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cis-($R'_2PC_2H_4PR'_2$)PdH(SnR_3) Complexes: Trapped Intermediates in the Palladium-Catalyzed Hydrostannation of Alkynes[†]

Roman Trebbe, Frank Schager, Richard Goddard, and Klaus-Richard Pörschke*

Max-Planck-Institut für Kohlenforschung, Postfach 101353,
45466 Mülheim an der Ruhr, Germany

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The complexes ($R'_2PC_2H_4PR'_2$)Pd(C_2H_4) ($R' = {}^iPr$, ${}^tBu$) react with R_3SnH ($R = Me$, ${}^nBu$) by displacement of the ethene ligand and oxidative addition of the Sn−H bond to generate the chelating phosphane stabilized *cis* Pd^{II} hydrido stannyl complexes ($R'_2PC_2H_4PR'_2$)PdH(SnR_3) ($R' = {}^iPr$ (**1**), ${}^tBu$ (**2**)). Complex **1a** ($R' = {}^iPr$, R = Me), containing the smallest substituents, is only transiently formed but has been detected at −80 °C by NMR spectroscopy. It reacts further with Me_3SnH, even at −120 °C, by eliminating hydrogen to give (d^ippe)Pd($SnMe_3$)$_2$ (**3**). In contrast, the isolated (d^ippe)PdH(Sn^nBu_3) (**1b**) is briefly stable at ambient temperature, whereas the sterically encumbered species (d^tbpe)PdH(SnR_3) (R = Me (**2a**), ${}^nBu$ (**2b**)) are stable well above 100 °C. The molecular structure of **2a** has been determined by X-ray crystallography. Complex **2a** reacts with 2 equiv of $C_2R''_2$ ($R'' = CO_2Me$) to give (d^tbpe)Pd($C_2R''_2$) (**4**) and predominantly the corresponding (*E*)-vinylstannane (*E*)-(R'')(H)C═C($SnMe_3$)-(R'') (***E*-5**). Since **2a** also catalyzes the hydrostannation of the alkyne, the *cis* Pd^{II} hydrido stannyl complexes **1a,b** and **2a,b** represent trapped intermediates in the Pd-catalyzed hydrostannation of alkynes. The existence of the complexes also sheds light on the mechanism of the Pd-catalyzed degradation of R_3SnH into Sn_2R_6 and H_2.

Introduction

Hydrostannation of alkynes[1] provides a convenient route to the synthetically useful vinylstannanes.[2] The spontaneous reaction is thought to proceed either by an ionic or free radical *trans*-mechanism to generate (*Z*)-vinylstannanes, which may eventually isomerize into the thermodynamically favored (*E*)-vinylstannanes.[3a] In contrast, the L_2Pd^0-catalyzed hydrostannation of alkynes leads regio- and stereospecifically to the (*E*)-vinylstannanes.[4] This reaction implies oxidative addition of R_3-Sn−H to Pd^0 to generate a Pd^{II} hydrido stannyl intermediate,[4a] which then undergoes *cis* addition of either the Pd−H or Pd−Sn[5] bond to the alkyne C≡C bond, followed by reductive elimination of the (*E*)-vinylstannane. The supposed *cis* Pd^{II} hydrido trialkylstannyl intermediates have so far remained elusive (Scheme 1).

In contrast, *trans*-(Ph_3P)$_2$PtH($SnMe_3$) has been known for a long time.[6] Moreover, we recently reported that chelating phosphane stabilized ($R'_2PC_2H_4PR'_2$)Pd^0 stannylene complexes react reversibly with weak acids such as water by HX addition across the Pd═Sn bond to give relatively stable ($R'_2PC_2H_4PR'_2$)Pd(H)SnR_2X (**A**; R = $CH(SiMe_3)_2$, X = OH, OMe).[7] While ($R'_2PC_2H_4PR'_2$)Pd-(H)SnR_3-type complexes should be accessible from **A** by substituting R for X, a more direct and general synthetic route is the oxidative addition of R_3Sn−H to a suitable ($R'_2PC_2H_4PR'_2$)Pd^0 starting complex. Here we report, for the first time, the synthesis and properties of *cis* Pd^{II} hydrido *trialkyl*stannyl complexes, ($R'_2PC_2H_4PR'_2$)Pd-(H)SnR_3.[8]

Results and Discussion

When the yellow-brown solutions of ($R'_2PC_2H_4PR'_2$)-Pd(C_2H_4) ($R' = {}^iPr$, ${}^tBu$)[9] in pentane are reacted with 1 equiv of R_3SnH (R = Me, ${}^nBu$) at 20 °C, ethene is liberated. Subsequent cooling of the reaction mixtures to −30 or −78 °C affords colorless or beige crystals of

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[†] Abbreviations: d^ippe, bis(diisopropylphosphino)ethane, ${}^iPr_2PC_2H_4P{}^iPr_2$; d^tbpe, bis(di-*tert*-butylphosphino)ethane, ${}^tBu_2PC_2H_4P{}^tBu_2$; dmad, dimethyl acetylenedicarboxylate.

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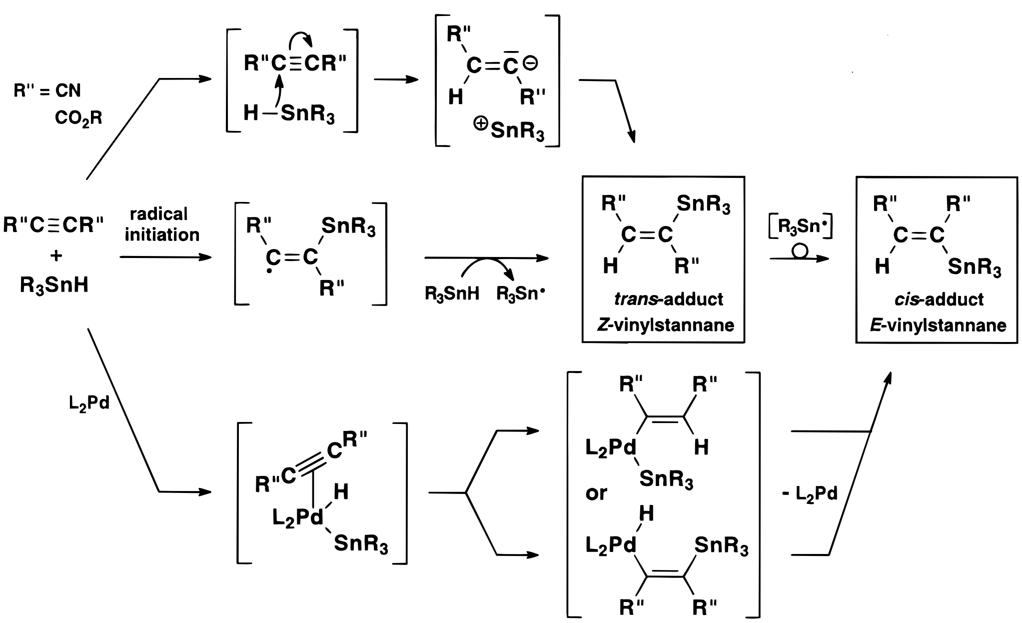
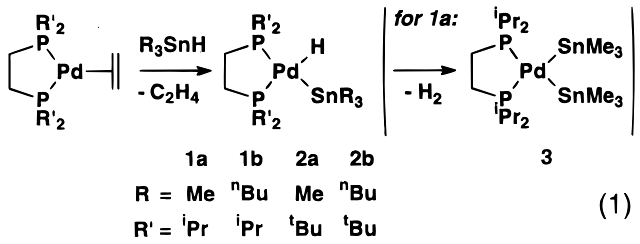
Scheme 1



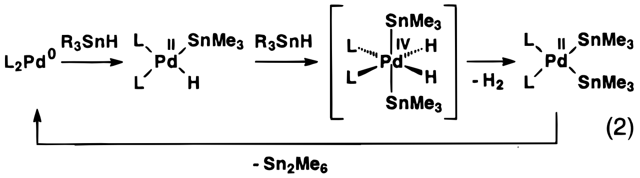
the $(R'_2PC_2H_4PR'_2)PdH(SnR_3)$ complexes **1b** (42%), **2a** (87%), and **2b** (81%). Complex **1a** ($R' = {}^iPr$, $R = Me$), in which the substituents are smallest, is unstable and has not been isolated. The reactions also proceed at −78 °C (eq 1). Remarkably, in all cases the ethene ligand of the starting complexes is extruded and does not insert into either the Pd−H or Pd−Sn bond of the product complexes.



(1)

The isolated compounds differ considerably in their thermal properties. Complex **1b** melts with slow decomposition below 20 °C. Complex **2a** decomposes at 144 °C without melting, while **2b** already melts at 52 °C but appears to decompose only at about 160 °C. Thus, thermal stability appears to increase with the bulk of the phosphane ($d^ippe < d^tbpe$) and, interestingly, with increasing chain length of R ($Me < {}^nBu$). The melting points decrease with increase in chain length of R.

Complex **1a** was observed and has been characterized by its NMR spectra when the reaction was performed at −78 °C. This complex reacts further with Me_3SnH, even at −120 °C, to yield $(d^ippe)Pd(SnMe_3)_2$ (**3**)[10] and hydrogen (eq 1). The reaction probably proceeds through an octahedral $[(d^ippe)Pd(H)_2(SnMe_3)_2]$ intermediate, which reductively eliminates the hydrogen. Considering that the known *cis,cis,trans*-$L_2Pt(H)_2(SnR_3)_2$ complexes, with L = phosphane, reversibly eliminate hydrogen,[11] we tentatively assume a similar structure for the $[(d^ippe)Pd(H)_2(SnMe_3)_2]$ intermediate, although an *all-cis* structure cannot be ruled out. The stability of **3** can be contrasted with the fact that in the presence of L_n-Pd complexes ($L = PPh_3$, for example) trialkylstannanes tend to catalytically eliminate hydrogen to give Sn_2R_6.[12] It would seem that the chelating d^ippe ligand in **3** stabilizes this type of complex so that reductive elimination of Sn_2R_6 is inhibited. It therefore follows that the transient complexes **1a** and $[(d^ippe)Pd(H)_2(SnMe_3)_2]$ and isolable **3** serve as model intermediates in the Pd-catalyzed hydrogen elimination from R_3SnH to give Sn_2R_6, giving weight to a mechanism involving a $Pd^0 \leftrightarrow Pd^{II} \leftrightarrow Pd^{IV}$ change in oxidation states (eq 2).



(2)

Spectroscopic Characterization of 1a,b and 2a,b. In the EI mass spectra of the thermally stable d^tbpe complexes **2a**,**b**, the molecular ions are observed, which characteristically fragment by loss of an R substituent to generate $[(d^tbpe)Pd(H)SnR_2]^+$. Further successive degradation affords $[(d^tbpe)Pd]^+$ as a prominent (**2b**) or the base ion (**2a**). Interestingly, M^+ does not undergo RH elimination to give $[(d^tbpe)Pd{=}SnR_2]^+$, although HX elimination was observed for **A**.[7] In the IR spectra the PdH stretching band of the d^tbpe complexes **2a**,**b** appears at 1837 cm^{-1}, and for the d^ippe derivative **1b** it lies at an even lower wavenumber (1816 cm^{-1}).

Selected ^1H, ^{13}C, and ^{31}P NMR data of complexes **1a**,**b** and **2a**,**b** are listed in Table 1. The PdH resonances were found for **1a**,**b** at $\delta(H)$ −3.0 and for **2a**,**b** at $\delta(H)$ −4.0

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Table 1. Selected ^{1}H, ^{13}C, and ^{31}P NMR Data of Complexes 1a,b and 2a,b[a]

	δ(H)		δ(C)	δ(P)[b]	
	$SnCH_n$	PdH	$SnCH_n$	$P_{trans\ to\ Sn}$	$P_{cis\ to\ Sn}$
1a[b]	*c*	−3.08	*c*	75.2	76.35
		^2J(PH) 178, <1		^2J(PP) 10	^2J(PP) 10
		^2J(SnH) 94		$^2J(^{119}$SnP) 1700	^2J(SnP) ~50
1b	0.81	−3.00	14.6	76.1	78.9
		^2J(PH) 175, <1		^2J(PP) <1	^2J(PP) <1
	^2J(SnH) ~36	$^2J(^{119}$SnH) 102	$^1J(^{119}$SnC) 168	$^2J(^{119}$SnP) 1571	^2J(SnP) 61
2a	0.07	−3.98	−2.4	94.9	95.6
		^2J(PP) 4		^2J(PP) 4	^2J(PP) 4
		^2J(PH) 171, <5			
	^2J(SnH) 36	$^2J(^{119}$SnH) 133	^1J(SnC) 145	$^2J(^{119}$SnP) 1789	^2J(SnP) 51
2b	~0.8[c]	−3.92	14.9	93.7	96.5
		^2J(PH) 167, <5		^2J(PP) <2	^2J(PP) <2
		$^2J(^{119}$SnH) 141	$^1J(^{119}$SnC) 164	$^2J(^{119}$SnP) 1603	^2J(SnP) 61

[a] Conditions: solvent THF-d_8, temperature 27 °C, if not indicated otherwise. Coupling constants are given in hertz. [b] Temperature −80 °C. [c] Partially obscured.

and thus occur at somewhat lower field than for **A** (δ(H) −4.2 to −5.5). The signals appear as doublets due to strong $^2J(PH)_{trans}$ coupling ($^2J(PH)_{cis}$ is insignificant). The additional $^2J(SnH)_{cis}$ couplings are larger for the d^{t}bpe (**2a**, 133 Hz; **2b**, 141 Hz) than for the d^{i}ppe complexes (**1a**, 94 Hz; **1b**, 102 Hz) and larger for the Sn^nBu_3 than for the $SnMe_3$ derivatives, possibly reflecting the proximity of the substituents in the molecular structure.[13] The ^{1}H and ^{13}C signals of the SnR_3 groups are generally similar to those of R_3SnH, with the distinction that in **1b** and **2a,b** Sn*C*H$_n$ is somewhat deshielded and the magnitudes of ^1J(SnC) are markedly smaller (145−168 Hz) than those of the free tin hydrides (~350 Hz).[14] In the ^{31}P NMR spectra two signals are observed for the inequivalent ^{31}P nuclei, for which the coupling ^2J(PP) is very small and is not always detected. The couplings $^2J(SnP)_{trans}$ = 1570−1790 Hz and $^2J(SnP)_{cis}$ = 50−60 Hz are significantly different from those of **A** (~2300 and 25−40 Hz).[7] The NMR signals of the $(R'_2PC_2H_4PR'_2)Pd$ moieties indicate that the complexes have C_s point symmetry. Although the NMR spectra are almost temperature independent between 20 and −80 °C, the ^{31}P NMR spectra were best resolved at low temperature. As can be seen from the above data, replacing the oxygen substituents (X) in the SnR_2X groups by R leads to marked changes in the spectra.

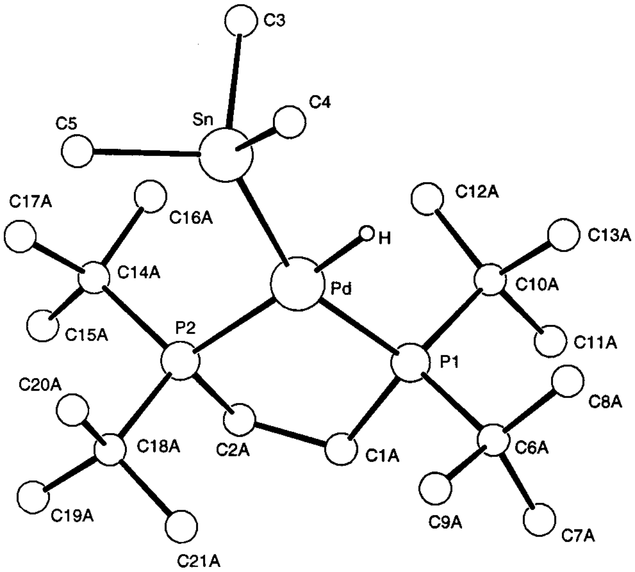

Figure 1. Molecular structure of **2a** (H atoms, except for the hydride H atom, and one of the two conformations adopted by the d^{t}bpe ligand are omitted for clarity). Selected bond distances (Å) and angles (deg): Pd−P1 = 2.349(1), Pd−P2 = 2.356(1), Pd−Sn = 2.6082(3), Pd−H = 1.59(3); P1−Pd−P2 = 88.80(2), P1−Pd−Sn = 158.44(1), P2−Pd−Sn = 111.11(1), P1−Pd−H = 93(1), P2−Pd−H = 178(1), Sn−Pd−H = 67(1), Pd−Sn−C3 = 107.92(8), Pd−Sn−C4 = 120.51(6), Pd−Sn−C5 = 123.09(6).

Molecular Structure of (d^{t}bpe)PdH(SnMe$_3$) (2a). The molecular structure of **2a** has been determined by X-ray crystallography (Figure 1). Although the d^{t}bpe group was found to be disordered over two conformations in all the samples studied (see Experimental Section), the diffraction data are good (R_{int} = 0.022, for 30 399 reflections) and all non-H atoms, together with the hydrogen atom bonded to Pd, could be located and refined satisfactorily (U_H = 0.041(7) Å^2). The Pd atom in **2a** is coordinated in a distorted-square-planar fashion by the d^{t}bpe P atoms, the $SnMe_3$ substituent, and the hydride H atom. The bite angle of the chelating d^{t}bpe ligand at 88.80(2)° falls within the range typically observed (86−89°) for $(R_2PC_2H_4PR_2)Pd$ complexes (R = ^{i}Pr,[7,15−17] ^{t}Bu[10]). The deviations of the P1−Pd−Sn angle (158.44(1)°) from linearity and P2−Pd−Sn angle (111.11(1)°) from 90° are, however, larger than those for (d^{i}ppe)Pd(H)Sn(OH){CH(SiMe$_3$)$_2$}$_2$ (**A′**; P−Pd−P = 87.5°; P_{trans}−Pd−Sn = 162.7°; P_{cis}−Pd−Sn = 108.9°),[7] presumably a result of steric repulsion. The hydride H atom lies almost *trans* to P2 (P2−Pd−H = 178(1)°) but, because of the small P1−Pd−Sn angle, only makes an angle of 67° to Sn at the Pd atom. The resulting relatively short Sn···H distance (2.47(3) Å) is thus

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(13) (a) The magnitude of the couplings $^2J(^{119}SnH)_{cis}$ is substantially larger than for the SnR_2X compounds **A** (10−45 Hz)[7] and is directed opposite to $^1J(^{119}$SnH) of the parent stannanes (Bu_3SnH, 1610 Hz; Me_3SnH, 1740 Hz; $\{(Me_3Si)_2CH\}_2(HO)SnH$, 1991 Hz[13b]). (b) Schager, F.; Goddard, R.; Seevogel, K.; Pörschke, K.-R. *Organometallics* **1998**, *17*, 1546.

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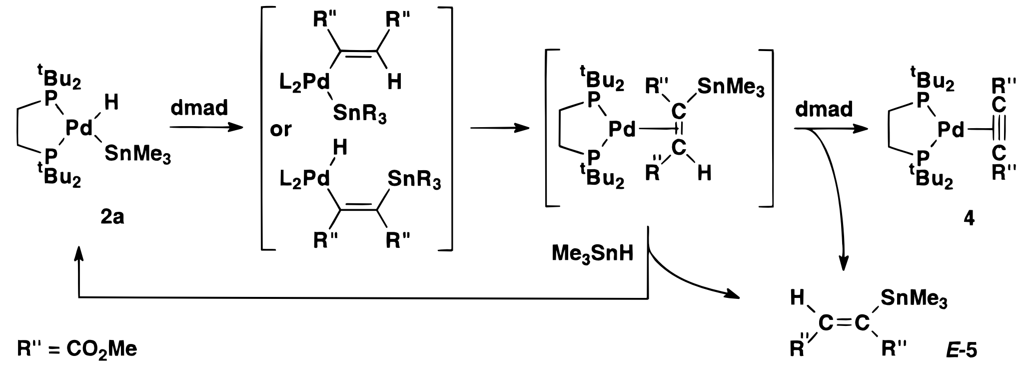
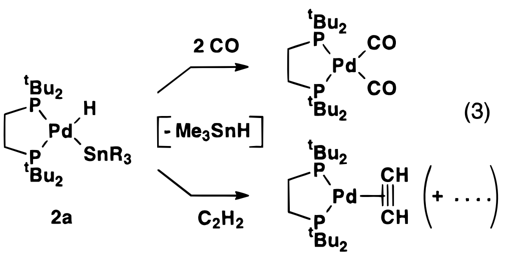
Scheme 2



probably not a result of a direct interaction but, rather, is due to the steric repulsion in the remainder of the molecule. Indeed, the Sn atom appears to be forced 0.36 Å out of a mean plane through Pd, the two P atoms, and the H atom, and the Pd−Sn−C angles are significantly different (108−123°), with those C atoms nearest to the coordination plane of the Pd atom exhibiting the largest angles.

The bonds Pd−P1 (2.349(1) Å) (*trans* to Sn) and Pd−P2 (2.356(1) Å) (*trans* to H) are almost equal in length, but both are somewhat longer than those for **A′**.[18] Similarly, the Pd−Sn bond length in **2a** at 2.6082(3) Å is also greater than that for **A′** [18] but is equal to that in (d^{t}bpe)Pd(SnMe$_3$)$_2$.[10] The Pd−H distance is 1.59(3) Å and compares favorably with Pd−H distances found in other Pd hydrides (average 1.55(6) Å).

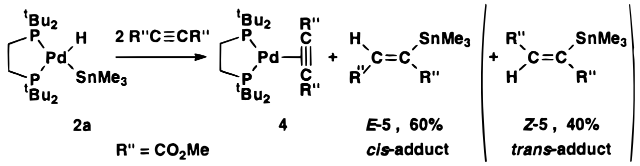
Reactivity of (d^{t}bpe)Pd(H)SnMe$_3$ (2a). The reactivity of **2a** has been studied in detail. Even on prolonged exposure, the compound is surprisingly inert toward water (12 h), ethene (6 h), or hydrogen (6 h) at ambient temperature. However, **2a** reacts with CO in pentane or ether to afford (d^{t}bpe)Pd(CO)$_2$[17] by formal Me$_3$SnH elimination (the actual products are Sn$_2$Me$_6$ and H$_2$ under the reaction conditions). When a pentane solution of **2a** is treated with ethyne for 1 h at 20 °C and the volatiles are evaporated under vacuum, a beige solid is left which consists of unreacted **2a** and the ethyne adduct (d^{t}bpe)Pd(C$_2$H$_2$) (δ_P 91.3),[9] among other unidentified components (eq 3).



(3)

The reaction (20 °C) of **2a** and 2 equiv of the strongly electron withdrawing dimethyl acetylenedicarboxylate[19] in diethyl ether or pentane affords, in the course of 1 h, a beige precipitate of (d^{t}bpe)Pd(dmad) (**4**), which is poorly soluble at low temperature and thus is easily separated. The remaining solution contains, besides some residual **4**, an isomeric mixture comprising mainly (*E*)-(R″)(H)C=C(SnMe$_3$)(R″) (***E*-5**, R″ = CO$_2$Me, *cis* adduct, 60%; $^3J(^{119}\mathrm{SnH})_{\mathrm{cis}}$ = 53 Hz),[4f] together with a smaller amount of (*Z*)-(R″)(H)C=C(SnMe$_3$)(R″) (***Z*-5**, *trans* adduct, 40%; $^3J(^{119}\mathrm{SnH})_{\mathrm{trans}}$ = 93 Hz) (eq 4). The isomeric vinylstannanes are readily distinguishable on the basis of the characteristic Sn,H spin−spin couplings of their vinyl protons.[3b] In contrast, the direct reaction of ^{n}Bu$_3$SnH with a slight excess of dmad (toluene-d_8, 20 °C, 1 h) leads exclusively to the formation of the corresponding *trans* adduct, (*Z*)-(R″)(H)C=C(Sn^{n}Bu$_3$)-(R″),[20] most likely by the ionic mechanism (Scheme 1), and the product does not isomerize within 1 week.

(4)



Since R$_3$SnH reacts directly with dmad to give exclusively the (*Z*)-vinylstannane, the formation of the (*Z*/*E*)-vinylstannane isomer mixture in the presence of **2a** (eq 4) indicates that more than half of **2a** reacts by alkyne insertion into the Pd−H or Pd−Sn bond to generate a Pd^{II} alkenyl intermediate, which by coupling of the substituents is converted into a Pd^0 (*E*)-vinylstannane π-complex, from which ***E*-5** is displaced by dmad to give **4** (cf. Scheme 2). The remainder of **2a** can undergo reductive Me$_3$SnH elimination, similar to the reactions shown in eq 3, and the generated [(d^{t}bpe)Pd^0] is trapped by dmad, also giving **4**, while the eliminated Me$_3$SnH reacts directly with dmad to give the (*Z*)-vinylstannane ***Z*-5**. The yields suggest that the rates of both stoichiometric reactions are about the same.

To determine whether the reaction of molar equivalents of Me$_3$SnH and dmad can be catalyzed by **2a** to produce the (*E*)-vinylstannane ***E*-5**, a corresponding mixture of Me$_3$SnH and dmad, containing 2% of **2a**, was reacted at 20 °C for 2 days and the solution subsequently filtered to remove the precipitated **4**. A 1:13 mixture of ***E*-5** (resulting from Pd catalysis) and ***Z*-5**

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[18] **A′**: Pd−P1 = 2.294(2) Å, Pd−P2 = 2.322(2) Å, Pd−Sn1 = 2.575(1) Å. The shorter Pd−P bonds are most likely due to the fact that the structure was determined at room temperature.[7]

[19] For an early study on the Pd-catalyzed ^{n}Bu$_3$SnH addition to dmad, see ref 4c.

[20] (a) For the (uncatalyzed) reaction of R$_3$SnH (R = Me, ^{n}Bu) with neat diethyl acetylenedicarboxylate, see: Leusink, A. J.; Marsman, J. W.; Budding, H. A. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 689. (b) The possibility of coordination of a carbonyl group to the R$_3$Sn^{IV} center in the intermediate cannot be neglected when discussing the mechanism of dmad hydrostannation.[3c]

(due to spontaneous reaction) was obtained, with a total yield of 80%. Thus, 5.7% of the original dmad was converted into ***E*-5**, corresponding to the formation of 2.8 molecules of ***E*-5** per Pd atom. Assuming that up to 0.6 molecule of ***E*-5** per Pd atom is created by the stoichiometric reaction of **2a** with dmad (eq 4), we estimate that the turnover number for catalytically produced ***E*-5** is 2.2. Although a much larger amount of the *Z* isomer ***Z*-5** is formed by the simultaneous uncatalyzed reaction of Me_3SnH and dmad, which outperforms the Pd catalysis, the reaction clearly shows that **2a** can function as an intermediate in the Pd-catalyzed hydrostannation of dmad. The mechanism of the catalysis can thus be thought of as two stoichiometric reactions in which **2a** is consecutively converted into Pd^{II} alkenyl[21] and Pd^0 (*E*)-vinylstannane intermediates. The latter either reacts with Me_3SnH with re-formation of **2a**, thereby closing the catalytic cycle, or reacts with dmad to give **4** (Scheme 2).

Complex **4** is very stable; it decomposes without melting only at about 200 °C, and solutions of the compound are stable at ambient temperature for a long period. In the EI mass spectrum of **4** a weak molecular ion is observed, which fragments by cleavage of the dmad ligand to give $[(d^tbpe)Pd]^+$ as base ion. The IR and NMR data of **4** are very similar to those of (d^ippe)Pd(dmad).[16] When **4** is reacted with Me_3SnH, the latter is catalytically decomposed into Sn_2Me_6 and H_2, and neither vinylstannane ***Z/E*-5** is formed. **4** is therefore not a catalyst for the hydrostannation of dmad, and formation of **4** represents loss of catalyst from the catalytic cycle (Scheme 2).

Conclusions

Whereas the spontaneous hydrostannation of alkynes affords (*Z*)-vinylstannanes, the L_2Pd^0-catalyzed reaction leads regio- and stereospecifically to the (*E*)-vinylstannanes, but the exact course of the reaction is dependent on the nature of the phosphane ligands L_2. For example, while the monodentate phosphane complexes, such as $Pd(PPh_3)_4$,[4a,e,f] are effective catalysts, the chelating phosphane derivative $Pd(Ph_2PC_2H_4PPh_2)_2$ is not.[4d] Here we show that the chelating phosphane containing fragments $[(R'_2PC_2H_4PR'_2)Pd]$ ($R' = {}^iPr, {}^tBu$) are best suited to *stabilize intermediates* such as the Pd^{II} hydrido stannyls, since the use of a chelating phosphane retards loss of one phosphane ligand. In addition, we find that the intermediates are the same for both the Pd-catalyzed degradation of R_3SnH into Sn_2R_6 and H_2 and the Pd-catalyzed hydrostannation of alkynes. The presence of the Pd^{II} hydrido stannyl intermediates in both reactions seems to imply a $Pd^0 \leftrightarrow Pd^{II} \leftrightarrow Pd^{IV}$ change in oxidation states and hence the existence of an additional octahedral Pd^{IV} intermediate.

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by using standard Schlenk techniques. For the NMR spectra solutions of the compounds in THF-d_8 were used if not indicated otherwise. Mass spectra were recorded at 70 eV and refer to ^{106}Pd and ^{120}Sn. Details of the spectroscopic instruments are given in ref 16. ***E*-5** has been decribed elsewhere.[4f]

($^iPr_2PC_2H_4P^iPr_2$)Pd(H)SnMe$_3$ (1a). A solution of (d^ippe)Pd(C_2H_4) (40 mg, 0.1 mmol) in 1 mL of THF-d_8 was treated with Me_3SnH (17 mg, 0.1 mmol) at −78 °C, and the ^1H and ^{31}P NMR spectra were recorded within 1 h. The spectra revealed the presence of **1a**, (d^ippe)Pd($SnMe_3$)$_2$ (δ_P 75.5), and unreacted (d^ippe)Pd(C_2H_4) (δ_P 62.7) in a 1:1:1 ratio among traces of other components. ^1H NMR (300 MHz, −80 °C) and ^{31}P NMR (121.5 MHz, −80 °C): see Table 1.

($^iPr_2PC_2H_4P^iPr_2$)Pd(H)Sn^{n}Bu$_3$ (1b). A yellow-brown solution of (d^ippe)Pd(C_2H_4) (397 mg, 1.00 mmol) in 10 mL of pentane was combined with $^nBu_3SnH$ (0.27 mL, 1.00 mmol) at −30 °C. When the mixture was slowly warmed to ambient temperature, ethene evolved, and the mixture turned brown. After filtration to remove some insoluble impurities, the clear, brown solution was cooled to −78 °C to obtain off-white intergrown crystals, which were freed from the mother liquor, washed with some cold pentane, and dried under vacuum at −30 °C: yield 280 mg (42%); $C_{26}H_{60}P_2PdSn$ ($M_r = 659.8$). The compound liquefied at ambient temperature to form a dark brown oil, and thus no elemental analysis was performed. IR (KBr): 1816 cm^{-1} (PdH). EI-MS: the compound decomposed. ^1H NMR (300 MHz, 27 °C; for PdH, see Table 1): δ 2.14 (4H, PCH and P′CH), 1.83, 1.81 (each 2H, PCH_2 and $P'CH_2$), 1.16, 1.14, 1.06, 1.06 (each 6H, Me), d^ippe; 1.55 (m, 6H, $C_\beta H_2$), 1.30 (m, 6H, $C_\gamma H_2$), 0.85 (t, 9H, Me), 0.81 (m, 6H, $^2J(SnH) \approx 34$ Hz, $SnCH_2$), Sn^nBu_3. ^{13}C NMR (75.5 MHz, 27 °C): δ 26.8, 26.5 (each 2C, PCH and P′CH), 24.2, 22.2 (each m, 1C, PCH_2 and $P'CH_2$); 20.7, 20.3, 19.2, 18.7 (each 2C, Me), d^ippe; 32.4 (3C, $^2J(SnC) = 8$ Hz, $C_\beta H_2$), 28.7 (3C, $^3J(SnC) = 44$ Hz, $C_\gamma H_2$), 14.6 (m, 3C, $^1J(^{119}SnC) = 168$ Hz, $SnCH_2$), 14.3 (3C, Me), Sn^nBu_3. ^{31}P NMR (121.5 MHz, 27 °C): see Table 1.

($^tBu_2PC_2H_4P^tBu_2$)Pd(H)SnMe$_3$ (2a). The reaction was performed as for **1b** by reacting (d^tbpe)Pd(C_2H_4) (453 mg, 1.00 mmol) with Me_3SnH (0.13 mL, 1.00 mmol) at 20 °C. At −30 °C colorless cubes crystallized, which were isolated as described above and dried under vacuum (20 °C): yield 515 mg (87%); mp 144 °C dec. IR (KBr): 1837 (PdH), 737 cm^{-1} ($SnMe_3$). EI-MS (100 °C): *m/e* (%) 590 (M^+, 9), 575 ($[M - Me]^+$, 11), 424 ($[(d^tbpe)Pd]^+$, 100). ^1H NMR (300 MHz, 27 °C; for $SnMe_3$ and PdH, see Table 1): δ 1.96 (4H, PCH_2 and $P'CH_2$), 1.26, 1.22 (each s, 18H, P^tBu_2 and P'^tBu_2), d^tbpe. ^{13}C NMR (75.5 MHz, 27 °C; for $SnMe_3$, see Table 1): δ 35.0, 35.1 (each 2C, PC and P′C), 30.8, 30.7 (each s, 6C, $PC\mathit{Me}_3$ and $P'C\mathit{Me}_3$), ∼26.7, ∼23.6 (each 1C, PCH_2 and $P'CH_2$), d^tbpe. ^{31}P NMR (121.5 MHz, −80 °C): see Table 1. Anal. Calcd for $C_{21}H_{50}P_2PdSn$ ($M_r = 589.7$): C, 42.77; H, 8.55; P, 10.51; Pd, 18.05; Sn, 20.13. Found: C, 42.66; H, 8.59; P, 10.39; Pd, 17.98; Sn, 19.97.

($^tBu_2PC_2H_4P^tBu_2$)PdH(Sn^{n}Bu$_3$) (2b). The reaction was performed as for **1b** by reacting (d^tbpe)Pd(C_2H_4) (453 mg, 1.00 mmol) with $^nBu_3SnH$ (0.27 mL, 1.00 mmol) at 20 °C. At −78 °C off-white intergrown crystals were obtained, which were isolated as described above and dried under vacuum (20 °C): yield 560 mg (78%); mp 52 °C. IR (KBr): 1837 cm^{-1} (PdH). EI-MS (120 °C): *m/e* (%) 716 (M^+, 4), 659 ($[M - {}^nBu]^+$, 33), 424 ($[(d^tbpe)Pd]^+$, 66). ^1H NMR (300 MHz, 27 °C; for PdH, see Table 1): δ 1.97 (4H, PCH_2 and $P'CH_2$), 1.25 (36H, P^tBu_2 and P'^tBu_2), d^tbpe; 1.56 (m, 6H, $C_\beta H_2$), 1.32 (m, 6H, $C_\gamma H_2$), 0.85 (t,

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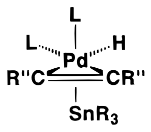
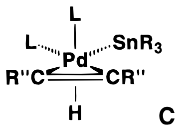
[21] (a) Adduct formation of the L_2Pd^{II} hydrido stannyl with the alkyne probably creates the octahedral, formally Pd^{IV} intermediate **B** or **C**, in which the alkyne ligand is coplanar with either the Pd−H (**B**) or Pd−Sn bond (**C**), followed by insertion, triggered by dissociation of the ligand L.[15a,21b−d] It still remains to be determined into which of these bonds alkyne insertion takes place. (b) Martinez, M.; Muller, G.; Panyella, D.; Rocamora, M.; Solans, X.; Font-Bardía, M. *Organometallics* **1995**, *14*, 5552. (c) Groen, J. H.; Delis, J. G. P.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 68. (d) Yu, J.; Spencer, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 5257.



B



C

9H, Me), 0.84 (m, 6H, SnCH$_2$), Sn^{n}Bu$_3$. ^{13}C NMR (50.3 MHz, 27 °C): δ ∼34.9 (4C, PC and P′C), 30.8, 30.6 (each s, 6C, PC*Me*$_3$ and P′C*Me*$_3$), ∼26.8, ∼23.4 (each 1C, PCH$_2$ and P′CH$_2$), d^{t}bpe; 32.4 (3C, ^2J(SnC) = 8 Hz, C$_\beta$H$_2$), 28.7 (3C, ^3J(SnC) = 45 Hz, C$_\gamma$H$_2$), 14.9 (“t”, 3C, ^1J(^{119}SnC) = 164 Hz, SnCH$_2$), 14.2 (s, 3C, Me), Sn^{n}Bu$_3$. ^{31}P NMR (121.5 MHz, −80 °C): See Table 1. Anal. Calcd for $C_{30}H_{68}P_2PdSn$ ($M_r = 715.9$): C, 50.33; H, 9.57; P, 8.65; Pd, 14.86; Sn, 16.58. Found: C, 50.23; H, 9.49; P, 8.49; Pd, 14.95; Sn, 16.71.

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd{C$_2$(CO$_2$Me)$_2$} (4). A light brown solution of **2a** (590 mg, 1.00 mmol) in diethyl ether (10 mL) was combined with dmad (284 mg, 2.00 mmol) at 20 °C. When the mixture was stirred for 1 h, a beige solid precipitated, which was separated by filtration, washed with pentane (−30 °C), and dried under vacuum (20 °C): yield 440 mg (78%); mp 201 °C dec. IR (KBr): 1844 (C≡C + C═O), 1686, 1223 cm^{-1} (CO$_2$Me). EI-MS (170 °C): *m*/*e* (%) 566 (M$^+$, 1), 424 ([(d^{t}bpe)Pd]$^+$, 100). ^{1}H NMR (200 MHz, CDCl$_3$, 27 °C): δ 3.73 (6H, OMe), alkyne; 1.79 (m, 4H, PCH$_2$), 1.20 (d, 36H, ^{t}Bu), d^{t}bpe. ^{13}C NMR (50.3 MHz, CDCl$_3$, 27 °C): δ 168.4 (“t”, 2C, ^3J(PC) = 16 Hz, *C*O$_2$Me), 121.7 (d, 2C, ^2J(PC)$_{\text{trans}}$ = 75 Hz, C≡C), 51.5 (s, 2C, OMe), alkyne; 34.4 (m, 4C, PC), 30.1 (m, 12C, PC*Me*$_3$), 23.7 (“t”, 2C, PCH$_2$), d^{t}bpe. ^{31}P NMR (81 MHz, CDCl$_3$, 27 °C): δ 95.5. Anal. Calcd for $C_{24}H_{46}O_4P_2Pd$ ($M_r = 567.0$): C, 50.84; H, 8.18; O, 11.29; P, 10.93; Pd, 18.77. Found: C, 51.02; H, 8.12; P, 10.82; Pd, 18.56.

Stoichiometric Reaction of 2a with dmad. A solution of **2a** (590 mg, 1.00 mmol) and dmad (284 mg, 2.00 mmol) in diethyl ether or pentane (10 mL) was stirred for 1 h at 20 °C. Precipitated **4** was removed by filtration, and the solvent was evaporated under vacuum. NMR analysis of the residue indicated the presence of ***Z*/*E*-5** as a 40:60 isomeric mixture.

Reaction of dmad with Me$_3$SnH in the Presence of 2a. A solution of dmad (142 mg, 1.00 mmol) and Me$_3$SnH (165 mg, 1.00 mmol) in diethyl ether or pentane (10 mL) was combined with **2a** (12 mg, 0.02 mmol), and the mixture was stirred for 2 days at 20 °C. The mixture was worked up as described above. According to NMR analysis, 20% of the dmad was left unreacted and 80% was converted into a 13:1 mixture of ***Z*/*E*-5**.

NMR Data for *Z*-5. $C_9H_{16}O_4Sn$ ($M_r = 306.9$). ^{1}H NMR (300 MHz, 27 °C): δ 6.84 (1H, ^3J(^{119}SnH)$_{\text{trans}}$ = 93 Hz, ═CH−), 3.76, 3.74 (each 3H, CO$_2$Me), 0.24 (9H, ^2J(^{119}SnH) = 58 Hz, SnMe$_3$). ^{13}C NMR (75.5 MHz, 27 °C): δ 172.1, 167.5 (each 1C, *C*O$_2$Me), 161.4 (1C, ═CSn), 134.6 (1C, ═CH), 52.1, 52.0 (each 1C, Me), −6.7 (3C, ^1J(^{119}SnC) = 386 Hz, SnMe$_3$).

Crystal Structure Determination of 2a. Crystal data: $C_{21}H_{50}P_2PdSn$, $M_r = 589.64$, light brown prism, crystal size 0.35 × 0.41 × 0.57 mm, $a = 8.164(2)$ Å, $b = 18.358(1)$ Å, $c = 18.803(1)$ Å, $\beta = 94.77(1)°$, $U = 2808.4(6)$ Å^3, $T = 100$ K, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $d_{\text{calcd}} = 1.40$ g cm^{-3}, $\mu = 1.65$ mm^{-1}; Siemens SMART diffractometer, λ(Mo Kα) = 0.710 73 Å; 30 399 measured reflections, spherical absorption correction ($T_{\min} = 0.398$ 46; $T_{\max} = 0.414$ 59), 9951 unique, 8096 (gt) with $I > 2.0\sigma(F_o^2)$. The structure was solved by direct methods (SHELXS-97)[22] and refined by full-matrix least squares (SHELXL-97)[22b] on F_o^2 for all data with Chebyshev weights to $R = 0.030$ (gt) and $R_w = 0.067$ (all data): 212 parameters, $S = 1.03$, d^{t}bpe ligand disordered over two conformations (C atoms isotropic, 50:50), H atom attached to Pd isotropic ($U_H = 0.041(7)$ Å^2), remaining H riding, maximum shift/error 0.004, residual $\rho_{\max} = 0.728$ e Å^{-3}.

Acknowledgment. This paper is dedicated to Professor Dirk Walther on the occasion of his 60th birthday. We thank the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Tables of X-ray data collection information, atom coordinates and thermal parameters, and bond lengths and angles for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM9908128

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