ORGANOMETALLICS

Addition/Correction

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Correction to 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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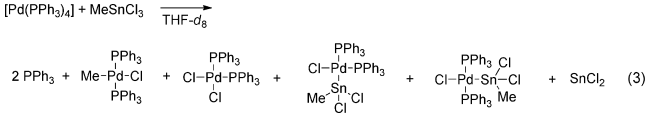
Supporting Information

Additional NMR spectroscopic data and the outcome of two X-ray crystallographic studies have led to a reinterpretation of the previous results and a revision of our earlier conclusions. Note that the first three authors in the author list above are additions to the original authors of the paper (E.J.D. and S.W., Organic Chemistry & Catalysis, Utrecht University; J.J.M.d.P., ARKEMA Vlissingen B.V.). Also note that the new street address for Organic Chemistry and Catalysis, Utrecht University, is Universiteitsweg 99.

Reaction of $RSnCl_3$ (R = Me, Ph) with $[Pd(PPh_3)_4]$ and $[Pd(2\text{-}PyPPh_2)_3]$. In the article it was argued that the reaction between $MeSnCl_3$ and $[Pd(PPh_3)_4]$ in THF-d_8 resulted in trichlorostannyl species *cis*- and *trans*-$[PdMe(SnCl_3)(PPh_3)_2]$ (*cis*-**4** and *trans*-**4**, respectively) next to minor products *cis*-$[PdCl_2(PPh_3)_2]$ (**2**) and *trans*-$[PdCl(Me)(PPh_3)_2]$ (**3**) (original eq 3). Re-examination of the NMR spectroscopic data supplemented by a $^1H/^{13}C$ HSQC NMR analysis[1] indicated that the Me groups in species **4** were in fact positioned on the Sn atom.

Initially, we argued that the small J_{H-Sn} values observed for the Me groups of **4** were evidence that the Me groups were on palladium, since a smaller coupling constant is expected for a three-bond interaction. However, we later noted that Al-Allaf also reported fairly small $^2J_{HSn}$ coupling constants of only 48 and 42 Hz for stannyl complexes $[PtCl(SnCl_nMe_{3-n})(COD)]$ (n = 1, 0) and $[PtMe(SnMe_3)(COD)]$, (see refs 1b and 1c in the original paper), respectively, while no $^3J_{HSn}$ was observed for the Pt−Me moiety in the latter. Similar values for the $^2J_{HSn}$ coupling constants were also reported by Eaborn et al. for *cis*- and *trans*-$[PtCl(SnCl_2Me)(PPh_3)_2]$ ($^2J_{HSn}$ = 47.2 and 43.9 Hz, respectively) (see ref 1a in the original paper) and structurally characterized methylstannylene [**5**][$MeSnCl_4$] (see below). The similarity of these $^2J_{HSn}$ values with those of **4** and the absence of a $^3J_{HP}$ coupling on the methyl protons is more in line with a methylated stannyl moiety. A $^1H/^{13}C$ HSQC NMR experiment (THF-d_8, −50 °C) afforded conclusive evidence for the Me group being on positioned on Sn, as it allowed the observation of the $^1J_{C-Sn}$ coupling constants on the Me signals (δ 11.6 (s, $^1J_{CSn}$ = 228 Hz), δ 14.0 (s, $^1J_{CSn}$ = 298 Hz)) that can be compared to those of Me_3SnCl ($^1J_{CSn}$ = 379 Hz), $SnMe_4$ ($^1J_{CSn}$ = 337 Hz), and Sn^nBu_4 ($^1J_{CSn}$ = 314 Hz).[2] In addition, the stannyl moieties of isomeric compounds **4** were also observed in the ^{119}Sn NMR spectrum (THF-d_8: δ 83.8 (t, $^2J_{SnP}$ = 93 Hz, *trans*-**4**), −11.4 (dd, $^2J_{SnP}$ = 270 Hz, $^2J_{SnP}$ = 3414 Hz, *cis*-**4**).

The observations above indicate that the structures of the tin-containing species **4** should be reformulated as being a mixture of *cis*- and *trans*-$[PdCl(SnCl_2Me)(PPh_3)_2]$ (*cis*- and *trans*-**4**), as indicated in the corrected eq 3:



A corrected Table 1 (revised) is also supplied.

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

[a] Coupling constant not detected.

In the original article complexes *trans*-$[PdR(SnCl_2(2\text{-}PyPPh_2)_2)][RSnCl_4]$ (R = Me ([**5**][$MeSnCl_4$]), Ph ([**6**]-[$PhSnCl_4$]), ^{n}Bu ([**11**][$^n BuSnCl_4$])) were proposed to be produced in the reaction of $[Pd(2\text{-}PyPPh_2)_3]$ with monoorganotin chlorides $RSnCl_3$ (eq 4 in the original paper). The structural characterization of these complexes was based on a comparison of NMR spectroscopic data obtained for [**5**]-[$MeSnCl_4$] with that of [**5**][BF_4] and its Pt analogue *trans*-$[PtMe(SnCl_2(2\text{-}PyPPh_2)_2)][BF_4]$ (see ref 3a in the original paper). The unequivocal structural assignment of product [**5**][$MeSnCl_4$], as opposed to the assignment published in the article, was recently achieved when crystals suitable for a single-crystal X-ray crystallographic study were obtained from the reaction of $[Pd(dba)_2]$ with $MeSnCl_3$ in the presence of excess 2-$PyPPh_2$. The resulting molecular structure indicates that the structure of [**5**][$MeSnCl_4$] had to be reformulated as $[PdCl(SnCl(Me)(2\text{-}PyPPh_2)_2)][MeSnCl_4]$, with the methyl

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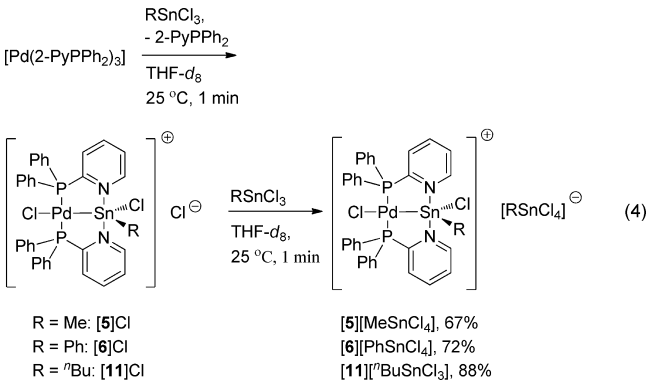
group positioned on the stannylene moiety rather than on the palladium center (see corrected eq 4):



(4)

The structural details of [**5**][$MeSnCl_4$] will be discussed in a forthcoming article.

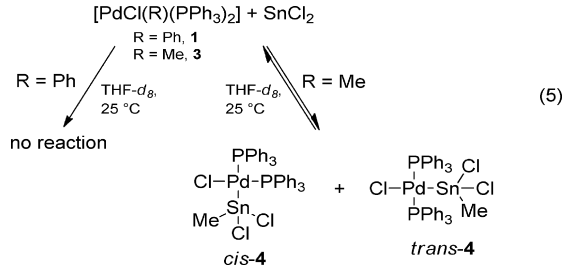
The NMR spectroscopic data of the isolated crystals dissolved in chloroform-d_1 were identical with those obtained previously for the reaction starting from [$Pd(2\text{-}PyPPh_2)_3$], indicating that the nature of the reaction product is not influenced by the specific Pd(0) starting material used. When the ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data for [**5**][$MeSnCl_4$] are compared with those for the tetrafluoroborate derivative [**5**][BF_4], it is clear that the structure of the latter should also be reformulated as *trans*-[PdCl{SnCl(Me)(2-$PyPPh_2$)$_2$}][BF_4] ([**5**][BF_4]) (see ref 3a in the original article).

The weak $^2J_{HSn}$ coupling constant observed on the methylstannylene signal of [**5**][$MeSnCl_4$] in the ^1H NMR spectrum (δ 1.36, $^2J_{HSn}$ = 45 Hz) can be compared to the Pt–Sn–Me fragments of related stannyl complexes [PtCl($SnCl_nMe_{3-n}$)(COD)] (n = 1, 0), [PtMe($SnMe_3$)(COD)] (see refs 4 and 5 in the original article), and *cis*- and *trans*-[PtCl($SnCl_2Me$)(PPh_3)$_2$] (see ref 1a in the original article). The new structural assignment of [**5**][$MeSnCl_4$] is further evidenced by the absence of a $^3J_{HP}$ coupling between the methyl protons and the phosphorus atoms, a coupling that was clearly visible for the methyl–platinum complex *trans*-[PtMe{$SnCl_2$(2-$PyPPh_2$)$_2$}][BF_4] (see ref 3a in the original article).

The ^1H NMR spectrum of a newly prepared sample of [**5**][BF_4] in dichloromethane-d_2 contained a broad signal at δ 1.69 with a $^2J_{HSn}$ (63 Hz) coupling constant that was previously thought to be due to residual water in the NMR solvent but that can now be assigned to a methylstannylene group, indicating that *trans*-[PdCl(SnCl(Me)(2-$PyPPh_2$)$_2$)][BF_4] is the correct formulation of [**5**][BF_4].

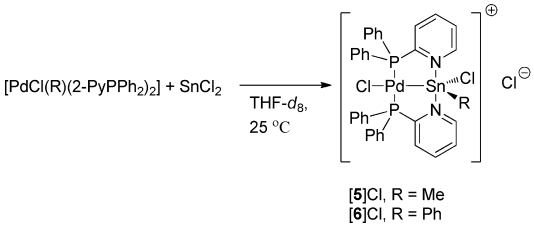
No carbon–tin satellites could be observed on the methylstannylene resonance in the $^{13}C\{^1H\}$ NMR spectrum of [**5**][$MeSnCl_3$], due to the low intensity of the signal. However, $^1J_{CSn}$ values of 360 and 930 Hz for the Sn(Cl)Me-fragment and the [$MeSnCl_4$]$^-$ anion, respectively, could be observed in the $^1H/^{13}C$ HSQC NMR spectrum (400 MHz, in dichloromethane-d_2).[1] The reasonably large carbon–tin coupling constant observed for the methyl signal of the cation confirmed the presence of a direct carbon–tin bond.[2]

As the ^1H and ^{31}P NMR spectroscopic data of the products formed from the reaction of tin dichloride with *trans*-[PdCl(Me)(PPh_3)$_2$] (**3**) (eq 5 in the original article, right) were identical with the products resulting from the reaction of eq 3 (except for the formation of free PPh_3 and **2**) it can be concluded that structural assignment of these products should also be revised (see corrected eq 5):



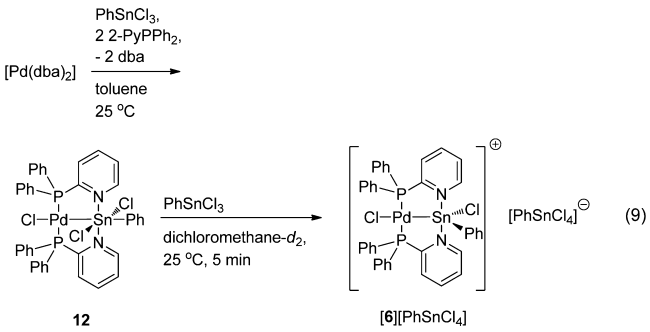
(5)

On the basis of similarities in the NMR data between [**5**][$MeSnCl_4$] and the product observed from the reaction of *trans*-[PdCl(Me)(2-$PyPPh_2$)$_2$] with $SnCl_2$ eq 6 in the original article also has to be revised (see corrected eq 6 for R = Me):



(6)

To verify its structure, the synthesis of [**6**]Cl was attempted on a preparative scale in toluene starting from [$Pd(dba)_2$], 2-$PyPPh_2$ (2 equiv), and $PhSnCl_3$ (1 equiv). Surprisingly, this led after crystallization from dichloromethane to the neutral phenyldichlorostannyl derivative *trans*-[PdCl($SnCl_2$(Ph)(2-$PyPPh_2$)$_2$)] (**12**) (eq 9), which was structurally fully



(9)

characterized by means of a single-crystal X-ray diffraction study (structural data will be discussed elsewhere). The lower polarity of dichloromethane in comparison to THF is most likely responsible for the fact that neutral **12** was isolated rather than [**6**]Cl. Crystals of **12** dissolved in dichloromethane-d_2 resulted in [**6**]Cl, which reacted with another 1 equiv of $PhSnCl_3$ to produce ionic [**6**][$PhSnCl_4$] within 5 min, according to the NMR spectral data (eq 9). Given the structure of intermediate **12**, it can now also be concluded that the correct structural assignments of [**6**]Cl and [**6**][$PhSnCl_4$] are *trans*-[PdCl(SnCl(Ph)(2-$PyPPh_2$)$_2$)]Cl (eq 6) and *trans*-[PdCl(SnCl(Ph)(2-$PyPPh_2$)$_2$)][$PhSnCl_4$] (eqs 4 and 9), respectively.

Reaction of ^{n}BuSnCl$_3$ with [Pd(2-PyPPh$_2$)$_3$]. Having determined that $MeSnCl_3$ and $PhSnCl_3$ undergo Sn–Cl bond activation by Pd(0), we also started to doubt the outcome of the reaction of [$Pd(2\text{-}PyPPh_2)_3$] with ^{n}BuSnCl$_3$ (eq 4 in the original article). The poor solubility of the product hindered its complete structural characterization. However, the related derivative *trans*-[PdCl(SnCl(^{n}Bu)(2-ImPPh$_2$)$_2$)][^{n}BuSnCl$_4$] ([**13**][^{n}BuSnCl$_4$], Im = 2-(1-methylimidazolyl)) has been structurally characterized by a X-ray crystallographic study (detailed results will be published in a forthcoming paper).

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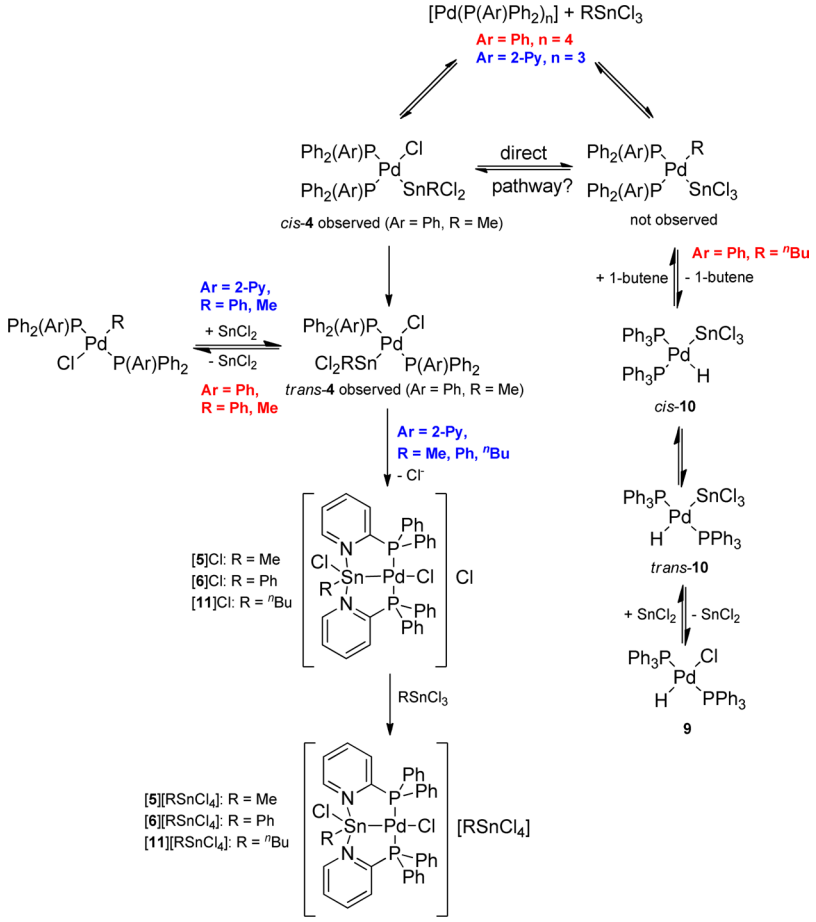
Scheme 1 (revised). Rationalization of the Reactions of $RSnCl_3$ Reagents on Pd(0)−Phosphine Precursors



From a comparison of the spectroscopic data of [**11**]-[^{n}BuSnCl$_4$] with those of [**13**][^{n}BuSnCl$_4$] (Sn*C*H$_2$ signals at δ 33.2 and 32.7, respectively, in the $^{13}C\{^1H\}$ NMR spectra) as well as [**5**][MeSnCl$_4$] (^{31}P NMR signals at δ 62.5 and 63.6, respectively) together with the fact that Sn−Cl activation is the dominant pathway observed for MeSnCl$_3$ and PhSnCl$_3$, it is most likely that [**11**][^{n}BuSnCl$_4$] is a butylstannylene complex (see revised eq 4 above). This is also in line with the rather high stability observed for this complex.

DISCUSSION

In light of the new interpretation of the previous results we have to revise our earlier conclusions. It appears that formal Sn−Cl oxidative addition is the dominant process when Pd(0) complexes [Pd(P(Ar)Ph$_2$)$_n$] (Ar = Ph, n = 4; Ar = 2-Py, n = 3) are reacted with monoorganotin trichlorides RSnCl$_3$ (R = Me, Ph, ^{n}Bu), resulting in transient organostannylpalladium complexes *cis*-[PdCl(SnCl$_2$R)(P(Ar)Ph$_2$)$_2$] (see left part of Scheme 1 (revised)). This complex can then undergo *cis* → *trans* isomerization/(partial) SnCl$_2$ elimination (Ar = Ph) or *cis* → *trans* isomerization/chloride elimination (Ar = 2-Py). The latter process is clearly favored by the intramolecular coordination of the pyridyl groups to the Sn center. The elimination of SnCl$_2$ from *trans*-[PdCl(SnCl$_2$R)(P(Ar)Ph$_2$)$_2$] (Ar = Ph) is reversible, as reaction of SnCl$_2$ with *trans*-[PdCl(Me)(PPh$_3$)$_2$] (**3**) was shown to produce the insertion product (as an equilibrium mixture of *trans*- and *cis*-**4**). For the pyridylphosphine complexes *trans*-[PdCl(SnCl$_2$R)(P(2-Py)-Ph$_2$)$_2$] the equilibrium is totally shifted to the side of the insertion products [**5**]Cl (R = Me) and [**6**]Cl (R = Ph), which can again be explained by the stabilizing N → Sn coordination.

The reaction with ^{n}BuSnCl$_3$ and [Pd(PPh$_3$)$_4$] is an intriguing one. On the basis of the reactions with PhSnCl$_3$ and MeSnCl$_3$, the primary product expected is the Sn−Cl oxidative addition product *cis*-[PdCl(SnCl$_2$^{n}Bu)(PPh$_3$)$_2$]. However, the Pd hydride and butene products observed suggest a β-hydride elimination pathway involving a Pd−^{n}Bu species. As was suggested in the original article, this would point to the formation of *cis*-[Pd^{n}Bu(SnCl$_3$)(PPh$_3$)$_2$] as an intermediate (Scheme 2 in the original article). The fact that [Pd(PPh$_3$)$_4$] is also an active catalyst for the dehydrostannylation of β-H-containing alkyltin trichlorides also suggested the involvement of such Pd−alkyl species.[3] To explain the current experimental results, we need to assume that an alkyl species, e.g. *cis*-[PdR(SnCl$_3$)(PPh$_3$)$_2$], can somehow be generated in kinetically relevant concentrations from *cis*-[PdCl(SnCl$_2$R)(PPh$_3$)$_2$]. A possible mechanism for this process is one that involves the reversibility of the Sn−Cl oxidative addition step and competing Sn−C bond activation (top right part of Scheme 1 (revised)). In the original article it was already shown by DFT calculations on a model system that a concerted Sn−C bond oxidative addition is in principle feasible. Another possibility is a direct R/Cl exchange between Sn and Pd through an intramolecular process. However, due to the dominance of the Sn−Cl activation, Sn−C bond activation is only expected to result in significant amounts of observable products if it is coupled to a thermodynamically favorable followup reaction as in the case of R = ^{n}Bu (elimination and isomerization of 1-

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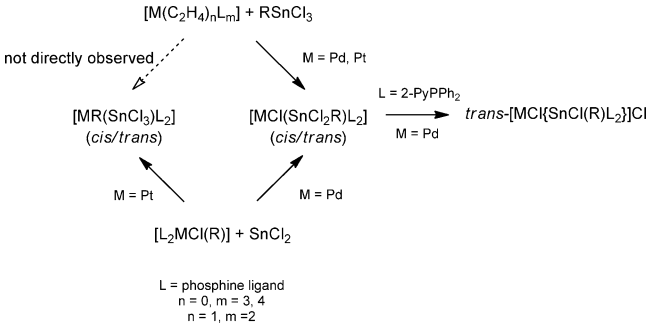
butene). The replacement of the triphenylphosphine ligands by 2-pyridyldiphenylphosphine effectively prevents the reversibility of the Sn−Cl oxidative addition step by stabilizing the Sn−Cl oxidative products such as [**11**]Cl.

When the observed Pd chemistry is compared to the Pt chemistry reported by Eaborn and Pidcock (references provided in the original article), it can be conluded that the Pd(0) and Pt(0) precursors in a qualitative sense display similar chemistry with respect to monoorganotin trichlorides (Scheme 3 (revised)). Concerning the insertion of $SnCl_2$ in *trans*-

Scheme 3 (revised). Comparison of the Reactivity of $RSnCl_3$ on Pt(0) and Pd(0) Precursors



[MCl(R)L_2] (L = phosphine ligand; M = Pd, Pt; R = Ph, Me, ^{n}Bu) there is a striking difference. Whereas for Pt the reaction results in the well-known trichlorostannyl derivatives *cis*- and *trans*-[MR($SnCl_3$)L_2], for Pd the reaction products observed are the organostannyl derivatives *cis*- and *trans*-[MCl($SnCl_2$R)-L_2], which can be trapped in their ionic form if 2-pyridyldiphenylphosphine is used as the ligand rather than triphenylphosphine.

CONCLUSIONS

The above studies show that the reaction of monoorganotin trichlorides with Pd(0)−phosphine complexes proceeds predominantly through an oxidative addition of the Sn−Cl bond, which is qualitatively similar to observations for related Pt(0) precursors, although the stability of the resulting complexes appears to be lower for Pd. 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−organostannyl products and to synthesize in a single step cationic alkylstannylenepalladium complexes that are stabilized by intramolecular coordination of the pyridyl groups of two 2-pyridyldiphenylphosphine ligands to the stannylene moiety. The latter is in strong contrast to organostannyl derivatives obtained from [Pd(PPh_3)$_4$] that undergo facile *cis*−*trans* isomerization, elimination of $SnCl_2$, and/or degradation through 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

All reactions and manipulations were performed under a nitrogen atmosphere in a glovebox or using conventional Schlenk techniques. All nondeuterated solvents were dried using an MBraun SPS-800 solvent purification system and degassed prior to use, except for dichloromethane-d_2 and chloroform-*d*, which were dried over and distilled from CaH_2. [Pt(dba)$_2$][4] and 2-(diphenylphosphino)-1-methylimidazole[5] were prepared by literature methods. All other reagents were purchased form Sigma-Aldrich. NMR data were recorded on a Varian MRF 400 or a Varian VNMRS 400 spectrometer at room temperature unless stated otherwise. Chemical shifts are reported relative to the residual solvent signals (^{1}H, ^{13}C), external H_3PO_4 85% in water (^{31}P), or external $SnMe_4$ (1 M, ^{119}Sn) in benzene.

Synthesis of *trans*-[PdCl($SnCl_2$(Ph)(2-$PyPPh_2$)$_2$)] (12). A Schlenk flask was charged with [Pd(dba)$_2$] (230 mg, 0.4 mmol) and 2-$PyPPh_2$ (0.22 g, 0.4 mmol). A 10 mL portion of dry, degassed toluene was then added, and the resulting orange-brown solution was stirred for 1 h at room temperature. The reaction mixture was filtered by cannula, resulting in a clear, bright orange solution to which was added $PhSnCl_3$ (116 mg, 0.063 mL, 0.4 mmol). After 1 h, the resulting suspension was concentrated in vacuo, followed by washing with diethyl ether (3 × 20 mL). The resulting solid was then dissolved in 20 mL of dichloromethane and filtered over a plug of Celite. The product was obtained as an analytically pure off-white solid after concentration of the resulting solution and drying in vacuo. Yield: 0.33 g (325 mg, 0.35 mmol, 91%). Crystals suitable for single-crystal X-ray analysis were obtained from layering a dichloromethane solution with toluene. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.70 (d, $^3J_{HH}$ = 6.8 Hz, 2H, 6-Py-H), 7.88 (m, $^3J_{HH}$ = 8.4 Hz, 2H, 4-Py-H), 7.77 (d, $^3J_{HH}$ = 6.4 Hz, 8H, o-PPh-H), 7.62 (dd, $^3J_{HH}$ = 8.4 Hz, 6.8 Hz, 2 H, 5-Py-H), 7.60 (m, 2H, SnPh-H), 7.50 (t, $^3J_{HH}$ = 7.2 Hz, 4H, p-PPh-H), 7.45−7.40 (m, 11 H, m-PPh-H, SnPh-H), 7.36 (m, 2H, 3-Py-H). ^{13}C{^{1}H} NMR (100.54 MHz, CD_2Cl_2): δ 150.3 (t, J_{PC} = 30.0 Hz, 2-Py-CH), 148.8 (s, i-SnPh-C), 147.8 (t, J_{PC} = 8.4 Hz, 6-Py-CH), 139.7 (s, 4-Py-CH), 136.3 (s, o-SnPh-CH), 134.3 (t, J_{PC} = 6.9 Hz, o-PPh-CH), 131.5 (t, J_{PC} = 8.3 Hz, 3-Py-CH), 131.1 (s, p-PPh-CH), 129.9 (t, J_{PC} = 24.4 Hz, i-PPh-C), 129.7 (s, p-SnPh-CH), 128.8 (s, m-SnPh-CH), 128.5 (t, J_{PC} = 8.3 Hz, m-PPh-CH), 126.8 (s, 5-Py-CH). ^{31}P{^{1}H} NMR (161.85 MHz, CD_2Cl_2): δ 62.4 (J_{SnP} = 443 Hz). ^{119}Sn{^{1}H} NMR (149.07 MHz, CD_2Cl_2): δ −274.1 (broad, lwhh = 2990 Hz). HRMS (ESI): exact mass (monoisotopic) calcd for $PdSnCl_2P_2N_2C_{40}H_{33}$ m/z 898.9580, found 898.9531 [M − Cl]$^+$.

Synthesis of *trans*-[PdCl(SnCl(^{n}Bu)(2-$ImPPh_2$)$_2$)][^{n}$BuSnCl_4$] ([13][^{n}$BuSnCl_4$]). In a Schlenk flask containing neat [Pd(dba)$_2$] (102 mg, 0.18 mmol) was placed 2-(diphenylphosphino)-1-methylimidazole (115 mg, 0.43 mmol, 2.5 equiv) in toluene (5 mL). The mixture was stirred at room temperature for 1 h, and a small amount of palladium black was removed by cannula filtration. Monobutyltin trichloride (101 mg, 0.36 mmol, 2 equiv) was added slowly to the orange-brown solution. After 1 h the solvent was removed under vacuum and the residue was washed with ether (3 × 10 mL) to give [**13**][^{n}$BuSnCl_4$] (182 mg, 0.15 mmol, 84% yield) as a yellow powder. Crystals suitable for single-crystal X-ray analysis were obtained by recrystallization from diethyl ether. ^{1}H NMR (399.80 MHz, CD_2Cl_2): δ 7.66−7.61 (m, 12H, H_2, H_6, H_8, H_9), 7.54−7.53 (m, 12H, H_3, H_4, H_5), 3.24 (s, 6H, N−CH_3), 2.18 (t, J_{HH} = 7.4 Hz, 2H, $Cl_4SnCH_2CH_2CH_2CH_3$), 1.96 (t, J_{HH} = 7.7 Hz, 2H, $ClSnCH_2CH_2CH_2CH_3$), 1.92−1.84 (m, 2H, $Cl_4SnCH_2CH_2CH_2CH_3$), 1.51−1.38 (m, 4H, $ClSnCH_2CH_2CH_2CH_3$, $Cl_4SnCH_2CH_2CH_2CH_3$), 1.18−1.09 (m, 2H, $ClSnCH_2CH_2CH_2CH_3$), 0.94 (t, J_{HH} = 7.3 Hz, 3H, $Cl_4SnCH_2CH_2CH_2CH_3$), 0.65 (t, J_{HH} = 7.2 Hz, 3H, $ClSnCH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR (100.54 MHz, CD_2Cl_2): δ 139.5 (t, $^1J_{CP}$ = 34 Hz, C_7), 133.7 (t, $^2J_{CP}$ = 7 Hz, C_2, C_6), 133.3 (broad, C_4, C_9), 130.5 (t, $^3J_{CP}$ = 6 Hz, C_3, C_5), 128.5 (t, $^3J_{CP}$ = 8 Hz, C_8), 125.9 (t, $^1J_{CP}$ = 26 Hz, C_1), 45.4 (s, $Cl_4SnCH_2CH_2CH_2CH_3$), 37.1 (s, N-CH_3), 32.7 (s, $ClSnCH_2CH_2CH_2CH_3$), 29.1 (s, $ClSnCH_2CH_2CH_2CH_3$), 28.4 (s, $Cl_4SnCH_2CH_2CH_2CH_3$), 27.4 (s, $ClSnCH_2CH_2CH_2CH_3$), 26.3 (s, $Cl_4SnCH_2CH_2CH_2CH_3$), 14.3 (s, $Cl_4SnCH_2CH_2CH_2CH_3$), 14.1 (s, $ClSnCH_2CH_2CH_2CH_3$). ^{31}P{^{1}H} NMR (161.85 MHz, CD_2Cl_2): δ 30.6 (s, J_{PSn} = 87 Hz). ^{119}Sn{^{1}H} NMR (149.07 MHz, CD_2Cl_2): δ −121.1 (broad, $\omega_{1/2}$ = 173 Hz, SnCl^nBu), −248.1 (broad, $\omega_{1/2}$ = 745 Hz, $SnCl_4$^{n}Bu). HRMS (ESI): exact mass (monoisotopic) calcd for $C_{36}H_{39}Cl_2N_4P_2PdSn$ 885.0085, found 885.0146 [M − BuSnCl]$^+$.

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■ ASSOCIATED CONTENT

Supporting Information

Figures giving ESI-HRMS data for [**11**][$BuSnCl_4$] (in the original article the data for [**5**][$MeSnCl_4$] were provided twice) and the $^{1}H/^{13}C$-HSQC spectrum for the reaction of [Pd(PPh_3)$_4$] with $MeSnCl_3$ (400 MHz in THF-d_8 at −50 °C). This material is available free of charge via the Internet at http://pubs.acs.org.

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