Synthesis of Novel Trialkyl(trichlorostannyl)platinum(IV) Complexes through $SnCl_2$ Insertion into the Pt−Cl Bond

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*Summary: Reaction of $SnCl_2$ with the trialkylplatinum(IV) complexes $[PtClMe_2(R)(bipy)]$ (**1**) resulted in the formation of the novel trialkyl(trichlorostannyl)platinum(IV) complexes $[PtMe_2(R)(SnCl_3)(bipy)]$ (R = allyl (**2a**), Me (**2b**), Bz (**2c**)). The solid-state molecular structure of fac-$[PtMe_3(SnCl_3)(bipy)]$ revealed a direct Pt−Sn bond (2.6497(2) Å) and three almost identical Pt−Me bond lengths (2.065(5) and 2.068(8) Å both cis and 2.069(5) Å trans to $SnCl_3$). The presence of platinum satellites ($^1J_{SnPt} = 3267{-}4260$ Hz) in the ^{119}Sn NMR spectra of complexes **2** indicates that the direct platinum−tin bond is maintained in solution. Addition of 1 equiv of PPh_3 to complexes **2** resulted in the formation of the trichlorostannate complexes fac-$[PtMe_2(R)(bipy)(PPh_3)][SnCl_3]$ (**3**). The absence of platinum satellites on the ^{119}Sn NMR signal of **3** confirmed the ionic character of these complexes in solution.*

Introduction

Heterobimetallic complexes of tin and group 10 metals have been known for several decades.[1] M(II) trihalostannyl complexes can be prepared via SnX_2 insertion into the M−X bond (M = Pt, Pd; X = Cl, Br) and are excellent catalysts for hydrogenation of olefins and alkynes[2] as well as for the hydroformylation of alkenes.[3] In these catalytic reactions, the $[SnX_3]^-$ anion serves as a weakly coordinating anionic ligand, which allows the facile creation of a vacant coordination site at the metal center.

It was Kuyper who reported the first examples of platinum(IV) trichlorostannyl complexes, i.e., $[PtClMe_2(SnCl_3)(N\text{-}N)]$ (N-N = 2,2′-bipyridine, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline),[4] which were obtained from oxidative addition of $SnCl_4$ on $[PtMe_2(N\text{-}N)]$. $[PtClMe_2(SnCl_3)(paen\text{-}me_2)]$[5] (paen-me$_2$ = *N*-(β-(dimethylamino)ethyl)pyridinealdimine) and $[PtClMe_2(SnMe_nCl_{3-n})(bipy)]$ ($n = 1{-}3$)[4] can be prepared in a similar way. Other Pt(IV)−stannyl complexes obtained by reaction of organoplatinum(II) complexes with tin(IV) reagents are $[Pt(SnMe_3)(Ph)(H)_2(PEt_3)_2]$,[6] $[PtIMe_2(SnMe_3)(Bu^t{}_2bpy)]$,[5] $[PtMe_2(SnMe_3)((pz)_3BH)]$[7] ($(pz)_3BH$ = tris(pyrazol-1-yl)borate), ionic $[PtMe_2(Me_2SnCl)(Bu^t{}_2bpy)]^+[Y]^-$, and $[PtClMe_2(SnPh_{3-x}Cl_x)(Bu^t{}_2bpy)]$[8] (Y = BF_4, PF_6; X = 1−3; $Bu^t{}_2bpy$ = 4,4′-di-*tert*-butyl-2,2′-bipyridine).[9] In all these Pt(IV) stannyl complexes, the stannyl substituent was introduced by oxidative addition of a tin(IV) species to a Pt(II) complex. Recently, Puddephatt et al. reported on the reductive elimination of Me_3SnX and Me_4Sn from $[PtXMe_2(SnMe_3)(diimine)]$ (X = Cl, Br, I) complexes, underlining the intermediacy of Pt(IV)−stannyl complexes in Sn−C bond formation.[10]

Here we report on the novel trialkyl(trichlorostannyl)platinum(IV) complexes $[PtMe_2(R)(SnCl_3)(bipy)]$ (**2**) and related stannate complexes $[PtMe_2(R)(PPh_3)(bipy)][SnCl_3]$ (**3**), which were synthesized through the unprecedented insertion of $SnCl_2$ into the Pt^{IV}−Cl bond. As these alkyl(trichlorostannyl)platinum complexes show a tendency to undergo reductive Sn−C bond formation, they are relevant for the oxidative alkylation of stannous halides. This aspect will be the subject of a subsequent paper.

Results and Discussion

Synthesis of $PtMe_2(R)(SnCl_3)(bipy)$ (2). Reaction of complexes $[PtClMe_2(R)(bipy)]^{11a-c}$ (**1**) with $SnCl_2$

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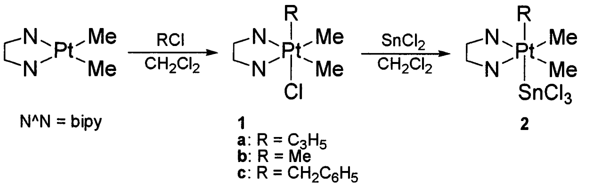
Table 1. ^1H NMR Data for [$PtClMe_2R$(bipy)] (1) and the Novel Pt(IV) Complexes [$PtMe_2R(SnCl_3)$(bipy)] (2) and [$PtClMe_2R(PPh_3)$(bipy)][$SnCl_3$] (3)[a]

complex	R	bipy ligand	α-H of R				Pt−Me (trans to bipy)				
			δ	$^2J_{HPt}$	$^3J_{HP}$	$^3J_{HSn}$	δ	$^2J_{HPt}$	$^3J_{HP}$	$^3J_{HSn}$	other
1a[b]	allyl	7.58 (t, 2H), 8.06 (t, 2H), 8.18 (d, 2H), 8.88 (d, 2H)	2.13 (d, 2H)	95			1.37 (s, 6H)	70			4.15−4.36 (m, 2H), 5.00−5.23 (ps sext, 1H, $^3J_{HH}$ = 9.2 Hz)
1b[c]	Me	7.61 (t, 2H), 8.04 (t, 2H), 8.24 (d, 2H), 8.91 (d, 2H)	0.47 (s, 3H)	82			1.36 (s, 6H)	69			
1c[d]	Bz	7.45 (t, 2H), 7.86−7.00 (m, 4H), 8.71 (d, 2H)	2.81 (s, 2H)	94			1.47 (s, 6H)	70			6.27−6.34 (d, 2H, $^3J_{HH}$ = 7.0 Hz), 6.53−6.67 (m, 3H)
2a	allyl	7.72 (t, 2H), 8.13 (t, 2H), 8.32 (d, 2H), 8.84 (d, 2H)	2.25 (d, 2H)	84		18.0	1.30 (s, 6H)	69		*f*	4.17−4.32 (m, 2H), 5.00 (ps sext, 1H, $^3J_{HH}$ = 8.8 Hz)
2b	Me	7.74 (t, 2H), 8.17 (t, 2H), 8.34 (d, 2H), 8.93 (d, 2H)	0.71 (s, 3H)	68		6.0	1.34 (s, 6H)	69		4.5	
2c	Bz	7.55 (d, 2H), 8.01 (m, 4H), 8.70 (d, 2H)	2.88 (s, 2H)	82		19.2	1.41 (s, 6H)	69		*f*	6.20 (d, 2H, $^3J_{HH}$ = 7.0 Hz), 6.61 (t, 2H, $^3J_{HH}$ = 7.8), 6.71 (t, 1H, $^3J_{HH}$ = 7.2 Hz)
3a	allyl	8.00 (d, 2H), 8.27 (t, 2H), 8.92 (d, 2H)[e]	1.98 (d, 2H)	75	8.8		1.30 (d, 6H)	67	10.2		4.16−4.23 (m, 2H), 4.81−5.03 (ps sext, 1H, $^3J_{HH}$ = 6.2 Hz), 6.98 (t, 6H, $^3J_{HH}$ = 9.4 Hz), 7.21−7.68 (m, 11 H)
3b	Me	8.16 (d, 2H), 8.31 (t, 2H), 8.86 (d, 2H)[e]	0.48 (d, 3H)	59	7.2		1.32 (d, 6H)	67	7.6		6.93 (t, 6H, $^3J_{HH}$ = 8.2 Hz), 7.20−7.46 (m, 11H)
3c	Bz	7.88 (d, 2H), 8.17 (t, 2H), 8.60 (d, 2H)[e]	2.65 (d, 2H)	73	12.0		1.40 (d, 6H)	67	6.8		6.15 (d, 2H, $^3J_{HH}$ = 8.1 Hz), 6.59 (m, 3H), 6.91 (t, 6H, $^3J_{HH}$ = 8.0 Hz), 7.18−7.37 (m, 11H)

[a] Recorded at 200.13 MHz in $CDCl_3$ at ambient temperature. [b] See ref 11c. [c] See ref 11b. [d] See ref 11a. [e] Overlap of bipy resonances with PPh_3 resonances. [f] Not observed.

afforded the novel platinum(IV) trichlorostannyl complexes [$PtMe_2(R)(SnCl_3)$(bipy)] (R = allyl (**2a**), Me (**2b**), Bz (**2c**)) in high yield (eq 1).



(1)

Complexes **2** are yellow solids, which are soluble in CH_2Cl_2, $CHCl_3$, THF, and acetone. The identity of complexes **2** was established by elemental analysis and ^1H and ^{119}Sn NMR spectroscopy. The ^1H NMR spectra of complexes **2** recorded in $CDCl_3$ (Table 1) show one signal for the two methyl ligands trans to the bipy ligand and four signals for the bipy ligand itself, pointing to a complex with the R and $SnCl_3$ substituents in trans positions. The resonances of the two PtMe groups trans to the bipy ligand show platinum satellites of 69 Hz, which is a typical value for a $Pt^{IV}Me$ resonance.[5−9] In the case of **2a** and **2c**, the $^3J_{HSn}$ sattelite signals flanking the PtMe resonance trans to the bipy ligand are not observed. A small coupling of $^3J_{HSn}$ = 4.5 Hz is seen for **2b**. This value is in agreement with the $^3J_{HSn}$ values reported for other platinum(IV)−stannyl complexes.[5]

The methylene proton resonances of R are shifted downfield by ca. 0.09−0.24 ppm relative to **1**, as a result of the introduction of the strongly electron-withdrawing $SnCl_3$ substituent. Furthermore, a decrease of the coupling constant $^2J_{HPt}$ for these methylene protons by 10 Hz was found. For all three complexes we observed also $^3J_{HSn}$ coupling for the methylene protons (18.0 (**2a**), 6.0 (**2b**), and 19.2 Hz (**2c**), respectively). ^{119}Sn NMR spectra of complexes **2** recorded in CH_2Cl_2 solution showed one singlet (δ +20.6 (**2a**), −6.1 (**2b**), and +17.6 (**2c**), respectively) with ^{195}Pt satellites ($^1J_{SnPt}$ = 3267, 4260, and 3415 Hz, respectively) (Table 2). The observation of ^{195}Pt satellites is direct proof for the presence of a platinum−tin bond in solutions of complexes **2**.

Table 2. $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR Data for the Novel Pt(IV) Complexes [$PtMe_2R(SnCl_3)$(bipy)] (2) and [$PtClMe_2R(PPh_3)$(bipy)][$SnCl_3$] (3)[a]

compd	^{119}Sn		^{31}P	
	δ (ppm)	$^1J_{SnPt}$ (Hz)	δ (ppm)	$^1J_{PPt}$ (Hz)
2a[b]	20.6	3267		
2b[b]	−6.1	4260		
2c[b]	17.2	3415		
3a	−48.9		−0.69	972
3b	−49.6		−2.40	984
3c	−46.3		−1.23	967

[a] Recorded at 81.02 MHz (^{31}P) and 74.63 MHz (^{119}Sn) in $CDCl_3$ at ambient temperature. [b] Recorded in CH_2Cl_2 at ambient temperature.

The magnitude of the platinum−tin coupling constants of **2** are at the low end of the range (2 500−35 000 Hz) found in the literature,[12] indicating a weak Pt−Sn interaction. Unfortunately, no reference data for Pt−$SnCl_3$ complexes with bidentate nitrogen ligands are available. For complexes of the type *trans*-[$Pt(SnCl_3)(Y)(PEt_3)_2$], $^1J_{PtSn}$ values of 6620 and 5775 Hz were found for Y = Me, CH_2Ph, respectively.[13] The magnitude of these values is comparable to those found for **2**.

Dissociation of the $SnCl_3$ ligand from the Pt center to give [$PtMe_2R$(bipy)][$SnCl_3$] can be excluded, even in coordinating solvents such as acetone; ^1H NMR spectra of **2b** recorded in acetone-d_6 showed platinum and tin satellites for the PtMe resonance in a position trans to the $SnCl_3$ substituent, indicating the covalent Pt−Sn bond is retained in solution.

Molecular Structure of *fac*-[$PtMe_3(SnCl_3)$(bipy)] (2b). The structure of **2b** in the solid state was solved by a single-crystal X-ray diffraction study (Figure 1). Selected bond distances and bond angles are listed in Table 3.

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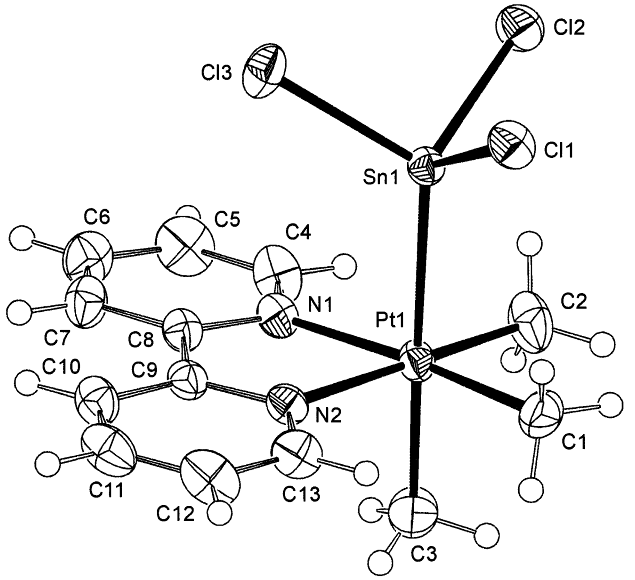


Figure 1. Displacement ellipsoid plot (50% probability) of *fac*-[$PtMe_3(SnCl_3)(bipy)$] (**2b**).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *fac*-$PtMe_3(SnCl_3)(bipy)$ (2b)

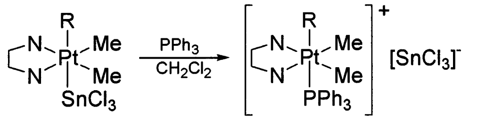
	Bond Lengths		
Pt(1)−Sn(1)	2.6497(2)	Pt(1)−C(3)	2.069(5)
Pt(1)−N(1)	2.147(3)	Sn(1)−Cl(1)	2.3896(9)
Pt(1)−N(2)	2.143(5)	Sn(1)−Cl(2)	2.3981(13)
Pt(1)−C(1)	2.065(5)	Sn(1)−Cl(3)	2.3958(12)
Pt(1)−C(2)	2.068(8)		
	Bond Angles		
Sn(1)−Pt(1)−N(1)	90.87(8)	N(2)−Pt(1)−C(3)	90.3(2)
Sn(1)−Pt(1)−N(2)	90.82(8)	C(1)−Pt(1)−C(2)	88.1(3)
Sn(1)−Pt(1)−C(1)	90.92(13)	C(1)−Pt(1)−C(3)	88.25(18)
Sn(1)−Pt(1)−C(2)	92.31(13)	C(2)−Pt(1)−C(3)	86.7(2)
Sn(1)−Pt(1)−C(3)	178.7(2)	Pt(1)−Sn(1)−Cl(1)	119.10(2)
N(1)−Pt(1)−N(2)	77.07(16)	Pt(1)−Sn(1)−Cl(2)	117.97(3)
N(1)−Pt(1)−C(1)	174.3(2)	Pt(1)−Sn(1)−Cl(3)	119.77(3)
N(1)−Pt(1)−C(2)	97.3(2)	Cl(1)−Sn(1)−Cl(2)	98.74(4)
N(1)−Pt(1)−C(3)	90.05(15)	Cl(1)−Sn(1)−Cl(3)	97.91(4)
N(2)−Pt(1)−C(1)	97.4(2)	Cl(2)−Sn(1)−Cl(3)	99.00(4)
N(2)−Pt(1)−C(2)	173.58(7)		

The six-coordinated platinum center has a distorted-octahedral geometry. The equatorial plane is formed by the bipy and the two methyl ligands, while the apical positions are occupied by the third methyl group and a trichlorostannyl group, respectively. The donor atoms in the equatorial plane are essentially coplanar with the Pt center (largest deviation 0.069(4) Å). The apical groups are in a linear arrangement with a Me−Pt−Sn angle of 178.72(13)°. The largest deviation from the ideal octahedral geometry arises from the bipy bite angle of 77.09(11)°. The Pt−Sn distance of 2.6497(3) Å is irrefutable proof of a direct Pt−Sn bond in the solid state. The Pt−Me distances have the same length (2.065(4)−2.069(4) Å), irrespective of their position to the stannyl ligand. The three Sn−Cl distances (2.3896(9)−2.3981(13) Å) are slightly longer than the Sn−Cl bond distances observed in trichlorostannyl platinum(II) complexes.[14]

Since the $SnCl_3$ ligand is a substituent with moderate trans influence,[1e,f,15] it was expected that the Pt−Me bond of **2b** trans to the stannyl ligand would be longer than the other two Pt−Me bonds. However, since all Pt−Me distances found were nearly of the same length, we can only conclude that there is a low trans influence of the stannyl group, presumably caused by the relatively long Pt−Sn distance (2.6497(3) Å). As expected, the Pt^{IV}−Sn distance is longer than in Pt(II) compounds[14] but also significantly longer than in other known Pt(IV) compounds (2.54−2.57 Å).[5,7a,9] We assume that this long bond length is a consequence of the electron-withdrawing effect of the three chloro substituents. The long Pt−Sn bond found in the crystal structure is also in agreement with the small $^1J_{SnPt}$ value found in the ^{119}Sn NMR spectrum.

The sum of the Cl−Sn−Cl angles (295.7°) indicates that some hybridization has occurred (270° for nonhybridized $[SnCl_3]^-$). This deviation is quite small and is in accordance with the long Pt−Sn distance. The conformation of the trichlorostannyl group is best described as eclipsed relative to the two equatorial methyl groups, giving rise to an approximate, noncrystallographic C_s symmetry of the octahedron. The conformation of the $SnCl_3$ group may be assisted by weak intramolecular C−H···Cl interactions (3.0738 Å) between the equatorial Me groups and the $SnCl_3$ chlorine atoms.

Synthesis of [$PtMe_2(R)(bipy)(PPh_3)$][$SnCl_3$] (3). Kollár et al. reported that addition of triarylphosphine (P) to Pt(II)−trichlorostannyl complexes [$PtCl(SnCl_3)$-(P-P)] (P-P = bidendate diphosphine ligand) resulted in the formation of stable stannate complexes [PtCl(P)(P-P)][$SnCl_3$], which were found to be soluble in most organic solvents.[16] In a similar fashion it was possible to replace the weakly coordinated $SnCl_3$ ligand in complexes **2** by PPh_3, resulting in the formation of cationic platinum(IV) complexes $[PtMe_2(R)(bipy)(PPh_3)]^+$ (**3**) with a noncoordinating $[SnCl_3]^-$ anion (eq 2).



(2)

2, N^N = bipy
a: R = C_3H_5
b: R = Me
c: R = $CH_2C_6H_5$

3

Complexes **3** are highly soluble in $CDCl_3$ and CH_2Cl_2, and elemental analyses were in agreement with the proposed formulation. The ^1H NMR resonances of Pt*Me* trans to the bipy ligand and the resonances of the methylene group trans to the phosphorus atom in complexes **3** display ^{195}Pt satellites and ^{31}P coupling but no ^{119}Sn satellites. The latter confirms that triphenylphosphine instead of $[SnCl_3]^-$ is bonded to the platinum center. The introduction of PPh_3 caused an upfield shift relative to **2** of ca. 0.23 ppm for the methylene positioned trans to phosphorus (**3a**, **3c**) and methyl groups (**3b**). In addition, a decrease (by ca. 9 Hz) of the $^2J_{HPt}$ values was found for the methylene resonances of the R substituent. For the signals of the PtMe groups trans to the bipy ligand, no significant changes in the

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chemical shifts and the $^2J_{\mathrm{HPt}}$ values were observed. The NMR data of complex **3b** fit well with the literature data for the closely related complexes $[\mathrm{PtMe_3(bipy)(PPh_3)}][\mathrm{BF_4}]$[17] and $[\mathrm{PtMe_3(bipy)(PPh_3)}][\mathrm{O_3SCF_3}]$.[18] The ^{31}P NMR spectra showed a single resonance (δ −0.69 (**3a**), −2.04 (**3b**), −1.23 (**3c**), respectively) with ^{195}Pt satellites ($^1J_{\mathrm{PPt}}$ = 972, 984, and 964 Hz, respectively). None of the signals in the ^{1}H and ^{31}P NMR spectra displayed tin satellites, in line with the noncoordinating character of the $[\mathrm{SnCl_3}]$ anion. The ^{119}Sn NMR spectra of **3a**−**c** each showed a singlet at δ −48.9, −49.6 and −46.3, respectively, in close agreement with those found for the $[\mathrm{SnCl_3}]$ anion in ionic stannate complexes $[\mathrm{AsPh_4}][\mathrm{SnCl_3}]$ (δ −51), $[\mathrm{NBu^n{}_4}][\mathrm{SnCl_3}]$ (δ −52), and, to a lesser extent, $[\mathrm{PBu^t{}_3H}][\mathrm{SnCl_3}]$ (δ −30).[19]

Conclusion

Three novel platinum(IV)−trichlorostannyl complexes $[\mathrm{PtMe_2(R)(SnCl_3)(bipy)}]$ have been prepared successfully by the reaction of $\mathrm{SnCl_2}$ with $[\mathrm{PtClMe_2(R)(bipy)}]$ (R = allyl, Me, Bz). These complexes represent the first examples of Pt(IV) stannyl complexes that were prepared through $\mathrm{SnCl_2}$ insertion into the $\mathrm{Pt^{IV}}$−Cl bond. NMR studies of **2a**−**c** and a crystal structure of **2b** prove the presence of a direct tin−platinum bond. The weakly coordinated $\mathrm{SnCl_3}$ ligand can be easily substituted by triphenylphosphine, resulting in the ionic $[\mathrm{PtMe_2(R)(PPh_3)(bipy)}][\mathrm{SnCl_3}]$ complexes.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an inert atmosphere of $\mathrm{N_2}$ using standard Schlenk techniques. All solvents were dried and distilled prior to use. $[\mathrm{PtMe_2(bipy)}]$,[20] $[\mathrm{PtClMe_2(benzyl)(bipy)}]$,[11a] $[\mathrm{PtClMe_3(bipy)}]$,[11b] and $[\mathrm{PtClMe_2(allyl)(bipy)}]$[11c] were prepared according to literature procedures. Anhydrous $\mathrm{SnCl_2}$ was used as supplied. Elemental analyses were carried out by H. Kolbe, Mikroanalytische Laboratorium, Mülheim an der Ruhr, Germany. NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer.

$[\mathrm{PtMe_2(allyl)(SnCl_3)(bipy)}]$ (2a). To a solution of $[\mathrm{PtClMe_2(allyl)(bipy)}]$ (148 mg, 0.33 mmol) in dichloromethane (7.5 mL) was added tin(II) chloride (61.6 mg, 0.33 mmol). After a few minutes an intense yellow solution was formed. The volume of the solution was reduced in vacuo to 1 mL, and pentane (5 mL) was added to precipitate the product as a yellow solid, which was isolated by filtration, washed with pentane (5 mL), and dried in vacuo. The yield was quantitative. Anal. Calcd for $\mathrm{C_{15}H_{19}Cl_3N_2PtSn}$: C, 27.83; H, 2.96; Cl, 16.43; N, 4.33. Found: C, 27.74; H, 3.10; Cl, 16.40; N, 4.26.

***fac*-$[\mathrm{PtMe_3(SnCl_3)(bipy)}]$ (2b).** *fac*-$[\mathrm{PtClMe_3(bipy)}]$ (100 mg, 0.23 mmol) was dissolved in dichloromethane (5 mL). Next, tin(II) chloride (44 mg, 0.23 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and filtered. Evaporation of the solvent gave 140 mg (98%) of a yellow solid. The yellow compound (50 mg) was dissolved in 5 mL of $\mathrm{CH_2Cl_2}$ and crystallized at −20 °C. After 1 week, light yellow crystals suitable for an X-ray crystallographic study had formed. Anal. Calcd for $\mathrm{C_{13}H_{17}Cl_3N_2PtSn}$: C, 25.13; H, 2.76; Cl, 17.11; N, 4.51. Found: C, 25.20; H, 2.71; Cl, 17.05; N, 4.43.

Crystal Structure Determination of 2b. Crystal data: $\mathrm{C_{13}H_{17}Cl_3N_2PtSn}$, fw = 621.42, yellowish plate, 0.45 × 0.24 × 0.06 mm^3, monoclinic, $P2_1/c$ (No. 14), a = 10.5494(1) Å, b = 15.4508(2) Å, c = 14.6084(1) Å, β = 130.6525(6)°, V = 1806.49(3) Å^3, Z = 4, ρ = 2.285 g/cm^3. A total of 39 957 reflections were measured on a Nonius Kappa CCD diffractometer with a rotating anode (λ = 0.710 73 Å) at a temperature of 150(2) K; 4139 reflections were unique (R_{int} = 0.0706). Absorption correction was performed with PLATON[21] (routine DELABS, μ = 9.55 mm^{-1}, 0.08−0.54 transmission). The structure was solved with direct methods (SIR97)[22] and refined with SHELXL97[23] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Methyl hydrogen atoms were refined with a rotating model and phenyl hydrogen atoms with a riding model; there were 184 refined parameters and no restraints. R values ($I > 2\sigma(I)$): R1 = 0.0240, wR2 = 0.0623. R values: R1 = 0.0258, wR2 = 0.0634. GOF = 1.084. The residual electron density was between −1.37 and 0.77 e/Å^3. Molecular illustration, structure checking, and calculations were performed with the PLATON package.[21]

$[\mathrm{PtMe_2(Bz)(SnCl_3)(bipy)}]$ (2c). This complex was prepared by following the same procedure described for **2a** from $[\mathrm{PtClMe_2(Bz)(bipy)}]$ (135 mg (0.27 mmol), dichloromethane (7.5 mL), and tin(II) chloride (50 mg, 0.27 mmol). The yellow product was isolated in 80% yield. Crystallization of **2a** from hot $\mathrm{CH_2Cl_2}$ afforded yellow plate-shaped crystals. Anal. Calcd for $\mathrm{C_{19}H_{21}Cl_3N_2PtSn}$: C, 32.72; H, 3.03; N, 4.02; Sn, 17.02. Found: C, 32.88; H, 3.04; N, 3.93; Sn, 17.18.

$[\mathrm{PtMe_2(allyl)(bipy)(PPh_3)}][\mathrm{SnCl_3}]$ (3a). *fac*-$[\mathrm{PtClMe_2(allyl)(bipy)}]$ (95 mg, 0.21 mmol) was dissolved in 10 mL of $\mathrm{CH_2Cl_2}$. Next 40 mg (0.21 mmol) of tin(II) chloride and 54 mg (0.21 mmol) of $\mathrm{PPh_3}$ were added to the solution. Stirring for 10 min at room temperature afforded a light yellow solution. Filtration of the reaction mixture and evaporation of the solvent gave 169 mg of a yellow solid (90%). Anal. Calcd for $\mathrm{C_{33}H_{34}Cl_3N_2PPtSn}$: C, 43.57; H, 3.77; Cl, 11.69; N, 3.08; P, 3.40. Found: C, 43.64; H, 3.85; Cl, 11.54; N, 3.60.

***fac*-$[\mathrm{PtMe_3(bipy)(PPh_3)}][\mathrm{SnCl_3}]$ (3b).** This complex was prepared by following the same procedure described for **3a** from *fac*-$[\mathrm{PtClMe_3(bipy)}]$ (88 mg, 0.20 mmol), dichloromethane (5 mL), tin(II) chloride (39 mg, 0.27 mmol), and triphenylphosphine (53 mg, 0.20 mmol). The product was obtained as an off-white solid in quantitative yield. Anal. Calcd for $\mathrm{C_{31}H_{32}Cl_3N_2PPtSn}$: C, 42.13; H, 3.65; Cl, 12.04; N, 3.17; P, 3.50. Found: C, 42.18, H, 3.61; Cl, 12.11; N, 3.15; P, 3.54.

$[\mathrm{PtMe_2(Bz)(bipy)(PPh_3)}][\mathrm{SnCl_3}]$ (3c). This complex was prepared by following the same procedure described for **3a** from *fac*-$[\mathrm{PtClMe_2(Bz)(bipy)}]$ (240 mg, 0.47 mmol), dichloromethane (20 mL), tin(II) chloride (89 mg, 0.47 mmol), and triphenylphosphine (124 mg, 0.47 mmol). The product was isolated as a yellow solid in 80% yield. Anal. Calcd for $\mathrm{C_{37}H_{36}Cl_3N_2PPtSn}$: C, 46.30; H, 3.78; N, 2.92; P, 3.23; Cl, 11.08. Found: C, 46.18; H, 3.88; N, 2.97; P, 3.30; Cl, 11.19.

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Supporting Information Available: Tables of X-ray crystallographic data for **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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