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Oxidative Addition of Sn−C Bonds on Palladium(0): Identification of Palladium−Stannyl Species and a Facile Synthetic Route to Diphosphinostannylene−Palladium Complexes

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Methyl-, phenyl-, and *n*-butyltin trichloride $RSnCl_3$ (R = Me, Ph, ^{n}Bu) react selectivily with palladium(0)−phosphine precursors through the unprecedented oxidative addition of the Sn−C bond. With [Pd(2-$PyPPh_2$)$_3$] (2-$PyPPh_2$ = 2-pyridyldiphenylphoshine), the reaction cleanly leads to stable cationic dichlorostannylene palladium complexes of the general formula *trans*-[PdR($SnCl_2$(2-$PyPPh_2$)$_2$)][X] (X = Cl, R = Me ([**5**]Cl), R = Ph ([**6**]Cl), R = ^{n}Bu ([**11**]Cl); X = $RSnCl_4$, R = Me ([**5**][$MeSnCl_4$]), R = Ph ([**6**][$PhSnCl_4$]), R = ^{n}Bu ([**11**][^{n}$BuSnCl_4$])). The $SnCl_2$(2-$PyPPh_2$)$_2$ fragment, formed by intramolecular coordination of the pyridyl groups to the dichlorostannylene moiety, can be considered as a self-assembled pincer-type ligand with a remarkable ability to suppress β-H elimination in its Pd−alkyl derivatives: [**11**][^{n}$BuSnCl_4$], containing a Pd−^{n}Bu moiety, was found to be stable up to 70 °C. Oxidative addition of $SnCl_4$ on [Pd(2-$PyPPh_2$)$_3$] resulted in *trans*-[PdCl($SnCl_2$(2-$PyPPh_2$)$_2$)]Cl ([**7**]Cl) and *trans*-[PdCl($SnCl_3$(2-$PyPPh_2$)$_2$)] (**8**). The molecular structure of **8** was determined by single-crystal X-ray crystallography, indicating that the Sn atom of the trichlorostannyl function has an octahedral coordination geometry. In contrast, oxidative addition of the Sn−C bond of $RSnCl_3$ on [Pd(PPh_3)$_4$] resulted in palladium trichlorostannyl complexes that were not stable toward *cis*−*trans* isomerization, (partial) elimination of $SnCl_2$ (R = Me, Ph), or β-H elimination (R = ^{n}Bu). The resulting mixtures of palladium alkyl and palladium hydride species were analyzed by multinuclear NMR, resulting in the identification of novel *cis*-[PdMe($SnCl_3$)(PPh_3)$_2$] (*cis*-**4**), *trans*-[PdMe($SnCl_3$)(PPh_3)$_2$] (*trans*-**4**), and *cis*-[PdH($SnCl_3$)(PPh_3)$_2$] (*cis*-**10**) along with previously observed *trans*-[PdPh(Cl)(PPh_3)$_2$] (**1**), *trans*-[PdMe(Cl)(PPh_3)$_2$] (**3**), *trans*-[PdH($SnCl_3$)(PPh_3)$_2$] (*trans*-**10**), and *trans*-[PdH(Cl)(PPh_3)$_2$] (**9**).

Introduction

The reactivity of organotin chloride reagents on platinum(0)−phosphine precursors has been the subject of many studies in the last decades.[1] In the case of monoorganotin trichloride $RSnCl_3$ (R = Me, Ph), the reaction was found to occur exclusively through oxidative addition of the Sn−Cl bond, resulting in bisphosphine(monoorganodichlorostannyl)-platinum chloride complexes [PtCl(Sn(R)Cl_2)(phosphine)$_2$].[1a] It appears that this reactivity, well-described for platinum(0), has never been extended to palladium(0) precursors despite the interest in organotin(IV) derivatives in some important palladium-catalyzed transformations.[2]

We recently reported that the presence of 2-pyridyldiphenylphosphine ligands (2-$PyPPh_2$) affects the coordination of tin-containing ligands in the vicinity of a group 10 metal (eq 1).[3] It was found that the reaction of $SnCl_2$ with [M(X)(Cl)(2-$PyPPh_2$)$_2$] precursors (X = Cl, Me) does not result in neutral trichlorostannyl complexes but in cationic complexes [M(X)-($SnCl_2$(2-$PyPPh_2$)$_2$)]$^+$, in which the dichlorostannylene moiety

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(1) (a) Butler, G.; Eaborn, C.; Pidcock, A. *J. Organomet. Chem.* **1979**, *181*, 47. (b) Al-Allaf, T. A. K. *Asian J. Chem.* **1999**, *11*, 348, and references therein. (c) Al-Allaf, T. A. K. *J. Organomet. Chem.* **1999**, *590*, *25* (phosphines are introduced after oxidative addition on [Pt(COD)$_2$)]).

(2) Well-known examples are hydrostannylation and Stille-type cross-coupling. In the latter, the reaction of an activated alkynyltrialkyltin with a palladium(0)−iminophosphine precursor has been demonstrated to occur through oxidative addition of the Sn−alkynyl bond, which was claimed to be the first case of a Sn−C bond undergoing oxidative addition on palladium. Theoretical work has also been published on this system. (a) Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177. (b) Shirakawa, E.; Hiyama, T. *J. Organomet. Chem.* **1999**, *576*, 169. (c) Matsubara, T. *Organometallics* **2003**, *22*, 4286. (d) Matsubara, T. *Organometallics* **2003**, *22*, 4297.

(3) (a) Cabon, Y.; Kleijn, H.; Siegler, M. A.; Spek, A. L.; Klein Gebbink, R. J. M.; Deelman, B.-J. *Dalton Trans.* **2010**, *39*, 2423. (b) These results were recently communicated at The 17th International Symposium on Homogeneous Catalysis (ISHC-17), July 2−9, 2010, Poznan, Poland.

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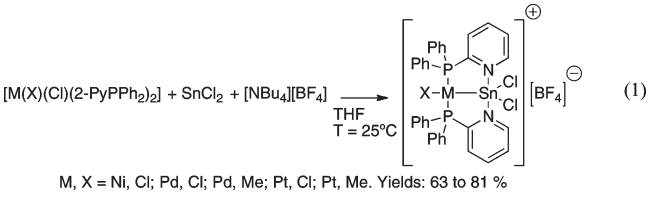
is stabilized by intramolecular coordination of the pyridyl groups to the tin center and exerting a strong *trans*-influence.

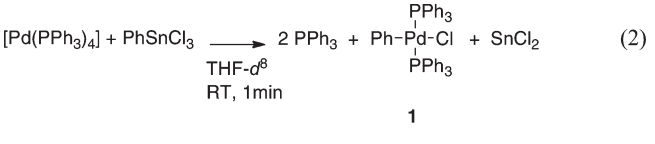


(1)

Because the 2-$PyPPh_2$ ligand appears to stabilize otherwise inaccessible species, we decided to study the reactivity of [Pd(2-$PyPPh_2$)$_3$] toward $RSnCl_3$ (R = Ph, Me, and ^{n}Bu) and to compare it to the reactivity of the more common [$Pd(PPh_3)_4$] precursor.[3b]

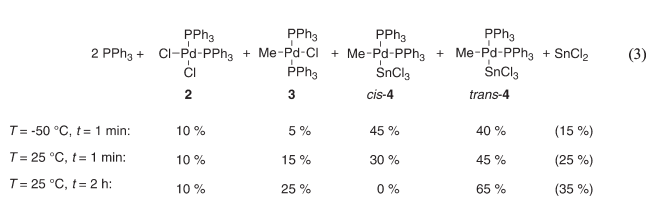
Results

Reaction of $RSnCl_3$ (R = Me, Ph) with [$Pd(PPh_3)_4$] and [Pd(2-$PyPPh_2$)$_3$]. The equimolar reaction of [$Pd(PPh_3)_4$] with $PhSnCl_3$ in THF-d_8 in an NMR tube at room temperature (eq 2) led within 1 min to the formation of free PPh_3 (2 equiv), *trans*-[PdPh(Cl)(PPh_3)$_2$] (**1**, 1 equiv), and $SnCl_2$ (detected by ^{119}Sn NMR, 1 equiv). The NMR data were assigned to **1** by comparison with literature values.[4] High-resolution mass spectroscopy analysis of the reaction mixture diluted with MeCN showed the expected [PdPh(PPh_3)$_2$]$^+$ and [PdPh(MeCN)(PPh_3)$_2$]$^+$ cations along with a weak signal for [PdPh(PPh_3)(PPh_3O)]$^+$ that was most probably due to oxidation during sample preparation.



(2)

In a similar reaction where $PhSnCl_3$ was replaced by $MeSnCl_3$ (eq 3), the resulting product mixture after 1 min consisted of the known compounds PPh_3 (2 equiv), *cis*-[$PdCl_2(PPh_3)_2$] (**2**, 10%),[5] and *trans*-[PdMe(Cl)(PPh_3)$_2$] (**3**, 15%) along with the new compounds *trans*- and *cis*-[PdMe($SnCl_3$)(PPh_3)$_2$] (*trans*-**4** and *cis*-**4**, 45% and 30%, respectively) and $SnCl_2$ (25%, according to the stoichiometry). This ratio evolved after 2 h at room temperature to PPh_3 (2 equiv), **2** (10%), **3** (25%), *trans*-**4** (65%), and $SnCl_2$ (35%). An experiment at −50 °C afforded a similar product mixture within a minute after addition of $MeSnCl_3$ with a slightly higher *cis*-**4**/*trans*-**4** ratio (eq 3). The NMR spectra obtained gave no indication of any intermediates other than **4**.



(3)

All compounds were identified on the basis of their NMR data at −50 °C (Table 1). The assignment of the resonances

Table 1. ^{31}P and ^{1}H NMR Data (T = −50 °C, THF-d_8) of the Products Resulting from the Reaction of $MeSnCl_3$ with [$Pd(PPh_3)_4$]

	^{31}P NMR			^{1}H NMR (Me group)		
compound	δ	$^2J_{P-P}$ (Hz)	$^2J_{P-Sn}$ (Hz)	δ	$^3J_{H-P}$ (Hz)	$^3J_{H-Sn}$ (Hz)
PPh_3	−5.4					
2	+24.4					
3	+31.2			−0.16	11.5	
cis-**4**	+37.2	36	271	+0.29	[a]	42.6
	+26.7	36	[a]			
trans-**4**	+27.9		96	+1.00	[a]	48.0

[a] Coupling constant not detected.

for the known compounds PPh_3, **2**, and **3** was done by comparison with literature data.[6] The remaining signals were attributed to the new products *cis*-**4** and *trans*-**4**. This attribution was consistent with the presence of a $^2J_{P-P}$ coupling constant for the *cis* compound and tin satellites in both the ^{31}P and ^{1}H NMR spectra for both compounds. Moreover, mass spectroscopy of the reaction mixture in the presence of acetonitrile exhibited two major signals at m/z = 645.1108 and 686.1337, corresponding to the fragments [PdMe(PPh_3)$_2$]$^+$ and [PdMe(PPh_3)$_2$(MeCN)]$^+$. This observation is consistent with the assignment to complexes **4**, as the $SnCl_3^-$ ligand has a well-established labile character[7] and can easily dissociate from the complexes during the ionization process. No attempts were made to separate and isolate the products.

The equimolar reaction of [Pd(2-$PyPPh_2$)$_3$] with $MeSnCl_3$ in THF-d_8 in an NMR tube at room temperature cleanly led within 1 min to the formation of free 2-$PyPPh_2$ (1 equiv) and the ionic dichlorostannylene complex *trans*-[PdMe($SnCl_2$(2-$PyPPh_2$)$_2$)]Cl ([**5**]Cl, 1 equiv, eq 4), which was indentified on the basis of the stoichiometry of the reaction and by comparison of its ^{1}H and ^{31}P NMR data with the previously described analogue [**5**][BF_4].[3a] When the reaction was run with 2 equiv of $MeSnCl_3$, [**5**][$MeSnCl_4$] was formed, as indicated by the detection of the [$MeSnCl_4$]$^-$ anion by ^{1}H and ^{119}Sn NMR (eq 4).[8] [**5**][$MeSnCl_4$] was isolated in good yield on a preparative scale (67%) and characterized by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, and ^{119}Sn) and high-resolution mass spectroscopy. The reaction of [Pd(2-$PyPPh_2$)$_3$] with 2 equiv of $PhSnCl_3$ in THF-d_8 in an NMR tube at room temperature also cleanly led within 1 min to the formation of free 2-$PyPPh_2$ (1 equiv) and *trans*-[PdPh($SnCl_2$(2-$PyPPh_2$)$_2$)][$PhSnCl_4$] ([**6**][$PhSnCl_4$], 1 equiv, eq 4). On a preparative scale, complex [**6**][$PhSnCl_4$] was isolated in 72% yield and characterized by multinuclear NMR (^{1}H, ^{13}C, ^{31}P, and ^{119}Sn) and high-resolution mass spectroscopy. The structure of [**6**][$PhSnCl_4$] was attributed to be analogous to [**5**][$MeSnCl_4$] and [**5**][BF_4] on the basis of similar analytical observations (downfield shifted ^{31}P NMR

(4) Herrmann, W. A.; Brossmer, C.; Priermeier, T.; Ofele, K. *J. Organomet. Chem.* **1994**, *481*, 97.

(5) The small quantities of *cis*-[$PdCl_2(PPh_3)_2$] detected as a minor signal at δ 24.4 in the ^{31}P NMR spectrum and m/z = 665.0547 ([$PdCl(PPh_3)_2$]$^+$) in the HRMS spectrum for the experiments using [$Pd(PPh_3)_4$] in combination with $MeSnCl_3$ or ^{n}$BuSnCl_3$ are most likely due to some protonolysis of the generated Pd−R bond (R = Me, H) by small quantities of HCl that are generated from hydrolysis of the starting alkyltin trichloride reagent by moisture.

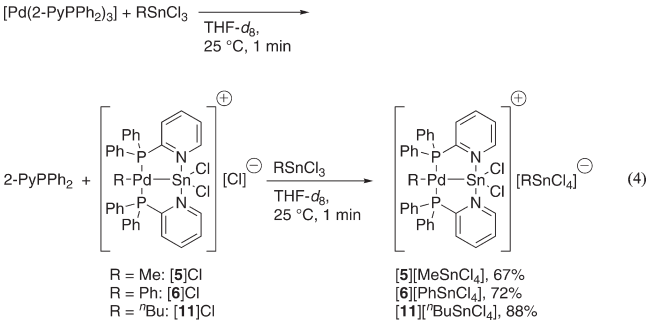
(6) Knight, L. K.; Freixa, Z.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Organometallics* **2006**, *25*, 954.

(7) Fernandez, D.; Garcia-Seijo, M. I.; Kegl, T.; Petocz, G.; Kollar, L.; Garcia-Fernandez, M. E. *Inorg. Chem.* **2002**, *41*, 4435.

(8) Organotin trichlorides can easily act as chloride anion acceptors to form organotin tetrachloride anions. Dakternieks, D.; Zhu, H. *Organometallics* **1992**, *11*, 3820.

Table 2. Comparison of ^{31}P NMR and High-Resolution MS Data for the Products [PdR(SnCl$_2$(2-PyPPh$_2$)$_2$)][RSnCl$_4$] (R = Me, Ph, and ^{n}Bu)

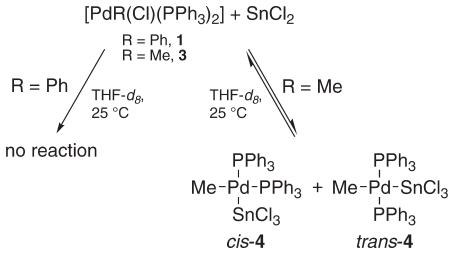
analytical method	[**5**][MeSnCl$_4$] (R = Me)	[**6**][PhSnCl$_4$] (R = Ph)	[**11**][^{n}BuSnCl$_4$] (R = ^{n}Bu)
^{31}P NMR (δ)	63.6	64.3	62.5
ESI-HRMS (m/z, (calcd for [PdR(SnCl$_2$(2-PyPPh$_2$)$_2$)]$^+$))	836.9351 (836.9391)	898.9539 (898.9547)	878.9868 (878.9860)



(4)

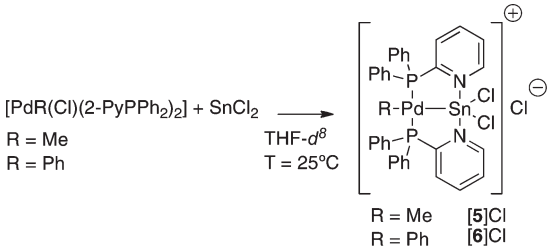
signal and detection of only the [PdR(SnCl$_2$(2-PyPPh$_2$)$_2$)]$^+$ cation in mass spectroscopy, Table 2).

To verify the nature of the products obtained from the previous experiments, the chloride precursors *trans*-[PdR(Cl)(PPh$_2$Ar)$_2$] (Ar = Ph, R = Me (**3**), Ph (**1**); Ar = 2-Py, R = Ph)[4,6] were reacted with SnCl$_2$.[1a] For the case Ar = Ph, NMR analysis of the equimolar reaction of SnCl$_2$ with **1** in THF-d_8 indicated that it does not react to form a trichlorostannyl species [PdPh(SnCl$_3$)(PPh$_3$)$_2$] (eq 5 left). However, the equimolar reaction of SnCl$_2$ with **3** exhibited the formation of the same mixture of **3**, *cis*-**4**, and *trans*-**4** complexes as the one found in the reaction of [Pd(PPh$_3$)$_4$] with MeSnCl$_3$ (eq 5 right, cf. eq 3), except for the presence of free PPh$_3$ and the impurity of **2**.[5]



(5)

For the case Ar = 2-Py, we already reported that the equimolar reaction of SnCl$_2$ with *trans*-[PdMe(Cl)(2-PyPPh$_2$)$_2$] led to the formation of the ionic complex [**5**]Cl (eq 6, R = Me).[3a] In a similar fashion, we determined that the equimolar reaction of SnCl$_2$ with *trans*-[PdPh(Cl)(2-PyPPh$_2$)$_2$] in THF-d_8 instantaneously led to the ionic complex [**6**]Cl (eq 6), confirming that [**6**]Cl is also the product of the reaction of [Pd(2-PyPPh$_2$)$_3$] with PhSnCl$_3$.



(6)

Although NMR analysis of a solution resulting from the equimolar reaction of [Pd(2-PyPPh$_2$)$_3$] with SnCl$_4$ in THF-d_8

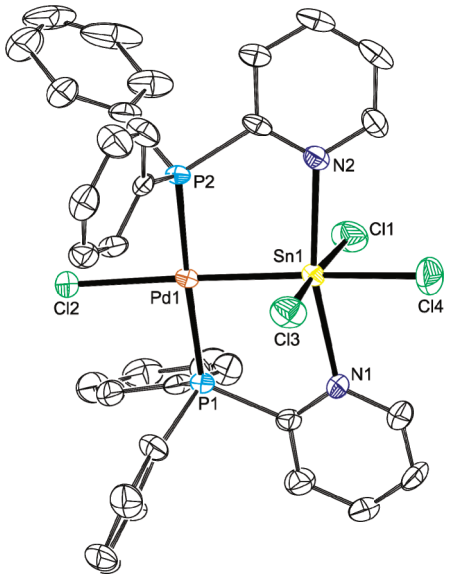
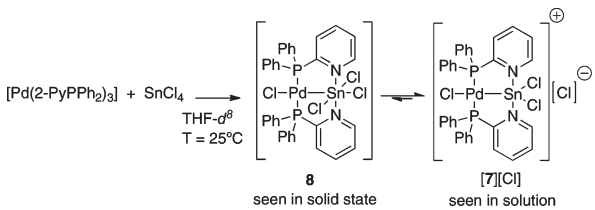


Figure 1. Displacement ellipsoid plot (50% probability level) of complex **8** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−Cl2 2.3987(14), Pd1−P1 2.2815(14), Pd1−P2 2.2966(14), Pd1−Sn1 2.5201(6), Sn1−Cl1 2.4819(17), Sn1−Cl3 2.5175(16), Sn1−Cl4 2.3903(16), Sn1−N1 2.368(4), Sn1−N2 2.378(4), Cl2−Pd1−P1 90.37(5), P1−Pd1−Sn1 88.51(4), Sn1−Pd1−P2 88.14(4), P2−Pd1−Cl2 92.91(5), Cl1−Sn1−Pd1 96.70(4), Pd1−Sn1−Cl3 88.82(4), Cl3−Sn1−Cl4 84.53(6), Cl4−Sn1−Cl1 89.95(6), Cl1−Sn1−Cl3 174.43(6), N1−Sn1−N2 166.05(14).

(eq 7) showed the quatitative formation of the previously described cationic dichlorostannylene complex *trans*-[PdCl(SnCl$_2$(2-PyPPh$_2$)$_2$)]Cl ([**7**]Cl),[3a] the crystals obtained from the reaction mixture correspond to *trans*-[PdCl(SnCl$_3$(2-PyPPh$_2$)$_2$)] (**8**) according to a single-crystal X-ray diffraction analysis. The molecular structure of **8** (Figure 1) exhibits a square-planar palladium(II) complex (sum of the angles around Pd1 is 359.93(9)°) bearing a SnCl$_3^-$ ligand. However, the trichlorostannyl ligand does not adopt the usual tetrahedral geometry but is octahedral instead with intramolecular coordination of both pyridyl groups of the phosphine ligands to the Sn center. This octahedral geometry is slightly distorted, as the Pd1, Cl1, Cl3, and Cl4 atoms form a plane (sum of the angles around Sn1 is 360.00(10)°), but the N1−Sn1−N2 angle is only 166.05(14)°.



(7)

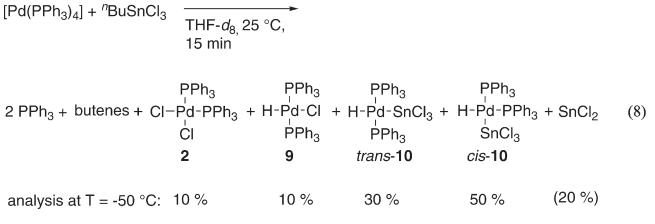
Reaction of ^{n}BuSnCl$_3$ with [Pd(PPh$_3$)$_4$] and [Pd(2-PyPPh$_2$)$_3$]. The equimolar reaction of [Pd(PPh$_3$)$_4$] with ^{n}BuSnCl$_3$ in THF-d_8

Table 3. ^{31}P and ^{1}H NMR Data ($T = -50$ °C, THF-d_8) of the Products Resulting from the Reaction of ^{n}BuSnCl$_3$ with [Pd(PPh$_3$)$_4$] after 15 min of Reaction at Room Temperature

	^{31}P NMR			^{1}H NMR (Pd−H)	
compound	δ	$^2J_{P-P}$ (Hz)	$^2J_{P-Sn}$ (Hz)	δ	relative amount of each species
PPh_3	−5.4				2 equiv
2	24.4				10%
9	30.8			−12.6	10%
trans-**10**	28.3		101	−7.0	30%
cis-**10**	38.3	36	211, 287	−7.0	50%
	26.6	36	[a]		

[a] Coupling constant not detected.

in an NMR tube at room temperature led to several products (eq 8). ^{1}H NMR analysis of the reaction mixture after 15 min showed the quantitative transformation of ^{n}BuSnCl$_3$ into butene isomers (both internal and terminal) and a palladium hydride function (^{1}H NMR δ −9.4 ppm, br, line width at half-height (lwhh) = 297 Hz at 25 °C). The ^{31}P NMR spectrum of the reaction mixture displayed a broad signal at room temperature (δ 9 ppm, lwhh = 470 Hz), indicating a fast exchange between the free phosphine and phosphine−palladium species. Compound **2** was also detected as an impurity (10%).[5] At −50 °C, the hydride signal is split into two broad signals at δ −7.0 and −12.6 ppm (9:1 ratio, Table 3); lowering the temperature to −90 °C did not significantly improve the line width of the signals, but the relative ratio of the hydride resonances evolved to 26:1. The broad ^{31}P NMR signal also decoalesced at −50 °C to give six signals, which were assigned (Table 3) to the known compounds PPh_3 (2 equiv), **2** (10%), *trans*-[PdH(Cl)(PPh$_3$)$_2$] (**9**, 10%),[9] and *trans*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] (*trans*-**10**, 30%)[9,10] as well as to the new complex *cis*-[PdH(SnCl$_3$)(PPh$_3$)$_2$] (*cis*-**10**, 50%). Involvement of an ionic [PdH(PPh$_3$)$_3$][SnCl$_3$] complex, resulting from the interaction of [PdH(SnCl$_3$)(PPh$_3$)$_2$] complexes **10** with free PPh_3, cannot be completely excluded, as such [PdH(PPh$_3$)$_3$]$^+$ compounds have been reported to display hydride signals in the same region (δ −7.0 ppm)[11] and as the ^{31}P NMR signal measured for free PPh_3 remained broad at −50 °C (δ −5.4 ppm, lwhh = 271 Hz). Determination of the activation parameters of the underlying processes involved proved impossible due to the simultaneous occurrence of at least two, if not three, dynamic processes (*cis*/*trans* isomerization, $SnCl_2$ insertion−elimination, and potentially $SnCl_3^-$-PPh_3 ligand exchange; see Discussion). The solution containing the three different palladium hydride species did not show any sign of decomposition in the ^{1}H NMR (two days at room temperature), but attempts to isolate a product by removing the solvent under vacuum or precipitating it with a different solvent resulted in the loss of the palladium hydride functionality (no longer detected in the ^{1}H NMR spectrum), probably because of the loss of the stabilizing excess of PPh_3.



In constrast to [Pd(PPh$_3$)$_4$], the equimolar reaction of ^{n}BuSnCl$_3$ with [Pd(2-PyPPh$_2$)$_3$] in THF-d_8 in an NMR tube at room temperature cleanly led within 1 min to the formation of free 2-PyPPh$_2$ (1 equiv) and an ionic palladium complex that was identified as *trans*-[Pd^{n}Bu(SnCl$_2$(2-PyPPh$_2$)$_2$)]Cl ([**11**]Cl, 1 equiv, eq 4) on the basis of multinuclear NMR and mass spectroscopic analysis (Table 2). Once again, the chloride counteranion was not formally identified, but performing the reaction with 2 equiv of ^{n}BuSnCl$_3$ led to [**11**][^{n}BuSnCl$_4$], the anion of which could be directly observed by ^{1}H and ^{119}Sn NMR (eq 4).[8] Remarkably, [**11**][^{n}BuSnCl$_4$] was stable enough to allow its isolation in 88% yield and its complete characterization (^{1}H, ^{13}C, ^{31}P, and ^{119}Sn NMR, high-resolution MS). Despite the presence of β-H atoms in the Pd−^{n}Bu moiety, no decomposition of [**11**][^{n}BuSnCl$_4$] was detected by NMR in THF-d_8 at 70 °C for 6 h.

Discussion

Two types of equilibria have to be considered when trying to explain the experimental results obtained for the reactions of RSnCl$_3$ (R = Me, Ph, and ^{n}Bu) on Pd(0)−phosphine precursors. The first equilibrium concerns the *cis*/*trans* isomerization of [MR(SnCl$_3$)(phosphine)$_2$] complexes. For platinum, Scrivanti showed that [PtEt(SnCl$_3$)(PPh$_3$)$_2$], obtained by insertion of ethene into *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$], exists in solution as both its *cis*- and *trans* isomers. *cis*-[PtEt(SnCl$_3$)-(PPh$_3$)$_2$] was found to be the kinetic product, which evolved to the thermodynamically more stable *trans*-[PtEt(SnCl$_3$)-(PPh$_3$)$_2$].[12a] The second equilibrium concerns the (reversible) deinsertion of $SnCl_2$ from a M−SnCl$_3$ bond to form the corresponding M−Cl species. It is known to occur for group 10 metal complexes, probably involving five-coordinate intermediates, and has been proven to be more facile for palladium than for platinum centers.[13] With this in mind, the results of the reactions of RSnCl$_3$ (R = Ph, Me, ^{n}Bu) can be fully rationalized (Scheme 1). The results suggest that, in every case, oxidative addition of the Sn−C bond of the RSnCl$_3$ reagent initially leads in a rapid process to the key intermediate *cis*-[PdR(SnCl$_3$)(PArPh$_2$)$_2$] (R = Me, Ph, ^{n}Bu ; Ar = Ph, 2-Py), which rapidly evolves depending on the nature of the R and Ar groups.

Case of R = Me and Ph. For R = Me and Ph with the [Pd-(PPh$_3$)$_4$] precursor, *cis*-[PdR(SnCl$_3$)(PPh$_3$)$_2$] is first formed and isomerized to give *trans*-[PdR(SnCl$_3$)(PPh$_3$)$_2$]. This complex can then (reversibly) eliminate $SnCl_2$ to form *trans*-[PdR(Cl)-(PPh$_3$)$_2$]. For R = Ph, the equilibria are completely shifted to the side of *trans*-[PdPh(Cl)(PPh$_3$)$_2$], **1**, and the fact that **1** does not insert $SnCl_2$ suggests that the elimination of $SnCl_2$ from [PdPh(SnCl$_3$)(PPh$_3$)$_2$] is indeed highly favorable. In contrast, for R = Me, both equilibria are observed as the initial mixture of *cis*-**4** and *trans*-**4** complexes evolved to the thermodynamically favored *trans*-isomer after a 2 h equilibration

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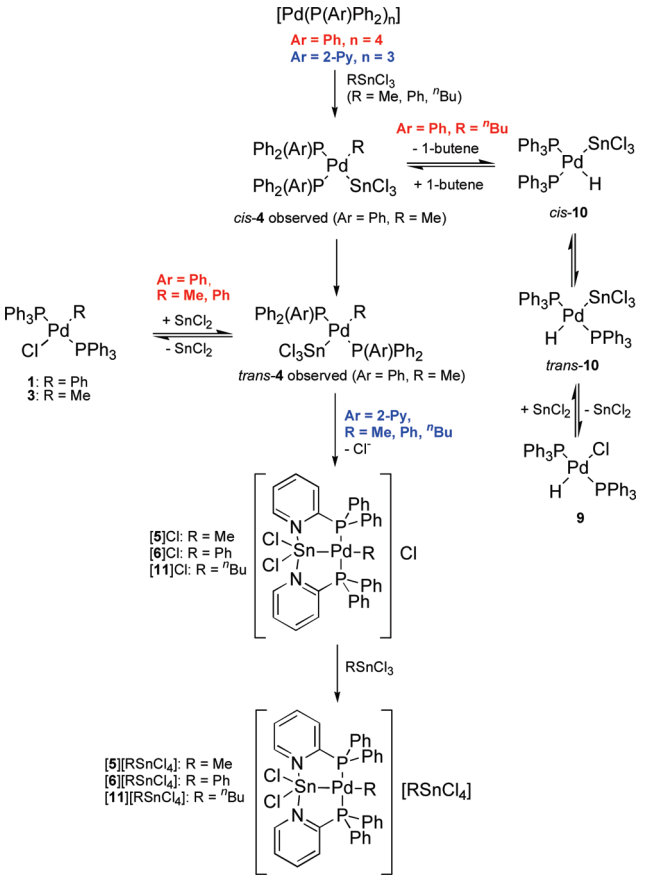
Scheme 1. Rationalization of the Reactions of $RSnCl_3$ Reagents on Pd(0)−Phosphine Precursors



period along with the presence of a significant amount of **3** from the beginning of the reaction. As no *cis*-[PdR(Cl)-$(PPh_3)_2$] is detected in our experiments, we suggest that the (reversible) elimination of $SnCl_2$ from [PdR$(SnCl_3)(PPh_3)_2$] complexes takes place only from the *trans*- isomer. However, elimination of $SnCl_2$ from *cis*-[PdR$(SnCl_3)(PPh_3)_2$] to form directly either *trans*-[PdR(Cl)$(PPh_3)_2$] or a transient *cis*-[PdR-(Cl)$(PPh_3)_2$] that would rapidly evolve to its *trans*-isomer cannot be completely ruled out at this stage.

For R = Me and Ph with the [Pd(2-PyPPh$_2)_3$] precursor, we believe that *cis*-[PdR$(SnCl_3)(PPh_3)_2$] is also initially formed followed by isomerization to *trans*-[PdR$(SnCl_3)$(2-PyPPh$_2)_2$]. However in that case, further stabilization occurs through intramolecular coordination of the pyridyl groups of the phosphine ligands to the tin center to lead to a *trans*-[PdR-$(SnCl_3$(2-PyPPh$_2)_2)$] complex, as exemplified in the X-ray structure of **8** (Figure 1). This neutral six-coordinate trichlorostannyl complex then eventually evolves further to form the cationic five-coordinate dichlorostannylene complex *trans*-[PdR$(SnCl_2$(2-PyPPh$_2)_2)]^+[X]^-$ by elimination of a chloride anion (to form [**5**]Cl and [**6**]Cl) or by transferring it to a second $RSnCl_3$ molecule that acts as a chloride acceptor (to form the five-coordinate $[RSnCl_4]^-$ counteranion in [**5**][$MeSnCl_4$] and [**6**][$PhSnCl_4$]).[8] In both cases, the $SnCl_2$(2-PyPPh$_2)_2$ moiety behaves as a P−Sn−P terdentate ligand that forces the resulting complex into a *trans*-geometry in which the intramolecular coordination of the pyridyl groups to the tin center hamper elimination of $SnCl_2$.

Case of R = ^{n}Bu. ^{n}BuSnCl_3 reacts with [Pd$(PPh_3)_4$] and [Pd(2-PyPPh$_2)_3$] through oxidative addition of the Sn−C bond, as in the $PhSnCl_3$ and $MeSnCl_3$ cases, but the end products differ dramatically depending on which phosphine ligand is used (Scheme 1). With [Pd$(PPh_3)_4$], we detected the formation of butene isomers and a mixture of at least three different palladium hydride compounds. As it is known that (i) the oxidative addition of $MeSnCl_3$ gives a mixture of *cis*-**4** and *trans*-**4** complexes both containing a $SnCl_3^-$ ligand, (ii) the $SnCl_3^-$ ligand has a labile character,[7] and (iii) a ^{n}Bu ligand on palladium can suffer β-H elimination when a *cis*- vacant site becomes available on the Pd center,[14] this result is consistent with the formation of a transient *cis*-[Pd^{n}Bu$(SnCl_3)(PPh_3)_2$] complex that rapidly undergoes β-H elimination to form 1-butene and *cis*-[PdH$(SnCl_3)(PPh_3)_2$] (*cis*-**10**, Scheme 1). *cis*-**10** then isomerizes into *trans*-**10**, which partially eliminates $SnCl_2$ to form **9**, as for the R = Me case, thus explaining the formation of all three palladium hydride species detected in the ^{1}H and ^{31}P NMR spectra. As (i) the reported ^{1}H NMR chemical shift for *trans*-**10** (δ −6.9 ppm)[10] lies very close to the one reported for [PdH$(PPh_3)_3$][CF_3-COO] (δ −7.0 ppm),[11] (ii) $SnCl_3^-$ is known for its labile character,[7] and (iii) in our experiment the ^{31}P NMR resonance of free PPh_3 is broad even at −50 °C, it is possible that [PdH$(PPh_3)_3$][$SnCl_3$] is also formed in solution. However, the absence of the corresponding characteristic doublet and triplet signals in the ^{31}P NMR spectrum[11] suggests that such a species is only transient in nature or highly dynamic even at low temperature. The detection of internal isomers of butene in the reaction can be explained by a palladium-hydride-catalyzed isomerization of the initially generated 1-butene through a 2,1-insertion/β-H elimination sequence.[14] We favor a mechanism involving the dissociation of the $SnCl_3^-$ ligand (Scheme 2) rather than one involving a pentacoordinated [PdH(butene)$(SnCl_3)(PPh_3)_2$] intermediate, which was, for example, proposed in related platinum chemistry,[12] because in [**11**][$BuSnCl_4$] β-H elimination and isomerization are efficiently blocked (see below). This is clearly due to the reduced lability of the Pd−Sn bond rather than lack of availability of a fifth coordination site on the Pd center.

The difference in behavior when ^{n}Bu$SnCl_3$ is reacted with [Pd(2-PyPPh$_2)_3$] hardly could have been more striking. In this case, oxidative addition of the Sn−C bond results in a stable alkyl species [**11**]X (X = Cl, [$BuSnCl_4$], Scheme 1) that shows no tendency to undergo β-H elimination up to 70 °C (6 h). This last observation is truly remarkable, as β-H elimination from an alkyl ligand is normally a facile process on palladium complexes containing triarylphosphine ligands.[14] To avoid β-H elimination usually requires strongly bound and bulky monodentate phosphines or polydentate ligands.[14] In that respect, strongly bound terdentate pincer ligands have been used successfully to generate stable *n*-alkyl−palladium complexes containing β-H atoms.[15] The fact that [**11**][X] (X = Cl, ^{n}Bu$SnCl_4$) does not undergo β-H elimination strongly supports the potential of the $SnCl_2$(2-PyPPh$_2)_2$ ligand to act as a terdentate diphosphinostannylene ligand and underlines the strength of the N−Sn interaction.

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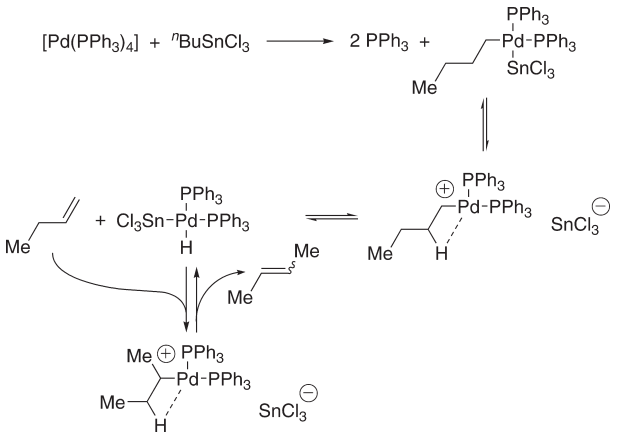
Scheme 2. Proposed Mechanism for the Formation of Internal Butenes in the Reaction of ^{n}BuSnCl$_3$ with [Pd(PPh$_3$)$_4$]



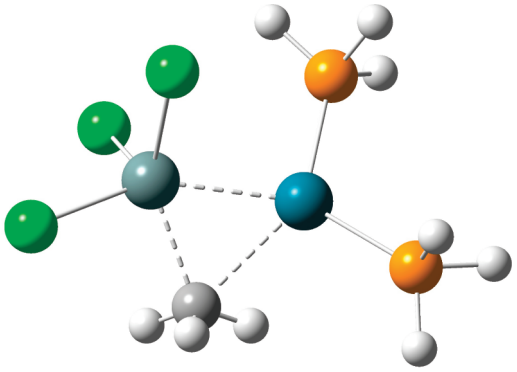
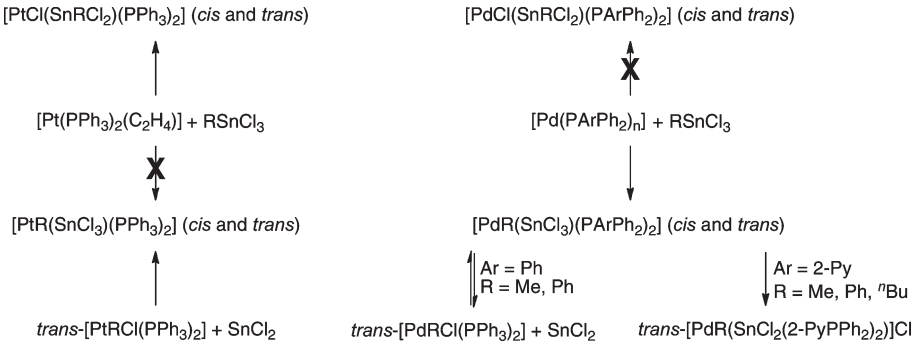


Figure 2. Representation of the transition state of the direct activation of the Me−SnCl$_3$ bond by the [Pd(PH$_3$)$_2$] fragment as calculated by DFT (Gaussian 09, RB3LYP, H/C/P/Cl 6-31G*, Pd/Sn LANL2DZ).

Scheme 3. Comparison of the Reactivity of RSnCl$_3$ Reagents on Pt(0) and Pd(0) Precursors



Comparison with the Platinum Case and Mechanism of the Sn−C Bond Oxidative Addition. With respect to studies on the oxidative addition of alkyltin derivatives on zero oxidation-state group 10 metal complexes in the literature, only Eaborn and Pidcock reported the case of RSnCl$_3$ reagents (R = Me, Ph), which underwent an oxidative addition of the Sn−Cl bond on the platinum(0) precursor [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], resulting in *cis*- and *trans*-isomers of [PtCl(SnRCl$_2$)(PPh$_3$)$_2$] (Scheme 3, left).[1a] From the work reported here, it can be concluded that the reactivity of RSnCl$_3$ (R = Ph, Me, ^{n}Bu) towards the Pd(0) precursors [Pd(PPh$_3$)$_4$] and [Pd(2-PyPPh$_2$)$_3$] differs significantly from the structurally related Pt(0) precursor (Scheme 3, right). Oxidative addition is formally taking place in the Sn−C bond, which results exclusively in transient *cis*-[Pd(alkyl)(SnCl$_3$)(phosphine)$_2$] species (Scheme 1), which can undergo *cis*−*trans* isomerization followed by, in the case of [Pd(PPh$_3$)$_4$], reversible SnCl$_2$ elimination or, in the case of [Pd(2-PyPPh$_2$)$_3$], chloride elimination to form stable palladium dichlorostannylene species.

Several mechanisms can be envisioned for the observed Sn−C bond activation reactions that, at least formally, lead to the oxidative addition on Pd. The first one would involve a preliminary oxidative addition of the Sn−Cl bond to give [PdCl(SnRCl$_2$)(phosphine)$_2$] complexes, as was observed in the analogous platinum chemistry. Those would then have to evolve rapidly to the observed [PdR(SnCl$_3$)(phosphine)$_2$] complexes, either through deinsertion of SnCl$_2$ from the SnRCl$_2^-$ ligand and its reinsertion into the Pd−Cl bond or through redistribution of the substituents on Sn with another RSnCl$_3$ molecule. However, [PdCl(SnMeCl$_2$)(PPh$_3$)$_2$] intermediates were not detected when the reaction between [Pd(PPh$_3$)$_4$] and MeSnCl$_3$ was monitored at low temperature (T = −50 °C, eq 3) by ^{1}H and ^{31}P NMR. Certainly, in the case of [Pd(2-PyPPh$_2$)$_3$] as starting compound, one would expect such intermediates to be stabilized by intramolecular coordination of the pyridyl groups to the Sn atom. No complexes of this type were detected, however. Moreover, in the formation of complex [**11**][^{n}BuSnCl$_4$], such a reaction pathway would involve [Pd^{n}Bu(Cl)(2-PyPPh$_2$)$_2$] as an intermediate that is expected to be unstable toward β-H elimination and would result in formation of butenes. The latter are not observed. The absence of R$_2$SnCl$_2$ species also excludes a redistribution of [PdCl(SnRCl$_2$)(phosphine)$_2$] and RSnCl$_3$.

Another possible reaction route for the formal oxidative addition reactions observed is an S$_N$2-type reaction of a [Pd(phosphine)$_3$] fragment with RSnCl$_3$ leading to a transient ionic [PdR(phosphine)$_3$][SnCl$_3$] intermediate. The SnCl$_3^-$ anion would then substitute one of the phosphine ligands to give the observed complexes. Pentacoordinated [PdR(SnCl$_3$)(phosphine)$_3$] complexes could then be envisioned as intermediates or transition states, which would provide a good explaination for the *cis*/*trans* isomerization of the [PdMe(SnCl$_3$)(PPh$_3$)$_2$] complexes via a Berry pseudorotation. However, when the reaction by [Pd(PPh$_3$)$_4$] and MeSnCl$_3$ was carried out and monitored by NMR at low temperature (T = −50 °C), *cis*-[PdMe(SnCl$_3$)(PPh$_3$)$_2$] is initially the major product of the reaction, suggesting a concerted activation of the Sn−C bond. Those observations make us favor a reaction pathway involving the direct activation of the Sn−C bond by [Pd(phosphine)$_2$] or [Pd(phosphine)$_3$] species. This

hypothesis is further supported by DFT calculations on a model system, which show that the activation barrier for such a process starting from the encounter complex is indeed low ($\Delta G^{\ddagger} = 24$ kJ·mol^{-1}, Figure 2).[16]

Conclusions

The above studies show that the reaction of alkyltin trichlorides on Pd(0)−phosphine complexes exclusively proceeds through an oxidative addition of the Sn−C bond, which is in sharp contrast to the related Pt(0) case. By using [Pd(2-PyPPh$_2$)$_3$] as a precursor instead of [Pd(PPh$_3$)$_4$], it became possible to efficiently block degradation of the initially formed palladium−alkyl products and to synthesize in a single step a cationic (bis(2-(diphenylphosphino)pyridine)-dichlorostannylene)−palladium−alkyl complex that showed no tendency to undergo β-H elimination. The unique P−Sn(II)−P terdentate ligand, through its stannylene donor function, can be expected to induce new interesting properties to derived metal complexes, the synthesis and reactivity of which are currently under investigation.

Experimental Section

General Considerations. All operations were performed in dry, degassed (deuterated) solvents under a dinitrogen atmosphere using standard Schlenk techniques or a glovebox. PhSnCl$_3$, MeSnCl$_3$, and ^{n}BuSnCl$_3$ were purchased from Sigma-Aldrich. Metal precursors [Pd(PPh$_3$)$_4$], *trans*-[PdMe(Cl)(PPh$_3$)$_2$], *trans*-[PdPh(Cl)(PPh$_3$)$_2$], [Pd(2-PyPPh$_2$)$_3$], and *trans*-[PdPh(Cl)(2-PyPPh$_2$)$_2$] were prepared according to literature procedures.[4,6] Toluene was distilled from sodium; THF-d_8 was distilled from sodium benzophenone. NMR data were recorded on a Varian Oxford 300 MHz or Varian Oxford AS 400 MHz, and chemical shifts are reported relative to SiMe$_4$ (^{1}H, ^{13}C), external 85% H$_3$PO$_4$ in water (^{31}P), or SnMe$_4$ (1 M) in benzene (^{119}Sn). The ^{119}Sn NMR signal of the stannylene ligand in complexes [**5**][MeSnCl$_4$], [**6**][PhSnCl$_4$], and [**11**][^{n}BuSnCl$_4$] could not be observed, which is presumably due to a very broad signal caused by a significant chemical shift anisotropy for the tin atom.[17] High-resolution mass spectroscopy (HRMS) has been performed on a Waters LCT Premier XE Micromass instrument using the electrospray ionization technique.

Preparation of [5][MeSnCl$_4$]. MeSnCl$_3$ (108.0 mg, 0.45 mmol) dissolved in toluene (1 mL) was slowly added to a stirred solution of [Pd(2-PyPPh$_2$)$_3$] (200.0 mg, 0.22 mmol) in toluene (10 mL) at room temperature. Within 10 min, a white precipitate formed, which was recovered by filtration, washed with toluene (3 × 5 mL), and dried under vacuum to lead to a white solid (166.4 mg, 15 mmol, 67%). ^{1}H NMR (CDCl$_3$, 25 °C, 300 MHz): δ 9.09 (d, $^3J_{H-H}$ = 5.3 Hz, 2*H*, Py), 8.17 (m, 2*H*, Py), 7.94 (m, 2*H*, Py), 7.66 (d, $^3J_{H-H}$ = 7.7 Hz, 2*H*, Py), 7.59−7.52 (m, 12*H*, Ph), 7.48−7.44 (m, 8*H*, Ph), 1.55 (s, $^2J_{H-Sn}$ = 112.9 and 117.9 Hz, 3*H*, *Me*SnCl$_4^-$), 1.36 (s, $^3J_{H-Sn}$ = 45.1 Hz, *Me*-Pd). ^{13}C NMR (CDCl$_3$, 25 °C, 101 MHz): δ 149.6 (t, J_{P-C} = 62 Hz), 149.3 (t, J_{P-C} = 17 Hz), 141.8 (s), 134.2 (t, J_{P-C} = 13 Hz), 132.5 (s), 131.5 (t, J_{P-C} = 12 Hz), 129.6 (t, J_{P-C} = 11 Hz), 129.2 (s), 127.3 (t, J_{P-C} = 51 Hz), 24.3 (s), 15.2 (s). ^{31}P NMR (CDCl$_3$, 25 °C, 121 MHz): δ 63.6 (s). ^{119}Sn NMR (CDCl$_3$, 25 °C, 112 MHz): δ −244.7 (br, [Me*Sn*Cl$_4$]$^-$). ESI-HRMS (in CH$_2$Cl$_2$): found 836.9351 (calculated for [**5**]$^+$ 836.9391, with the correct isotope pattern).

Preparation of [6][PhSnCl$_4$] and [11][^{n}BuSnCl$_4$]. Synthesis was performed using the same procedure as for the synthesis of [**5**][MeSnCl$_4$] except that PhSnCl$_3$ (74.0 μL, 0.45 mmol) or ^{n}BuSnCl$_3$ (75.0 μL, 0.45 mmol) was slowly introduced as the neat compound (and, for [**6**][PhSnCl$_4$], an extra washing with 2 × 5 mL of Et$_2$O). A white solid was obtained ([**6**][PhSnCl$_4$], 198.8 mg, 16 mmol, 72%; [**11**][^{n}BuSnCl$_4$], 235.1 mg, 20 mmol, 88%).

[**6**][PhSnCl$_4$]: ^{1}H NMR (CDCl$_3$, 25 °C, 300 MHz): δ 8.52 (m, 2*H*), 8.25 (m, 1*H*), 8.08 (m, 2*H*), 7.91 (m, 1*H*), 7.77 (m, 2*H*), 7.68−7.35 (m, 30*H*). ^{13}C NMR (CDCl$_3$, 25 °C, 101 MHz): δ 149.2 (t, J_{C-P} = 8.6 Hz), 149.1 (t, J_{C-P} = 31.3 Hz), 145.9 (s), 141.5 (s), 135.7 (s), 135.4 (s), 134.2 (t, J_{C-P} = 6.8 Hz), 132.4 (s), 131.2 (s), 131.0 (s), 130.3 (s), 130.0 (s), 129.8 (s), 129.5 (t, J_{C-P} = 5.5 Hz), 128.6 (s), 128.5 (s), 127.5 (t, J_{C-P} = 25.5 Hz). ^{31}P NMR (CDCl$_3$, 25 °C, 121 MHz): δ 64.3 (s, $^2J_{P-Sn}$ = 145 Hz). ^{119}Sn NMR (CDCl$_3$, 25 °C, 112 MHz): δ −321.7 (br, [PhSnCl$_4$]$^-$). ESI-HRMS (in CH$_2$Cl$_2$): found 898.9539 (calculated for [**6**]$^+$ 898.9547, with the correct isotope pattern).

[**11**][^{n}BuSnCl$_4$]: ^{1}H NMR (CDCl$_3$, 25 °C, 300 MHz): δ 9.05 (d, $^3J_{H-H}$ = 5.2 Hz, 2*H*, Py), 8.17 (m, 2*H*, Py), 7.94 (m, 2*H*, Py), 7.57 (d, ^{3}J$_{H-H}$ = 7.7 Hz, 2*H*, Py), 7.48−7.34 (m, 20*H*, Ph), 2.15 (t, $^3J_{H-H}$ = 7.6 Hz, $^2J_{H-Sn}$ = 107 Hz, 2*H*, [^{n}Pr-C*H*$_2$-SnCl$_4$]$^-$), 1.92 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, ^{n}Pr-C*H*$_2$-Pd), 1.82 (m, 2*H*, [^{n}Et-C*H*$_2$-CH$_2$SnCl$_4$]$^-$), 1.37 (m, 2*H*, [Me-C*H*$_2$-C$_2$H$_4$SnCl$_4$]$^-$), 0.84 (m, 2*H*, ^{n}Et-C*H*$_2$-CH$_2$-Pd), 0.81 (t, $^3J_{H-H}$ = 7.3 Hz, 3*H*, [*Me*-C$_3$H$_6$SnCl$_4$]$^-$), 0.74 (m, 2*H*, Me-C*H*$_2$-C$_2$H$_4$-Pd), 0.27 (t, $^3J_{H-H}$ = 7.1 Hz, 3*H*, *Me*-C$_3$H$_6$-Pd). ^{13}C NMR (CDCl$_3$, 25 °C, 101 MHz): δ 149.8 (m), 149.7 (m), 142.0 (s), 134.1 (t, J_{C-P} = 6.7 Hz), 132.6 (s), 131.9 (t, J_{C-P} = 6.0 Hz), 129.7 (t, J_{C-P} = 5.5 Hz), 129.4 (s), 127.1 (t, J_{C-P} = 25.6 Hz), 44.5 (s), 33.2 (s), 28.0 (s), 27.8 (s), 26.6 (s), 25.7 (s), 14.0 (s), 13.7 (s). ^{31}P NMR (CDCl$_3$, 25 °C, 121 MHz): δ 62.5 (s). ^{119}Sn NMR (CDCl$_3$, 25 °C, 112 MHz): δ −249.6 (br, [^{n}BuSnCl$_4$]$^-$). ESI-HRMS (in CH$_2$Cl$_2$): found 878.9868 (calculated for [**11**]$^+$ 878.9860, with the correct isotope pattern).

Monitoring of the Reactions of [Pd(PPh$_3$)$_4$] with MeSnCl$_3$, PhSnCl$_3$, or ^{n}BuSnCl$_3$ by NMR. [Pd(PPh$_3$)$_4$] (11.5 mg, 0.01 mmol) was introduced in an NMR tube and dissolved in 0.5 mL of THF-d_8. MeSnCl$_3$ (2.4 mg, 0.01 mmol), PhSnCl$_3$ (1.65 μL, 0.01 mmol), or ^{n}BuSnCl$_3$ (1.67 μL, 0.01 mmol) was then introduced in the tube, and the resulting solution was shaken and then analyzed by ^{31}P and ^{1}H NMR as well as by mass spectroscopy (except for the ^{n}BuMeSnCl$_3$ case).

[Pd(PPh$_3$)$_4$] and MeSnCl$_3$. The spectra were recorded at −50 °C because broad signals were observed at room temperature. NMR analysis indicated the formation of the known compounds PPh$_3$ (2 equiv), *cis*-[PdCl$_2$(PPh$_3$)$_2$] (**2**, 10%), and *trans*-[PdMe(Cl)(PPh$_3$)$_2$][6] (**3**, 15% at t = 1 min, 25% at t = 2 h), as well as the new compounds *trans*-[PdMe(SnCl$_3$)(PPh$_3$)$_2$] (*trans*-**4**, 45% at t = 1 min, 65% at t = 2 h) and *cis*-[PdMe(SnCl$_3$)(PPh$_3$)$_2$] (*cis*-**4**, 30% at t = 1 min, 0% at t = 2 h). As a mixture of products was present, only the methyl signals were attributed by ^{1}H NMR. PPh$_3$: ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ −5.4 (s). **2**: ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 24.4 (s). **3**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ −0.16 (t, $^3J_{H-P}$ = 11.6 Hz). ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 31.2 (s). *trans*-**4**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ 1.00 (s, $^3J_{H-Sn}$ = 48.0 Hz). ^{31}P

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NMR (THF-d_8, −50 °C, 121 MHz): δ 27.9 (s, $^2J_{P-Sn}$ = 96 Hz). *cis*-**4**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ 0.29 (s, $^3J_{H-Sn}$ = 42.6 Hz). ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 37.2 (d, $^2J_{P-P}$ = 36 Hz, $^2J_{P-Sn}$ = 271 Hz), 26.7 (d, $^2J_{P-P}$ = 36 Hz). ESI-HRMS of the reaction mixture (in DCM/MeCN): found 645.1248 and 686.1473 corresponding respectively to $[PdMe(PPh_3)_2]^+$ (calculated 645.1087) and $[PdMe(MeCN)(PPh_3)_2]^+$ (calculated 686.1352).

[Pd(PPh$_3$)$_4$] and PhSnCl$_3$. Analysis of the solution by ^{1}H and ^{31}P NMR after 1 min indicated the complete formation of PPh_3 (2 equiv) and *trans*-[PdPh(Cl)(PPh$_3$)$_2$] (**1**, 1 equiv) assigned by comparison with literature data.[4] PPh_3: ^{31}P NMR (THF-d_8, 25 °C, 121 MHz): δ −5.4 (s). **1**: ^{31}P NMR (THF-d_8, 25 °C, 121 MHz): δ 24.2 (s). ESI-HRMS of the reaction mixture (in DCM/MeCN): found 707.1136, 723.1086, 748.1352 corresponding respectively to $[PdPh(PPh_3)_2]^+$ (calculated 707.1265), $[PdPh(PPh_3)(PPh_3O)]^+$ (calculated 723.1198), and $[PdPh(MeCN)(PPh_3)_2]^+$ (calculated 748.1514).

[Pd(PPh$_3$)$_4$] and ^{n}BuSnCl$_3$. The NMR spectra were recorded at −50 °C because broad signals were observed at room temperature. NMR analysis of the solution indicated the formation of the known compounds PPh_3 (2 equiv), butene isomers (1 equiv, isomer ratio evolves from initially >80% 1-butene to >95% 2-butene after 2 h), *cis*-[$PdCl_2(PPh_3)_2$] (**2**, 10%), *trans*-[PdH(Cl)(PPh$_3$)$_2$] (**9**, 10%),[9,10] and *trans*-[PdH($SnCl_3$)(PPh$_3$)$_2$] (*trans*-**10**, 30%)[10] as well as the new compound *cis*-[PdH($SnCl_3$)(PPh$_3$)$_2$] (*cis*-**10**, 50%). As a mixture of products is present, only the hydride signals were attributed by ^{1}H NMR. PPh_3: ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ −5.4 (br, lwhh = 271 Hz). 1-Butene: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ 5.90 (m, 1H), 5.02 (m, 1H), 4.93 (m, 1H), 2.07 (m, 2H), 1.01 (t, 3H, J_{H-H} = 14.9 Hz). 2-Butenes (*Z* and *E* mixture): ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): 5.46 (m, 2H), 1.84 (m, 6H). **2**: ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 24.4 (s). **9**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ −12.6 (br). ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 30.8 (s). *trans*-**10**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ −7.0 (br). ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 28.3 (s, $^2J_{P-Sn}$ = 101 Hz). *cis*-**10**: ^{1}H NMR (THF-d_8, −50 °C, 300 MHz): δ −7.0 (br). ^{31}P NMR (THF-d_8, −50 °C, 121 MHz): δ 38.3 (d, $^2J_{P-P}$ = 36 Hz, $^2J_{P-Sn}$ = 211 and 287 Hz), 26.6 (d, $^2J_{P-P}$ = 36 Hz).

Monitoring of the Reactions of *trans*-[PdR(Cl)(PPh$_3$)$_2$] (R = Me, Ph) and *trans*-[PdPh(Cl)(2-PyPPh$_2$)$_2$] with $SnCl_2$ by NMR. *trans*-[PdMe(Cl)(PPh$_3$)$_2$] (**3**, 6.8 mg, 0.01 mmol), *trans*-[PdPh(Cl)(PPh$_3$)$_2$] (**1**, 7.4 mg, 0.01 mmol), or *trans*-[PdPh(Cl)(2-PyPPh$_2$)$_2$] (7.5 mg, 0.01 mmol) was introduced in an NMR tube and dissolved in 0.5 mL of THF-d_8. $SnCl_2$ (1.9 mg, 0.01 mmol) was then introduced, and the tube was shaken. The resulting mixture was then analyzed by ^{31}P and ^{1}H NMR. For *trans*-[PdPh(Cl)(2-PyPPh$_2$)$_2$], quantitative formation of the cationic dichlorostannylene cation $[\mathbf{6}]^+$ was observed, suggesting the formation of [**6**]Cl. For the *trans*-[PdR(Cl)(PPh$_3$)$_2$] precursors, no reaction was observed for **1**, whereas for **3** partial formation of *cis*-**4** and *trans*-**4** was detected. See previous sections for NMR data.

Synthesis and X-ray Crystal Structure Determination of Compound 8. [Pd(2-PyPPh$_2$)$_3$] (10 mg, 0.011 mmol) was reacted with $SnCl_4$ (1.3 μL mg, 0.011 mmol) in THF-d_8 (0.5 mL) in an NMR tube. The ^{1}H and ^{31}P NMR spectra were recorded and indicated the quantitative formation of free 2-$PyPPh_2$ (1 equiv) and [**7**][Cl] (1 equiv).[3a] The THF-d_8 solution in the tube was covered with an *n*-hexane layer and left at room temperature (7 days) until single white crystals suitable for X-ray analysis were formed. $C_{34}H_{28}Cl_4N_2P_2PdSn$, fw = 893.41, yellow needle, 0.24 × 0.03 × 0.03 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 14.4729(6) Å, b = 12.5944(13) Å, c = 22.8027(11) Å, β = 124.973(2)°, V = 3405.9(4) Å^3, Z = 4, D_x = 1.742 g/cm^3, μ = 1.70 mm^{-1}. A total of 45 500 reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.55 Å^{-1} at a temperature of 150(2) K. Intensity integration was performed with Eval15 using a model for large mosaicity.[18] The SADABS program was used for absorption correction and scaling based on multiple measured reflections (0.61−0.75 correction range).[19] A total of 4725 reflections were unique (R_{int} = 0.071), of which 3581 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SHELXS-97.[20] The structure was refined with SHELXL-97 against F^2 of all reflections.[20] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. A total of 397 parameters were refined with no restraints. R1/wR2 [$I > 2\sigma(I)$]: 0.0338/0.0678. R1/wR2 [all refls]: 0.0573/0.0760. S = 1.035. Residual electron density was between −0.52 and 0.81 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[21]

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Supporting Information Available: For experiments with [Pd(PPh$_3$)$_4$] in NMR tubes, ^{31}P and ^{1}H NMR spectra (at RT or −50 °C) and HRMS spectra. For experiments with [Pd(2-PyPPh$_2$)$_3$], full analytical data (^{1}H, ^{13}C, and ^{31}P NMR, HRMS) of complexes [**5**][$MeSnCl_4$], [**6**][$PhSnCl_4$], and [**11**][^{n}BuSnCl$_4$]. Crystallographic details of compound **8** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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