



Selective synthesis of monoorganotin trihalides: the direct reaction of allylic halides with tin(II) halides catalyzed by platinum and palladium complexes

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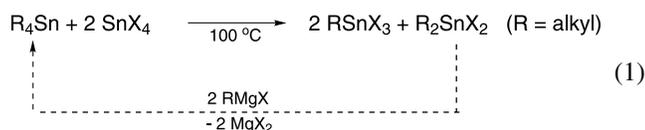
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Abstract—The reaction of 3-haloalkenes (3-chloropropene, 3-bromopropene, 3-chloro-2-methylpropene, 1-chloro-2-butene) with SnX₂ (X=Cl, Br) to form mono-allyltin trihalides, was catalyzed by several platinum and palladium complexes of the type MZ₂L (M=Pt, Pd; Z=Me, Cl; L=2,2'-bipyridine, 1,10-phenanthroline or dppe). The highest yield of allyltin trichloride was obtained for the reaction of 3-chloropropene with SnCl₂ catalyzed by PdMe₂(phen) (83%) while the yield obtained with the other catalysts decreased in the order PdCl₂(phen), PdCl₂(bipy) > PdMe₂(bipy) > PtCl₂(phen) > PtMe₂(bipy) > PtMe₂(phen) > PtCl₂(bipy). Interestingly, PdCl₂(PhCN)₂ and Pd(PPh₃)₄ had no activity at all. The yield of allyltin trichloride was not only dependent on the activity of the catalyst but also on the decomposition rate of the product in the presence of the catalyst. 3-Bromopropene gave 19% of allyltin tribromide when reacted with SnBr₂. The other 3-haloalkenes did react but the resulting monoallyltin trihalides were not stable enough to produce significant yields. Reaction of both, benzyl chloride and chlorobenzene, led to catalyst decomposition. In addition, SnCl₂ catalyzed formation of polybenzyl was observed in the case of benzyl chloride.

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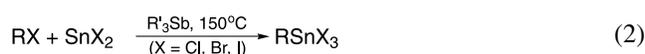
1. Introduction

Monoalkyltin trihalides, RSnX₃, (X=Cl, Br, I; R=alkyl) find application as precursors for PVC stabilizers,¹ as catalysts for polyurethane production and as precursors for the deposition of SnO₂-coatings on glass.² They are produced industrially by a redistribution reaction, which is controlled by the stoichiometry of the reactants and which usually involves X=Cl (Eq. (1)).³ For economic reasons, the R₄SnX₂ is converted in a subsequent step into the R₄Sn starting material. Full conversion of R₄Sn into 4 equiv. of RSnCl₃ is only successful for allyl,⁴ vinyl⁵ and phenyltins⁶ or requires a catalyst in the case of alkyltins.⁷



Another alternative, the direct reaction of alkyl halides with stannous halides (Eq. (2)), was studied extensively in the past but yields and selectivities are generally poor (for X=Cl) or the reaction involves the use of environmentally

less desirable trialkylantimony catalysts.^{8a–c} For example, octyltin trichloride is obtained in a low, 31%, yield after a reaction time of 96 h at a temperature of 150°C.^{8b}



In a relatively recent publication on the carbonyl allylation reaction it was shown that certain palladium complexes are able to catalyze the reaction of tin(II) halides with allyl halides.⁹ This reaction is believed to involve the in situ formation of solvated monoallyltin trichlorides and subsequent addition of the allyl–Sn bond across the carbonyl function of a range of aldehydes and ketones. The use of strongly coordinating solvents such as DMF, DMSO or THF renders this reaction unsuitable as a synthetic method for allyltin trihalides. To investigate the potential of several palladium and platinum complexes for the preparation of solvent free monoorganotin trichlorides, we decided to study their catalytic activity in the reaction of tin(II) halides with organic halides (Eq. (2)) in less strongly coordinating solvents like dichloromethane.

2. Results and discussion

3-Chloro-1-propene was reacted with tin(II) chloride in the presence of catalytic amounts of the complexes MZ₂L

Keywords: monoorganotin trihalides; allylic halides; direct reaction; platinum and palladium catalyzed; polybenzyl.

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Table 1. Maximum yield of (allyl)SnCl₃ for the reaction of C₃H₅Cl with SnCl₂ in the presence of 5 mol% of catalyst MZ₂L^a

Entry	L–L	M	Z	Solvent	Max. yield (%) ^b	t (h)	Yield (%) at t=120 h	Note
1	bipy	Pt	Cl	CH ₂ Cl ₂	41	26	0	
2	bipy	Pt	Me	CH ₂ Cl ₂	67	26	19	2% MeSnCl ₃
3	phen	Pt	Cl	CH ₂ Cl ₂	75	30	52	
4	phen	Pt	Me	CH ₂ Cl ₂	62	30	14	2% MeSnCl ₃
5	bipy	Pd	Cl	CH ₂ Cl ₂	82	26	69	
6	bipy	Pd	Me	CH ₂ Cl ₂	80	26	48	2% MeSnCl ₃
7	phen	Pd	Cl	CH ₂ Cl ₂	82	30	57	
8	phen	Pd	Me	CH ₂ Cl ₂	83	30	64	4% MeSnCl ₃
9	dppe	Pt	Me	CH ₂ Cl ₂	13	53	8	4% MeSnCl ₃
10	phen	Pd	Me	CH ₂ Cl ₂	52	70	43	T=35°C
11	phen	Pd	Me	CH ₂ Cl ₂	71	17	35	T=65°C
12	phen	Pd	Me	Toluene	61	53	40	
13	phen	Pd	Me	C ₃ H ₅ Cl	64	30	9	
14	phen	Pd	Me	THF	66	46	39	
15	phen	Pd	Me	C ₆ H ₄ Cl ₂ -1,2	74	46	22	
16	phen	Pd	Me	DMF	0	24	0	
17	phen	Pd	Me	Acetone	5	24	0	

^a Reaction conditions: 5 mL of solvent, [RX]=1.0 mol L⁻¹, [SnX₂]=0.2 mol L⁻¹, 5 mol% of catalyst (relative to SnCl₂ amount), 45°C.

^b Percentage of SnCl₂ converted into (allyl)SnX₃, determined by GC analysis. phen=1,10-phenanthroline; bipy=2,2'-bipyridine. n.d.=not determined.

(M=Pt, Pd; Z=Cl, Me; L=chelating nitrogen or phosphorus ligand), as well as PdCl₂(PhCN)₂ and Pd(PPh₃)₄. The progress of the reaction was monitored by treating reaction samples with an excess of EtMgBr (to convert the allyltin chlorides to the corresponding allyl ethyl tetraorganotin species) and subsequent analysis of these mixtures with GC (Table 1). The GC analyses were complicated by the fact that the sample pre-treatment procedure unfortunately afforded a redistribution mixture of SnEt₄, (allyl)SnEt₃ and Allyl₂SnEt₂ even for authentic samples of allyltin trichloride. However, the sum of the three integrated signals was found to correlate linearly with the amount of allyltin trichloride present. The reaction profile obtained by GC analysis was verified by ¹H NMR spectroscopy (Fig. 1) for the best catalyst (entry 8, Table 1) and was found to be in good agreement.

In general, the yields were significantly lower than quantitative as a result of the limited stability of the end product (vide infra). By comparing the maximum yields and

the yield after 120 h and by inspection of Figure 1, this feature is immediately apparent. The data in Table 1 show that the reactions catalyzed by the palladium complexes give higher yields of allyltin trichloride than those catalyzed by the analogous platinum complexes (entries 1–8). Of the palladium complexes tested, PdMe₂(phen) gave the highest yield (83%). Dppe complexes of the type MZ₂(dppe) (M=Pt, Pd; Z=Me, Cl) were also tested but only PtMe₂(dppe) was found to display some activity. A maximum yield of 13% after 53 h (entry 9) was obtained. Pd(PPh₃)₄ and PdCl₂(PhCN)₂, two typical catalysts for the carbonyl allylation reaction,⁹ were also tested but did not afford significant amounts of allyltin trichloride in CH₂Cl₂. The catalyst decomposed to Pd-black at an early stage of the reaction.

When dimethyl platinum or palladium complexes were used, the presence of small amounts (2–4%) of methyltin trichloride (δ 1.69; ²J_{HSn}=99.6 Hz) was observed next to allyltin trichloride (Table 1).¹⁰ This indicates that part of

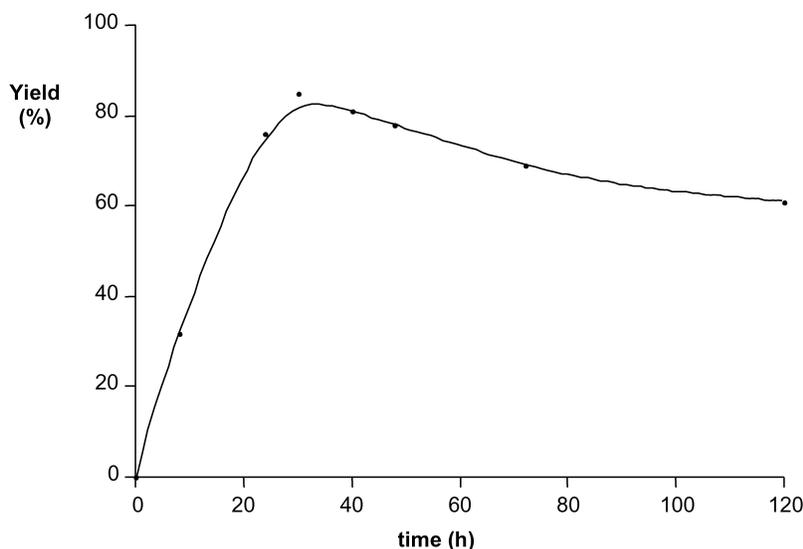


Figure 1. Plot of the yield of allyltin trichloride (%) versus time (h) for the reaction of 3-chloropropene with SnCl₂ catalyzed by PdMe₂(phen) in CH₂Cl₂ at 45°C.

the methyl ligands of the catalyst were transferred to tin as well.

The experiment corresponding to entry 8 in Table 1 was also performed on preparative scale and stopped after 30 h. At that time, just 10% of the initial amount of the poorly soluble SnCl_2 could be recovered from the reaction mixture. Allyltin trichloride was isolated from the organic phase as a liquid in 84% yield. The ^1H NMR spectrum of the product revealed the presence of 5% of decomposition products. The isolated yield of allyltin trichloride is in good agreement with the yields determined by GC and ^1H NMR spectroscopic analysis of the reaction mixture.

After prolonged heating at the reaction temperature (45°C), the decomposition of allyltin trichloride becomes apparent and is accompanied by the appearance of broad resonances at δ 0.6–2.6 and 5.3–5.9 in the ^1H NMR spectrum. The decomposition reaction was studied independently by monitoring solutions of pure allyltin trichloride over a period of time at 25 and 45°C , respectively. The monitoring at 45°C was also carried out in the presence of catalyst (Fig. 2). From the data in Figure 2 it is obvious that the decomposition reaction is not only accelerated by the presence of catalyst but is even significant in the absence of catalyst. As both the platinum and the palladium catalyzed reactions are slow, we conclude that the yield of allyltin trichloride is determined by the relative rates of the catalyzed formation and the decomposition of allyltin trichloride. With the platinum catalysts, the decomposition reaction is faster than with the palladium catalysts, resulting in lower yields of product.

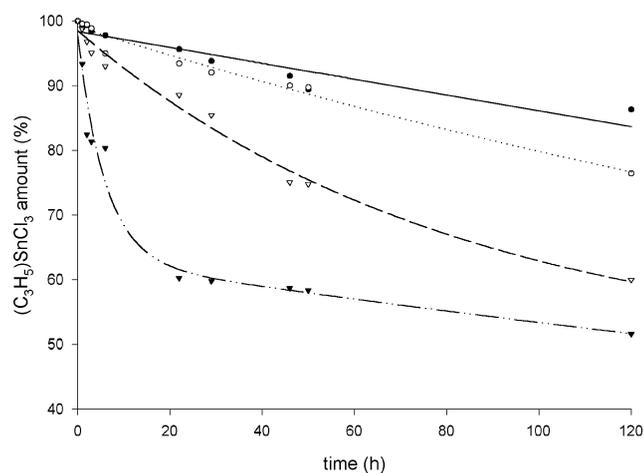


Figure 2. Plot of the (allyl) SnCl_3 amount (%) versus time (h) at 25°C (—), at 45°C (···), at 45°C with 5 mol% of $\text{PdMe}_2(\text{bipy})$ (- - -) and at 45°C with 5 mol% of $\text{PtMe}_2(\text{bipy})$ (-----).

The instability of allyl tin compounds has been discussed before and it was suggested that they decompose by cationic polymerization.^{4b} To obtain more information on the decomposition products of allyltin trichloride, a sample was stored for several weeks in the dark at room temperature. After this period it had decomposed to a white solid and a sticky brown oil. The elemental analysis data of the white solid showed a Sn/Cl molar ratio of 1:2.3 which is close to the theoretical 1:2 ratio for SnCl_2 , but the analogous data for the brown oil was more ambiguous. The

presence of numerous resonances in the region δ 30–50 and 120–140 in the ^{13}C NMR spectrum as well as broad resonances in the ^1H NMR spectrum made it difficult to identify the nature of the products which most likely are polymeric in nature.

In our catalytic system, non-coordinating CH_2Cl_2 was used as solvent. In this way, allyltin trichloride can easily be obtained just by filtration of the reaction mixture followed by evaporation of all volatile components. This is in contrast to the system of Masuyama,¹¹ which makes use of polar solvents, such as DMF, 1,3-dimethyl-2-imidazolidinone (DMI), DMSO, EtOH, DME or THF. These solvents coordinate to the Lewis acidic allyltin trichloride to give discrete 1:2 complexes (allyl) $\text{SnCl}_3(\text{solvent})_2$ (e.g. ^{119}Sn NMR: δ -488 with DMF as solvent). These reactions are considerably faster which most likely relates to the difference in solubility of SnCl_2 in the solvents used by Masuyama (soluble in DMF) and in the present study (insoluble in CH_2Cl_2).

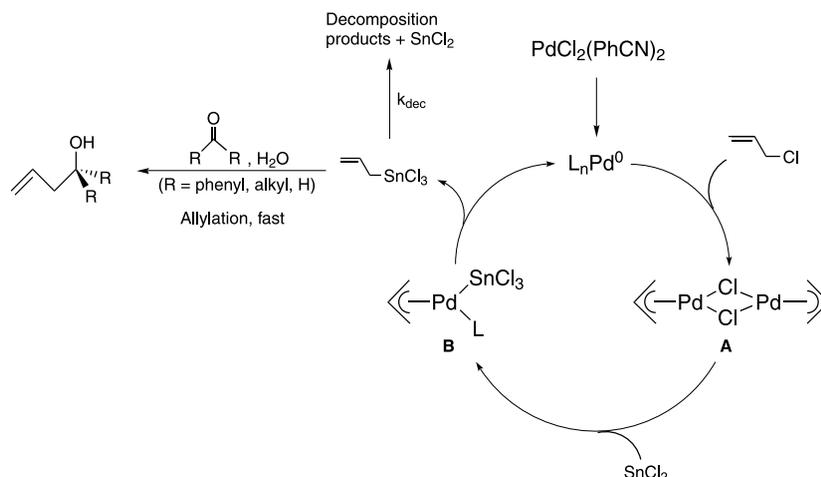
When the reaction (CH_2Cl_2 with $\text{PdMe}_2(\text{phen})$ as catalyst) was performed at 35 or 65°C instead of at 45°C , the yields of allyltin trichloride were decreased (entry 10 and 11). At 35°C , the highest yield was reached after a significantly longer reaction time (70 h). Entries 12–17 of Table 1 show that with the other solvents tested, lower yields and faster decomposition of the formed allyltin trichloride occurred. Even the use of solvents such as THF and DMF, which are successfully applied in the carbonyl allylation of ketones and aldehydes, resulted in poor yields.

Next to 3-chloropropene, the reagents 3-chloro-2-methylpropene, 1-chloro-2-butene, 3-bromopropene, benzyl chloride and chlorobenzene were tested in the reaction with tin(II) halides with $\text{PdMe}_2(\text{phen})$ and $\text{PtMe}_2(\text{bipy})$ as catalyst.

3-Chloro-2-methylpropene and 1-chloro-2-butene were found to react with tin(II) chloride in CH_2Cl_2 at 45°C . ^1H NMR spectroscopic analysis of the reaction mixtures after 24 h showed the presence of considerable amounts of decomposition products, whereas, resonances assigned to methallyl- or crotyltin trichloride were absent.^{4b} Methallyltin trichloride and crotyltin trichloride are probably even less stable and decompose faster than allyltin trichloride under these conditions. This was confirmed by the presence of similar broad resonances in the ^1H NMR spectra as observed in the reaction of 3-chloropropene with tin(II) chloride.

3-Bromopropene reacted with SnBr_2 in the presence of $\text{PdMe}_2(\text{phen})$ (5 mol%) in CH_2Cl_2 at 45°C to give allyltin tribromide in 19% yield after 48 h.^{12,13} This yield is considerable lower than the yield of allyltin trichloride obtained in the reaction of allyl chloride with SnCl_2 under comparable reaction conditions. Furthermore, significant formation of side-products was already observed after 24 h, while for 3-chloropropene almost no side-product was formed at that time.

Reaction of benzyl chloride with SnCl_2 led to the formation of considerable amounts of polybenzyl.¹⁴ In the ^1H NMR



Scheme 1. Proposed mechanism for the palladium catalyzed formation of allyltin trichloride in the carbonyl allylation reaction with ketones and aldehydes with L=coordinating solvent or 3-chloropropene.

spectrum, broad resonances at δ 7.0 and 3.8 were visible. The ^{13}C NMR chemical shift values corresponded with values reported in the literature.¹⁴ To investigate whether $\text{PtMe}_2(\text{bipy})$ is responsible for the polymerization reaction, an independent reaction without catalyst was carried out. Also in this case, formation of polybenzyl was significant suggesting that not the platinum complex, but SnCl_2 itself acts as a catalyst for the polycondensation of benzyl chloride. Similar polymerization reactions of benzyl chloride catalyzed by other Lewis acids like TiCl_3 and AlCl_3 have been reported.^{14,15}

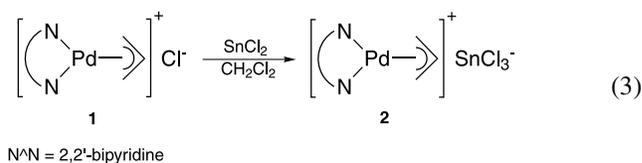
For chlorobenzene, only decomposition of the catalyst into metal-black was observed ($\text{PdMe}_2(\text{phen})$, CH_2Cl_2 , 45°C).

2.1. Mechanistic aspects

Work by Masuyama and Kurosawa et al. on the palladium-catalyzed carbonyl allylation of ketones and aldehydes by in situ generated allyltin trichloride suggested that this reaction most likely involves a $\text{Pd}^0/\text{Pd}^{\text{II}}$ catalytic cycle.^{11,16} It was shown that the allyltin(IV) formation proceeds via the η^3 -allyl(trichlorostannyl)palladium(II) intermediate **B** (Scheme 1).¹⁶ The formation of allyltin trichloride via reductive elimination is the rate-determining step and is followed by a fast allylation reaction of the carbonyl function of ketone or aldehyde to give the allylated product.^{9,16} Finally, it can be concluded that all through the reaction the actual concentration of allyltin trichloride will remain low. Most likely, a polar solvent is required for the latter step to be fast (vide supra).

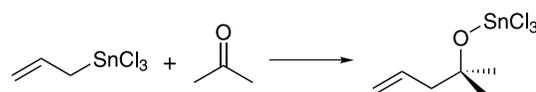
In our system, allyltin trichloride is the end-product and does not subsequently react with a substrate to give a stable end-product. Consequently, the success of our system is highly dependent on the stability of allyltin trichloride and therefore, a small k_{dec} is required to obtain good yields.

By analogy and by taking into account that we are using palladium dichloride complexes with strongly coordinating bidentate ligands, the initial step in the catalysis might involve the formation of ionic $[\text{Pd}(\eta^3\text{-allyl})(\text{bipy})][\text{Cl}]$ (**1**), which is a known compound.¹⁷

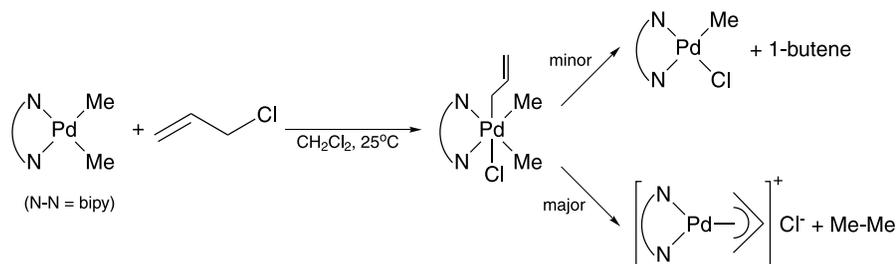


Addition of 1 equiv. of SnCl_2 to (**1**) in a separate reaction indeed resulted in quantitative formation of ionic $[\text{Pd}(\eta^3\text{-allyl})(\text{bipy})][\text{SnCl}_3]$ (**2**) (Eq. (3)), which has a ^1H NMR spectrum similar to that reported for related $[\text{Pd}(\eta^3\text{-allyl})(\text{bipy})][\text{BF}_4]$.¹⁸ In addition, the ^{119}Sn NMR chemical shift of $\delta -37.0$ is in agreement with the value found for a $[\text{SnCl}_3]^-$ anion like in $[\text{PBu}_5\text{H}][\text{SnCl}_3]$ ($\delta -30$), $[\text{tBu}_4\text{N}][\text{SnCl}_3]$ ($\delta -42$) and $[\text{AsPh}_4][\text{SnCl}_3]$ ($\delta -51$) (all measured in CH_2Cl_2).¹⁹ As reported for $[\text{Pd}(\eta^3\text{-allyl})(\text{PPh}_3)_2][\text{SnCl}_3]$,²⁰ also **2** did not reductively eliminate allyltin trichloride, neither in CH_2Cl_2 nor in a polar solvent as acetone- d_6 , not even at the reaction temperature applied in the catalytic reaction (45°C). However, when **2** was used as catalyst in the reaction of 3-chloropropene with SnCl_2 , activities similar to that of $\text{PdCl}_2(\text{bipy})$ were found.

Compound **2** was not reactive towards 3-chloropropene (excess in CD_2Cl_2 or acetone- d_6 , 25 and 45°C), whereas, **2** reacts with an excess of SnCl_2 in CD_2Cl_2 to afford an unidentified allylic species but not allyltin trichloride. However, when the latter reaction was performed in acetone- d_6 , slow formation of the butenylalkoxide $\text{CH}_2=\text{CH}-\text{CH}_2\text{C}(\text{CD}_3)_2\text{OSnCl}_3$ was observed (44% after 0.5 h) which is the result of direct reaction of acetone with allyltin trichloride (Scheme 2, see also Section 4).^{9,11} The ^1H NMR resonances perfectly matched those of an independently prepared sample of (allyl)SnCl₃ recorded in acetone- d_6 .^{4b} It can thus be concluded that reductive elimination of allyltin trichloride from **2** is possible but only leads to appreciable build-up of allyl chloride if its formation is competing effectively with decomposition. The



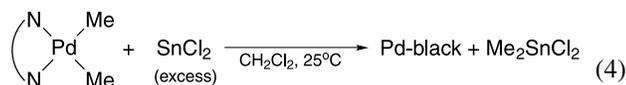
Scheme 2. Reaction of (allyl)SnCl₃ with acetone.



Scheme 3. Reaction of PdMe₂(bipy) with 3-chloropropene.

latter is only realized under catalytic conditions in the presence of sufficient amounts of both substrates. In addition, there is apparently also an effect of the excess SnCl₂ on the reductive elimination step.

For the dimethyl palladium complexes PdMe₂L, a different cycle could be operative. In order to obtain more insight in the reactivity of this pre-catalyst, independent reactions of PdMe₂(bipy) with both SnCl₂ and 3-chloropropene were studied. When an excess of SnCl₂ was added to a solution of PdMe₂(bipy) in CH₂Cl₂, the color of the solution turned orange instantaneously while deposition of palladium black became clearly visible. Analysis of the solution by ¹H NMR spectroscopy showed the absence of the initial palladium complex. Instead, the presence of the methylated product Me₂SnCl₂ (δ 1.22; ¹J_{H-Sn}=84 Hz)²¹ in the reaction mixture was observed. This indicates that the methyl ligands of the initial palladium complex have been transferred from palladium(II) to tin(II). Apparently, SnCl₂ has acted as reducing agent in the reaction with PdMe₂(bipy) (Eq. (4)).



(N^N = 2,2-bipyridine)

The reaction of 3-chloropropene (excess) with PdMe₂(bipy) afforded in ca. ten minutes [Pd(η³-allyl)(bipy)][Cl]¹⁷ (**1**) along with traces of PdMe(Cl)(bipy) (Scheme 3).¹⁸ This result is in line with the observations made by Canty et al. for the reaction of allyl bromide with PdMe₂(bipy).¹⁸

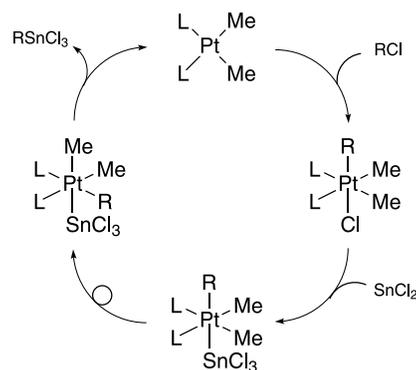
To study the extent of competition of the reactions of PdMe₂(bipy) with either SnCl₂ (Eq. (4)) or 3-chloropropene (Scheme 3), respectively, SnCl₂ and 3-chloropropene (both 1 equiv.) were added to a solution of PdMe₂(bipy) in CD₂Cl₂. After ten minutes at room temperature, two singlet Me resonances without tin satellites were visible in the ¹H NMR spectrum (δ 0.90 and 1.71). Analysis of the solution by ¹H NMR after 24 h showed the presence of Me₂SnCl₂, [Pd(η³-allyl)(bipy)][SnCl₃] and several unidentified singlet resonances (δ 0.66, 0.86 and 1.67) which may originate from ethane and butene formation. The formation of Me₂SnCl₂ and [Pd(η³-allyl)(bipy)][SnCl₃] would suggest a Pd⁰/Pd^{II} catalytic cycle similar to that of PdCl₂(bipy). However, under catalytic conditions, no Me₂SnCl₂ but MeSnCl₃ (2–4%) was detected. Formation of MeSnCl₃ may well be the result of reductive elimination from [Pd(Me)(bipy)][SnCl₃] (minor route in Scheme 3 followed by SnCl₂ insertion). [Pd(η³-allyl)(bipy)][SnCl₃] may well be resulting from SnCl₂ insertion in the Pd–Cl bond of [PdCl(η³-allyl)(bipy)] but is part of both catalyst activation

mechanisms. Even if a Pd^{IV} species is involved, once the methyl groups have been transferred, the catalyst enters the same cycle as was proposed for the palladium chloride complexes (Scheme 1).

Next to the palladium complexes the analogous platinum complexes were investigated and subjected to stoichiometric reactions with the substrate. The platinum dichloride complex PtCl₂(bipy) was found not to react with a four-fold excess of 3-chloropropene. On the other hand, when a four-fold excess of SnCl₂ was added, the color of the reaction mixture changed from yellow to bright orange. The reaction mixture was stirred for 24 h at 45°C, after which a orange solid was isolated from the solution. A ¹H NMR spectrum recorded in acetone-*d*₆ showed no resonances of the initial platinum compound. The resonances in the aromatic region pointed towards a complex mixture of several newly-formed bipy complexes that might include species like PtCl(SnCl₃)(bipy) and Pt(SnCl₃)₂(bipy). Attempts to identify these complexes were without any success, due to the overlap of several resonances, preventing further mechanistic investigations.

The platinum analogue PtMe₂(bipy), was reacted with SnCl₂ and 3-chloropropene. When an excess of SnCl₂ was added to a solution of PtMe₂(bipy) in CH₂Cl₂, no reaction was observed within ten minutes. A sample of the reaction mixture analyzed by ¹H NMR spectroscopy, showed PtMe₂(bipy)²² to be the only compound present. On the other hand, PtMe₂(bipy) reacted completely with 3-chloropropene within one minute and resulted in quantitative formation of the expected *trans*-oxidative addition product [PtMe₂(allyl)(Cl)(bipy)].²³

These results suggest that an oxidative addition reaction of 3-chloropropene with PtMe₂(N^N) (N^N=bipy, phen)



Scheme 4. Postulated catalytic cycle for the PtMe₂L catalyzed formation of allyltin trichloride (R=C₃H₅; N^N=bipy, phen).

takes place at first (Scheme 4). Previously, it was demonstrated that the insertion of tin(II) chloride into the platinum–chloride bond of [PtMe₂(allyl)(Cl)(bipy)] is also fast and results in the formation of [PtMe₂(allyl)(SnCl₃)(bipy)] (**3**).²⁴ Before reductive elimination of allyltin trichloride can take place, the octahedral complex has to rearrange to position the allyl ligand *cis* to the SnCl₃ ligand.²⁵ This *trans* to *cis* isomerization takes place via a five-coordinate intermediate²⁶ by dissociation of a weakly coordinating ligand such as SnCl₃.²⁷ Next, reductive elimination of allyltin trichloride results in the re-formation of the starting complex PtMe₂L. To investigate whether complex **3** does indeed undergo reductive formation of Sn–C bonds, a solution of **3** in acetone-*d*₆ was examined by ¹H NMR spectroscopy. While complex **3** was stable for 2 days at 25°C, at 60°C **3** gave in 12 h almost quantitative formation of butenylalkoxide (vide supra) that results from consecutive reaction of (allyl)SnCl₃ with acetone (Scheme 2). These results confirm that **3** can undergo reductive elimination to afford allyltin trichloride. While the oxidative addition of 3-chloropropene and the insertion of SnCl₂ are fast, reductive elimination step is slow and probably the rate determining step in the catalytic cycle.

In the postulated catalytic cycle, not only an allyl substituent, but also a Me substituent is orientated in the *cis* position to the SnCl₃ ligand. Consequently, formation of MeSnCl₃ that is observed in the catalytic reaction, can be explained by this mechanism.

3. Conclusion

Despite its thermal instability, allyltin trichloride could be prepared under mild conditions by the direct reaction of 3-chloropropene and SnCl₂ catalyzed by platinum and palladium 2,2'-bipyridine and 1,10-phenanthroline complexes. In general, the palladium catalysts give higher yields of allyltin trichloride than the analogous platinum complexes. This effect is ascribed to a lower decomposition rate of the product when palladium catalysts are used. Unfortunately, this approach fails for other organic halides. Some brief mechanistic studies show that most likely a Pd⁰/Pd^{II} catalytic cycle is operative for the PdCl₂L complexes. The PtMe₂L complexes follow a Pt^{II}/Pt^{IV} cycle, while the mechanism involved for PtCl₂L and PdMe₂L remains less well defined.

4. Experimental

4.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. PtMe₂(bipy),²⁸ PtCl₂(bipy),²⁹ PtMe₂(dppe),³⁰ PtCl₂(dppe),³¹ PtCl₂(phen),³² PtMe₂(phen),²² PdMe₂(bipy),³³ PdCl₂(bipy),³⁴ PdMe₂(dppe),³⁵ PdCl₂(dppe),³⁶ PdMe₂(phen),³³ PdCl₂(phen),³⁴ PdCl₂(PhCN)₂,³⁷ Pd(PPh₃)₄,³⁸ PdCl₂(allyl)(bipy)¹⁷ and allyltin trichloride³⁹ were prepared according to literature procedures. Dichloromethane was distilled from CaH₂; all organic halides were distilled and stored on molsieves 3 Å. Commercially available anhydrous SnCl₂

and SnBr₂ were stored under a nitrogen atmosphere; CCl₄ was stored under a nitrogen atmosphere on molsieves 3 Å. Toluene was used as internal standard to determine the yields by ¹H NMR spectroscopy (100 μL of toluene in 10 mL of CDCl₃). ¹H, ¹³C{¹H} and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker AC 200 MHz or on Varian Inova 300 MHz NMR spectrometer with Me₄Si (¹H and ¹³C) and Me₄Sn (¹¹⁹Sn) as external references. GC analysis were carried out on a Perkin–Elmer instrument consisting of an Autosystem XL GC. GC–MS analysis were carried out on a Perkin–Elmer instrument consisting of an Autosystem XL GC and a Turbomass MS. Elemental analysis were carried out by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

4.1.1. Typical procedure for the reaction of organic halide with SnX₂ (X=Cl, Br) catalyzed by 5 mol% of catalyst. To anhydrous tin(II) halide (1 mmol) in a Schlenk flask, 5 mL of dry solvent was added. After addition of the organic halide (5 mmol), internal standard *n*-tridecane (100 μL) and the catalyst (0.05 mmol, 5 mol%), the reaction mixture was heated to the desired temperature. A 50 μL sample was taken from the reaction mixture at regular intervals and reacted with 1.0 M EtMgBr in Et₂O (3 mL). The sample was quenched with 5 mL of water and the upper Et₂O layer was analyzed by GC and GC–MS. The yield of allyltin trichloride was calculated from the sum of the integrals of SnEt₄, Sn(C₃H₅)Et₃ and Sn(C₃H₅)₂Et₂ signals and calibrated to the internal standard (*n*-tridecane). The total area of the three signals was found to correlate well with the amount of allyltin trichloride.

Analysis of the reaction mixture by NMR spectroscopy was carried out as follows: after cooling of the reaction mixture to room temperature, a 500 μL sample was taken and evaporated till dryness. Next, 600 μL of CDCl₃ with internal toluene standard was added to the residue. The sample was analyzed by ¹H, ¹³C and ¹¹⁹Sn NMR spectroscopy. NMR data of allyltin trichloride, ¹H NMR (CDCl₃, 25°C): δ 3.14 (d, 2H, J_{HSn}=119 Hz, CH₂–Sn), 5.19–5.66 (m, 2H, CH₂), 5.75–6.14 (m, 1H, CH). ¹³C NMR (CDCl₃, 25°C): δ 36.3 (¹J_{CSn}=314.9 Hz), 122.0 (²J_{CSn}=72.3 Hz), 127.2 (³J_{CSn}=65.4 Hz). ¹¹⁹Sn NMR (CDCl₃, 25°C): δ –29.0. GC–MS *m/e* (rel. intensity): 236 (3, M⁺), 207 (82), 179 (98), 149 (100), 58 (121); SnEt₄, 219 (12, M⁺–C₂H₅), 207 (45), 179 (50), 149 (100), 121 (47); Sn(C₃H₅)Et₃, 231 (12, M⁺–C₂H₅), 219 (35), 161 (38), 149 (100), 121 (33); Sn(C₃H₅)₂Et₂.

NMR data of allyltin tribromide, ¹H NMR (CDCl₃, 25°C): δ 3.23 (d, 2H, J_{HSn}=108 Hz, CH₂–Sn), 5.28–5.47 (m, 2H, CH₂), 5.74–6.14 (m, 1H, CH). The concentration of allyltin tribromide was too low to obtain satisfactorily ¹³C and ¹¹⁹Sn NMR spectra.

The reaction on a preparative scale was carried out as described above using SnCl₂ (0.95 g, 5 mmol), 3-chloropropene (1.9 g, 25 mmol), PdMe₂(phen) (79 mg, 0.25 mmol, 0.5 mol%) and CH₂Cl₂ (25 mL). After the reaction mixture was heated for 30 h at 45°C, it was cooled to room temperature and filtered. Evaporation of the solvent from the residue in vacuo resulted in 1.18 g of a slightly yellow colored oil. The oil was analyzed by ¹H NMR and

found to contain allyltin trichloride in 95% purity along with some decomposition product (see text), corresponding to an 84% yield.

4.1.2. Decomposition studies of allyltin trichloride.

Without solvent. A sample of freshly prepared (allyl)SnCl₃ (3.4 g) was stored for several weeks in the dark at room temperature. CH₂Cl₂ (10 mL) was added and the suspension was filtrated. The white solid was washed two times with CH₂Cl₂ (5 mL) and dried in vacuo (0.25 g). Elem. anal. Found: Sn, 47.07; Cl, 31.43%. The volatiles from the filtrate were removed in vacuo to give a brown sticky material (3.0 g). Elem. anal. Found: C, 16.08; H, 2.38; Sn, 40.02; Cl, 36.03%. ¹H NMR (CDCl₃, 25°C): δ 0.6–2 (br, 3H), 2.2–2.6 (br, 9H), 5.3–5.6 (m, 2H), 5.7–5.9 (m, 1H). ¹³C NMR (CDCl₃, 25°C): δ 33.5, 39.8 (*J*_{C-Sn}=69.8 Hz),⁴⁰ 43.4, 123.5, 132.9 ppm.

In CH₂Cl₂. Four aliquots of freshly prepared (allyl)SnCl₃ (200 mg, 0.75 mmol) in 5 mL of CH₂Cl₂ with *n*-tridecane (100 μL) were prepared. To the first and the second, PtMe₂(bipy) (38 mg, 0.1 mmol) and PdMe₂(bipy) (29 mg, 0.1 mmol), respectively, were added. These two solutions together with a solution that did not contain the metal complex, were stored at 45°C. The fourth solution was stored at 25°C. For the analysis of the reaction mixtures a 50 μL sample was taken and was reacted with 1.0 M EtMgBr in Et₂O (3 mL). The sample was quenched with 5 mL of water and the upper Et₂O layer was analyzed by GC.

4.1.3. Synthesis of [Pd(η³-allyl)(bipy)][SnCl₃] (2). PdCl(allyl)(bipy) (130 mg, 0.39 mmol) was suspended in 10 mL of CH₂Cl₂. SnCl₂ (73 mg, 0.39 mmol) was added to the suspension and the reaction mixture was stirred for 3 days at room temperature. Filtration of the reaction mixture resulted in the isolation of a light yellow powder (133 mg, 65% yield). Mp 182°C (dec). ¹H NMR (CD₂Cl₂, -25°C): δ 3.56 (d, 2H, ³*J*_{HH}=12.6 Hz, Pd-CH₂), 4.28 (d, 2H, ³*J*_{HH}=6.9 Hz, allylic CH₂), 6.09 (m, 1H, ³*J*_{HH}=9.0 Hz), 7.71 (t, 2H, ³*J*_{HH}=7.2 Hz, bipy), 8.28 (t, 2H, ³*J*_{HH}=8.7 Hz, bipy), 8.42 (d, 2H, ³*J*_{HH}=8.1 Hz, bipy), 8.83 (d, 2H, ³*J*_{HH}=4.8 Hz, bipy). ¹¹⁹Sn (CD₂Cl₂, 25°C): δ -37.0. Anal. calcd. for C₁₃H₁₃Cl₃N₂PdSn: C, 29.53; H, 2.48; N, 5.30; Cl, 20.12. Found: C, 29.44; H, 2.40; N, 5.21; Cl, 20.16.

4.1.4. Reaction of [Pd(η³-allyl)(bipy)][SnCl₃] (2) with 3-chloropropene or SnCl₂. A solution of **2** (10 mg, 0.02 mmol) in 1 mL of CD₂Cl₂ or acetone-*d*₆ was transferred in a NMR tube. Next, SnCl₂ (15 mg, 0.08 mmol) or 3-chloropropene (7 μL, 0.08 mmol) was added. After the tube was sealed, it was stored at room temperature or it was placed in an oil bath of 45°C. The solution was analysed by ¹H NMR spectroscopy at regular intervals. ¹H NMR of the reaction with SnCl₂ in CD₂Cl₂ (25°C): δ 3.40 (d, 2H, CH₂, ³*J*_{HH}=13.2 Hz), 5.10 (d, 2H, CH₂, ³*J*_{HH}=7.4 Hz), 5.23–5.44 (m, 1H, CH), 7.72 (t, 2H, bipy, ³*J*_{HH}=13.2 Hz), 8.27 (t, 2H, bipy, ³*J*_{HH}=8.3 Hz), 8.35 (d, 2H, bipy, ³*J*_{HH}=7.4 Hz), 8.82 (d, 2H, bipy, ³*J*_{HH}=6.4 Hz). ¹H NMR of the reaction with SnCl₂ in acetone-*d*₆ (25°C): δ 2.19 (d, 2H, CH₂, ³*J*_{HH}=5.0 Hz), 4.96–5.10 (m, 2H, CH₂), 5.81–6.02 (m, 1H, CH) for CH₂=CH-CH₂C(CD₃)₂OSnCl₃ and δ 8.09 (t, ³*J*_{HH}=

5.4 Hz, bipy 1), 8.25 (t, ³*J*_{HH}=6.9 Hz, bipy 2), 8.56 (t, ³*J*_{HH}=8.1 Hz, bipy 1), 8.70 (d, ³*J*_{HH}=8.1 Hz, bipy 2), 8.86 (d, ³*J*_{HH}=8.1 Hz, bipy 1), 9.04 (d, ³*J*_{HH}=8.1 Hz, bipy 2), 9.39 (d, ³*J*_{HH}=5.4 Hz, bipy 1), 9.57 (d, ³*J*_{HH}=5.4 Hz, bipy) for the bipy resonances. An independently prepared sample of (allyl)SnCl₃ in acetone-*d*₆ showed the same characteristic resonances for CH₂=CH-CH₂C(CD₃)₂OSnCl₃ in the ¹H NMR spectrum.^{4b}

4.1.5. Reaction of (allyl)SnCl₃ with acetone. Allyltin trichloride (0.5 g, 1.8 mmol) was added dropwise to acetone (5 mL) at room temperature. After ten minutes, H₂O (2 mL) was added to the reaction mixture followed by extraction with Et₂O (2x5 mL). The collected organic fractions were dried with MgSO₄ and filtered. Evaporation of the solvent in vacuo yielded 0.15 g of a colourless oil. ¹H NMR (CDCl₃, 25°C): δ 1.25 (s, 6H, CH₃), 2.11 (s, 1H, OH), 2.25 (d, 2H, ³*J*_{HH}=8.0 Hz, CH₂=CHCH₂), 4.95–5.17 (m, 2H, CH₂=CHCH₂), 5.71–5.88 (1H, m, CH₂=CHCH₂). GC-MS analysis 100 (1, M⁺), 85 (10, M⁺-CH₃), 59 (100), 43 (55, M⁺-C₃H₅), 31 (22) (2-methyl-4-pentene-2-ol).

4.1.6. Reactions of MZ₂(bipy) (M=Pd, Pt; Z=Me, Cl) with 3-chloropropene or SnCl₂. All experiments were performed with 0.4 mmol of platinum- or palladium complex and SnCl₂ (302 mg, 1.6 mmol) or 3-chloropropene (122 mg, 1.6 mmol) in 10 mL of CH₂Cl₂. The reaction mixtures were analyzed by ¹H NMR spectroscopy with CDCl₃ or acetone-*d*₆ as solvent.

4.1.7. Stoichiometric reaction of PdMe₂(bipy) with 3-chloropropene and SnCl₂. To a mixture of 3-chloropropene (3 μL, 0.032 mmol), SnCl₂ (6 mg, 0.032 mmol) and CD₂Cl₂ (0.5 mL) in a NMR tube, PdMe₂(bipy) (10 mg, 0.032 mmol) was added. The tube was stored at room temperature and the solution was analysed by ¹H NMR spectroscopy at regular intervals.

4.1.8. Decomposition of [PtMe₂(allyl)(SnCl₃)(bipy)] (3). A solution of 16 mg (0.024 mmol) of **3** in 1 mL of acetone-*d*₆ was transferred. After the tube was sealed, it was submerged in a oil bath at 60°C for 2 days. The NMR-tube was cooled to room temperature and the solution was analysed by ¹H NMR spectroscopy at regular intervals. After 48 h, an orange solid had precipitated from the solution. ¹H NMR (acetone-*d*₆, 25°C): δ 2.19 (d, 2H, CH₂, ³*J*_{HH}=5.0 Hz), 4.96–5.10 (m, 2H, CH₂), 5.81–6.02 (m, 1H, CH). An independently prepared sample of (allyl)SnCl₃^{4b} showed the same resonances in the ¹H NMR spectrum recorded in acetone-*d*₆.

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