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Ligand behaviour of P-functionally substituted organotin halides: palladium(II) and platinum(II) complexes with $Ph_2PCH_2CH_2SnCl_3$

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Abstract

The P-functional organotin chloride $Ph_2PCH_2CH_2SnCl_3$ reacts with $[(COD)MCl_2]$ and *trans*-$[(Et_2S)_2MCl_2]$ (M = Pd, Pt) in molar ratio 1:1 to the zwitterionic complexes $[(COD)M^+(Cl)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**1**: M = Pd; **2**: M = Pt) and *trans*-$[(Et_2S)_2M^+(Cl)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**3**: M = Pd; **4**: M = Pt). The same reaction with [(COD)Pd(Cl)Me] yields under transfer of the methyl group from palladium to tin the complex $[(COD)M^+(Cl)(PPh_2CH_2CH_2Sn^-MeCl_3)]$ (**5**) which changes in acetone into the dimeric adduct $[Cl_2Pd(PPh_2CH_2CH_2SnMeCl_2\cdot 2Me_2CO)]_2$ (**6**). In molar ratio 2:1 $Ph_2PCH_2CH_2SnCl_3$ reacts with $[(COD)MCl_2]$ to the complexes $[Cl_2Pd(PPh_2CH_2CH_2SnCl_3)_2]$ (**7**: M = Pd, mixture of *cis*/*trans* isomer; **8**: M = Pt, *cis* isomer). In a subsequent reaction **8** is transformed in acetone into the 16-membered heterocyclic complex *cis*-$[Cl_2Pt(PPh_2CH_2CH_2)_2SnCl_2]_2$ (**9**). *trans*-$[(Et_2S)_2PtCl_2]$ and $Ph_2PCH_2CH_2SnCl_3$ in molar ratio 1:2 yields the zwitterionic complex $[(Et_2S)M^+(Cl)(PPh_2CH_2CH_2SnCl_3)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**10**). The results of crystal structure analyses of **1**, **3**, **6**, **9** and of the adduct of the *trans*-isomer of **7** with acetone (**7a**) are reported. ^{31}P- and ^{119}Sn-NMR data of the complexes are discussed.
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Keywords: Organotin; Crystal structures; Hexacoordination; Pentacoordination; NMR spectroscopy

1. Introduction

P-functional tetraorganotin compounds of the type $R_2PCH_2CH_2SnR'_3$ (R, R′ = Me, Ph) and $(Me_2PCH_2CH_2)_2SnMe_2$ and the distannanes $[Ph_2P(CH_2)_nMe_2Sn-]_2$ ($n = 2$, 3) react with low-valent transition metal compounds in a chelate assisted oxidative addition reaction as bidentate ligands to form metallacycles with the structural element $\overline{[M] \leftarrow PR_2(CH_2)_nSnR'_2}$ ($n = 2$, 3) [1–4]. But, with compounds of transition metals in their usual oxidation state these ligands are coordinated only with the phosphorus atom without any detectable interaction between the tin and the transition metal [5–7].

Recently, we found that in complexation reactions of the P-functional triorganotin chloride $Ph_2PCH_2CH_2Sn(Cl)Me_2$ with $[Rh(Cl)(CO)_2]_2$ and various Ni^{II}, Pd^{II} and Pt^{II} chloride complexes the tin compound is bonded in a chelate ligand mode by P→[M] coordination and intra- or intermolecular [Sn]–Cl···[M] bridges (M = Rh, Ni, Pd, Pt) [8,9]. The complexes formed in this way can undergo further reactions [9].

In continuation of these studies we recently synthesized the ω-diphenylphosphinoalkyltin di- and trichlorides $[Ph_2P(CH_2)_3]_2SnCl_2$ and $Ph_2P(CH_2)_nSnCl_2R$ ($n = 2$, 3; R = Cl, Me) as new potential ligands with a high Lewis acidity of the tin centre and different lengths of the $(CH_2)_n$-bridge between the tin and the phosphorus atom [10].

In the following paper we report the synthesis and structure of Pd^{II} and Pt^{II} chloride complexes with the ligand $Ph_2PCH_2CH_2SnCl_3$.

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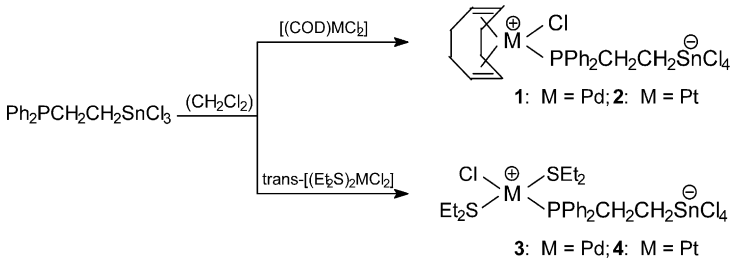
2. Results and discussion

2.1. Synthetic aspects

2.1.1. Complexes of Pd^{II} and Pt^{II} with $Ph_2PCH_2CH_2SnCl_3$ in molar ratio 1:1

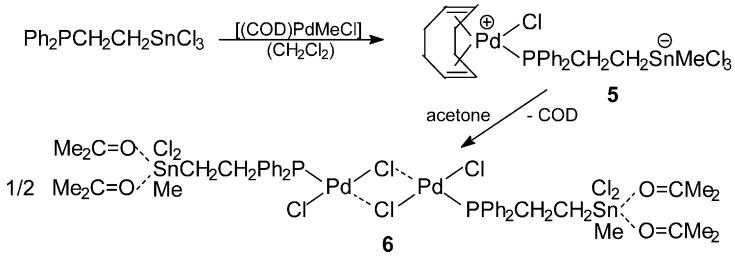
[(COD)MCl_2] and *trans*-[$(Et_2S)_2MCl_2$] (M = Pd, Pt) react with one equivalent of $Ph_2PCH_2CH_2SnCl_3$ in CH_2Cl_2 to give the zwitterionic complexes [(COD)-M^+(Cl)($PPh_2CH_2CH_2Sn^-Cl_4$)] (**1**: M = Pd; **2**: M = Pt) and *trans*-[$(Et_2S)_2M^+$(Cl)($PPh_2CH_2CH_2Sn^-Cl_4$)] (**3**: M = Pd; **4**: M = Pt) (Eq. (1)). Due to the high Lewis acidity of the tin atom in the ligand the formation of **1**–**4** is connected with the transfer of a chloride anion from the transition metal to the tin centre. Consequently, in the same reaction with the tin monochloride $Ph_2PCH_2CH_2Sn(Cl)Me_2$ as ligand this Cl^- transfer could not be observed [9].



(1)

Compounds **1** and **2** precipitate after the reaction of the educts. Compounds **3** and **4** were isolated after concentration of the reaction solution and addition of *n*-pentane as microcrystalline powders. The palladium complexes **1** and **3** are yellow and the analogous platinum complexes are colourless compounds, respectively. Whereas **1** is slightly soluble in CH_2Cl_2 **2** is only soluble in strong donor solvents, e.g. in DMSO, under decomposition after some hours. Compounds **3** and **4** are soluble in CH_2Cl_2, $CHCl_3$ and donor solvents.

In the analogous reaction to Eq. (1) between $Ph_2PCH_2CH_2SnCl_3$ and [(COD)MMeCl] (M = Pd, Pt) in CH_2Cl_2 obviously a transfer of the methyl group instead of the chloride ligand from the transition metal to tin takes place. Whereas [(COD)PtMeCl] gives a colorless unsoluble compound which decomposes in strong donor solvents the reaction of [(COD)PdMeCl] with $Ph_2PCH_2CH_2SnCl_3$ results in a green–yellow solution with NMR data which indicate the formation of the complex [(COD)Pd^+(Cl)(PPh_2 $CH_2CH_2Sn^-MeCl_3$)] (**5**). Unfortunately, after evaporation of the solvent the remained crude product of **5** could not be crystallized in an unpolar solvent. But, from the solution of **5** in acetone after layering with *n*-pentane red crystals of the acetone adduct of the dimeric complex [Cl_2Pd(PPh_2CH_2-$CH_2SnMeCl_3$)]$_2$ (**6**) are obtained. The molecular structure of **6** (Fig. 3) reveals the following structural changes by transformation of **5** into **6**: (a) transfer of a chloride ligand from tin to palladium and increasing of the coordination number of the tin atom to six by coordination of two molecules of acetone, (b) replacement of COD at the palladium atom as a result of the dimerization of the complex with formation of Sn–Cl···Sn bridges. Eq. (2) summarizes the reaction course.



(2)

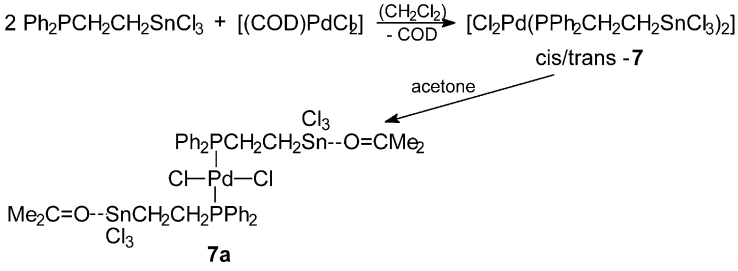
2.1.2. Complexes of Pd^{II} and Pt^{II} with $Ph_2PCH_2CH_2SnCl_3$ in molar ratio 1:2

In the first step of the reactions of the Pd^{II} and Pt^{II} starting compounds with $Ph_2PCH_2CH_2SnCl_3$ the complexes **1**–**4** are formed (Eq. (1)). The result of the reaction of the second ligand molecule with **1**–**4** depends on the strength of the coordinating ligand groups which shows the following sequence: $Ph_2P > Et_2S > \eta^2$-COD $\sim Cl > \eta^1$-COD.

$Ph_2PCH_2CH_2SnCl_3$ reacts with $[(COD)PdCl_2]$ in molar ratio 2:1 to give an amorphous yellow powder which is only soluble in donor solvents. NMR data of a solution of this compound in acetone indicate the formation of a mixture of *cis*/*trans*-$[Cl_2Pd(PPh_2CH_2CH_2SnCl_3)_2]$ (**7**). The same complex is formed with **1** as starting compound. As a consequence of the substitution of the bidentate COD in **1** by the second molecule of $Ph_2PCH_2CH_2SnCl_3$ the chloride anion changes from tin to palladium to occupy the vacant coordination site. From acetone/*n*-pentane single crystals of the adduct of the *trans* isomer of **7** with acetone (**7a**) are available (Eq. (3)).

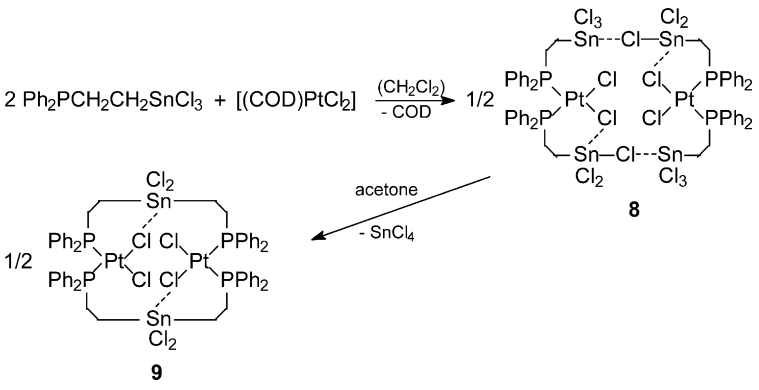
The same reaction of $Ph_2PCH_2CH_2SnCl_3$ with *trans*-$[(Et_2S)_2PdCl_2]$ instead of $[(COD)PdCl_2]$ results in a mixture of products with only a share of **7** less than 10%.

In the same way as the corresponding palladium complex $[(COD)PtCl_2]$ reacts according to Eq. (4) with $Ph_2PCH_2CH_2SnCl_3$ to the complex *cis*-$[Cl_2Pt(PPh_2CH_2CH_2SnCl_3)_2]$ (**8**) which is dimeric with intermolecular Sn–Cl···Sn bridges. In acetone the strong intermolecular Sn–Cl···Sn bridges in **8** give rise to the elimination of $SnCl_4$ and the formation of the 16-membered heterocyclic complex **9** what reminds a template reaction.



(3)

In comparison with $[(COD)PtCl_2]$ the reaction of *trans*-$[(Et_2S)_2PtCl_2]$ with two equivalents of $Ph_2PCH_2CH_2SnCl_3$ shows another course and gives the zwitterionic complex **10** illustrated by Eq. (5). Also in this case the 1:1 complex **4** (Eq. (1)) is an intermediate compound in which the second molecule of $Ph_2PCH_2CH_2SnCl_3$ substitutes one Et_2S ligand. But, the higher ligand strength of Et_2S compared with COD prevents in **10** the transfer of the chloride anion from tin to platinum under substitution of the second Et_2S ligand and formation of complex **8**.



(4)

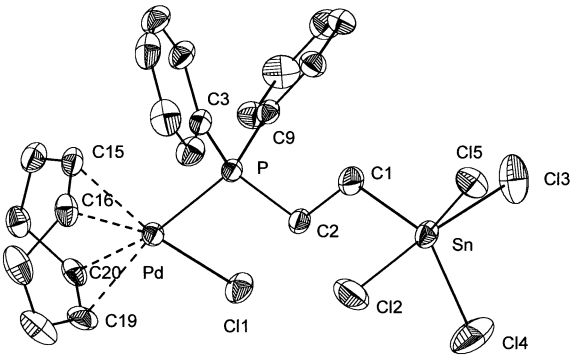


Fig. 1. Molecular structure of $[(COD)Pd^{+}(Cl)(PPh_2CH_2CH_2Sn^{-}Cl_4)]$ (**1**) with atom-numbering.

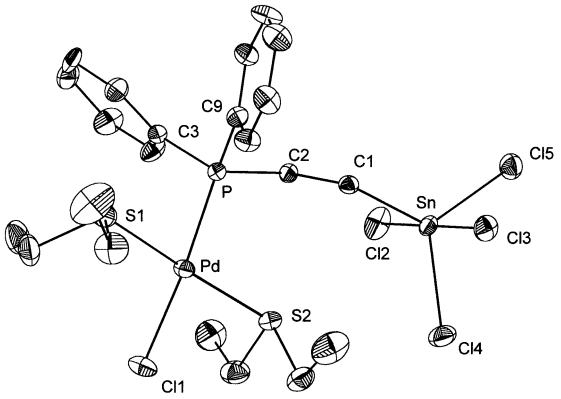
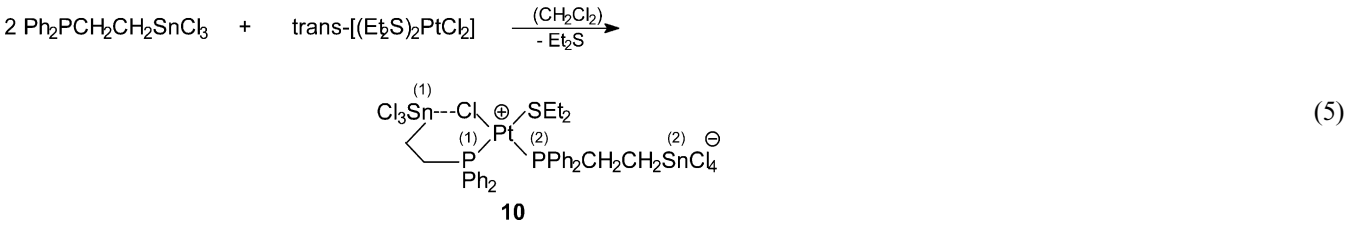


Fig. 2. Molecular structure of *trans*-$[(Et_2S)_2Pd^{+}(Cl)(PPh_2CH_2CH_2Sn^{-}Cl_4)]$ (**3**) with atom-numbering.

Compound **10** is soluble both in CH_2Cl_2 and in donor solvents. Its postulated structure follows unambigously from NMR data in CD_2Cl_2 (see Section 2.3).



(5)

2.2. Molecular structures of *1*, *3*, *6*, *7a* and *9*

The molecular structures of **1**, **3**, **6**, **7a** and **9** are shown in Figs. 1–5 along with the atom-numbering schemes. The crystallographic data are given in Table 5 and selected interatomic parameters are listed in Tables 1–3. The main feature of the molecular structures of **1** and **3** (Figs. 1 and 2) is their existence as intramolecular zwitterions without any interaction between the palladium cation and the anionic $-CH_2SnCl_4^{-}$ part of the molecule.

Compounds **1** and **3** contain the Pd atom in a square-planar coordination geometry. Due to the different coordination mode of the COD and the two Et_2S ligands the P and the Cl ligand are arranged *cis* in **1** and *trans* in **3**, respectively. According to the different *trans* influence of the opposite ligands the Pd–P and Pd–Cl bond distances in **1** and **3** are different. Furthermore, the small aperture angle C15/C16–Pd–C19/C20 of the COD ligand of 85.3(1)° gives rise to a more distorted ligand polyhedron of the palladium in **1** compared with **3**.

The pentacoordinated tin in the anionic $-CH_2SnCl_4^{-}$ part of the molecule both in **1** and **3** shows an only slightly distorted trigonal-bipyramidal ligand polyhedron with the CH_2 group in an equatorial position. The structural data of the $-CH_2SnCl_4^{-}$ part both in **1** and **3** are in good agreement with those of the $[MeSnCl_4]^{-}$ anion [11,12].

The molecular structure of compound **6** (Fig. 3) confirms the postulated transfer of a methyl group from the palladium to the tin atom in the reaction between [(COD)PdMeCl] and $Ph_2PCH_2CH_2SnCl_3$ according to Eq. (2). Compound **6** represents a centrosymmetric dimer with Pd–Cl···Pd bridges forming a planar four-membered $[PdCl_2Pd]$ ring. The bond distances and angles of the central structural element [P(Cl)$PdCl_2$Pd(Cl)P] are in good agreement with those of comparable phoshine complexes of palladium [13], e.g. $[(n\text{-}PrPh_2P)PdCl_2]_2$ [14].

As in most of the octahedrally coordinated diorganotin dihalide adducts of the type $R_2SnCl_2 \cdot 2D$ (D = donor molecule) also in **6** the two organo groups are in *trans* position. Both the two chlorine and oxygen atoms are in *cis* positions. As a consequence of the low donor strength of acetone the ligand octahedron of the tin atom in **6** is strongly distorted. This is demonstrated by the long Sn–O bond distances with the corresponding low values of the Pauling-type bond order (BO) [15], by the small C–Sn–C bond angle and by the varying values

Table 1
Selected bond lengths (Å) and bond angles (°) of $[(COD)(Cl)Pd^{+}(PPh_2PCH_2CH_2Sn^{-}Cl_4)]$ (**1**) and $[(Et_2S)_2(Cl)Pd^{+}(PPh_2PCH_2CH_2Sn^{-}Cl_4)]$ (**3**)

Compound **1**		Compound **3**	
Bond lengths			
Pd–Cl(1)	2.297(2)	Pd–Cl(1)	2.337(1)
Pd–P	2.301(2)	Pd–P	2.280(1)
Pd–C(15)/C(16)	2.09(1)	Pd–S(1)	2.341(1)
Pd–C(19)/C(20)	2.23(1)	Pd–S(2)	2.352(1)
Sn–C(1)	2.124(7)	Sn–C(1)	2.154(4)
Sn–Cl(2)	2.453(2)	Sn–Cl(2)	2.460(1)
Sn–Cl(3)	2.479(2)	Sn–Cl(3)	2.463(1)
Sn–Cl(4)	2.314(2)	Sn–Cl(4)	2.351(1)
Sn–Cl(5)	2.342(2)	Sn–Cl(5)	2.367(1)
Bond angles			
P–Pd–Cl(1)	87.3(1)	P–Pd–S(1)	87.2(1)
P–Pd–C(15)/C(16)	96.3(1)	P–Pd–S(2)	92.2(1)
C(15)/C(16)–Pd–C(19)/C(20)	85.3(1)	Cl(1)–Pd–S(1)	90.3(1)
C(19)/C(20)–Pd–Cl(1)	91.0(1)	Cl(2)–Sn–Cl(4)	90.3(1)
P–Pd–C(19)/C(20)	177.3(1)	Cl(2)–Sn–Cl(5)	87.9(1)
Cl(1)–Pd–C(15)/C816)	175.6(1)	Cl(2)–Sn–C(1)	95.3(1)
Cl(2)–Sn–C(1)	94.6(3)	Cl(3)–Sn–Cl(4)	89.0(1)
Cl(2)–Sn–Cl(4)	89.1(1)	Cl(3)–Sn–Cl(5)	89.0(1)
Cl(2)–Sn–Cl(5)	88.1(1)	Cl(3)–Sn–C(1)	88.2(1)
Cl(3)–Sn–C(1)	91.6(3)	Cl(1)–Pd–S(2)	90.6(1)
Cl(3)–Sn–Cl(4)	88.8(1)	Cl(1)–Pd–P	175.5(1)
Cl(3)–Sn–Cl(5)	87.2(1)	S(1)–Pd–S(2)	175.6(1)
C(1)–Sn–Cl(4)	127.8(2)	C(1)–Sn–Cl(4)	122.8(1)
C(1)–Sn–Cl(5)	116.1(2)	C(1)–Sn–Cl(5)	123.7(1)
Cl(4)–Sn–Cl(5)	116.1(1)	Cl(4)–Sn–Cl(5)	113.3(1)
Cl(2)–Sn–Cl(3)	173.4(1)	Cl(2)–Sn–Cl(3)	176.2(1)

Table 2
Selected bond lengths (Å) and angles (°) of $[Cl_2Pd\{PPh_2CH_2CH_2Sn(Me)Cl_2(OCMe_2)_2\}]_2$ (**6**) and *trans*-$[Cl_2Pd\{PPh_2CH_2CH_2SnCl_3(OCMe_2)\}_2]$ (**7a**)

Compound **6**		Compound **7a**	
Bond lengths			
Pd–Cl(1)	2.342(1)	Pd–Cl(1)	2.308(1)
Pd–Cl(2)	2.270(1)	Pd–P	2.314(1)
Pd–P	2.210(1)	Sn–C(1)	2.137(3)
Pd–Cl(1)′	2.418(1)	Sn–Cl(2)	2.330(1)
Sn–C(1)	2.139(3)	Sn–Cl(3)	2.331(1)
Sn–C(3)	2.146(3)	Sn–Cl(4)	2.365(1)
Sn–Cl(3)	2.400(1)	Sn–O	2.541(2)
Sn–Cl(4)	2.400(1)		
Sn–O(1)	2.711(3)		
Sn–O(2)	2.690(3)		
Bond angles			
P–Pd–Cl(1)	91.5(1)	P–Pd–Cl(1)	92.4(1)
P–Pd–Cl(2)	91.1(1)	P–Pd–Cl(1)′	87.6(1)
Cl(1)′–Pd–Cl(1)	86.4(1)	P–Pd–P′	180.0(3)
Pd–Cl(1)–Pd′	93.6(1)	Cl(1)–Pd–Cl(1)′	180.0
Cl(1)′–Pd–Cl(2)	90.9(1)	Cl(4)–Sn–C(1)	106.3(1)
Cl(1)–Pd–Cl(2)	176.4(1)	Cl(4)–Sn–Cl(2)	96.5(1)
Cl(1)′–Pd–P	176.3(4)	Cl(4)–Sn–Cl(3)	95.8(1)
C(1)–Sn–Cl(3)	100.3(1)	O–Sn–C(1)	75.3(1)
C(1)–Sn–Cl(4)	99.1(1)	O–Sn–Cl(2)	85.3(1)
C(1)–Sn–O(1)	78.9(1)	O–Sn–Cl(3)	80.3(1)
C(1)–Sn–O(2)	77.3(1)	C(1)–Sn–Cl(2)	125.1(1)
C(3)–Sn–Cl(3)	101.5(1)	C(1)–Sn–Cl(3)	119.1(1)
C(3)–Sn–Cl(4)	105.2(1)	Cl(2)–Sn–Cl(3)	106.9(1)
C(3)–Sn–O(1)	78.0(1)	O–Sn–Cl(4)	176.0(1)
C(3)–Sn–O(2)	81.2(1)		
C(1)–Sn–C(3)	145.2(1)		
Cl(3)–Sn–O(2)	177.3(1)		
Cl(4)–Sn–O(1)	176.3(1)		
Cl(4)–Sn–Cl(3)	96.2(1)		
Cl(4)–Sn–O(2)	83.3(1)		
Cl(3)–Sn–O(1)	81.3(1)		
O(1)–Sn–O(2)	99.2(1)		

of the angles between the *cis* standing ligands of **6** [$d_{(Sn-O)} = 2.690$, 2.711 Å, (BO: 0.31, 0.29); $\measuredangle$C–Sn–C = 145.2°; *cis*-$\measuredangle$ = 77.3–105.2°]. The corresponding data of the adduct $Me_2SnCl_2 \cdot 2Me_2S{=}O$ with the stronger donor $Me_2S{=}O$ and the smaller distorsion of the ligand octahedron are $d_{(Sn-O)} = 2.273$, 2.310 Å (BO = 0.73, 0.69), $\measuredangle$C–Sn–C = 170.3° and *cis*-$\measuredangle$ = 82.8–95.0 [16].

Although compound **7** exists in solution both as *cis* and *trans* isomer only the *trans* isomer could be obtained in the crystalline state as the acetone adduct **7a**. The crystal structure of **7a** (Fig. 4) consists of centrosymmetric molecules with the palladium atom residing on a centre of symmetry. The coordination of the ligands is nearly square-planar with both the phosphorus and the chlorine atoms in *trans* position. The bond lengths and angles within the ligand sphere of the palladium in **7a** agree with those of numerous known *trans*-dichloro bis-phoshine palladium complexes [13].

In contrast to the hexacoordinated tin in compound **6** the tin in **7a** is merely penta-coordinated in spite of its higher Lewis acidity. **7a** represents a rare example of a 1:1 adduct of an organotin trichloride $RSnCl_3$ with an external donor. The few so far known pentacoordinated complexes with $RSnCl_3$ are formed by intramolecular coordination when R is an C,Y-chelating ligand (Y = heteroatom-containing substituent) [17].

The low donor strength of acetone gives rise to a considerable distortion of the trigonal-bipyramide around the tin atom in **7a** towards a monocapped tetrahedron. This is indicated by the long Sn–O distance of 2.541(2) Å (BO = 0.46) and particularly by the relatively small value of 52.5° for the difference between the sum of the three equatorial and the three axial angles (to the chlorine atom) in the trigonal-bipyramidal coordination sphere around the tin atom ($\Sigma \measuredangle Sn_{eq} - \Sigma \measuredangle Sn_{ax}$: TBP = 90°, tetrahedron = 0° [18,19]). In **7a** the geometry of the ligand polyhedron around the tin is comparable with that of the pentacoordinated tin in the organotin trichloride $Cl_3Sn(CH_2)_4OC(O)Me$ [20] which is dimeric in the solid state caused by intermolecular C=O···Sn interactions [$d_{Sn-O} = 2.463(3)$ Å (BO = 0.54), $\Sigma \measuredangle Sn_{eq} - \Sigma \measuredangle Sn_{ax} = 58.4°$].

Table 3
Selected bond lengths (Å), bond angles (°) and endocyclic torsion angles (°) of *cis*-$[Cl_2Pt(PPh_2CH_2CH_2)_2SnCl_2]_2$ (**9**)

Bond lengths			
Pt–P(1)	2.247(1)	Pt–Cl(1)	2.372(1)
Pt–P(2)	2.251(1)	Pt–Cl(2)	2.337(1)
Sn–C(1)	2.123(8)	Sn–Cl(3)	2.346(2)
Sn–C(3)′	2.101(7)	Sn–Cl(4)	2.410(3)
Sn–Cl(1)	3.012(2)		
Bond angles			
P(1)–Pt–Cl(1)	83.3(1)	Cl(2)–Pt–P(2)	91.6(1)
P(1)–Pt–P(2)	97.9(1)	P(1)–Pt–Cl(2)	170.4(1)
Cl(2)–Pt–Cl(1)	87.4(1)	P(2)–Pt–Cl(1)	177.4(1)
C(1)–Sn–Cl(1)	83.5(2)	C(3)′–Sn–Cl(4)	102.7(2)
C(1)–Sn–Cl(3)	104.4(3)	Cl(1)–Sn–Cl(3)	82.0(1)
C(1)–Sn–Cl(4)	97.1(2)	Cl(1)–Sn–Cl(4)	179.1(1)
C(3)′–Sn–Cl(1)	77.5(2)	Cl(3)–Sn–Cl(4)	97.0(1)
C(3)′–Sn–Cl(3)	111.4(2)	C(1)–Sn–C(3)′	136.1(3)
Torsion angles			
Pt–P(1)–C(2)–C(1)	−40.5(1)	C(1)–Sn–Cl(1)–Pt	−48.1(1)
P(1)–C(2)–C(1)–Sn	98.6(1)	Sn–Cl(1)–Pt–P(1)	79.2(1)
C(2)–C(1)–Sn–Cl(1)	−35.9(1)	Cl(1)–Pt–P(1)–C(2)	−48.0(1)

The molecular structure of compound **9** shown in Fig. 5 characterizes the compound as a centrosymmetric 16-membered heterocyclic system which is formally the result of the cyclizising coordination of $Cl_2Sn(CH_2CH_2PPh_2)_2$ with $PtCl_2$. Additionally there are two weak Pt–Cl···Sn interactions inside the macrocycle. Bond lengths and angles at the nearly square-planar coordinated platinum centres are in good agreement with those of other *cis*-dichloro bis-phosphine platinum complexes [13], e.g. *cis*-$[Cl_2Pt(PMePh_2)_2]$ [21].

In **9** the tin atoms exhibit a trigonal-bipyramidal coordination sphere which is strongly distorted towards a monocapped tetrahedron as a consequence of the relatively weak Pt–Cl···Sn coordination [$d_{Sn-Cl(1)} = 3.012(2)$ Å (BO = 0.35); $\Sigma \measuredangle Sn_{eq} - \Sigma \measuredangle Sn_{ax} = 55.1°$]. These data agree with those of the Me_2SnCl_3 structural element in chloro-dimethyl(*N*-methylpyrrolidinone)tin-(IV)-μ-chloro-dichlorodimethyltin(IV) [22] [$d_{Sn\cdots Cl} = 3.116$ Å (BO = 0.24); $\Sigma \measuredangle Sn_{eq} - \Sigma \measuredangle Sn_{ax} = 56.6°$].

On the basis of the endocyclic torsion angles an unambiguous assignment of a conformation to the six-membered ring fragments in **9** is not possible.

2.3. NMR investigations of *1–10*

As a consequence of the formation both of intra and intermolecular M–Cl···M bridges (M = Pd, Pt, Sn) in the structures of **1–10** some of these compounds show an only sligth solubility in unpolar solvents and their NMR spectra are recorded in donor solvents. Furthermore, **1–10** undergo in some cases concentration dependent dynamic processes causing broad signals. Therefore the NMR data of **1–10** in Table 4 give only a rough insight into the behaviour of these compounds in solution and allow in some cases no unambiguous structural assignments.

The solid state structure of **1–4** is confirmed also in solution. **1** and **2** are only soluble in strong donor solvents. The ^{119}Sn-NMR chemical shifts of **3** ($\delta^{119}Sn = -275$ ppm) and **4** ($\delta^{119}Sn = -274$ ppm) in CD_2Cl_2 are in good agreement with that of the pentacoordinated anions $[RSnCl_4]^-$ in $CDCl_3$ (R = Me: $\delta^{119}Sn = -259.6$ ppm; R = *n*-Bu: $\delta^{119}Sn = -271.0$ ppm) [12]. In agreement with the structure is also the high value of the ^3J(SnCCP) coupling constant in the same solvent of 654 Hz (**3**) and 693 Hz (**4**), respectively. Furthermore, the coupling constant ^1J(PPt) of 3331 Hz indicates the *trans* position of the P and Cl atom in the ligand sphere of the platinum in compound **4** [9,23,24]. In the strong donor solvent DMSO in which also **1** and **2** are soluble **1–4** show nearly the same ^{119}Sn-NMR shift of ∼ −460 ppm and increased ^3J(SnCCP) coupling constants between 828 and 867 Hz, both indicating hexacoordination of the tin atom in **1–4** by coordination of one DMSO molecule at the tin atom.

For **5** in DMSO the ^{119}Sn-NMR signal at lower field ($\delta^{119}Sn = -261$ ppm) and the decreased value of the coupling constant ^3J(SnCCP) compared with the corresponding data of **1–4** indicate the lower degree of chlorination in **5**. Furthermore, the δ^{119}Sn-value of −261 ppm for **5** is in agreement with that of the also hexacoordinated tin of $Ph_2P(CH_2)_3SnMeCl_2$ in pyridine ($\delta^{119}Sn = -278$ ppm) [10].

Because of the low solubility of compound **7** in unpolar solvents its NMR data are recorded in acetone. In this solvent no M–Cl···Sn contacts (M = Pd, Pt, Sn) can be detected. As already reported for complexes of

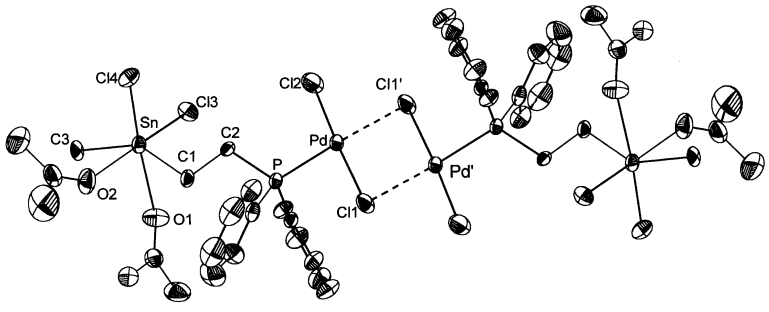


Fig. 3. Molecular structure of *trans*-$[Cl_2Pd(PPh_2CH_2CH_2SnMeCl_2{\cdot}2Me_2CO)]_2$ (**6**) with atom-numbering.

Table 4
^{119}Sn- and ^{31}P-NMR data of **1**–**10**

Compound	δ (^{119}Sn) (ppm)	δ (^{31}P) (ppm)	^{3}J(^{119}Sn,^{31}P) (Hz)	^{1}J(^{31}P^{195}Pt) (Hz)	Solvent
1	−467 (b)	38.0 (s)	828		DMSO-d_6
2	−465 (b)	19.7 (s)	867	3638	DMSO-d_6
3	−275 (b)	31.4 (s)	654		CD_2Cl_2
	−459 (b)	35.7 (s)	863		DMSO-d_6
4	−274 (b)	11.6 (s)	693	3331	CD_2Cl_2
	−463 (b)	15.5 (s)	854	3641	DMSO-d_6
5	−261 (b)	40.5 (s)	754		DMSO-d_6
7 *cis*	−236 (m) [a]	38.0 (s)	609		Acetone-d_6
trans	−205 (m) [b]	26.7 (s)	698		Acetone-d_6
8	−132 (d)	13.4 (s)	338	3715	CD_2Cl_2
10	−114 (d, b) [c]	18.6 (s)	520	3173	CD_2Cl_2
	−262 (d, b) [d]	10.6 (s)	703	3426	CD_2Cl_2

[a] ^{2}J(PPdP) < 10 Hz.
[b] ^{2}J(PPdP) = 685 Hz; ^{5}J(P,Sn) < 10 Hz.
[c] Sn(1), P(1).
[d] Sn(2), P(2) (see Eq. (5)).

the type [M($PPh_2CH_2CH_2SnClMe_2$)$_2$] (M = Rh(CO)Cl, $PdCl_2$, $PtCl_2$) [8,9] as a consequence of the natural abundance of the ^{119}Sn isotope of 8.58% the dominant isotopomer of **7** in solution contains only one ^{119}Sn atom (the portion of the isotopomer with two ^{119}Sn atoms is only 0.74%). That means the ^{119}Sn-NMR spectrum and the satellite part of the ^{31}P-NMR spectrum of **7** are parts of an ABX spin system (A,B = ^{31}P, X = ^{119}Sn) because the two phosphorus atoms are chemically but not magnetically equivalent. The coupling constants (see Table 4) are determined by computer simulation [25]. The different values of the ^{2}J(PPdP) coupling constants allow the unambiguous assignment of the NMR signals to the isomers of **7**. The *trans*-isomer with ^{2}J(PPdP) of 685 Hz is the dominating one.

Compound **8** exists in CD_2Cl_2 as *cis*-isomer. This is illustrated by the small ^{2}J(PPtP) coupling constant (J < 10 Hz) and the high value for the ^{1}J(PPt) coupling of 3715 Hz indicating the *trans*-position of the phosphorus and the chlorine atoms in the square-planar ligand

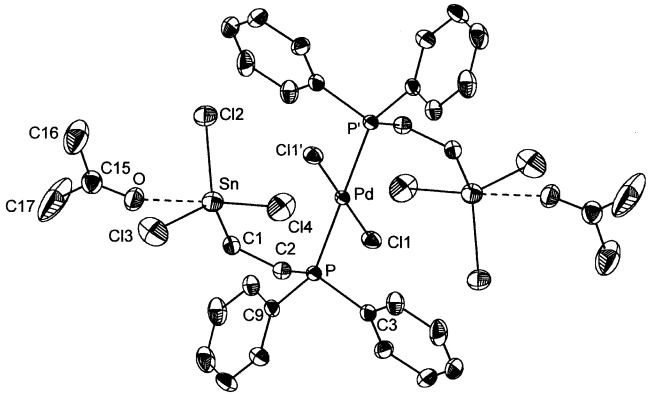


Fig. 4. Molecular structure of *trans*-[$Cl_2Pd(PPh_2CH_2CH_2SnCl_3\cdot Me_2CO)_2$] (**7a**) with atom-numbering.

sphere of the central platinum atom [9,23,24]. Furthermore, the high field position of the ^{119}Sn-NMR signal of **8** at −132 ppm compared with the free ligand $Ph_2PCH_2CH_2SnCl_3$ (δ^{119}Sn = −69 ppm) [10] indicates hypervalent tin caused by intramolecular Pt–Cl···Sn and intermolecular Sn–Cl···Sn interactions, respectively. This bond situation is already described for the analogous complex *cis*-[$Cl_2Pt(PPh_2CH_2CH_2$ $SnClMe_2)_2$] [9].

Unfortunately, the NMR investigation of the interesting structure of the product **9** formed from **8** according to Eq. (4) failed because the compound is nearly insoluble in the common solvents.

The structure of the 2:1 complex of $Ph_2PCH_2CH_2SnCl_3$ with [$(Et_2S)_2PtCl_2$] (**10**) which is postulated in Eq. (5) is confirmed by the NMR data in CD_2Cl_2. The ^{31}P-NMR spectrum of **10** is of the AB type with a coupling constant of 19.5 Hz which is in the typical range for bis-phosphine platinum complexes. The assignment of the ^{31}P-NMR signals follows from the different values for the ^{1}J(PPt) coupling constant. The higher value of 3426 Hz for ^{1}J(P(2)Pt) (δ^{31}P = 10.6 ppm) indicates the P(2) atom to be in *trans*-position to the chlorine atom which has a lower *trans* influence as the Et_2S ligand [26]. The assignment of the ^{119}Sn-NMR signal at −262 ppm to the Sn(2) atom with the value of the ^{3}J(SnCCP) coupling constant of 703 Hz follows from the good agreement of this data with those of the complex **4**. The high field position of the NMR signal of the Sn(1) atom at −114 ppm compared with the free ligand $Ph_2PCH_2CH_2SnCl_3$ (δ^{119}Sn = −69 ppm) [10] confirms the postulated intramolecular Pt–Cl···Sn(1) interaction. Finally, the smaller value of the ^{1}J(P(1)Pt) coupling constant compared with that of ^{1}J(P(2)Pt) confirms the *cis*-position of the P(1) and the Cl atom in **10**.

Table 5
Crystal data and details of the refinement

	1	3	6	7a	9
Formula	$C_{23}H_{28}Cl_7PPdSn$	$C_{22}H_{34}Cl_5PPdS_2Sn$	$C_{42}H_{58}Cl_8O_4P_2Pd_2Sn_2$	$C_{34}H_{40}Cl_8O_2P_2PdSn_2$	$C_{62}H_{68}Cl_8O_2P_4Pt_2Sn_2$
Formula weigth (g mol^{-1})	808.66	795.92	1422.60	1169.98	1880.32
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Temperature (K)	r.t.	220(2)	220(2)	220(2)	220(2)
Unit cell dimensions					
a (Å)	13.776(6)	14.734(2)	8.608(2)	10.493(3)	10.735(3)
b (Å)	14.144(6)	15.425(1)	11.723(3)	12.778(2)	12.677(4)
c (v)	16.045(7)	14.916(2)	15.316(4)	16.642(3)	12.861(4)
α (°)	90	90	96.96(3)	90	91.10(3)
β (°)	107.56(3)	112.34(1)	97.70(3)	105.30(3)	90.50(4)
γ (°)	90	90	108.62(3)	90	101.75(3)
V (Å^3)	2981(2)	3135.4(6)	1429.1(6)	2152.2(8)	1713.1(8)
Z	4	4	1	2	1
D_{calc} (g cm^{-3})	1.802	1.686	1.653	1.805	1.821
Absorption coefficient (mm^{-1})	2.135	1.991	1.948	2.166	5.236
2θ Range (°)	3.42–52.04	3.96–51.92	3.72–52.10	5.08–51.78	5.04–51.90
hkl indices	$-17 \le h \le 16$, $0 \le k \le 17$, $-19 \le l \le 19$	$-18 \le h \le 16$, $-17 \le k \le 18$, $-18 \le l \le 18$	$-10 \le h \le 10$, $-14 \le k \le 14$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-14 \le k \le 15$, $-20 \le l \le 20$	$-13 \le h \le 13$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections, measured	7387	17840	11127	16033	13972
Reflections, unique	5821	6044	5148	4093	6182
Reflections, unique	4426	4344	4710	3600	4918
R_{int} [$F_o > 4\sigma(\|F_o\|)$]	0.0467	0.0488	0.0355	0.0603	0.0487
No. of refined parameters	411	425	327	279	441
R_1, wR_2 (all data)	0.0716, 0.1112	0.0567, 0.0779	0.0308, 0.0777	0.0347, 0.0768	0.0472, 0.0856
R_1, wR_2 [$I > 2\sigma(I)$]	0.0447, 0.0947	0.0333, 0.0729	0.0272, 0.0732	0.0294, 0.0741	0.0340, 0.0813
Largest difference peak and hole (e Å^{-3})	1.699 and −0.850	1.069 and −0.483	0.736 and −0.929	1.003 and −0.893	1.236 and −1.330

Detailed investigations of the behaviour of **1**–**10** in solution are in progress.

3. Experimental

All manipulations were performed under dry argon. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemical Department of the University of Halle. The NMR spectra were recorded on Gemini (200 and 400 MHz) (Varian) or Unity (500 MHz) (Varian) spectrometers. Me_4Sn (^{119}Sn) and 85% H_3PO_4 (^{31}P) were used as external references.

3.1. [(COD)Pd$^+$(Cl)(PPh$_2$CH$_2$CH$_2$Sn$^-$Cl$_4$)] (1)

$Ph_2PCH_2CH_2SnCl_3$ (0.307 g, 0.7 mmol) [10] dissolved in 30 ml of CH_2Cl_2 was added to a stirred solution of 0.2 g (0.7 mmol) of [(COD)$PdCl_2$] [27] in 10 ml of CH_2Cl_2 at room temperature (r.t.). A yellow solid precipitates immediately. After stirring for 12 h at r.t. the half of the solvent is removed in vacuo, the solid is filtered, washed with *n*-pentane and dried. After recrystallization from 50 ml of CH_2Cl_2 0.46 g (81%) yellow crystalline **1** was obtained; m.p. 137–139 °C. Compound **1** crystallized with one molecule of CH_2Cl_2. Anal. (Exp./Calc.) for $C_{22}H_{26}Cl_5PdPSn \cdot CH_2Cl_2$ (808.7): C, 34.08/34.16; H, 3.53/3.49; Cl, 29.98/30.69%.

3.2. [(COD)Pt$^+$(Cl)(PPh$_2$CH$_2$CH$_2$Sn$^-$Cl$_4$)] (2)

The same procedure described for **1** was carried out with 0.2 g (0.53 mmol) of [(COD) $PtCl_2$] [28] in 10 ml of CH_2Cl_2 and 0.24 g (0.55 mmol) of $Ph_2PCH_2CH_2SnCl_3$ in 30 ml of CH_2Cl_2 yielded 0.38 g (78%) of **2** as a colourless microcrystalline powder; m.p. 159–161 °C. The low solubility of **2** prevents its recrystallization from

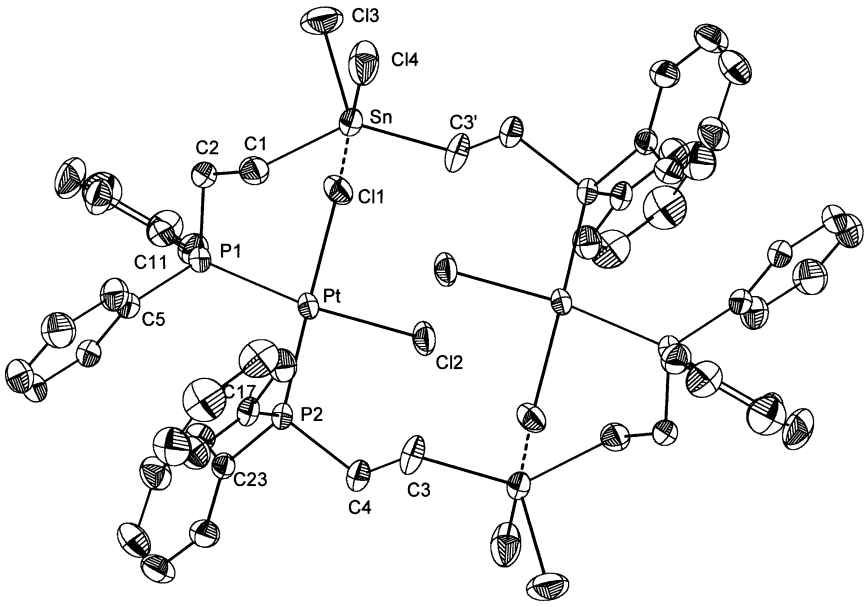


Fig. 5. Molecular structure of *cis*-$[Cl_2Pt(PPh_2CH_2CH_2)_2SnCl_2]_2$ (**9**) with atom-numbering.

CH_2Cl_2. Like **1**, **2** was also formed as an adduct with one molecule of CH_2Cl_2.

Anal. (Exp./Calc.) for $C_{22}H_{26}Cl_5PPtSn \cdot CH_2Cl_2$ (897.4): C, 30.79/30.78; H, 3.24/3.15; Cl, 27.40/27.65%.

3.3. *trans*-$[(Et_2S)_2Pd^+(Cl)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**3**)

A solution of 0.245 g (0.56 mmol) of $Ph_2PCH_2CH_2SnCl_3$ in 20 ml of CH_2Cl_2 was added dropwise at r.t. to a stirred solution of 0.2 g (0.56 mmol) of *trans*-$[(Et_2S)_2PdCl_2]$ [29] in 10 ml of CH_2Cl_2. After stirring for 3 h at the same temperature the reaction solution was evaporated to dryness and the yellow powdered solid was filtered, washed with *n*-pentane and dried. The recrystallization of this product from CH_2Cl_2–*n*-pentane gave 0.31 g (70%) of **3** as yellow to orange-coloured crystals; m.p. 156–157 °C.

Anal. (Exp./Calc.) for $C_{22}H_{34}Cl_5S_2PdPSn$ (796.0): C, 33.18/33.20; H, 4.51/4.31; Cl, 22.54/22.27; S, 8.15/8.06%.

3.4. *trans*-$[(Et_2S)_2Pt^+(Cl)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**4**)

The analogous reaction to compound **3** of 0.2 g (0.45 mmol) of *trans*-$[(Et_2S)_2PtCl_2]$ [29] and 0.2 g (0.46 mmol) of $Ph_2PCH_2CH_2SnCl_3$ both of the compounds dissolved in 10 ml of CH_2Cl_2 gave a colorless powder of **4** (0.32 g, 80%) which was not recrystallizable from CH_2Cl_2–*n*-pentane; m.p. 158–160 °C.

Anal. (Exp./Calc.) for $C_{22}H_{34}Cl_5S_2PPtSn$ (884.7): C, 29.61/29.87; H, 3.78/3.87; Cl, 19.49/20.04; S, 7.23/7.25%.

3.5. $[(COD)Pd^+(Cl)(PPh_2CH_2CH_2Sn^-MeCl_3)]$ (**5**) and *trans*-$[Cl_2Pd(PPh_2CH_2CH_2SnMeCl_2 \cdot 2Me_2CO)]_2$ (**6**)

$Ph_2PCH_2CH_2SnCl_3$ (0.33 g, 0.75 mmol) dissolved in 30 ml of CH_2Cl_2 was added to a solution of 0.2 g (0.75 mmol) of [(COD)PdMeCl] [30] in 10 ml of CH_2Cl_2 at r.t. The colour of the solution changed from yellow to green. After 2 h the solvent was completely removed in vacuo and the remained green–yellow powder of **5** was washed with *n*-pentane and dried (0.31 g, 58%); m.p. 84–87 °C.

Compound **5**: Anal. (Exp./Calc.) for $C_{23}H_{29}Cl_4PdPSn$ (703.4): C, 39.31/39.28; H, 4.00/4.16; Cl, 20.87/20.16%.

By layering of a concentrated solution of **5** in acetone with *n*-pentane compound **6** was formed as red crystals; m.p. 159–160 °C.

Compound **6**: Anal. (Exp./Calc.) for $C_{42}H_{58}Cl_8O_4Pd_2P_2Sn_2$ (1422.7): C, 35.67/35.46; H, 4.23/4.11; Cl, 19.39/19.94%.

3.6. *cis*/*trans*-$[Cl_2Pd(PPh_2CH_2CH_2SnCl_3)_2]$ (**7**) and *trans*-$[Cl_2Pd(PPh_2CH_2CH_2SnCl_3 \cdot Me_2CO)_2]$ (**7a**)

[(COD)$PdCl_2$] (0.2 g, 0.7 mmol) in 20 ml of CH_2Cl_2 was added dropwise to a solution of 0.614 g (1.4 mmol) of $Ph_2PCH_2CH_2SnCl_3$ in 40 ml of CH_2Cl_2 at r.t. The colour of the solution changed from colorless via light-green to yellow and after 2 h a voluminous yellow solid precipitated. After stirring for 6 h the pecipitate was filtered, washed with *n*-pentane and dried. Compound **7** was obtained as an amorphous yellow powder (0.43 g, 58%); m.p. 160–162 °C.

Compound **7**: Anal. (Exp./Calc.) for $C_{28}H_{28}Cl_8PdP_2Sn_2$ (1053.9): C, 32.31/31.91; H, 2.70/2.68; Cl, 26.88/26.91%.

Compound **7a**: slow crystallization of **7** from acetone/*n*-pentane yielded **7a** as yellow crystals.

3.7. *cis*-$[Cl_2Pt(PPh_2CH_2CH_2SnCl_3)_2]$ (**8**) and *cis*-$[Cl_2Pt(PPh_2CH_2CH_2)_2SnCl_2]_2$ (**9**)

From a reaction solution which was formed at r.t. by dropwise addition of a solution of 0.262 g (0.7 mmol) of $[(COD)PtCl_2]$ in 20 ml of CH_2Cl_2 to 0.614 g (1.4 mmol) of $Ph_2PCH_2CH_2SnCl_3$ dissolved in 40 ml of the same solvent a colourless solid precipitated. After stirring for 4 h at r.t. half of the solvent was removed in vacuo and the solid was filtered. After washing with *n*-pentane and drying, 0.39 g (49%) of **8** was obtained as a colourless powder; m.p. 149–152 °C.

Compound **8**: Anal. (Exp./Calc.) for $C_{28}H_{28}Cl_8PtP_2Sn_2$ (1142.6): C, 29.84/29.43; H, 2.53/2.47; Cl, 25.14/24.82%.

Compound **8** was transformed by slow crystallization from acetone–*n*-pentane into the colorless crystalline compound **9** which crystallized with two molecules of acetone; m.p. 159–161 °C.

Compound **9**: Anal. (Exp./Calc.) for $C_{56}H_{56}Cl_8Pt_2P_4Sn_2 \cdot 2\ C_3H_6O$ (1880.3): C, 39.15/39.60; H, 3.47/3.65; Cl, 15.53/15.08%.

3.8. $[(Et_2S)Pt^+(Cl)(PPh_2CH_2CH_2SnCl_3)(PPh_2CH_2CH_2Sn^-Cl_4)]$ (**10**)

trans-$[(Et_2S)_2PtCl_2]$ (0.312 g, 0.7 mmol) in 20 ml of CH_2Cl_2 was added dropwise at r.t. to a solution of 0.614 g (1.4 mmol) of $Ph_2PCH_2CH_2SnCl_3$ in 40 ml of CH_2Cl_2. After 4 h at the same temperature the solution evaporated in vacuo to dryness and the remaining solid was washed with *n*-pentane and dried. Compound **10** was obtained as a colourless powder (0.42 g, 49%); m.p. 164–167 °C.

Anal. (Exp./Calc.) $C_{32}H_{38}SCl_8P_2PtSn_2$ (1232.8): C, 31.32/31.18; H, 3.32/3.11; Cl, 23.29/23.01; S, 2.36/2.60%.

3.9. Crystallographic studies

Crystal data and details of the data collection and refinement are summarized in Table 5. The data collections were performed on a STOE IPDS diffractometer (**3**, **6**, **7a**, **9**) and on a STOE STADI-IV diffractometer (**1**) using Mo–K_α radiation. The structures were solved by direct methods and full-matrix least-squares refinements were performed [31]; all non-hydrogen atoms were refined with anisotropic displacement parameters. For molecular drawings DIAMOND 2.1 [32] was used.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 198677–198681 for compounds **1**, **3**, **6**, **7a**, and **9**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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