py)]$(PF_6)_2$, 62601-26-7; [Ru(phen)$_2$(napy)]$(PF_6)_2$, 62571-34-0; [Ru(phen)$_2$(ppyz)]$(PF_6)_2$, 62571-32-8; [Ru(bpy)$_3$]$(PF_6)_2$, 60804-74-2; [Ru(phen)$_3$]$(PF_6)_2$, 60804-75-3; napy, 254-60-4; 2-mnapy, 1569-16-0; 2,7-dmnapy, 14903-78-7; ppyz, 322-46-3; Ru(phen)$_2$Cl$_2$, 15453-59-5; Ru(bpy)$_2$Cl$_2$, 19542-80-4.

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Dimethyl Compounds of Platinum(II). 1. Oxidative Addition Reactions Involving Group 4 Element–Halogen Bonds

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Reactions of PtMe$_2$(N-N) (N-N = 2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) with methyltin– or aryltin–halogen compounds SnR$_n$Cl$_{4-n}$ (R = Me, Ph; n = 0–3), lead diphenyl dichloride, PbPh$_2$Cl$_2$, and lead triphenyl chloride, PbPh$_3$Cl, proceeded via an oxidative addition involving the Sn–Cl or Pb–Cl bond to give the new compounds PtMe$_2$Cl(N-N)(SnR$_n$Cl$_{3-n}$) and PtMe$_2$Cl(N-N)(PbPh$_m$Cl$_{3-m}$) (m = 1, 2) in almost quantitative yield. The compounds and their reactions were studied by ^{1}H NMR spectroscopy. Exchange reactions of PtMe$_2$Cl(bpy)(SnR$_n$Cl$_{3-n}$) with SnR′$_m$Cl$_{4-m}$ and reactions with MeI showed that their relative stability decreased in the order SnPhCl$_2$ > SnMeCl$_2$ > SnPh$_2$Cl > SnMe$_2$Cl > SnPh$_3$ > SnMe$_3$. With MeI no reaction was observed, PtMe$_3$Cl(bpy) was formed, or PtMe$_3$I(bpy) depending upon the stability of the platinum–tin bond. In contrast with the SnR$_n$Cl$_{4-n}$ compounds themselves, the platinum–tin compounds were not affected by Lewis bases such as H$_2$O, ROH, pyridine, and PPh$_3$. Although there was evidence that the platinum–lead bonds were stronger than the corresponding tin bonds, the former compounds decomposed in CH$_2$Cl$_2$ solution except PtMe$_2$Cl(Ph$_2$Me$_2$phen)(PbPh$_2$Cl), which was stable. In addition a halogen exchange between PtMe$_3$Cl(bpy) and MeI was observed.

Introduction

The formation of Pt–M bonds (M is a group 4 element: Si, Ge, Sn, or Pb) by oxidative addition of group 4 compounds to Pt(0)[1–6] or Pt(II)[6–10] compounds has received considerable attention.

Recently it was clearly established[1] that oxidative addition of SnR$_3$X (R = Me, Ph; X = Cl, Br, I, OH, NO$_3$) to Pt (C$_2$H$_4$)(PPh$_3$)$_2$ proceeded by "insertion" of platinum in the Sn–C bond rather than in the Sn–X bond, as was described earlier.[2] Similarly oxidative addition of SiRX$_2$H to square-planar Rh(I) and Ir(I) compounds involved the M–H instead of the M–X bond.[11,12] Reactions of MR$_3$H compounds (R = Me, Ph; M = Si, Ge, Sn) with Pt(0) compounds probably proceed via oxidative addition of M–H to platinum, followed by reaction with another molecule R$_3$MH. This results in H$_2$ elimination or again oxidative addition.[5–7] Also reactions of SiMe$_n$Cl$_{3-n}$*H* (n = 0, 1) with Pt(0) compounds proceeded similarly and did not involve rupture of the Si–Cl or Si–C bond.[5,6] Oxidative addition of SnMe$_3$H to Pt(II) also involved the Sn–H bond.[8–10]

Since no oxidative additions of MR$_n$Cl$_{4-n}$ (R = Me, Ph; M = Si, Ge, Sn, Pb; n = 0–3) with Pt(II) compounds are known, we became interested in reactions of MR$_n$Cl$_{4-n}$ with PtMe$_2$(bpy), a compound which is known to undergo oxidative additions very readily.[13] The results of this investigation with tin and lead compounds are presented in this paper.

Experimental Section

General Information. Although the compounds prepared in this study were stable in air, several of the starting materials were susceptible to atmospheric moisture. Therefore all preparations were carried out in a dry nitrogen atmosphere. The abbreviations bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Ph$_2$Me$_2$phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and pic = 4-picoline are used in the text.

Chemicals. Tin and lead alkyl or aryl chlorides are commercially available and were used without further purification. Reagent grade solvents were dried and distilled prior to use. ^{1}H NMR spectra in CH$_2$Cl$_2$ were recorded on a Varian HA100 NMR spectrometer. Melting and decomposition points were recorded on a DTA apparatus, Du Pont Model 900, and were checked visually. Elemental analyses were performed by Childers Laboratories, Milford, N.J. Analytical data are summarized in Table I.

Preparation of PtMe$_2$(bpy). Bipyridine (8.4 mmol) was added with rapid stirring to a warm solution (60 °C) of [PtMe$_2$(SEt$_2$)]$_2$[13] (4 mmol) in benzene (about 100 mL). As soon as all the bipyridine had dissolved, stirring was stopped. After 5 min at 60 °C and subsequently 24 h at 5 °C the red needles of PtMe$_2$(bpy) were collected on a filter and vacuum-dried for 1 h; yield 85% (two fractions). PtMe$_2$(phen) was

Table I. Analytical Results

Compd	Mp, dec pt,[a] °C	% C		% H		% Cl		% N		% others[c]	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$PtMe_2(Ph_2M_2phen)$	250 dec	57.83	57.23	4.52	4.80			4.31	4.77		
$PtMe_2Cl(bpy)(SnMe_3)$	164 dec	31.23	31.03	4.11	3.99	6.38	6.11	4.64	4.82		
$PtMe_2Cl(bpy)(SnMe_2Cl)$	185	27.98	27.98	3.41	3.35	11.93	11.80	4.47	4.66		
$PtMe_2Cl(bpy)(SnMeCl_2)$	205	25.39	25.12	2.85	2.76	17.13	17.12	4.15	4.51		
$PtMe_2Cl(bpy)(SnCl_3)$	>165 dec[b]	21.56	22.45	2.43	2.20	21.88	22.10	3.95	4.37	17.6 (Sn)	18.49 (Sn)
$PtMe_2Cl(bpy)(SnPhCl_2)$	186	31.67	31.63	2.93	2.80	15.85	15.56	4.00	4.10	27.7 (Pt)	28.54 (Pt)
$PtMe_2Cl(bpy)(SnPh_2Cl)\cdot CH_2Cl_2$	173	37.61	37.06	3.29	3.24	17.08	17.50	3.20	3.46		
$PtMe_2Cl(bpy)(SnPh_3)$	148	46.60	46.99	3.98	3.81	5.05	4.62	3.56	3.65		
$PtMe_2Cl(phen)(SnMeCl_2)$	205	27.58	27.91	2.66	2.66	17.25	16.48	3.98	4.34		
$PtMe_2Cl(Ph_2M_2phen)(SnMeCl_2)\cdot C_6H_6$	210	46.71	46.41	3.79	4.12	11.80	11.74	3.10	3.09		
$PtMe_2Cl(Ph_2M_2phen)(SnCl_3)$	230	40.53	40.35	3.42	3.29	16.25	16.53	3.07	3.27		
$PtMe_2I(bpy)(SnMeCl_2)$		21.85	21.90	2.40	2.40	9.51	9.95			18.1 (I)	17.80 (I)
$PtMe_2Cl(bpy)(PbPh_3)\cdot {}^1/_2THF$	97 dec[b]	43.04	43.11	3.79	3.73	4.14	3.98	3.16	3.14		
$PtMe_2Cl(bpy)(PbPh_2Cl)$[d]	~100 dec[b]	35.47	35.43	2.97	2.97	9.09	8.71	3.30	3.44	26.1 (Pb)	25.46 (Pb)
$PtMe_2Cl(phen)(PbPh_2Cl)$	~110 dec[b]	37.67	37.19	2.93	3.12	8.59	8.44				
$PtMe_2Cl(Ph_2M_2phen)(PbPh_2Cl)$	148 dec[b]	47.36	47.10	3.46	3.76	7.48	6.95	2.45	2.75		
$PtMe_2Cl(Ph_2M_2phen)(PbPh_3)$	130	52.10	52.04	3.89	4.08	3.41	3.34				

[a] Decomposition on melting or directly thereafter. [b] Only decomposition without melting. [c] Standard error for these analyses 0.5–1.3%. [d] Pt: calcd, 23.98%; found, 23.3%.

Table II. ^1H NMR Data of Pt-Sn and Pt-Pb Compounds[a]

Compd	Pt–Me resonances[b]	Sn–R resonances[c]	bpy, phen, or Ph_2M_2phen resonances[d]			
$PtMe_2(bpy)$	–4.35 (85 Hz)		3.86 (21 Hz)[f]	2.16	2.72	2.73
$PtMe_2(phen)$	–4.22 (86 Hz)		4.14 (22 Hz)[f]	2.47	3.27	2.56
$PtMe_2(Ph_2M_2phen)$	–4.27 (89 Hz)		–2.34 (4.5 Hz) (=Me)[f]	2.24 (7 Hz)	2.21 (=Ph)	2.44
$PtMe_3Cl(bpy)$	–4.06 (70 Hz), –4.89 (74 Hz)		3.56 (13.5 Hz)	2.31	2.71	2.94
$PtMe_3I(bpy)$	–3.83 (70 Hz), –4.69 (73 Hz)		3.65 (13.5 Hz)	2.32	2.74	2.94
$PtMe_2Cl(bpy)(SnMe_3)$[e]	–4.16 (59 Hz)		3.59 (14 Hz)	2.34	2.82	2.93
$PtMe_2Cl(bpy)(SnMe_2Cl)$	–4.01 (56 Hz)	–4.95 (49, 47 Hz)	3.57 (14 Hz)	2.35	2.79	2.97
$PtMe_2Cl(bpy)(SnMeCl_2)$	–3.84 (56, 5.5 Hz)	–4.28 (52, 50, 5.9 Hz)	3.55 (14 Hz)	2.41	2.84	3.00
$PtMe_2I(bpy)(SnMeCl_2)$	–3.54 (61, 7.6 Hz)	–4.31 (57, 55, 5 Hz)	3.62 (15 Hz)	2.38	2.82	3.00
$PtMe_2Cl(phen)(SnMeCl_2)$	–3.69 (57.5, 5.8 Hz)	–4.29 (52, 50, 5.8 Hz)	3.86 (15 Hz)	2.70	3.33	2.75
$PtMe_2Cl(Ph_2M_2phen)(SnMeCl_2)\cdot C_6H_6$	–3.60 (59, 6 Hz)	–4.57 (52, 50, 6.5 Hz)	–2.06 (3.3 Hz) (=Me)	2.38 (4.4 Hz)	2.23 (=Ph)	2.52
$PtMe_2Cl(Ph_2M_2phen)(SnCl_3)$	–3.35 (63, 14 Hz)		–2.05 (3 Hz) (=Me)	2.43 (4.2 Hz)	2.24 (=Ph)	2.57
$PtMe_2Cl(bpy)(SnPh_3)$	–3.78 (58 Hz)	1.82	3.26 (14 Hz)	2.34	2.60	2.78
$PtMe_2Cl(bpy)(SnPh_2Cl)\cdot CH_2Cl_2$	–3.79 (57 Hz)	1.90	3.41 (14 Hz)	2.18	2.66	2.86
$PtMe_2Cl(bpy)(SnPhCl_2)$	–3.72 (58, 5 Hz)	2.09	3.57 (14 Hz)	2.40	2.84	3.02
$PtMe_2Cl(phen)(SnPhCl_2)$	–3.59 (58, 5 Hz)	Not resolved	3.85 (14 Hz)	2.75	3.31	2.67
$PtMe_2Cl(bpy)(PbPh_3)\cdot {}^1/_2THF$	–3.73 (61, 6 Hz)	1.77	3.42 (15 Hz)	2.09	2.60	2.75
$PtMe_2Cl(Ph_2M_2phen)(PbPh_3)$	–3.41 (64, 6.7 Hz)	1.75 m, 1.57 m (64 Hz)	–2.01 (2.8 Hz) (=Me)	Not resolved		
$PtMe_2Cl(bpy)(PbPh_2Cl)$	–3.68 (62, 20 Hz)	1.92	3.54 (15 Hz)	2.28	2.74	2.91
$PtMe_2Cl(phen)(PbPh_2Cl)$	–3.52 (63, 20 Hz)	1.79 br	3.83 (15 Hz)	2.49	3.19	2.65
$PtMe_2Cl(Ph_2M_2phen)(PbPh_2Cl)$	–3.39 (64, 21 Hz)	1.82 m, 1.68m	–2.02 (3.1 Hz) (=Me)	Not resolved		

[a] Ppm relative to CH_2Cl_2. [b] $J(^{195}Pt–H)$ and if present $J(^{117,119}Sn–H)$ are given in parentheses. [c] If observed, $J(^{117}Sn–H)$, $J(^{119}Sn–H)$, and $J(^{195}Pt–H)$ are given in parentheses. [d] The chemical shifts for the H, Me, and/or Ph groups are given in the sequence obtained when starting from the N atom. Proton-proton couplings are omitted. [e] These are the resonances observed when a 10-fold excess of $SnMe_3Cl$ is present. Due to rapid exchange the only observed Sn–Me resonance is of $SnMe_3Cl$. [f] These resonances in the free ligands are respectively 3.32 ppm (bpy), 3.78 ppm (phen), and –2.40 ppm (Ph_2M_2phen).

prepared similarly as fine orange crystals in 80% yield.

Preparation of $PtMe_2(Ph_2Me_2phen)$. 2,9-Dimethyl, 4,7-diphenyl-1,10-phenanthroline (1 mmol) was added to a warm solution of $[PtMe_2(SEt_2)]_2$ (0.5 mmol) in benzene (25 mL). After a few minutes a dark red solution was obtained, which was slowly concentrated to 10 mL under vacuum. Warm hexane was added until the solution just became cloudy and the mixture was set aside at −10 °C for 24 h. Orange crystals of $PtMe_2(Ph_2Me_2phen)$ were obtained in 85% yield (two fractions).

Preparation of $PtMe_3Cl(bpy)$. In a 1-L flask $PtMe_2(bpy)$ (0.5 mmol) was dissolved in CH_2Cl_2 (25 mL) at 0 °C. The flask was purged with MeCl until most of the air was removed. The flask was tightly stoppered (some pressure will be developed) and the temperature was raised to 20 °C. After several hours the solution turned yellow. Slow evaporation of CH_2Cl_2 in air afforded light yellow crystals of $PtMe_3Cl(bpy)$ in quantitative yield.

Preparation of $PtMe_2Cl(bpy)(SnCl_3)$. A solution of $SnCl_4$ in CH_2Cl_2 (0.33 mmol) was added dropwise to a solution of $PtMe_2(bpy)$ in CH_2Cl_2. An orange-yellow highly insoluble precipitate formed immediately and was collected on a filter; yield 85% of $PtMe_2Cl(bpy)(SnCl_3)$.

Preparation of $PtMe_2Cl(bpy)(SnMeCl_2)$. $PtMe_2(bpy)$ (0.5 mmol) was suspended in dry benzene (10 mL) and subsequently $SnMeCl_3$ (0.52 mmol) was added with rapid stirring. A nearly colorless solution formed rapidly and soon a white-yellow precipitate formed. As soon as all $PtMe_2(bpy)$ had reacted, dry hexane (10 mL) was added, and the precipitate was collected on a filter and vacuum-dried for 2 h; yield 95%. About half a molecule of benzene is held tenaciously. Recrystallization from CH_2Cl_2/hexane afforded light yellow crystals without lattice solvent. The following compounds were prepared similarly: $PtMe_2Cl(bpy)(SnMe_2Cl)$, $PtMe_2Cl(bpy)(SnPhCl_2)$, $PtMe_2Cl(bpy)(SnPh_2Cl)\cdot CH_2Cl_2$, and $PtMe_2Cl(phen)(SnMeCl_2)$. They are crystalline and range from nearly white to yellow.

Preparation of $PtMe_2Cl(bpy)(SnPh_3)$. The preparation was similar to that described above. However a 10% excess of $SnPh_3Cl$ was necessary and a small amount should be added to the solution when recrystallizing the compound from CH_2Cl_2 to prevent dissociation; yield 90%.

Preparation of $PtMe_2Cl(bpy)(SnMe_3)$. A fivefold excess of $SnMe_3Cl$ was added to the benzene suspension of $PtMe_2(bpy)$ (0.5 mmol) and the mixture was stirred until all $PtMe_2(bpy)$ had reacted (about 12 h). Then 10 mL of hexane was added, and the precipitate was collected on a filter, washed with hexane, and vacuum-dried for 2 h; yield 92%. Because of excessive dissociation, recrystallization from CH_2Cl_2 was not possible. The dissociation was studied by NMR and it was shown that the chemical shift and the $J(^{195}Pt\text{-}H)$ coupling constant of the methyls bonded to platinum were largely dependent upon the concentration of $SnMe_3Cl$.

Preparation of $PtMe_2Cl(Ph_2Me_2phen)(SnCl_3)$. A solution of $SnCl_4$ in CH_2Cl_2 (0.25 mmol) was added dropwise to a solution of $PtMe_2(Ph_2Me_2phen)$ (0.25 mmol) in benzene (10 mL). The color of the solution changed from red to yellow and a small amount of a yellow precipitate formed which was removed by filtration. Subsequently the solution was evaporated to dryness (under vacuum). The resulting yellow residue was fractionally crystallized from benzene/hexane, the latter fractions being the purer ones; yield 60%.

Preparation of $PtMe_2Cl(Ph_2Me_2phen)(SnMeCl_2)\cdot C_6H_6$. $SnMeCl_3$ (0.52 mmol) was added to a solution of $PtMe_2(Ph_2Me_2phen)$ (0.5 mmol) in benzene (10 mL). As soon as the red color had disappeared, hexane was added slowly until the solution started to become cloudy. Yellow-white crystals of $PtMe_2Cl(Ph_2Me_2phen)(SnMeCl_2)\cdot C_6H_6$ were obtained at −20 °C in 93% yield (two fractions).

Preparation of $PtMe_2Cl(bpy)(PbPh_2Cl)$. $PbPh_2Cl_2$ (0.5 mmol) was added to a stirred solution of $PtMe_2(bpy)$ (0.5 mmol) in THF (10 mL). An immediate reaction occurred and the mixture soon became light yellow. The fine crystalline yellow precipitate was collected on a filter after 5 min, washed with THF and hexane, and subsequently vacuum-dried for 12 h; yield 82%.

Preparation of $PtMe_2Cl(bpy)(PbPh_3)\cdot{}^1/_2THF$. This compound was prepared similarly to the above compound with 0.53 mmol of $PbPh_3Cl$. Small yellow leaflet crystals were obtained in 90% yield. The compound slowly turns pink at room temperature. Both lead compounds decompose in CH_2Cl_2 or $CHCl_3$ and could not be recrystallized from these solvents. The NMR data of especially the latter compound could only be obtained with great difficulty, using successive runs at different intervals with new samples.

Preparation of $PtMe_2Cl(Ph_2Me_2phen)(PbPh_3)$. $PbPb_3Cl$ (0.53 mmol) was added to a stirred solution of $PtMe_2(Ph_2Me_2phen)$ (0.5 mmol) in THF (5 mL). A clear, light yellow solution was rapidly obtained, whereafter hexane was added dropwise to the solution until it started to become cloudy. A small amount of precipitate was removed and the clear solution set aside at −20 °C. After 24 h yellow crystals were obtained and vacuum-dried for 25 h; yield 90%. The compound decomposed in CH_2Cl_2 only after several hours. $PtMe_2Cl(Ph_2Me_2phen)(PbPh_2Cl)$ was prepared similarly in 85% yield. This compound showed no decomposition in CH_2Cl_2 after 3 days.

Reaction of $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ (R = Ph, Me; n = 1, 2) with Lewis Bases. Addition of pyridine, picoline, alcohol, H_2O, or PPh_3 to CH_2Cl_2 solutions of $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ did not result in any observable reaction (^1H NMR). Most of the compound could be recovered at low temperatures after 24 h.

Reaction of $PtMe_2(bpy)$ with $SnMeCl_3(pic)_2$. $SnMeCl_3(pic)_2$ reacted rapidly with $PtMe_2bpy$ in CH_2Cl_2 solution. $PtMe_2Cl(bpy)(SnMeCl_2)$ was isolated at −20 °C. ^1H NMR showed that the reaction afforded quantitatively 4-picoline and $PtMe_2Cl(bpy)(SnMeCl_2)$. A similar reaction was observed for $PtMe_2(bpy)$ and $SnMeCl_3(PPh_3)$ and afforded PPh_3 and $PtMe_2Cl(bpy)(SnMeCl_2)$ in high yield.

Reaction of $[PtMe_2((i\text{-}Pr)_2S)]_2$ with $SnMeCl_3(bpy)$. $SnMeCl_3(bpy)$ was added to a solution of $[PtMe_2((i\text{-}Pr)_2S)]_2$[13] ($i\text{-}Pr_2S$ = diisopropyl sulfide) in CH_2Cl_2 with stirring. After several days nearly all $SnMeCl_3(bpy)$ had gone into solution and remaining traces were removed by filtration. $PtMe_2Cl(bpy)(SnMeCl_2)$ was obtained at −20 °C in 70% yield. The resulting solution contained mainly $(i\text{-}Pr)_2S$ among some other products.

Reaction of $PtMe_2Cl(bpy)(SnR_3)$ (R = Me, Ph) with MeI. MeI is added to a suspension or solution of $PtMe_2Cl(bpy)(SnR_3)$ in CH_2Cl_2. An immediate reaction took place and $PtMe_3I(bpy)$ and SnR_3Cl were formed quantitatively (^1H NMR).

Reaction of $PtMe_2Cl(bpy)(SnMe_2Cl)$ with MeI. A tenfold excess of MeI was added to a solution of $PtMe_2Cl(bpy)(SnMe_2Cl)$ in CH_2Cl_2 and the reaction was followed by ^1H NMR. New resonances of $PtMe_3Cl(bpy)$ appeared slowly, whereas the methyl resonances and the low-field bipyridine resonances of $PtMe_2Cl(bpy)(SnMe_2Cl)$ started to broaden. This broadening increased with further progress of the reaction. After about 1 day the yield of $PtMe_3Cl(bpy)$ was optimal and the very slow formation of $PtMe_3I(bpy)$ became observable. After 1 week the reaction was completed and $PtMe_3I(bpy)$ was formed nearly quantitatively. Almost no formation of MeCl (−2.32 ppm) was observed, while the resonances at −4.12 ppm (both relative to CH_2Cl_2) could be ascribed to $SnMe_2Cl_2$, indicating that halogen exchange occurred between $PtMe_3Cl(bpy)$ and $SnMe_2ClI$. The reaction of $PtMe_2Cl(bpy)(SnPh_2Cl)$ with MeI was somewhat slower but proceeded similarly. However in this case an appreciable amount of MeCl formed, showing that halogen exchange between $PtMe_3Cl(bpy)$ and MeI took place.

Reaction of $PtMe_2Cl(bpy)(SnRCl_2)$ (R = Ph, Me) with MeI. No reaction was observed with a 30-fold excess of MeI after 3 days.

Reaction of $PtMe_3Cl(bpy)$ with MeI. MeI (a tenfold excess) was added to a solution of $PtMe_3Cl(bpy)$ in CH_2Cl_2 and the reaction was followed by ^1H NMR. The slow formation of $[PtMe_3I(bpy)]$ and MeCl was observed and the reaction went to completion after about 1 week. The yield of $PtMe_3I(bpy)$ was quantitative after evaporation of the solution at room temperature.

Reaction of $PtMe_2(bpy)$ with $SnMeCl_3$ Followed by MeI. $SnMeCl_3$ (0.5 mmol) was added to $PtMe_2(bpy)$ (0.5 mmol) in CH_2Cl_2 (5 mL). Subsequently MeI (10 mL) was added to the nearly colorless solution. After 4 h the solution had turned yellow. Solvent was removed under vacuum and the residue recrystallized from CH_2Cl_2. Yellow crystals of $PtMe_2I(bpy)(SnMeCl_2)$ were obtained in 40% yield. However, no reaction was observed either when MeI was added to a solution of pure $PtMe_2Cl(bpy)(SnMeCl_2)$ in CH_2Cl_2 or when $PtMe_3I(bpy)$ or $SnMeCl_3$ was present. Only when both compounds were present simultaneously was a small amount of the iodine product obtained after 4 days.

Reaction of $PtMe_2Cl(bpy)(SnPh_2Cl)$ with $PbPh_2Cl_2$. Equimolar quantities of the compounds were shaken vigorously in CH_2Cl_2 and an ^1H NMR spectrum was run within 2 min. Quantitative formation of $SnPh_2Cl_2$ and $PtMe_2Cl(bpy)(PbPh_2Cl)$ was evident by comparison with standard samples. Decomposition of the lead compound was soon observed. A similar reaction occurred with $PbPh_3Cl$ and $PtMe_2Cl(bpy)(SnPh_3)$.

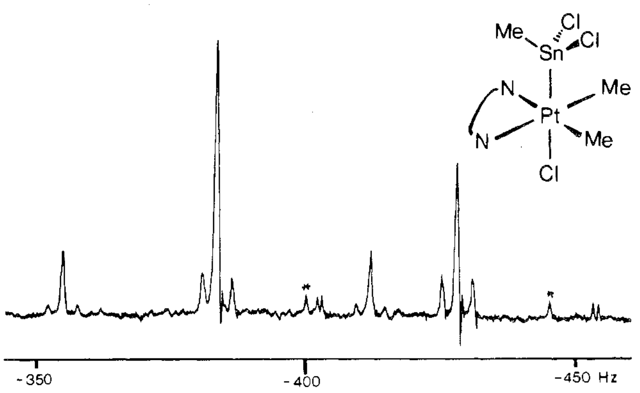

Figure 1. Methyl region of the ^{1}H NMR spectrum (100 MHz, in CH_2Cl_2, frequency shift relative to CH_2Cl_2) of $PtMe_2Cl(bpy)(SnMeCl_2)$ and its proposed structure.

Results and Discussion

I. Platinum–Tin Compounds. A novel series of platinum–tin compounds have been obtained in nearly quantitative yield according to

$$PtMe_2(N\text{-}N) + SnR_nCl_{4-n} \rightarrow PtMe_2Cl(N\text{-}N)(SnR_nCl_{3-n}) \qquad (1)$$

(N-N) = 2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; R = Me, Ph; n = 1–3.

The ^{1}H NMR data of these new compounds are summarized in Table II. The assignment of the methyls bonded to platinum or to tin is obvious from the coupling constants. $J(^{195}Pt\text{–}H)$ = 56–63 Hz corresponds to methyls bonded to platinum and $J(^{117,119}Sn\text{–}H)$ = ~50, ~52 Hz corresponds to methyls bonded to tin. The intensities of the ^{195}Pt and ^{117,119}Sn satellites were consistent with the natural abundance of 33.7% for ^{195}Pt and 7.7 and 8.7% for ^{117}Sn and ^{119}Sn. In addition low-field shifts were observed for the methyls bonded to platinum, while high-field shifts were observed for the methyls or phenyls bonded to tin (Tables II and III). Integration of the NMR spectra demonstrated that, in the case of $PtMe_2Cl(N\text{-}N)(SnMe_nCl_{3-n})$ compounds, no methyl transfer from tin to platinum or vice versa has occurred. Similarly in the case of the aryltin compounds only one type of aryl group was found indicating that no phenyl transfer has occurred. In the case of the compounds $PtMe_2Cl(N\text{-}N)(SnRCl_2)$ (R = Me, Ph) a simultaneous ^{195}Pt and ^{117,119}Sn coupling is found with the methyls bonded to platinum, $J(^{195}Pt\text{–}H)$ = 56–60 Hz and $J(^{117,119}Sn\text{–}H)$ = 5–6 Hz. The same is found for the methyls bonded to tin (R = Me), $J(^{195}Pt\text{–}H)$ = 5.8–6 Hz and $J(^{117,119}Sn\text{–}H)$ = 50, 52 Hz. This demonstrates clearly the presence of a platinum–tin bond in these compounds (Figure 1).

Similar evidence for a platinum–tin bond is present for the compound $PtMe_2Cl(Ph_2Me_2phen)(SnCl_3)$ in which the platinum methyls have $J(Sn\text{–}H)$ = 14 Hz. The fact that a metal–metal bond has formed and no methyl or aryl transfer has occurred is of interest, since methyl transfer has been observed in reactions of platinum dimethyl compounds with compounds of Au(I) and Hg(II),[14,15] which are isoelectronic with Sn(IV). Reaction 1 is also in contrast with the reaction of SnR_3X compounds with Pt(0) compounds, which resulted in the formation of a platinum–tin bond with the simultaneous transfer of an R group to platinum.[1]

The NMR data (Table II) also show that the methyls bonded to platinum are magnetically equivalent and that the bipyridine or phenanthroline ligands are (magnetically) symmetrically bonded to platinum. From these data it is concluded that the methyl groups are cis to each other and opposite to the nitrogens of the bipyridine or phenanthroline ligand. If this were not the case either they must be trans to each other and a $J(Pt\text{–}H) \approx 44$ Hz is expected[16,17] in contrast to the observed value of 56–63 Hz or one methyl and the SnR_nCl_{3-n} or Cl group must be opposite to the nitrogen atoms. This would mean that the methyl groups have to interchange positions very rapidly and intramolecularly in the NMR time scale, which is very unlikely but cannot be excluded.

Table III. ^{1}H NMR Data for SnR_nCl_{4-n}[a]

$SnMe_3Cl$	−4.68 (59, 56 Hz)
$SnMe_2Cl_2$	−4.11 (70, 67 Hz)
$SnMeCl_3$	−3.62 (100, 95 Hz)
$SnMeCl_3(pic)_2$	−3.94 (121, 116 Hz)
$SnPh_3Cl$	2.36 m (62 Hz), 2.16 m
$SnPh_2Cl_2$	2.44 m (76 Hz), 2.25 m
$SnPhCl_3$	2.33 m (119 Hz), ~2.33 m

[a] CH_2Cl_2 solution; in ppm relative to CH_2Cl_2. If resolved, $J(^{117}Sn\text{–}H)$ and $J(^{119}Sn\text{–}H)$ are given separately in parentheses.

The above results agree very well with a trans oxidative addition of the Sn–Cl bond to $PtMe_2(N\text{-}N)$, which is consistent with the common trans oxidative additions of RX (R = alkyl; X = halogen)[13,18] to various dimethylplatinum(II) compounds.

The structure proposed for these compounds is similar to the structure given for $PtMe_2Cl(N\text{-}N)(SnMeCl_2)$ in Figure 1.

No tin–hydrogen coupling was observed for the platinum methyls in the case of $PtMe_2Cl(N\text{-}N)(SnR_2Cl)$ and $PtMe_2Cl(N\text{-}N)(SnR_3)$ (R = Me, Ph). The coupling might be too small to observe due to the difference in the platinum–tin interaction with increasing methyl or phenyl substitution on tin. This is clearly demonstrated if one compares the $J(^{117,119}Sn\text{–}H)$ coupling constants of the platinum methyls in the compounds $PtMe_2Cl(Ph_2Me_2phen)(SnCl_3)$ (14 Hz) and $PtMe_2Cl(Ph_2Me_2phen)(SnMeCl_2)$ (6 Hz) or the other $(SnRCl_2)$ compounds of Table II. In the case of the $SnMe_3$ or $SnPh_3$ compounds the coupling is absent anyway due to intermolecular exchange. The methyl groups of $PtMe_2Cl(bpy)(SnPh_3)$ had broad resonances at 30 °C and slow exchange was observed with added $SnPh_3Cl$. With $PtMe_2Cl(bpy)(SnMe_3)$ not only was fast exchange observed (on the NMR time scale) with $SnMe_3Cl$ but also the value of $J(^{195}Pt\text{–}H)$ for the platinum methyls decreased, while its chemical shift went to lower field with increasing concentration of $SnMe_3Cl$, no doubt due to the equilibrium

$$PtMe_2(bpy) + SnMe_3Cl \rightleftarrows PtMe_2Cl(bpy)(SnMe_3) \qquad (2)$$

The lowest values of 56 Hz observed for the coupling constants $J(^{195}Pt\text{–}H)$ is noteworthy for the methyls bonded to platinum in the compounds $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$, compared with the values of 85–89 Hz (Table II) for $PtMe_2(N\text{-}N)$ and of 69–71 Hz for $PtMe_2XR(bpy)$;[13] the latter compounds are also of Pt(IV). Also on the basis of previous work[16,17] on dimethyl compounds of platinum(II) and -(IV), one would expect a higher J value since it was assumed that this coupling constant was mainly determined by the donor atom of the ligand trans to the methyl group. The low value of 56 Hz observed here clearly demonstrates that cis-bonded ligands can also have a large influence on the coupling constant $J(^{195}Pt\text{–}H)$ of the methyls bonded to platinum. The reactivity of the compounds $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ toward Lewis bases was investigated. They did not react with donor ligands such as alcohol, pyridine, 4-picoline, or triphenylphosphine (eq 3), and in fact

$$PtMe_2Cl(bpy)(SnR_nCl_{3-n}) + \text{donor ligand} \not\leftrightarrow \qquad (3)$$

these donor ligands were expelled from the coordination sphere of tin (alcohol was not studied in this case) as summarized by eq 4 and 5. (The $SnMe_3$ and $SnPh_3$ compounds were only partially studied due to very weak adduct formation of Lewis bases with $SnMe_3Cl$ and $SnPh_3Cl$.[19] The compound

$$\mathrm{PtMe_2(bpy) + SnMeCl_3(PPh_3) \rightarrow PtMe_2Cl(bpy)(SnMeCl_2) + PPh_3} \quad (4)$$

$$\mathrm{PtMe_2(bpy) + SnMeCl_3(pic)_2 \rightarrow PtMe_2Cl(bpy)(SnMeCl_2) + 2pic} \quad (5)$$

$PtMe_2Cl(bpy)(SnCl_3)$ was not studied as it was extremely insoluble.) The above behavior explains the stability of the compounds toward moisture, as apparently Lewis bases will not coordinate to tin in these compounds, protecting the compounds from hydrolysis. This is in contrast to the facile hydrolysis of SnR_nCl_{4-n} compounds, especially for low values of n.

The formation of $PtMe_2Cl(bpy)(SnMeCl_2)$ is noteworthy, eq 6. This might well be an elegant route to prepare platinum–tin compounds with ligands other than bipyridine or phenanthroline.

$$\mathrm{[PtMe_2(\mathit{i}\text{-}Pr)_2S)]_2 + 2(bpy)SnMeCl_3 \rightarrow 2PtMe_2Cl(bpy)(SnMeCl_2) + 2(\mathit{i}\text{-}Pr)_2S} \quad (6)$$

The relative stability of compounds of the type $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ was investigated by determining the course of the intermolecular exchange reactions as summarized by eq 7 and 8. Reaction 7 gives information about the lability of the platinum–tin bond (dissociation) and the following results were obtained (at 30 °C) for the rate of the intermolecular exchange (on the ^1H NMR time scale): $SnMe_3Cl$ very rapid, $SnMe_2Cl_2$ medium, $SnPh_3Cl$ slow, and not observable for $SnPh_2Cl_2$, $SnMeCl_3$, $SnPhCl_3$. Reaction 8 gives information about the relative stability of the platinum–tin bond and it was found, from successive replacements of SnR_nCl_{3-n} by SnR'_mCl_{3-m} on platinum, that two factors determine the stability (relative to reaction 8). Higher chlorinated $[SnR'_mCl_{4-m}]$ compounds form more stable platinum–tin bonded compounds than lower chlorinated SnR_nCl_{4-n} compounds ($4 - m > 4 - n$; R' = Me or Ph, R = Me or Ph; $n = 1, 2, 3$), and with the same number of chlorines $SnPh_nCl_{4-n}$ forms more stable compounds than $SnMe_nCl_{4-n}$. Although $PtMe_2Cl(bpy)(SnRCl_2)$ reacted with $SnCl_4$, the nature of the products was not clear. The displacements in all cases went to completion immediately except in the case of R = Me, R' = Ph, and $n = m = 1$ in which case the reaction was still not completed even after 24 h. Both factors are consistent with the idea that the platinum–tin bond is more stable when more electron-withdrawing groups are present on tin. In this way more charge is removed from the platinum atom, which has a high electron density because of the strongly electron-donating methyls bonded to platinum.

$$\mathrm{PtMe_2Cl(bpy)(SnR_\mathit{n}Cl_{3-\mathit{n}}) + Sn^*R_\mathit{n}Cl_{4-\mathit{n}} \rightleftarrows PtMe_2Cl(bpy)(Sn^*R_\mathit{n}Cl_{3-\mathit{n}}) + SnR_\mathit{n}Cl_{4-\mathit{n}}} \quad (7)$$

$$\mathrm{PtMe_2Cl(bpy)(SnR_\mathit{n}Cl_{3-\mathit{n}}) + SnR'_\mathit{m}Cl_{4-\mathit{m}} \rightarrow PtMe_2Cl(bpy)(SnR'_\mathit{m}Cl_{3-\mathit{m}}) + SnR_\mathit{n}Cl_{4-\mathit{n}}} \quad (8)$$

$$R, R' = \mathrm{Me, Ph};\ n, m = 1, 2, 3$$

MeI is known to react very rapidly (within seconds) with $PtMe_2(bpy)$[13] in a trans oxidative addition reaction to form the very stable $PtMe_3I(bpy)$. Since both tin and carbon are group 4 elements, it is of interest to study the reactivity of the platinum–tin bonded compounds toward MeI. The course of the reactions of $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ + MeI(excess) was found to be critically dependent upon the stability of the platinum–tin bond. The investigated reactions are represented in eq 9–11.

$$\mathrm{PtMe_2Cl(bpy)(SnR_3) + MeI \rightarrow PtMe_3I(bpy) + SnR_3Cl} \quad (9)$$

$$\mathrm{PtMe_2Cl(bpy)(SnR_2Cl) + MeI \rightarrow PtMe_3Cl(bpy) + SnR_2ClI} \quad (10)$$

$$\mathrm{PtMe_2Cl(bpy)(SnRCl_2) + MeI \nrightarrow} \quad (11)$$

Reaction 9 went to rapid completion and most likely an initial dissociation took place, the reverse of eq 2 followed by oxidative addition of MeI to resulting $PtMe_2(bpy)$. Reaction 10 was followed by reactions 12–14.

$$\mathrm{PtMe_2Cl(bpy)(SnR_2Cl) + SnR_2ClI \rightleftarrows PtMe_2Cl(bpy)(SnR_2I) + SnR_2Cl_2} \quad (12)$$

$$\mathrm{PtMe_3Cl(bpy) + MeI \rightarrow PtMe_3I(bpy) + MeCl} \quad (13)$$

$$\mathrm{PtMe_3Cl(bpy) + SnR_2ClI \rightleftarrows PtMe_3I(bpy) + SnR_2Cl_2} \quad (14)$$

The different course of reaction 10 excluded the possibility that it is due to a dissociation of the platinum–tin bond as otherwise reaction 9 would take place. Reaction 10 was somewhat more rapid for R = Me than for R = Ph, but in both cases it took several days to go to completion. Reaction 13 was studied separately and was appreciably slower than reaction 10, when using a tenfold excess of MeI in both cases. The equilibrium of reaction 14, which was studied by dissolving SnR_2Cl_2 and $PtMe_3I(bpy)$ in CH_2Cl_2 lay far to the right with or without the presence of MeI; the rate however could not be determined. In the case of R = Ph, the formation of $PtMe_3I(bpy)$ was certainly also due to reaction 13, which could be concluded from the formation of appreciable amounts of MeCl (^1H NMR) and by comparing the relative rates of formation of $PtMe_3Cl(bpy)$ (reaction 10) and its conversion to $PtMe_3I(bpy)$ as a function of the MeI concentration. Reaction 14 was present in the case of R = Me, since only a small amount of MeCl was formed. The difference in behavior might well be due to steric factors. The occurrence of reaction 12 was deduced from the fact that the resonances of the platinum methyls were broadened as the reaction proceeded and in addition no exchange could be observed between mixtures of $PtMe_2Cl(bpy)(SnR_2Cl)$ and $PtMe_3Cl(bpy)$ or $PtMe_3I(bpy)$.

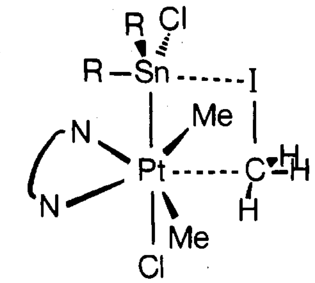

Figure 2. Proposed intermediate in the reaction of $PtMe_2Cl(bpy)(SnR_2Cl)$ with MeI.

Reaction 10 did not proceed via an initial dissociation of SnR_2Cl_2. Also initial iodine coordination of MeI to tin, followed by dissociation of the platinum–tin bond, is not likely to occur in this reaction in view of the fact that the platinum–tin compounds are unaffected by Lewis bases such as ROH. However, the course of the reaction of MeI with $PtMe_2Cl(bpy)(SnR_2Cl)$ can be explained if an intermediate is assumed as shown in Figure 2. The reason that no reaction is observed between $PtMe_2Cl(bpy)(SnRCl_2)$ and MeI is probably due to the higher stability of the platinum–tin bond. Moreover if steric factors or an initial coordination of iodine to tin were the rate-determining step, one would expect the reaction to go more rapidly in the case of higher halogen-substituted tin compounds, since these form more stable complexes with Lewis bases.[19]

II. Platinum–Lead Compounds. Reaction of $PtMe_2(N\text{-}N)$ (N-N = bpy, phen, Ph_2Me_2phen) with $PbPh_2Cl_2$ and $PbPh_3Cl$ proceeded analogously to the reactions with the corresponding tin compounds (reaction 15).

$$\mathrm{PtMe_2(N\text{-}N) + PbPh_\mathit{n}Cl_{4-\mathit{n}} \rightarrow PtMe_2Cl(N\text{-}N)(PbPh_\mathit{n}Cl_{3-\mathit{n}})} \quad (15)$$

$$\mathrm{N\text{-}N = bpy, phen, M_2Ph_2phen};\ n = 2, 3$$

These compounds were prepared in THF or acetone as decomposition took place in CH_2Cl_2 or $CHCl_3$ and the solubilities of the lead compounds were too low in benzene. The platinum–lead compounds are less stable to decomposition than the platinum–tin compounds which is reflected not only in their decomposition temperatures but also in their facile decomposition in CH_2Cl_2 or $CHCl_3$. In these solvents decomposition is observable after ~1 min for $PtMe_2Cl(bpy)(PbPh_3)$ and $PtMe_2Cl(phen)(PbPh_3)$, after ~5 min for $PtMe_2Cl(bpy)(PbPh_2Cl)$ and $PtMe_2Cl(phen)(PbPh_2Cl)$, and after several hours for $PtMe_2Cl(Ph_2Me_2phen)(PbPh_3)$ but is not observed for $PtMe_2Cl(Ph_2Me_2phen)(PbPh_2Cl)$ even after several days. The increased stability of the Ph_2Me_2phen compounds is probably caused by steric factors. In spite of the facile decomposition, no dissociation of the platinum–lead bond is observed in the NMR time scale and in all cases a ^{207}Pb coupling is observed with the platinum methyls. This clearly demonstrates the presence of the platinum–lead bond. Of particular interest is the fact that the $J(^{207}Pb–H)$ value is about 3 times smaller for the $PbPh_3$ compounds than for the $PbPh_2Cl$ compounds. The increased phenyl substitution on lead must cause this drastic lowering of the coupling constants, a property which was mentioned earlier for the tin compounds. Also a low value $J(^{195}Pt–H) \approx 61$ Hz was found for the methyls bonded to platinum, similar to the platinum–tin compounds. The proposed structure for the platinum–lead compounds is similar to the structure proposed for $PtMe_2Cl(SnMeCl_2)(bpy)$ (Figure 2).

The decomposition of $PtMe_2Cl(bpy)(PbPh_3)$ was complicated and will be investigated further. However, ^1H NMR studies provided strong indication that among the products three isomers of $PtMe_2PhCl(bpy)$ were present; only the one with the two methyl groups trans to each other seemed to be absent. Depending on the reaction conditions $[Pb(CH)Cl]_n$ and $PbPh_4$ were formed (elemental analysis and NMR) and also benzene, probably via an initial formation of unstable $PbPh_2$, which turned the solution red, followed by a decomposition involving also CH_2Cl_2. The results of this investigation and of other reactions involving addition of metal–halogen bonds to $PtMe_2(N-N)$ will be published elsewhere.

Although the platinum–lead compounds were less stable toward decomposition (in CH_2Cl_2) than the corresponding tin compounds, the platinum–lead bond itself seemed to be stronger than the platinum–tin bond. This could be inferred from the fact that there is no dissociation observed for $PtMe_2Cl(bpy)(PbPh_3)$ on the ^1H NMR time scale, whereas dissociation is observed for $PtMe_2Cl(bpy)(SnPh_3)$. Also addition of MeI did not affect the decomposition of $PtMe_2Cl(bpy)(PbPh_3)$ in CH_2Cl_2, whereas it reacted rapidly with the tin compound. Furthermore addition of $SnPh_2Cl_2$ to a solution (CH_2Cl_2) of $PtMe_2Cl(bpy)(PbPh_2Cl)$ did not affect the decomposition of the lead compound (NMR), while addition of $PbPh_2Cl_2$ to $PtMe_2Cl(bpy)(SnPh_2Cl)$ resulted in the rapid and quantitative formation of $PtMe_2Cl(bpy)(PbPh_2Cl)$ (NMR) which then decomposed. A similar behavior was observed for the corresponding $SnPh_3Cl$ and $PbPh_3Cl$ compounds.

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Registry No. $PtMe_2(Ph_2Mphen)$, 63133-64-2; $PtMe_2Cl(bpy)(SnMe_3)$, 63105-47-5; $PtMe_2Cl(bpy)(SnMe_2Cl)$, 63105-46-4; $PtMe_2Cl(bpy)(SnMeCl_2)$, 63105-45-3; $PtMe_2Cl(bpy)(SnCl_3)$, 63133-62-0; $PtMe_2Cl(bpy)(SnPhCl_2)$, 63105-44-2; $PtMe_2Cl(bpy)(SnPh_2Cl)$, 63105-35-1; $PtMe_2Cl(bpy)(SnPh_3)$, 63105-34-0; $PtMe_2Cl(phen)(SnMeCl_2)$, 63105-33-9; $PtMe_2Cl(Ph_2Mphen)(SnMeCl_2)$, 63105-32-8; $PtMe_2Cl(Ph_2Mphen)(SnCl_3)$, 63105-31-7; $PtMe_2I(bpy)(SnMeCl_2)$, 63105-30-6; $PtMe_2Cl(bpy)(PbPh_3)$, 63105-29-3; $PtMe_2Cl(bpy)(PbPh_2Cl)$, 63105-28-2; $PtMe_2Cl(phen)(PbPh_2Cl)$, 63105-27-1; $PtMe_2Cl(Ph_2Mphen)(PbPh_2Cl)$, 63105-26-0; $PtMe_2Cl(Ph_2Mphen)(PbPh_3)$, 63105-25-9; $PtMe_2(bpy)$, 52594-52-2; $PtMe_2(phen)$, 52594-55-5; $PtMe_3Cl(bpy)$, 38194-03-5; $PtMe_3I(bpy)$, 38194-05-7; $PtMe_2Cl(phen)(SnPhCl_2)$, 63105-20-4; $SnMe_3Cl$, 1066-45-1; $SnMe_2Cl_2$, 753-73-1; $SnMeCl_3$, 993-16-8; $SnMeCl_3(pic)_2$, 63105-19-1; $SnPh_3Cl$, 639-58-7; $SnPh_2Cl_2$, 1135-99-5; $SnPhCl_3$, 1124-19-2; $[PtMe_2(SEt_2)]_2$, 62343-09-3; MeCl, 74-87-3; $SnCl_4$, 7646-78-8; $PbPh_2Cl_2$, 2117-69-3; $PbPh_3Cl$, 1153-06-6; $SnMeCl_3(bpy)$, 19568-00-4; $[PtMe_2((i\text{-}Pr)_2S)]_2$, 62343-11-7; MeI, 74-88-4.

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