 (s; $C(\mathrm{CH_3})_3$), 31.4 (s; $\mathrm{C}(C\mathrm{H_3})_3$), 24.5–24.4 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 24.2–24.0 (not resolved; $\mathrm{CH}C\mathrm{H_3}$), 23.8–23.7 ppm (not resolved; $\mathrm{CH}C\mathrm{H_3}$); ^{31}P{^{1}H} NMR (121.49 MHz, $\mathrm{CD_2Cl_2}$): $\delta=27.5$ ppm (J(P,Sn) = 126 Hz, J(P,Pt) = 126 Hz); ^{119}Sn{^{1}H} NMR (111.92 MHz, $\mathrm{CD_2Cl_2}$): $\delta=-483$ ppm (t, J(Sn,P) = 130 Hz, J(Sn,Sn) = 1500 Hz, J(Sn,Pt) = 28 470 Hz); ^{195}Pt NMR (64.52 MHz, $\mathrm{CD_2Cl_2}$): $\delta=-4482$ ppm (quint., J(Pt,P) = 122 Hz, ^1J(Pt,Sn) = 28 480/27 190 Hz); IR (KBr): ν = 2981, 2935, 1467, 1386, 1180 (P=O), 1004, 896, 850, 559 cm^{-1}; MS (+ESI): *m/z*: 1461 $[M-\mathrm{Cl}]^+$; elemental analysis calcd (%) for $\mathrm{C_{44}H_{78}Cl_4O_{12}P_4PtSn_2\cdot C_7H_8}$: C 38.54, H 5.45; found: C 38.2, H 5.3.

***cis*-$[2,6\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3SnCl}]_2\mathrm{PdI_2}$ (5)** A solution of 2,6-$(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3SnCl}$ (187 mg, 0.54 mmol) in THF (40 mL) was stirred with $\mathrm{PdI_2}$ (97 mg, 0,27 mmol) for 2 d. The resulting mixture was filtered and the red solid residue was washed with hexane (2 × 10 mL) to give a red solid of **5** (yield 227 mg, 80 %).

M.p. 193–195 °C. ^{1}H NMR (500.13 MHz, $\mathrm{CDCl_3}$): $\delta=2.70$ (s, 6H; $\mathrm{NCH_3}$), 2.81 (s, 6H; $\mathrm{NCH_3}$), 3.95 (AB system, ^2J(H,H) = 12.1 Hz, 2H; $\mathrm{CH_2}$), 4.20 (AB system, ^2J(H,H) = 12.1 Hz, 2H; $\mathrm{CH_2}$), 7.12 (d, ^3J(H,H) = 6.1 Hz, 2H; ArH), 7.33 ppm (t, ^3J(H,H) = 6.1 Hz, 1H; ArH); ^{13}C NMR (125.77 MHz, $\mathrm{CDCl_3}$): $\delta=47.7$ ($\mathrm{NCH_3}$), 48.7 ($\mathrm{NCH_3}$), 64.1 ($\mathrm{NCH_2}$), 125.7, 130.5, 142.2, 145.3 ppm; ^{119}Sn{^{1}H} NMR (186.49 MHz, $\mathrm{CDCl_3}$): $\delta=-20$ ppm (J(Sn,Sn) = 3885 Hz); elemental analysis calcd (%) for $\mathrm{C_{24}H_{40}Cl_2I_2N_4PdSn_2}$ (1053.11): C 27.07, H 3.53; found: C 27.04, H 3.51.

***cis*-$[2,6\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3SnCl}]_2\mathrm{PtCl_2}$ (6)**: A solution of 2,6-$(\mathrm{Me_2NCH_2})_2\text{-}\mathrm{C_6H_3SnCl}$ (393 mg, 1.10 mmol) and $\mathrm{PtCl_2}$ (151 mg, 0.55 mmol) in THF (40 mL) was stirred for 3 d. The yellow solid residue was separated by filtration and washed with hexane (2 × 10 mL) to give 489 mg (yield 90 %) of compound **6** as a yellow solid.

M.p. 199 °C (decomp.); ^{1}H NMR (500.13 MHz, $\mathrm{CDCl_3}$): $\delta=2.63$ (s, 6H; $\mathrm{NCH_3}$), 2.87 (s, 6H; $\mathrm{NCH_3}$), 3.80 (AB system, ^2J(H,H) = 11.9 Hz, 2H; $\mathrm{CH_2}$), 4.16 (AB system, ^2J(H,H) = 11.9 Hz, 2H; $\mathrm{CH_2}$), 7.14 (d, ^3J(H,H) = 5.9 Hz, 2H; ArH), 7.36 ppm (t, ^3J(H,H) = 5.9 Hz, 1H; ArH); ^{13}C NMR (125.77 MHz, $\mathrm{CDCl_3}$): $\delta=47.2$ ($\mathrm{NCH_3}$), 64.1 ($\mathrm{NCH_2}$), 125.6, 130.6, 142.9, 143.8 ppm; ^{119}Sn{^{1}H} NMR (186.49 MHz, $\mathrm{CDCl_3}$,): $\delta=-254$ ppm (^1J-

(Sn,Pt) = 12 640 Hz); elemental analysis calcd (%) for $C_{24}H_{40}Cl_4N_4PtSn_2$ (958.90): C 29.76, H 3.90; found: C 29.73, H 3.87.

Synthesis of *trans*-[{2,6-($Me_2NCH_2)_2C_6H_3$}SnI]$_2$PtI$_2$ (7): A solution of **6** (0.40 g, 0.4 mmol) in CH_2Cl_2 (40 mL) to which had been added NaI (0.25 g, 1.6 mmol) was stirred for 3 d. The resulting mixture was filtered to remove NaCl and excess NaI. After the filtrate had been evaporated to dryness, the solid residue thus obtained was washed with hexane (2× 10 mL) to give 0.36 g (68 %) of complex **7** as a red solid.

M.p. 235 °C (decomp.); ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 2.88$ (s, 12 H; NCH_3), 4.13 (s, 4 H; CH_2N), 7.29 (d, ^3J(H,H) = 6.3 Hz, 2 H; ArH), 7.46 ppm (t, ^3J(H,H) = 6.3 Hz, 1 H; ArH); ^{13}C NMR (125.77 MHz, $CDCl_3$): $\delta = 47.8$ (NCH_3), 64.7 (CH_2N), 125.4, 130.3, 142.5, 147.5 ppm; ^{119}Sn {^{1}H} NMR (186.49 MHz, $CDCl_3$): $\delta = -80$ ppm; elemental analysis calcd (%) for $C_{24}H_{40}I_4N_4PtSn_2$ (1324.70): C, 21.76, H 3.06; found: C, 21.73, H 3.03.

Isolation of [(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2C_6H_2$SnCl)$_2$Pt(SnCl$_3$)$_2$]·2 C_7H_8 (10): 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2C_6H_2$SnCl (1.18 g, 1.92 mmol) was added to a suspension of $PtCl_2$ (0.17 g, 0.39 mmol) and $SnCl_2$ (0.24 g, 0.79 mmol) in toluene (5 mL). After the reaction mixture had been stirred for 12 h, the solution was filtered. Recrystallisation from toluene/*n*-hexane yielded red crystals (m.p. 185 °C (decomp.)) suitable for X-ray diffraction analysis. There was not enough material to perform an elemental analysis.

Isolation of [(4-*t*Bu-2,6-{P(O)(O*i*Pr)$_2$}$_2C_6H_2$SnCl)$_3$Pt(SnCl$_3$)$_2$]·C_7H_8·0.5 C_6H_{14} (11): 4-*t*Bu-2,6-[P(O)(O*i*Pr)$_2$]$_2C_6H_2$SnCl (1.0 g, 1.62 mmol) was added to a suspension of $PtCl_2$ (0.11 g, 0.41 mmol) in the presence of traces of $SnCl_2$ in toluene (5 mL). After the reaction mixture had been stirred for 12 h, the solution was filtered. Recrystallisation from toluene/*n*-hexane yielded a few red single crystals (m.p. 133 °C) suitable for X-ray diffraction analysis. Elemental analysis calcd (%) for $C_{76}H_{133}Cl_8O_{19}P_6PtSn_5$ (2608.96): C 34.99, H 5.14; found: C 35.0, H 4.7 (the crystals used for X-ray diffraction and elemental analyses contained one less Cl, replaced by one OH).

X-ray crystallography: Intensity data for the crystals **1**·C_6H_6, **2**·C_7H_8, **4**·1.5 C_7H_8, **5**, **6**, **7**·2 $CHCl_3$ and **11**·C_7H_8·0.5 C_6H_{14} were collected on a Nonius KappaCCD diffractometer (Bruker) and for the crystals **3**·C_7H_8, **8** and **10**·2 C_7H_8 on an XcaliburS CCD diffractometer (Oxford Diffraction) using $Mo_{K\alpha}$ radiation at 110 K. The structures were solved by direct methods (Sir92)[68] for **7**·2 $CHCl_3$ and for the remaining structures SHELXS-97[69] was used. Refinements were carried out against F^2 by using SHELXL-97.[69]. C–H hydrogen atoms were positioned in idealised geometries and refined by using a riding model. All non-hydrogen atoms were refined by using anisotropic displacement parameters except for disordered carbon atoms in compound **4**·1.5 C_7H_8, all methyl groups in compound **8**, and C1 to C10 in compound **10**·2 C_7H_8 to benefit the data/parameter ratio. For compound **10**·2 C_7H_8, twin refinement was carried out with a final BASF value of 0.508. At least two isopropyl groups and sometimes one *tert*-butyl group in compounds **1**·C_6H_6, **2**·C_7H_8, **4**·1.5 C_7H_8, **8**, **10**·2 C_7H_8 and **11**·C_7H_8·0.5 C_6H_{14} are affected by disorder and refined by a split model over two positions with occupancies of between 70:30 and 50:50. For more details, see the Supporting Information. In compound **4**·1.5 C_7H_8, one pincer-type ligand backbone (C13–C20) is disordered and split into two positions with equal occupancies (see Figure S7 in the Supporting Information). In compound **11**·C_7H_8·0.5 C_6H_{14}, the chlorine atoms Cl1 and Cl3 share their positions with hydroxy groups O1H and O3H (we were not able to localise the hydrogen atoms in the difference Fourier map). Their occupancies were allowed to refine freely until a constant number was obtained and rounded down to the integer values 50:50 to simplify the sum formula. The severely disordered and non-coordinating solvents of compounds **3**·C_7H_8 and **11**·C_7H_8·0.5 C_6H_{14} were removed by Platon/SQUEEZE[61] to improve the main part of their structures. Figures 1–8 were created by using Diamond 3..

CCDC-887667 (**1**·C_6H_6), -887668 (**2**·C_7H_8), -887669 (**3**·C_7H_8), -887670 (**4**·1.5 C_7H_8), -887671 (**5**), -887672 (**6**), -795540 (**7**·2 $CHCl_3$), -887673 (**8**), -887674 (**10**·2 C_7H_8) and -887675 (**11**·C_7H_8·0.5 C_6H_{14}), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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