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Synthesis and characterization of five-coordinate platinum(II) complexes [Pt(2,9-dimethyl-1,10-phenanthroline) (SnR_nX_{3-n})X(olefin)] (X = Cl or Br; R = Ph or Me). Molecular structure of [Pt(2,9-dimethyl-1,10-phenanthroline)($SnPh_2Cl$)Cl(ethylene)]

Vincenzo G. Albano*, Carlo Castellari
Dipartimento di Chimica "G. Ciamician", Università di Bologna, via F. Selmi 2, 40126 Bologna (Italy)

Vincenzo De Felice
Dipartimento di Scienze e Tecnologie, Università del Molise, via Tiberio 21/a, 86100 Campobasso (Italy)

Achille Panunzi and Francesco Ruffo*
Dipartimento di Chimica, Università di Napoli, via Mezzocannone 4, 80134 Napoli (Italy)

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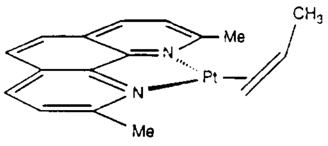
Abstract

Five-coordinate olefin complexes of platinum(II) of the general formula [Pt(2,9-Me_2-1,10-phen)(SnR_nX_{3-n})X(olefin)] have been synthesized through oxidative addition of organotin halides R_nSnX_{4-n} to three-coordinate platinum(0) complexes [Pt(2,9-Me_2-1,10-phen)(olefin)]. The X-ray crystal structure of the title complex has been determined. This crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 13.858(8)$, $b = 13.730(6)$, $c = 16.820(8)$ Å, $\beta = 102.44(5)°$, and $Z = 4$. Refinement converged at $R = 0.04$ ($R_w = 0.044$). The geometry of the five-coordinate platinum complex is bipyramidal, with anionic ligands in apical positions and the olefinic double bond in the equatorial plane. Some general features of the addition process, and the structural and NMR properties of the complexes, are also discussed.

Introduction

The chemistry of the Pt–Sn bond has been the object of extensive studies, owing to its involvment in many catalytic and stoichiometric processes [1]. For example, aryltrimethylstannanes are used in the arylation or diarylation of platinum(II) complexes such as [$PtCl_2$(cod)] [2] and tin chloride is used as a cocatalyst in platinum(II)-catalyzed hydroformylation and hydrogenation [3].

A large number of stable square-planar platinum(II) complexes of general formula [$PtL_2(SnX_nY_{3-n})X$] (X,Y = halogen and/or alkyl group, L = phosphine)



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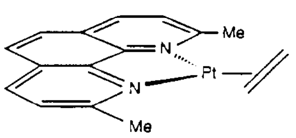

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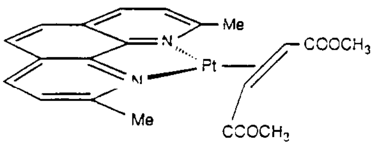

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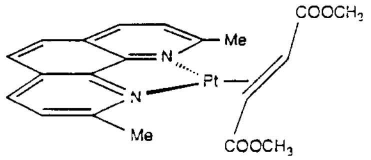

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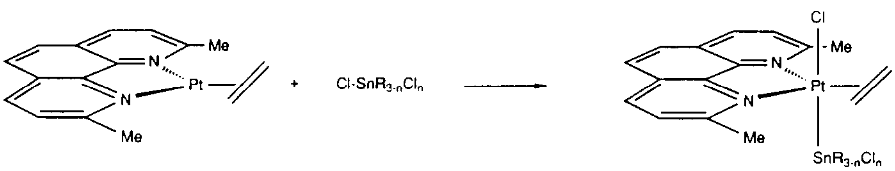
Fig. 1. Three-coordinate complexes used in this work. The organotin halides used are SnR_nCl_{4-n}: $SnMe_3Br$, $SnMe_3Cl$, $SnMe_2Cl_2$, $SnMeCl_3$, $SnPh_3Cl$ and $SnPh_2Cl_2$.

has been obtained through the oxidative addition of organotin halides to platinum(0) complexes [4]. Since the oxidative addition was generally accompanied by the irreversible dissociation of one or two ligands, five-coordinate complexes were generally not isolated *.

Recently [6], we described the oxidative addition of organic halides R–X to the platinum(0) species, [Pt(N–N′)(olefin)], where N–N′ is a ligand with steric properties suitable for stabilizing the five-coordinate product [PtRX(N–N′)(olefin)] [7]. This procedure led to the straightforward isolation of a variety of alkyl derivatives of platinum(II), not easily available through the previously reported synthetic pathways [8].

We now report the use of the same Pt^0 olefin precursors (Fig. 1) as substrates for the oxidative addition of organotin halides. This process affords a new class of five-coordinate olefin complex of platinum(II) with a Pt–Sn bond.



The molecular structure of a representative product is also reported.

We note that five-coordinate intermediates containing Pt–Sn bonds are involved in the catalytic processes [3] mentioned above.

* A remarkable exception was described by Ghilardi *et al.* [5a]. Few examples of five-coordinate complexes of d^8 ions with both an olefin and a σ-bonded SnR_3 group, are known, but see ref. 5b for a recent example of rhodium(I).

Results and discussion

Features of the oxidative addition reactions

Eaborn and Pidcock [4] have reported that the oxidative addition of organotin halides R_nSnX_{4-n} to $[Pt(PPh_3)_3]$ or $[Pt(PPh_3)_2(C_2H_4)]$ involves the insertion of platinum into an Sn–C or an Sn–X bond, depending on the value of n. The reaction with trichloride species leads to insertion into the Sn–X bond, whilst triorganotin halides afford platinum(II) complexes with a Pt–C bond. Two typical reactions are shown.

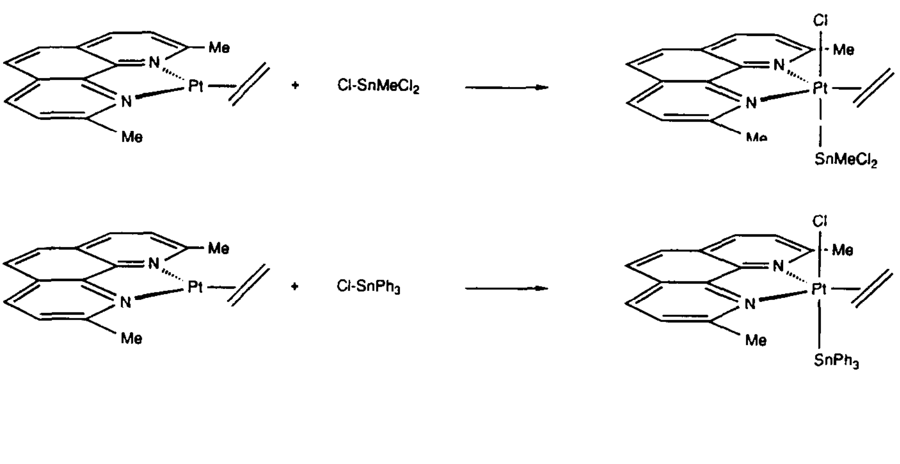
$$[Pt(PPh_3)_2(C_2H_4)] + RSnX_3 = \underset{\textbf{(a)}}{[Pt(PPh_3)_2(RSnX_2)X]} + C_2H_4$$

$$[Pt(PPh_3)_2(C_2H_4)] + R_3SnX = \underset{\textbf{(b)}}{[Pt(PPh_3)_2(R_2SnX)R]} + C_2H_4$$

It was suggested [9] that, for R = Me and X = Cl, in both cases, the first step of the reaction is the activation of the Sn–X bond, affording a chloro-derivative, such as (**a**) in the first equation. The formation of a product of type (**b**) was explained through the ready activation by the intermediate platinum(II) complex $[Pt(PPh_3)_2(R_3Sn)X]$ of the Sn–C bond of another molecule of organotin halide, to give $[Pt(PPh_3)_2(R_3Sn)(R_2SnX)X(R)]$, which eliminates R_3SnX to give (**b**).

On this basis we thought that the recently described complexes of general formula [Pt(N–N)(olefin)] (N–N = chelate ligands with suitable steric properties [7]), could activate the Sn–X bond of R_nSnX_{4-n} towards oxidative addition, to give the title compounds $[Pt(N–N)X(SnR_nX_{3-n})(olefin)]$. These were expected to be unreactive towards further addition, because of their coordination saturation, and, on the basis of the quoted mechanism, the formation of a Pt–C bond would not occur.

This belief has been confirmed by the experimental results: the reaction between R_nSnX_{4-n} and [Pt(N–N)(olefin)] affords platinum(II) complexes with Pt–X and Pt–Sn bonds, whatever the value of n, as the two examples below show.We also found that increasing the number of chlorine atoms on tin enhances the reactivity of the organotin halide, by increasing its electrophilicity. Thus, the triorganotin species SnR_3X appear to be the least reactive of the tin halides used,



leading to the formation of five-coordinate products only with complexes **1** and **2**. On the other hand, three-coordinate platinum(0) complexes show the behaviour exhibited in reactions with organic halides R–X [6]: the presence of electron-withdrawing substituents on the olefin lowers the nucleophilicity of the metal centre and therefore reduces reactivity. For instance, we did not detect any reaction between **3** or **4** and $SnPh_3Cl$ after 24 h in chloroform solution. The same electrophile reacts in a few hours with a toluene suspension of the more reactive ethylene compound **2**. On the other hand, complex **1**, prepared *in situ* in toluene solution (see Experimental), reacts immediately with $SnPh_3Cl$, owing to the presence of an electron-donating substituent on the olefinic double bond.

The addition of dichloro- and trichloro-species to all the three-coordinate platinum precursors we used readily takes place.

Oxidative additions to **2** should generally be performed in dry toluene rather than chlorinated solvents to avoid competitive addition reactions [6], but the high reactivity of dichloro- and trichloro-tin derivatives does allow the use of methylene chloride as solvent.

Characterization of the products

The five-coordinate complexes were characterized through NMR spectroscopy, elemental analysis (Tables 1–3) and conductivity measurements.

The products of oxidative addition show trigonal-bipyramidal geometry, which has been observed before in similar bimetallic compounds such as trichlorostannyl platinum(II) complexes [10] and Pt–Sn complexes with sterically demanding tridentate ligands [5a].

The assignation of a bipyramidal trigonal geometry has been inferred through ^1H NMR spectral evidence as throughly discussed elsewhere [7] for the related alkyl complexes. Here we point out the main features of the spectra *.

(i) Large high-field shifts of the olefinic proton resonances, as already observed for the five-coordinate haloalkyl complexes [7,8]. The shift is larger for olefins bearing withdrawing substituents (e.g., 2.64–2.54 ppm for dimethylmaleate, 2.35–1.80 for ethylene).

(ii) Equivalence of the two halves of 2,9-dimethyl-1,10-phenanthroline in complexes with olefins of C_{2v} symmetry (dimethylmaleate) or higher symmetry (ethylene).

(iii) The methyl protons on tin show coupling with tin nuclei ** (the range of the $^2J(Sn–H)$ is 44–65 Hz), and a detectable, though poorly measurable, coupling with platinum.

The ^1H NMR spectrum of the product obtained by the addition of $SnPh_2Cl_2$ to **4** does not contain any evidence of the insertion of platinum into the Sn–Cl bond. However, competitive insertion into the Sn–C bond can be ruled out by the presence of coupling between tin nuclei and the *ortho*-carbon atoms of both the diastereotopic phenyl rings, in the ^{13}C NMR spectrum.

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* ^1H NMR signals of the products of the addition to complexes **3** and **4** are accompanied by peaks owing to three-coordinate complexes and to free tin halides. Probably a reversible dissociation process occurs, and this is being investigated separately.

** The satellites owing to the coupling with ^{117}Sn and ^{119}Sn overlap.

Table 1

^{1}H NMR data [δ (ppm), J (Hz)] for the five-coordinate products [Pt(2,9-Me_2-1,10-phen)-(SnR_nX_{3-n})X(olefin)] [a]

Substrate [b]	Organotin halide	Resonances			
		Sn–CH_x (^2J(Sn–H))	N–CMe (J(Pt–H))	–CH (olefinic)	Other signals [c]
1	$SnMe_2Cl_2$	−0.08(50) (s, 6H)	3.40	3.82([d]) (m, 1H)	
			3.35	3.05([d]) (m, 2H)	
(as above, diastereomer) 40% abundance		0.12(50) (s, 6H)	3.42	3.82([d]) (m, 1H)	
			3.34	3.05([d]) (m, 2H)	
1	$SnPh_3Cl$		3.35	3.75([d]) (m, 1H)	7.11 (t, 3H)
			3.30	3.13([d]) (d, 1H)	6.98 (t, 6H)
				3.02(81) (d, 1H)	6.80 (d, 6H)
2	$SnMeCl_3$	0.62(45) (s, 3H)	3.38	3.22(65) (d, 4H)	
2	$SnMe_2Cl_2$	−0.03(44) (s, 6H)	3.36	3.05(80) (d, 2H) [e]	
				2.85(48) (d, 2H) [e]	
2	$SnPh_2Cl_2$		3.33	3.11(68) (d, 4H)	7.11 (t, 2H)
					6.98 (t, 4H)
					6.85 (d, 4H)
2	$SnMe_3Br$ [f]	−0.68(47) (s, 9H)	3.32	2.93(81) (d, 2H) [e]	
				2.50(54) (d, 2H) [e]	
2	$SnMe_3Cl$ [g]	−0.65(51) (s, 9H)	3.25	2.64([d]) (d, 2H) [e]	
				2.42(74) (d, 2H) [e]	
2	$SnPh_3Cl$		3.27	3.30(98) (d, 4H)	7.11 (t, 3H)
					6.95 (t, 6H)
					6.89 (d, 6H)
3	$SnMeCl_3$	1.35(43) (s, 3H)	3.27	4.24(70) (s, 2H)	3.90 (s, OHz)
3	$SnMe_2Cl_2$	0.30(61) (s, 6H)	3.32	4.34(80) (s, 2H)	3.87 (s, OMe)
3	$SnPh_2Cl_2$		3.10	4.34(81) (s, 2H)	7.36 (d, 4H)
					7.20–7.00 (m, 6H)
					3.46 (s, OMe)
4	$SnMeCl_3$	1.20(65) (s, 3H)	3.23	4.66(70) (d, 1H)	3.93 (s, OMe)
			3.53	4.34(70) (d, 1H)	3.79 (s, OMe)
4	$SnMe_2Cl_2$	0.90(65) (s, 3H)	3.50	4.24(80) (q, 2H) [h]	3.82 (s, OMe)
		0.19(65) (s, 3H)	3.15		3.76 (s, OMe)
4	$SnPh_2Cl_2$ [i]		3.48	4.54(71) (d, 1H)	3.82 (s, OMe)
			2.66	4.20(68) (d, 1H)	3.70 (s, OMe)
			[31.2]	[34.6 (480) [j]]	[136.0(47) [k]] [2C(α)]
			[29.2]	[29.7(500) [j]]	[135.6(47) [k]] [2C(α)]

[a] 270 or 200 MHz; in $CDCl_3$ solutions. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] See Fig. 1. [c] The aromatic protons of the phenanthroline rings are in the range 8.50–8.10 (2H), 7.90–7.70 (2H), 7.70–7.35 (2H). [d] ^2J(Pt–H) not evaluable. [e] Pseudodoublets, actually constituting a AA′XX′ of more complex multiplet. [f] Recorded at −20 °C. [g] In CD_2Cl_2, recorded at −30°C. [h] AB quartet. [i] Selected ^{13}C NMR resonances in square brackets. [j] ^1J(Pt–C) (Hz). [k] ^2J(Sn–C) (Hz).

The spectra of the complexes [Pt(2,9-dimethyl-1,10-phen)Br($SnMe_3$)(ethylene)] and [Pt(2,9-dimethyl-1,10-phen)Cl($SnMe_3$)(ethylene)] (see Table 1) have been recorded at low temperature in order to delay decomposition, which occurs very rapidly at room temperature.

In no case did we detect free rotation of the coordinated olefin around the Pt-double bond axis: the ethylene and the propylene patterns appear as doublets or multiplets, the olefinic protons of dimethylfumarate as AB quartets or doublets

Table 2

^{119}Sn and ^{195}Pt chemical shifts [a] for some five-coordinate complexes

Complex	$\delta(^{119}Sn)$ (ppm)	$\delta(^{195}Pt)$ (ppm)	$^1J(Pt-Sn)$ (Hz)
[Pt(2,9-Me_2-1,10-phen)Cl($SnMe_2Cl$)(propylene)]	−3.98	−3273.74	12909.0
As above, diastereomer, 40% abundance	−26.99	−3312.38	13816.4
[Pt(2,9-Me_2-1,10-phen)Cl($SnMe_2Cl$)(ethylene)]	−2.23	−3411.39	12573.2
[Pt(2,9-Me_2-1,10-phen)Cl($SnMe_2Cl$)(dimethylmaleate)]	−145.98	−3074.22	11216.1
[Pt(2,9-Me_2-1,10-phen)Cl($SnMeCl_2$)(ethylene)]	−141.69	−3262.51	16978.3

[a] Referred to $SnMe_4$ and H_2PtCl_6, respectively.

of doublets. Dimethylmaleate olefinic resonances actually appear as singlets. This result should be related to the presence of only one of the two possible isomers, (probably owing to steric repulsion between the tin group and the cis substituents on the olefin), more than to the free rotation of the olefin, which should be hindered as in the case of dimethylfumarate.

The complex [Pt(2,9-Me_2-1,10-phen)($SnPh_3$)Cl(propylene)] exists in only one of the two possible isomers, whereas the two expected isomers are observed for [Pt(2,9-Me_2-1,10-phen)Cl($SnMe_2Cl$)(propylene)], and the relative abundance (see Table 1) was evaluated by integration.

The molecular structure of [Pt(2,9-dimethyl-1,10-phenanthroline)Cl($SnPh_2Cl$)(ethylene)]

The structure of the title compound has been determined by X-ray diffraction and the molecular structure is illustrated in Fig. 2. Fractional atomic coordinates, bond distances, and angles are listed in Tables 4 and 5. The molecule exhibits the expected trigonal bipyramidal coordination with the axial sites occupied by Cl^- and $SnPh_2Cl^-$. The orientation of the $SnPh_2Cl$ group seems dictated by the need to minimize the molecular hindrance and its actual conformation deprives the molecule of the idealized mirror plane permitted by the coordination polyhedron. In spite of the lack of symmetry, the bond parameters do not exhibit significant

Table 3

Analytical data for the five-coordinate products [Pt(2,9-Me_2-1,10-phen)(SnR_nX_{3-n})X(olefin)]

Substrate	Organotin halide	Formula	Anal. Found (calc.) (%)		
			C	H	N
1	$SnMe_2Cl_2$	$C_{19}H_{24}Cl_2N_2PtSn$	34.3 (34.31)	3.7 (3.64)	4.4 (4.21)
1	$SnPh_3Cl$	$C_{35}H_{33}ClN_2PtSn$	50.5 (50.59)	4.0 (4.00)	3.5 (3.37)
2	$SnMeCl_3$	$C_{17}H_{19}Cl_3N_2PtSn$	30.4 (30.41)	2.9 (2.85)	4.3 (4.17)
2	$SnMe_2Cl_2$	$C_{18}H_{22}Cl_2N_2PtSn$	33.2 (33.21)	3.4 (3.41)	4.3 (4.30)
2	$SnPh_2Cl_2$	$C_{28}H_{26}Cl_2N_2PtSn$	43.2 (43.38)	3.6 (3.38)	3.6 (3.61)
2	$SnPh_3Cl$	$C_{34}H_{31}ClN_2PtSn$	50.0 (49.99)	3.9 (3.83)	3.5 (3.43)
3	$SnMeCl_3$	$C_{21}H_{23}Cl_3N_2O_4PtSn$	31.9 (32.03)	2.9 (2.94)	3.5 (3.56)
3	$SnMe_2Cl_2$	$C_{22}H_{26}Cl_2N_2O_4PtSn$	34.5 (34.44)	3.5 (3.42)	3.8 (3.65)
3	$SnPh_2Cl_2$	$C_{32}H_{30}Cl_2N_2O_4PtSn$	43.0 (43.12)	3.5 (3.39)	3.2 (3.14)
4	$SnMeCl_3$	$C_{21}H_{23}Cl_3N_2O_4PtSn$	32.0 (32.03)	2.9 (2.94)	3.7 (3.56)
4	$SnMe_2Cl_2$	$C_{22}H_{26}Cl_2N_2O_4PtSn$	34.4 (34.44)	3.5 (3.42)	3.7 (3.65)
4	$SnPh_2Cl_2$	$C_{32}H_{30}Cl_2N_2O_4PtSn$	43.1 (43.12)	3.4 (3.39)	3.2 (3.14)

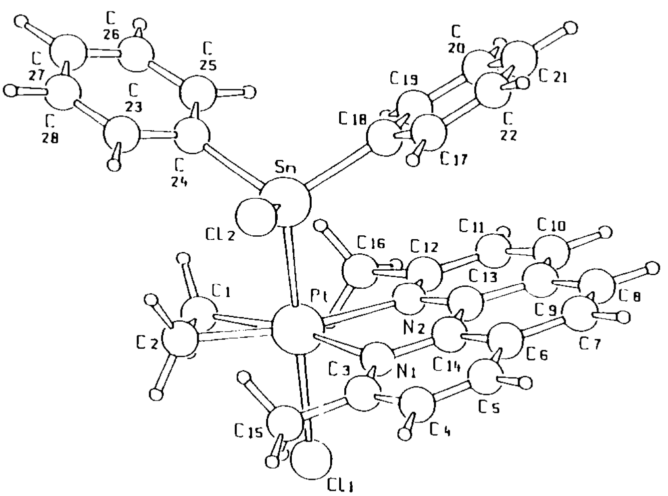

Fig. 2. View of the molecule [Pt(2,9-Me_2-1,10-phen)Cl($SnPh_2Cl$)(C_2H_4)].

deviations from regularity. The axial ligands are in line with the platinum atom [Sn–Pt–Cl(1) 177.3(1)°], and the coordinated equatorial atoms do not significantly deviate from planarity (range ± 0.05 Å). The average plane of the phenanthroline rings is 9.9(3)° out of the coordination plane and the Pt atom is 0.32 Å out of this plane on the side of the tin atom. The non-coincidence of the phenanthroline and coordination plane has already been pointed out and attributed to the methyl–platinum contacts [Pt–C(15,16) 3.4 Å] [11].

The Pt–N distances are equivalent and the average is 2.20(1) Å. The Pt–C(ethylene) average distance is 2.08(1) Å, while the C=C bond length is 1.41(2) Å. All these values are strictly comparable with those found in species of similar composition and geometry, as shown in Table 6.

The Pt–Sn bond [2.534(1)] is slightly longer than in other species in which Sn is *trans* to Cl, *e.g.* 2.514(1) Å in [PtCl($SnCl_3$)(PEt_3)($NH_2C_6H_4$-*p*-Cl)] [12], 2.501(1) Å in [PtCl($SnCl_3$)(PEt_3)(PhC(NH_2)=NOH] [13]. The lengthening is statistically significant and can be ascribed to the different *trans* substituents. The radius of Sn is greater in $SnPh_2Cl$ than in $SnCl_3$, where the electron-withdrawing effect of three chlorine atoms places some positive charge on Sn and shrinks its orbitals. The fact is confirmed by the Pt–Sn distances in [PtH($SnPh_3$)(PCy_3)$_2$] [14] and [PtH($SnCl_3$)(PCy_3)$_2$] [14], 2.654(1) and 2.600(2) Å, respectively.

The Pt–Cl distance [2.478(3) Å] is significantly longer than that found in five-coordinate dichloro-derivatives, e.g. 2.311(3) Å in [$PtCl_2$(2,9-Me_2-1,10-phen)(ethylene)] [15], but substantially equivalent to the values in species containing an alkyl group trans to the chloride ligand (see Table 6). This is a clear indication that the trans influence of the Sn atom in the observed molecule is as strong as that of an sp^3-hybridized carbon atom. This is consistent with the much shorter Pt–Cl distances of 2.311(1) and 2.325(3) Å found in [PtCl($SnCl_3$)(PEt_3)($NH_2C_6H_4$-*p*-Cl)] and [PtCl($SnCl_3$)(PEt_3)(PhC(NH_2)=NOH], respectively. Again the electronic properties of the substituents explain the effect; $SnPh_2Cl^-$ is a better donor than $SnCl_3^-$ and its *trans* influence is stronger, and more similar to those of alkyl groups.

Experimental

^1H NMR spectra were recorded at 60 MHz on a Jeol SI-60 spectrometer and at 270 or 200 MHz on a Bruker AC-270 or a Varian XL-200 spectrometer, respectively. $CDCl_3$ was used as solvent and as internal standard.

The platinum(0) complexes **1**, **2** and **4** were made by previously described procedures [6]. Solvents and reagents were of AnalaR grade and, unless otherwise stated, they were used without further purification.

Table 4

Fractional atomic coordinates for $[Pt(2,9\text{-}Me_2\text{-}1,10\text{-}phen)]Cl(SnPh_2Cl)(C_2H_4)]$ with their standard deviations in parentheses

Atom	*x*	*y*	*z*
Pt	0.00374(3)	0.04335(3)	0.77311(3)
Cl1	0.1629(2)	−0.0339(2)	0.7648(2)
C1	0.000(1)	−0.038(1)	0.8760(8)
C2	0.043(1)	0.053(1)	0.8998(7)
N1	0.0329(7)	0.1593(7)	0.6921(6)
N2	−0.0658(6)	−0.0102(7)	0.6505(6)
C3	0.087(1)	0.238(1)	0.7115(9)
C4	0.094(1)	0.310(1)	0.655(1)
C5	0.042(1)	0.300(1)	0.578(1)
C6	−0.016(1)	0.221(1)	0.553(1)
C7	−0.069(1)	0.200(2)	0.471(1)
C8	−0.115(1)	0.117(2)	0.449(1)
C9	−0.116(1)	0.042(1)	0.5074(8)
C10	−0.163(1)	−0.048(2)	0.492(1)
C11	−0.157(1)	−0.117(1)	0.553(1)
C12	−0.108(1)	−0.094(1)	0.630(1)
C13	−0.0676(8)	0.059(1)	0.5904(6)
C14	−0.0158(9)	0.147(1)	0.6119(8)
C15	0.144(1)	0.247(1)	0.797(1)
C16	−0.104(1)	−0.168(1)	0.698(1)
Sn	−0.15517(5)	0.13014(6)	0.78150(5)
Cl2	−0.1161(2)	0.2966(2)	0.8166(2)
C17	−0.271(1)	0.2294(9)	0.6247(8)
C18	−0.2611(8)	0.1432(7)	0.6709(6)
C19	−0.3123(9)	0.060(1)	0.6349(8)
C20	−0.378(1)	0.066(1)	0.5610(9)
C21	−0.392(1)	0.152(1)	0.520(1)
C22	−0.340(1)	0.231(1)	0.5522(9)
C23	−0.2065(9)	0.1329(9)	0.9527(6)
C24	−0.2243(8)	0.0855(7)	0.8763(7)
C25	−0.287(1)	0.004(1)	0.8654(9)
C26	−0.325(1)	−0.027(1)	0.930(1)
C27	−0.309(1)	0.018(1)	1.002(1)
C28	−0.250(1)	0.097(1)	1.0127(8)
C29	0.374(1)	0.0883(7)	0.7294(5)
Cl3	0.4087(6)	0.0145(5)	0.6592(4)
Cl4	0.4583(5)	0.0819(5)	0.8202(3)
Cl5	0.3545(4)	0.2060(4)	0.6976(5)

Table 5

Bond distances (Å) and angles (deg)

Bond distances			
Pt–Cl1	2.478(3)	C10–C11	1.38(3)
Pt–C1	2.07(1)	C11–C12	1.37(2)
Pt–C2	2.09(1)	C12–C16	1.52(2)
Pt–N1	2.19(1)	C13–C14	1.41(1)
Pt–N2	2.207(9)	Sn–Cl2	2.393(3)
Pt–Sn	2.534(1)	Sn–C18	2.11(1)
C1–C2	1.41(2)	Sn–C24	2.12(1)
N1–C3	1.31(1)	C17–C18	1.41(1)
N1–C14	1.38(1)	C17–C22	1.38(2)
N2–C12	1.30(1)	C18–C19	1.42(1)
N2–C13	1.38(1)	C19–C20	1.38(1)
C3–C4	1.39(2)	C20–C21	1.36(2)
C3–C15	1.49(2)	C21–C22	1.35(2)
C4–C5	1.35(3)	C23–C24	1.41(1)
C5–C6	1.36(2)	C23–C28	1.37(2)
C6–C7	1.45(2)	C24–C25	1.40(1)
C6–C14	1.43(2)	C25–C26	1.37(2)
C7–C8	1.31(4)	C26–C27	1.35(2)
C8–C9	1.43(3)	C27–C28	1.34(2)
C9–C10	1.39(3)	C29–Cl3	1.70(1)
C9–C13	1.43(1)	C29–Cl4	1.71(1)
		C29–Cl5	1.71(1)
Bond angles			
N2–Pt–Sn	89.9(2)	C18–C19–C20	120(1)
N1–Pt–Sn	88.4(2)	C19–C20–C21	121(1)
N1–Pt–N2	76.3(3)	C20–C21–C22	119(1)
C2–Pt–Sn	87.4(4)	C17–C22–C21	123(1)
C2–Pt–N2	160.3(5)	C24–C23–C28	119(1)
C2–Pt–N1	123.1(6)	Sn–C24–C23	122.2(8)
C1–Pt–Sn	91.6(5)	C23–C24–C25	118(1)
C1–Pt–N2	121.1(5)	Sn–C24–C25	119.8(9)
C1–Pt–N1	162.6(5)	C24–C25–C26	119(1)
C1–Pt–C2	39.6(5)	C25–C26–C27	124(1)
Cl1–Pt–Sn	177.31(9)	C26–C27–C28	118(1)
Cl1–Pt–N2	91.1(2)	C23–C28–C27	123(1)
Cl1–Pt–N1	89.5(2)	Cl4–C29–Cl5	111.2(6)
Cl1–Pt–C2	92.4(4)	Cl3–C29–Cl5	113.4(6)
Cl1–Pt–C1	89.9(4)	Cl3–C29–Cl4	110.5(7)
Pt–C1–C2	70.8(8)	C3–N1–C14	119(1)
Pt–C2–C1	69.6(7)	Pt–N2–C13	113.0(8)
Pt–N1–C14	113.5(8)	Pt–N2–C12	128.2(9)
Pt–N1–C3	127.9(9)	C12–N2–C13	119(1)
Pt–Sn–C24	116.4(3)	N1–C3–C15	118(1)
Pt–Sn–C18	116.0(3)	N1–C3–C4	122(1)
Pt–Sn–Cl2	108.0(1)	C4–C3–C15	120(1)
C18–Sn–C24	110.2(4)	C3–C4–C5	119(1)
Cl2–Sn–C24	101.9(3)	C4–C5–C6	122(2)
Cl2–Sn–C18	102.3(3)	C5–C6–C14	116(1)
C18–C17–C22	118(1)	C5–C6–C7	127(1)
Sn–C18–C17	121.6(9)	C7–C6	C14116(1)
C17–C18–C19	118(1)	C6–C7–C8	124(1)
Sn–C18–C19	119.8(8)	C7–C8–C9	121(1)
		C8–C9–C13	119(1)

Table 5 (continued)

Bond angles			
C8–C9–C10	126(1)	N2–C13–C9	122(1)
C10–C9–C13	115(1)	C9–C13–C14	120(1)
C9–C10–C11	121(2)	N2–C13–C14	118(1)
C10–C11–C12	119(1)	C6–C14–C13	121(1)
N2–C12–C11	124(1)	N1–C14–C13	118(1)
C11–C12–C16	120(1)	N1–C14–C6	121(1)
N2–C12–C16	117(1)		

Synthesis of 3

A solution of dimethylmaleate (0.040 g, 1.2 equiv.) in dry methanol (4 ml) was added with stirring to solid **2** (0.100 g). The colour of the suspension changed from red to yellow. After 10 min the precipitated product was recovered by filtration and washed with dry methanol. Yield: 90%. ^{1}H NMR ($CDCl_3$): 8.33 (d, 2H), 7.75 (s, 2H), 7.70 (d, 2H), 3.70 (s, OMe), 3.55(78) (s, =CH), 3.22 (s, NCMe) ppm.

Addition of SnR_nCl_{4-n} to 3 or 4 ($n = 2, 3, R = Me; n = 2, R = Ph$). A chloroform solution of the appropriate organotin chloride (1.2 equiv.) was added to a solution of the platinum complex (0.100 g) in the same solvent (3 ml). After filtration on Celite, addition of diethyl ether caused crystallization of the five-coordinate complex. Yield: 75–80%.

Addition of $SnPh_3Cl$, $SnMe_3Br$, or $SnMe_3Cl$ to 2. A solution of the organotin halide (1.5 equiv.) in dry toluene (4 ml) was added to solid **2** (0.100 g) in an ethylene atmosphere. The resulting suspension was stirred for 24 h, while the colour changed from red to light brown. The solid was separated, washed with dry toluene and dried *in vacuo*. The yield of the crude products was 80%. The complex [Pt(2,9-dimethyl-1,10-phen)Cl($SnPh_3$)(ethylene)] can be crystallized from $CHCl_3/Et_2O$, whereas the complexes [Pt(2,9-dimethyl-1,10-phen)Br($SnMe_3$)(ethylene)] and [Pt(2,9-dimethyl-1,10-phen)Cl($SnMe_3$)(ethylene)] have been characterized without further purification (see text).

Addition of SnR_nCl_{4-n} to 2 ($n = 2, 3, R = Me; n = 2, R = Ph$). A solution of the appropriate organotin halide (1.5 equiv.) in dry methylene chloride (4 ml) was added with stirring to the solid Pt complex (0.100 g) in an ethylene atmosphere. In a few seconds the resulting red solution became yellow. Filtration on Celite and addition of n-hexane caused the precipitation of the product. Crystallization was achieved from $CHCl_3/Et_2O$. Yield: 70–80%.

Table 6

Comparison of average bond lengths in related five-coordinate complexes of general formula [MClX(2,9-Me_2-1,10-phen)(olefin)] (M = Pt, Pd; X = Cl, C(alkyl), Sn)

Formula	M–C(olefin)	C=C	M–N	M–Cl	Ref.
[Pt(2,9-Me_2-1,10-phen)Cl($SnPh_2Cl$)(ethylene)]	2.08(1)	1.410(7)	2.20(1)	2.478(3)	
[Pt(2,9-Me_2-1,10-phen)Cl_2(ethylene)]	2.083(7)	1.41(1)	2.236(5)	2.311(3)	15
[Pt(2,9-Me_2-1,10-phen)Cl(CH(CH_2)$_2$CH=CH(CH_2)$_2$CH(OMe))]	2.06(1)	1.44(1)	2.24(1)	2.457(2)	11
[Pd(2,9-Me_2-1,10-phen)Cl(Me)(maleic anhydride)]	2.096(5)	1.410(7)	2.19(1)	2.492(1)	16

Table 7

Crystal data and details of the structure determination

Formula	$C_{28}H_{26}Cl_2N_2PtSn \cdot CHCl_3$	Crystal colour	Pale yellow
M_r (amu)	894.6	Crystal dimensions	$0.2 \times 0.2 \times 0.3$ mm^3
Crystal system	Monoclinic	Transmission factor range	67–100%
Space group	$P2_1/n$	Scan mode	$\omega/2\theta$
a (Å)	13.858(8)	θ range (deg)	2–25
b (Å)	13.730(6)	Scan width (deg) ($+0.35 \tan \theta$)	1.5
c (Å)	16.820(8)	Prescan acceptance $\sigma(I)/I$	0.5
β (deg)	102.44(5)	Required counting $\sigma(I)/I$	0.02
U (Å^3)	3125(3)	Prescan speed (deg/min)	5
Z	4	Maximum scan time (s)	120
$d_{calc.}$ (g/cm^3)	1.9	Collected octants	$\pm h, +k, +l$
μ (Mo-K_α) (cm^{-1})	5.95	Data collected	5985
$F(000)$	1712	Data used [$I > 2\sigma(I)$]	3134
		R (%), R_w (%)	4.0, 4.4
		k (g) [a]	5.9, 2×10^{-4}

[a] The weighting scheme employed was $w = k/[\sigma^2(F) + |g|F^2]$, where both k and g were independently determined.

Addition of $SnPh_3Cl$ and $SnMe_2Cl_2$ to 1. To a solution of the three-coordinate complex (0.100 g) in dry toluene [6], solid organotin chloride (1.5 equiv.) was added. Immediately the colour of the solution changed from red to yellow, followed by precipitation of the product. This was crystallized from $CHCl_3/Et_2O$, in 65–70% yield.

Crystallography of [Pt(2,9-Me_2-1,10-phen)Cl($SnPh_2Cl$)(ethylene)]

Crystals suitable for X-ray diffraction were obtained starting from a chloroform solution of the five-coordinate complex (0.050 g in 3 ml). A few drops of diethyl ether were added to the solution and, after 12 h at −40°C, pale yellow crystals were collected. Crystal data and experimental details are reported in Table 7. The diffraction experiments were carried out at room temperature on an Enraf–Nonius CAD-4 diffractometer with Mo-K_α radiation. The diffraction intensities were corrected for Lorentz, polarization, and absorption effects [17]. Scattering factors were taken from [18]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations. The thermal motion was treated anisotropically for all the non-hydrogen atoms. The hydrogen atoms were placed in calculated positions [C–H sp^3 1.08, C–H sp^2 1.05 Å] and allowed to ride on their carbon atoms. The final difference-Fourier map showed a maximum of residual electron density of 1.4 e Å^{-3} located at a distance of 1.5 Å from the platinum atom. The SHELX program was used for the computations [19].

Supplementary material. Tables of anisotropic thermal parameters of non-hydrogen atoms (2 pages), positional parameters of non-hydrogen atoms (1 page) and a listing of structure factors (19 pages) are available from the authors.

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