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Palladium-catalyzed dehydrostannylation of *n*-alkyltin trichlorides†

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[Pd(PPh$_3$)$_4$] catalyzes the dehydrostannylation of *n*-alkyltin trichlorides into HSnCl$_3$(THF)$_n$ and isomers of the corresponding alkene. The reaction mechanism involves oxidative addition of the Sn–C bond followed by β-H elimination from the resulting *n*-alkylpalladium trichlorostannyl species. Rate-determining reductive elimination of HSnCl$_3$ from *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] completes the catalytic cycle. Organotin trichlorides without β-H atoms either do not react or undergo thermal disproportionation. These results are relevant to understand some of the problems associated with the use of monoalkyltin compounds as coupling partner in Stille-type cross-coupling reactions as well as with the catalytic hydrostannylation of 1-alkenes to monoalkyltin trichlorides.

Introduction

Organotin compounds are important as reagents in the group 10 metal-catalyzed Stille-type cross-coupling reaction. Although this reaction commonly uses tetraorganotins, there has been recent interest in monoorganotins as alkylating reagents[1–5] because their tin tetrahalide by-products are less toxic than the triorganotin halides which are generated by a tetraorganotin coupling partner. However, if the alkyltin trihalide contains β-H atoms, this reaction is limited to highly reactive aryl iodide coupling partners and basic aqueous reaction conditions,[4,5] with significant amounts of homocoupling by-products being produced.[5] A different type of reaction, *i.e* the catalytic hydrostannylation of 1-alkenes using [Pd(PPh$_3$)$_4$] as catalyst to produce *n*-alkyltin trihalides, also appeared to face severe limitations. So far, only low conversions could be achieved.[6]

In order to better understand the specific issues related to both types of Pd-catalysis, we decided to have a closer look at the interaction of [Pd(PPh$_3$)$_4$)] with several alkyltin trichlorides and phenyltin trichloride. We have previously reported on the stoichiometric reactivity of monoorganotin trichlorides with [Pd(PPh$_3$)$_4$], which involved oxidative addition of the Sn–C bond, followed by rapid β-H elimination in the case of ^{n}BuSnCl$_3$.[7] We now present the discovery of a palladium-catalyzed dehydrostannylation that occurs if an excess of monoalkyltin trichloride is allowed to react with [Pd(PPh$_3$)$_4$].

Results and discussion

Reaction of ^{n}BuSnCl$_3$ with a catalytic amount of [Pd(PPh$_3$)$_4$]

A study in a sealed NMR tube containing a THF-*d*$_8$ solution of ^{n}BuSnCl$_3$ (0.6 M) did not exhibit any degradation of the alkyltin compound during a 3 h period at 70 °C. The same tube, but with an extra 1 mol% of [Pd(PPh$_3$)$_4$] added, did not show any significant conversion of ^{n}BuSnCl$_3$ over a 3 h period at room temperature either. However, when heated at 50 °C for 3 h, ^{1}H NMR analysis showed that 22% of the starting ^{n}BuSnCl$_3$ reagent had been converted into butene isomers. 1-Butene was initially formed as the major product but, under these conditions, concomittant isomerization led to its almost complete transformation into 2-butene isomers (>95%) within 2 h.

The reaction mixture exhibited two broad ^{119}Sn NMR signals at $\delta = -156$ and -197 ppm. The first signal corresponds to unreacted ^{n}BuSnCl$_3$. The second is similar to the signal observed for an independently prepared equimolar solution of SnCl$_2$ and HCl in THF-*d*$_8$, a mixture that is described in the literature as giving the "acidic complex" (HSnCl$_3$)(solvent)$_n$ in donor solvents such as Et$_2$O, DMSO and pyridine.[8] Accordingly, HSnCl$_3$(THF)$_n$ was identified as the coproduct of the butene isomers formation in the reaction of ^{n}BuSnCl$_3$ with a catalytic amount of [Pd(PPh$_3$)$_4$]. The overall reaction corresponds to a so far unprecedented dehydrostannylation of monoalkyltin trichlorides catalyzed by [Pd(PPh$_3$)$_4$] (eqn (1)). In the literature, only a non-catalytic version of a dehydrostannylation reaction was previously observed by Murai *et al.* in the specific case of β-trichlorostannyl ketones, leading to the corresponding enones and HSnCl$_3$(DMSO)$_n$.[9]

$$^{n}\mathrm{BuSnCl_3} \underset{\mathrm{THF},\,\Delta}{\overset{[\mathrm{Pd(PPh_3)_4}]}{\underset{1\,\mathrm{mol}\,\%}{\rightleftharpoons}}} \text{butene isomers} + (\mathrm{HSnCl_3})(\mathrm{THF})_n \qquad (1)$$

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of ^{n}OctSnCl$_3$. Van't Hoff plot of the concentration at equilibrium for the dehydrostannylation of ^{n}BuSnCl$_3$. Conversion *vs.* time plots of the kinetic studies of the dehydrostannylation of ^{n}OctSnCl$_3$ for the temperature-, ^{n}OctSnCl$_3$-, catalysis-, 1-octene-, HSnCl$_3$- and 2-octene-dependent studies. See DOI: 10.1039/c1dt10330j

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The catalytic dehydrostannylation of ^{n}BuSnCl$_3$ appeared to be an equilibrium reaction. Not only has the reverse reaction been claimed,[6] but this also became apparent from experiments at different temperatures in a sealed NMR tube. Within 2 h at 50 °C, the [butenes]/[^{n}BuSnCl$_3$] ratio returned to its initial value ([butenes]/[^{n}BuSnCl$_3$] = 22/78) after the NMR tube had been kept successively for 2 h at 60 °C ([butenes]/[^{n}BuSnCl$_3$] = 29/71) and 70 °C ([butenes]/[^{n}BuSnCl$_3$] = 36/64). By taking K = [butenes]^2/[^{n}BuSnCl$_3$] (as a measure for K = [butenes][HSnCl$_3$]/[^{n}BuSnCl$_3$]), K values in the range 37×10^{-3} to 121×10^{-3} M were obtained (50–70 °C). The thermodynamic parameters, $\Delta H^\circ = 55$ kJ mol^{-1} and $\Delta S^\circ = 125$ J mol^{-1} K^{-1}, were determined from a Van't Hoff plot and indicate that the dehydrostannylation reaction is entropically driven.

Substrate scope of the reaction

To test the scope of the reaction with respect to the organotin substrate, reactions were run with several RSnCl$_3$ compounds (R = Me, Ph, ^{n}Bu and ^{n}Oct). To this end, THF solutions of RSnCl$_3$ (0.6 M) in the presence of 1 mol% of [Pd(PPh$_3$)$_4$] were heated at 50 °C for 3 h. After a workup procedure with EtMgBr to convert the remaining RSnCl$_3$ into less reactive RSnEt$_3$, the reaction mixture was analyzed by GC using undecane as an internal standard. The results are presented in Table 1.

For R = ^{n}Bu, the results were identical to the NMR tube experiment with an observed conversion of 22%. The R = ^{n}Oct case is similar, with an observed conversion of 25% and the presence of octene isomers in the resulting gas chromatogram.[10] Both reactions required the presence of the [Pd(PPh$_3$)$_4$] catalyst, as was demonstrated in blank experiments (Table 1, entry b). For R = Me, no reaction was observed, irrespective of whether or not [Pd(PPh$_3$)$_4$] was used.

The case R = Ph is substantially different. Although the disappearance of 52% of the starting PhSnCl$_3$ was observed, it did not correspond to a dehydrostannylation reaction but rather to a disproportionation into equimolar amounts of Ph$_2$SnCl$_2$ and SnCl$_4$ which were both detected in 26% yield. This reaction did not require Pd as a catalyst, as was demonstrated in a blank experiment (Table 1, entry b). Consequently, it can be concluded that the observed disproportionation reaction is a thermal non-catalytic process.[11]

It is worthwhile to note that the dehydrostannylation of ^{n}BuSnCl$_3$ and ^{n}OctSnCl$_3$ can be made quantitative in 12 h at 50 °C when a nitrogen purge was introduced across the reaction vessel. Under these conditions, the volatile products, *i.e.* the olefin and/or HCl (from HSnCl$_3$ that is in equilibrium with HCl + SnCl$_2$)[8] can leave the system, drawing the dehydrostannylation reaction to completion.

Table 1 Conversion of the RSnCl$_3$ substrate as measured by GC (0.6 M in THF, 1 mol% of catalyst, 50 °C, reaction time: 3 h)

		Conversion of the RSnCl$_3$ substrate (%)			
Entry	Catalyst	R = Me	R = Ph	R = ^{n}Bu	R = ^{n}Oct
a	[Pd(PPh$_3$)$_4$]	0	52[a]	22 (100)[b]	25 (100)[b]
b	None	0	53[a]	0	0

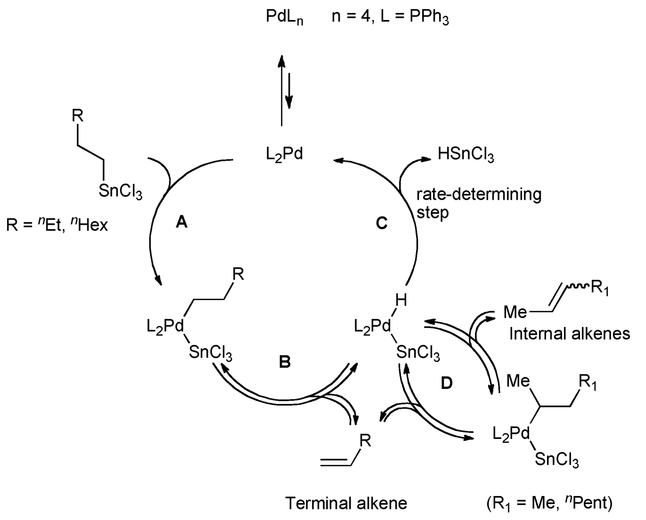
[a] Equimolar amounts of Ph$_2$SnCl$_2$ and SnCl$_4$ were observed. [b] Conversion after 12 h when a nitrogen purge was applied.

Reaction mechanism

We previously reported on the stoichiometric reaction of ^{n}BuSnCl$_3$ with [Pd(PPh$_3$)$_4$], which happens rapidly (<1 min) even at low temperature (−50 °C).[7] It was found that the Sn–C bond of ^{n}BuSnCl$_3$ was oxidatively added on the Pd(0) center (probably present as a [Pd(PPh$_3$)$_2$] fragment) and that the resulting *cis*-[Pd(^{n}Bu)(SnCl$_3$)(PPh$_3$)$_2$] species was only transient in nature. This species suffered immediate β-H elimination producing butenes and a mixture of three palladium-hydride species that were in equilibrium: *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$], *trans*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] and *trans*-[PdH(Cl)(PPh$_3$)$_2$] (the latter species was explained through deinsertion of SnCl$_2$ from the SnCl$_3^-$ ligand).[7] It was proposed that, among those Pd–H species, *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] was responsible for the isomerization of the initially formed 1-butene into 2-butenes through a 2,1-insertion/β-H elimination sequence.[7]

Based on these previous observations and the new results obtained, we propose a catalytic cycle for the dehydrostannylation of *n*-alkyltin trichlorides (Scheme 1). The cycle starts with the oxidative addition of the Sn–C bond of the substrate on a [Pd(PPh$_3$)$_2$] fragment (step A), followed by a β-H elimination from the transient *cis*-[Pd(*n*-alkyl)(SnCl$_3$)(PPh$_3$)$_2$] intermediate (step B). The main cycle is closed by the reductive elimination of HSnCl$_3$ (detected in the reaction mixture) from the *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] intermediate (step C), which also regenerates the active [Pd(PPh$_3$)$_2$] fragment. A secondary cycle is present (D), which leads to the formation of internal olefin isomers from the initially-formed terminal alkene through a 2,1-insertion/β-H elimination sequence catalyzed by *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$].

The first two steps of the cycle are rapid processes under stoichiometric conditions, even at low temperature, whereas the catalytic dehydrostannylation reaction requires heating for multiple hours. The most likely candidate for the rate limiting step is therefore the reductive elimination of the HSnCl$_3$ fragment from *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$]. Because this species itself could



Scheme 1 Proposed mechanism for the Pd-catalyzed dehydrostannylation of alkyltin trichlorides. For clarity, steps A and C are not indicated as such but should be considered as being reversible as well.

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Table 2 Results of the kinetic experiments for the determination of the activation energy and kinetic orders by the initial rate methodology

Entry	[^{n}OctSnCl$_3$]$_0$/M	[Pd(PPh$_3$)$_4$]/M	T/°C	Initial rate/M s^{-1}
a	0.60	0.0060	30	11.7×10^{-6}
b	0.60	0.0060	40	19.1×10^{-6}
c	0.60	0.0060	50	27.6×10^{-6}
d	0.60	0.0060	60	50.1×10^{-6}
e	0.60	0.0060	70	121×10^{-6}
f	0.10	0.0060	60	44.1×10^{-6}
g	0.20	0.0060	60	44.9×10^{-6}
h	0.30	0.0060	60	46.9×10^{-6}
i	1.20	0.0060	60	48.7×10^{-6}
j	0.60	0.0006	60	7.2×10^{-6}
k	0.60	0.0012	60	13.5×10^{-6}
l	0.60	0.0030	60	31.3×10^{-6}
m	0.60	0.012	60	63.1×10^{-6}
n	0.60	0.024	60	77.8×10^{-6}

not be isolated in pure form,[7] kinetic studies were undertaken to investigate this in more detail.

Kinetic studies

Kinetic measurements were performed using the initial rate methodology to further test the validity of the catalytic cycle proposed in Scheme 1. The case of ^{n}OctSnCl$_3$ over that of ^{n}BuSnCl$_3$ was preferred for these studies as the generated octene isomers are less volatile than the butene isomers. This reduced losses of alkenes during sampling, therefore improving the reproducibility of the experiments. The results of the kinetic experiments are reported in Table 2.

The reaction was found to be close to zero order in ^{n}OctSnCl$_3$ in the concentration range 0.1 to 1.2 M (Table 2; entries d, f, g, h and i; Fig. 1). A catalyst concentration-dependent study, in the range 0.0006 to 0.024 M, indicated that the reaction is first order in catalyst below 0.012 M (Table 2; entries d, j, k, l, m and n; Fig. 2). At higher loadings, the catalyst stock solution was visually turbid, which indicates an incomplete solubilization of [Pd(PPh$_3$)$_4$] and could explain the observation of a kinetic order inferior to one at these concentrations. Finally, a temperature-dependent study to determine the activation energy (E_a) allowed to estimate E_a = 50 kJ mol^{-1} at 50 °C through an Arrhenius plot (Table 2; entries a, b, c, d and e; Fig. 3).

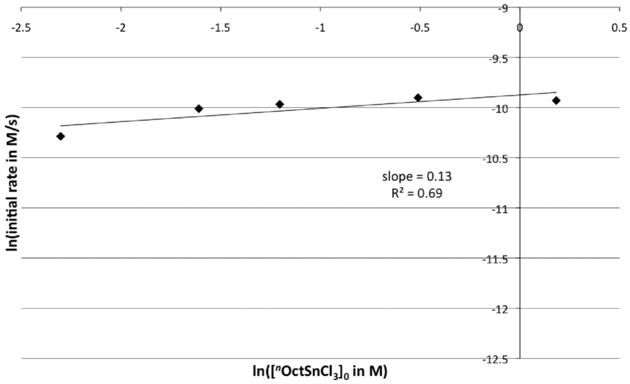

Fig. 1 Determination of the kinetic order in ^{n}OctSnCl$_3$.

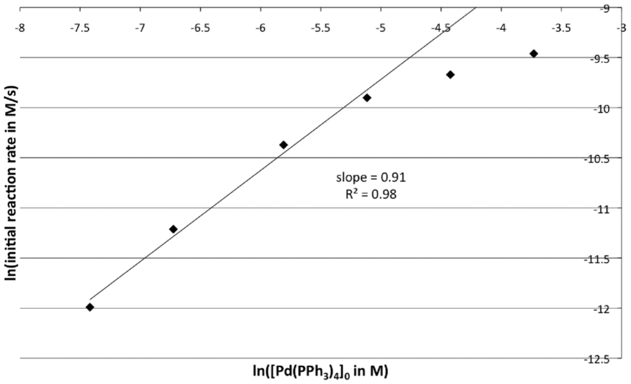

Fig. 2 Determination of the kinetic order in [Pd(PPh$_3$)$_4$].

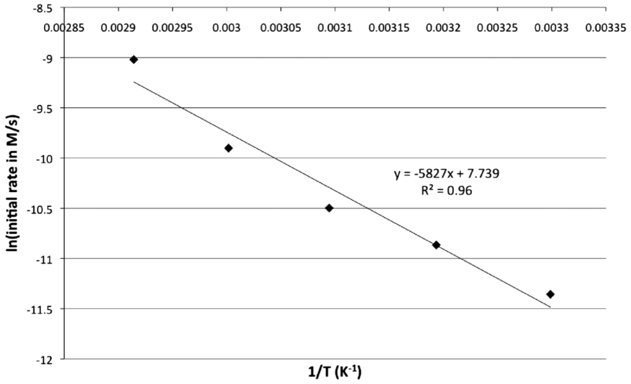

Fig. 3 Determination of the activation energy (Arrhenius plot).

Table 3 Results of the kinetic experiments for the inhibition studies ([^{n}OctSnCl$_3$], 0.20 M; [Pd(PPh$_3$)$_4$], 0.006 M; T, 60 °C)

Entry	[1-octene]$_0$ (mol%)	[2-octene]$_0$ (mol%)	[SnCl$_2$]$_0$ (mol%)	[HCl]$_0$ (mol%)	Initial rate/M s^{-1}
a	0	0	0	0	44.9×10^{-6}
b	10	0	0	0	33.4×10^{-6}
c	20	0	0	0	30.3×10^{-6}
d	50	0	0	0	15.5×10^{-6}
e	0	0	10	10	32.2×10^{-6}
f	0	0	20	20	17.7×10^{-6}
g	0	0	50	50	12.8×10^{-6}
h	0	50	0	0	42.8×10^{-6}

These three observations are in line with our proposal that the reductive elimination of a HSnCl$_3$ fragment from *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] is the rate limiting step of the dehydrostannylation process. Indeed, the kinetically observed zero order in ^{n}OctSnCl$_3$ and the first order in catalyst indicate that only a single palladium centre and no free ^{n}OctSnCl$_3$ are involved in the rate limiting step.

As the dehydrostannylation process is an equilibrium, the presence of a significant amount of the reaction products at the beginning of an experiment is expected to lower the reaction rate by favouring the backward reaction. Indeed, kinetic experiments performed in the presence of an initial concentration (10, 20 or 50 mol%) of 1-octene or HSnCl$_3$ (introduced as a HCl/SnCl$_2$ mixture) resulted in a dramatic decrease of the initial reaction rate (Table 3).

Furthermore, in the case of the experiments in which 1-octene was added, we observed that the inverse of the initial rate correlates linearly with the initial concentration of 1-octene (Fig. 4). This

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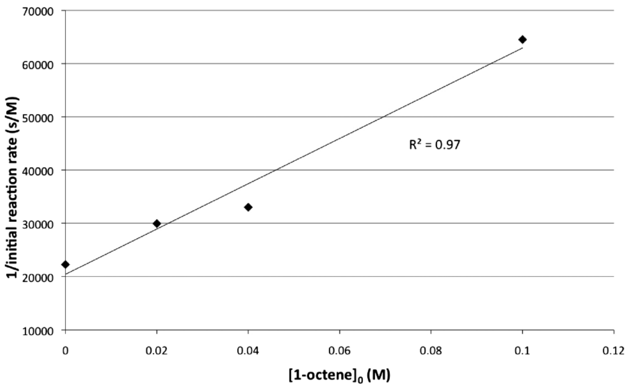

Fig. 4 Effect of a concentration of 1-octene on the initial reaction rate.

behavior suggests the existence of a pre-equilibrium between *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] + 1-octene and [Pd(Oct)(SnCl$_3$)(PPh$_3$)$_2$] species (Scheme 1).[12] Back insertion of 2-octene is apparently less important as no inhibiting effect was observed when 2-octene was added to the reaction mixture (entry h, Table 3).

Consequences for other Pd-catalyzed processes

The presently described [Pd(PPh$_3$)$_4$]-catalyzed dehydrostannylation of *n*-alkyltin trichlorides could explain the so far poor performance of β-H-containing monoalkyltins as alkylating reagents in Stille-type cross-coupling reactions. Indeed, our studies demonstrate that, within the generally accepted mechanism for Stille-type cross coupling reactions, the oxidative addition of the aryl halide substrate on Pd(0) would be in competition with the oxidative addition of the Sn–C bond of the monoalkyltin coupling partner, which results in its catalytic degradation. This may explain why only aryl iodide substrates, which react faster with Pd(0) than their bromide and chloride analogues, have been successfully coupled with monoalkyltins so far.

The limited conversions obtained in the [Pd(PPh$_3$)$_4$]-catalyzed hydrostannylation of 1-alkenes can be explained by the existence of the backward (dehydrostannylation) reaction. In this specific case, concomitant alkene isomerisation is probably playing an important role as well. Indeed, the previously described Pd-catalyzed hydrostannylation reaction required an initial excess of 1-alkene, the role of which can now be interpreted as being required to shift the equilibrium reaction towards the formation of the alkyltin trichloride product. During the reaction the excess of 1-alkene is rapidly converted into internal isomers, thereby resulting in the loss of driving force for the hydrostannylation reaction.

From a more general point of view, the dehydrostannylation of monoalkyltins could be relevant for the development of new processes. A possible application would concern the catalytic breakdown of alkyltin contaminants in waste water streams or the conversion of obsolete stocks of alkyltins back into useful inorganic tin and olefinic starting materials.[13]

Conclusions

In this article we demonstrate that monoalkyltin trichlorides containing β-H atoms suffer a dehydrostannylation reaction in the presence of catalytic amounts of [Pd(PPh$_3$)$_4$]. The reaction is an equilibrium, which lies to the side of the alkyltin starting material in closed systems at a 0.6 M concentration. Kinetic data combined with data obtained from previously reported stoichiometric studies suggest a catalytic cycle involving oxidative addition of the Sn–C bond followed by β-H elimination and rate-limiting reductive elimination of HSnCl$_3$ from a *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] species.

Experimental section

All operations were performed in dry degassed solvents (including the deuterated solvents) under a dinitrogen atmosphere using standard Schlenk techniques. THF and n-hexane were obtained from a solvent purification system MBraun SPS-800. THF-d_8 was distilled from sodium-benzophenone. All solvents were degassed by three freeze-pump-thaw cycles. MeSnCl$_3$, PhSnCl$_3$, ^{n}BuSnCl$_3$, 1-octene, anhydrous SnCl$_2$, HCl (1 M in Et$_2$O), undecane and EtMgBr (25% in THF) were purchased from Sigma-Aldrich. ^{n}OctSnCl$_3$ was obtained from ARKEMA Vlissingen B.V. [Pd(PPh$_3$)$_4$] was prepared according to literature procedures. NMR data were recorded on a Varian Oxford 300 MHz or Varian Oxford AS 400 MHz spectrometers, chemical shifts are reported relative to SiMe$_4$ (^{1}H, ^{13}C) or SnMe$_4$ (1 M in benzene, ^{119}Sn). Coupling constants are expressed in Hertz and coupling patterns are described using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Gas chromatograms were recorded on a Perkin Elmer Clarus 500 Gas Chromatograph with a Alltech ECONO-CAP EC-5 column (length 30 m, diameter 0.32 mm, packing 0.25 μm).

^{n}OctSnCl$_3$

^{1}H NMR (CDCl$_3$, 25 °C, 400 MHz): δ 2.39 (t, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, $J_{H\text{-}Sn}$ = 83.0 Hz), 1.93 (q, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, $J_{H\text{-}Sn}$ = 208.7 Hz), 1.48 (q, 2H, $^3J_{H\text{-}H}$ = 7.2 Hz), 1.41–1.22 (m, 8H), 0.89 (t, 3H, $^3J_{H\text{-}H}$ = 6.9 Hz). ^{13}C NMR (CDCl$_3$, 25 °C, 101 MHz): δ 33.5 (s, $^1J_{^{13}C\text{-}^{117}Sn}$ = 622, $^1J_{^{13}C\text{-}^{119}Sn}$ = 651 Hz), 32.7 (s, $^2J_{^{13}C\text{-}^{117/119}Sn}$ = 109 Hz, the ^{117}Sn and ^{119}Sn satellites were not resolved), 31.9 (s), 29.1 (s), 29.0 (s), 25.1 (s, $^3J_{^{13}C\text{-}^{117/119}Sn}$ = 61 Hz, the ^{117}Sn and ^{119}Sn satellites were not resolved), 22.8 (s), 14.3 (s).

Dehydrostannylation of ^{n}BuSnCl$_3$ in NMR tubes

[Pd(PPh$_3$)$_4$] (3.5 mg, 0.003 mmol) and ^{n}BuSnCl$_3$ (50 μL, 84.6 mg, 0.30 mmol) were dissolved in THF-d_8 (0.5 mL) in an NMR tube. The tube was sealed to prevent butenes leakage. The relative concentrations of ^{n}BuSnCl$_3$ and butene isomers were monitored by ^{1}H NMR by observing the integrals of the olefinic protons of butene isomers (1-butene: δ 5.90 (m, 1H), 5.02 (m, 1H), 4.93 (m, 1H); 2-butenes (*Z* and *E* mixture): δ 5.46 (m, 2H)) and of the ^{n}Pr-C*H*$_2$-SnCl$_3$ signal (δ 2.39). For the determination of the temperature-dependance of the concentrations at equilibrium (Van't Hoff plot), the same tube was heated successively at 50, 60 and 70 °C and then back to 60 and 50 °C. For each temperature, the concentrations were measured after a 2 h equilibration time.

Dehydrostannylation of RSnCl$_3$ (R = Ph, Me, ^{n}Bu, ^{n}Oct) in Schlenk tubes

Substrate screening experiments. RSnCl$_3$ (12.0 mmol; R = Me: 2.88 g; R = Ph: 1.97 mL; R = ^{n}Bu: 2.00 mL; R = ^{n}Oct: 4.06 g)

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was dissolved in THF (18.0 mL) together with undecane (internal standard, 5.00 mmol, 1.05 mL) and heated to 50 °C. A t = 0 min, the catalyst was introduced as 1.0 mL of a stock solution in THF ([Pd(PPh$_3$)$_4$]: 1.0 mol%, 1.39 g in 10 mL; blank experiments: 1.0 mL of THF) and the mixture was stirred at 50 °C for 3 h. After this time, a sample of the reaction mixture (2 mL) was evaporated to dryness under vacuum. *n*-Hexane (20 mL) was added under vigorous stirring resulting in a red precipitate which contained the palladium catalyst and HSnCl$_3$(THF)$_n$. EtMgBr (25% in THF, 2.0 mL, 3.70 mmol) was slowly added and the mixture stirred for 10 min (to transform the remaining RSnCl$_3$ into RSnEt$_3$ for GC analysis). The excess of Grignard reagent was then hydrolyzed by diluted aqueous H$_2$SO$_4$ (5%, 10 mL). A sample of the organic phase was passed through a plug of silica, diluted 20 times and analyzed by GC.

Kinetic experiments with ^{n}OctSnCl$_3$. The desired amount of ^{n}OctSnCl$_3$ was dissolved in THF (36.0 mL) together with undecane as internal standard (2.11 mL, 10.0 mmol) and an eventual additive. The reaction mixture was then heated to the desired temperature. A t = 0 min the desired amount of [Pd(PPh$_3$)$_4$] was introduced as 2.0 mL of a stock solution in THF and the system was stirred at the desired temperature. At t = 0, 15, 30, 60, 120 and 240 min a sample of the reaction mixture (2.0 mL) was poured in hexane (20 mL) and treated under vigorous stirring with three equivalents of EtMgBr for 10 min (to transform the remaining ^{n}OctSnCl$_3$ into ^{n}OctSnEt$_3$ for GC analysis). The excess of Grignard reagent was hydrolyzed by dilute aqueous H$_2$SO$_4$ (5%, 10 mL). A sample of the organic phase was passed through a plug of silica, diluted 20 times and analyzed by GC. The derived initial rate data are listed in Table 2 and Table 3. *As a function of the temperature*: ^{n}OctSnCl$_3$ (8.12 g, 24.0 mmol); [Pd(PPh$_3$)$_4$] (stock solution of 1.39 g in 10 mL of THF); EtMgBr (25% in THF, 2.0 mL, 3.7 mmol); temperatures of 30, 40, 50, 60 and 70 °C. *As a function of the substrate concentration*: [Pd(PPh$_3$)$_4$] (stock solution of 1.39 g in 10 mL THF); temperature 60 °C; ^{n}OctSnCl$_3$ (1.35 g, 4.00 mmol; 2.71 g, 8.00 mmol; 4.06 g, 12.00 mmol, 8.10 g, 24.0 mmol and 16.2 g, 48.0 mmol); EtMgBr (25% in THF; 0.33 mL, 0.60 mmol; 0.99 mL, 1.8 mmol; 2.0 mL, 3.7 mmol; 4.0 mL, 7.3 mmol). *As a function of the catalyst loading*: ^{n}OctSnCl$_3$ (8.12 g, 24.0 mmol); temperature 60 °C; EtMgBr (25% in THF; 2.0 mL, 3.7 mmol). [Pd(PPh$_3$)$_4$] (stock solution in 10 mL THF; 139 mg, 0.024 mmol, 0.1 mol%; 278 mg, 0.048 mmol, 0.2 mol%; 695 mg, 0.12 mmol, 0.5 mol%; 1.39 g, 0.24 mmol, 1 mol%; 2.78 g, 0.48 mmol, 2 mol%; 5.65 g, 0.96 mmol, 4 mol%). *With an initial concentration of 1-octene*: temperature 60 °C; [Pd(PPh$_3$)$_4$] (stock solution of 1.39 g in 10 mL THF); ^{n}OctSnCl$_3$ (2.70 g, 8.00 mmol); EtMgBr (25% in THF; 0.66 mL, 1.20 mmol); 1-octene (0.12 mL, 0.80 mmol, 10 mol%; 0.25 mL, 1.6 mmol, 20 mol%; 0.50 mL, 4.0 mmol, 50 mol%). *With an initial concentration of HSnCl$_3$*: temperature 60 °C; [Pd(PPh$_3$)$_4$] (stock solution of 1.39 g in 10 mL THF); ^{n}OctSnCl$_3$ (2.70 g, 8.00 mmol); EtMgBr (25% in THF, 0.66 mL, 1.20 mmol); HCl (1 M in Et$_2$O)/SnCl$_2$ (0.80 mL/151.7 mg, 0.80 mmol, 10 mol%; 1.60 mL/303.4 mg, 1.6 mmol, 20 mol%; 4.0 mL/758.5 mg, 4.0 mmol, 50 mol%). *With an initial concentration of 2-octene (cis-/trans- mixture)*: temperature 60 °C; [Pd(PPh$_3$)$_4$] (stock solution of 1.39 g in 10 mL THF); ^{n}OctSnCl$_3$ (2.70 g, 8.00 mmol); EtMgBr (25% in THF; 0.66 mL, 1.20 mmol); 1-octene (0.50 mL, 4.0 mmol, 50 mol%).

GC method for analysis of the reaction mixture. Injection temperature: 270 °C, Detector temperature: 270 °C. Oven temperature: ramp of 20 °C min^{-1} from 50 °C to 280 °C, then hold at 280 °C for 4 min. Detector type: FID. Retention times: 2.41 to 2.54 min (octene isomers), 3.38 min (MeSnEt$_3$), 4.45 min (undecane), 7.01 min (PhSnEt$_3$), 9.41 min (Ph$_2$SnEt$_2$), 4.10 min (SnEt$_4$), 5.28 min (^{n}BuSnEt$_3$) and 7.77 min (^{n}OctSnEt$_3$). Conversions were calculated by comparing the area of the peak corresponding to RSnEt$_3$ with its value at $t = 0$ min using undecane as internal standard.

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10 As for the ^{n}BuSnCl$_3$ case, the dehydrostannylation of ^{n}OctSnCl$_3$ initially leads mainly to the formation of the terminal olefin, in this case 1-octene. But, under the conditions employed, the terminal olefin is concomitantly isomerized into its internal isomers resulting in >95% of internal isomers after 3 h of reaction.

11 For a general discussion of thermal disproportionation of organotins see: S. H. L. Thoonen, B.-J. Deelman and G. van Koten, *J. Organomet. Chem.*, 2004, **689**, 2145 and references therein.

12 Without any initial concentration of 1-octene, SnCl$_2$ or HCl, the rate law is written $v = k[\mathrm{PdH(SnCl_3)(PPh_3)_2}]$ with $[\mathrm{PdH(SnCl_3)(PPh_3)_2}] = [\mathrm{Pd}]_{\mathrm{tot}}$. For example, in the presence of a pre-equilibrium K between [PdH(SnCl$_3$)(PPh$_3$)$_2$], octene and [Pd(Oct)(SnCl$_3$)(PPh$_3$)$_2$], the concentration of the key intermediate can be written as $[\mathrm{PdH(SnCl_3)(PPh_3)}] = [\mathrm{Pd}]_{\mathrm{tot}}/(1 + K[\mathrm{octene}])$. Thus, $1/v = A + B[\mathrm{octene}]$ ($A = 1/(k[\mathrm{Pd}]_{\mathrm{tot}})$; $B = KA$).

13 For a review on the interest of degrading alkyltin pollutants see *e.g.* R. De Carvalho Oliveira and R. E. Santelli, *Talanta*, 2010, **82**, 9.