804 *J. Am. Chem. Soc.* **1996,** *118,* 804−821

A Palladium-Catalyzed Stannole Synthesis[⊥]

Jochen Krause, Karl-Josef Haack, Klaus-Richard Pörschke,* Barbara Gabor,[†]
Richard Goddard,[‡] Christian Pluta,[§] and Klaus Seevogel[||]

Contribution from the Max-Planck-Institut für Kohlenforschung,
D-45466 Mülheim an der Ruhr, Germany

Received July 25, 1995[⊗]

Abstract: A palladium-catalyzed (2 + 2 + 1) cycloaddition reaction of two C_2H_2 and one SnR_2 to form *C*-unsubstituted stannoles $(C_4H_4)SnR_2$ [R = $CH(SiMe_3)_2$ **2a**, $R_2 = \{C(SiMe_3)_2CH_2\}_2$ **2c**] is described. Catalysts are *$(R'_2PC_2H_4PR'_2)$-Pd* complexes (slow reaction) and *$(R'_3P)_2Pd$* complexes (fast reaction). The mechanism of the catalysis has been elucidated in detail from stoichiometric reactions based on R = $CH(SiMe_3)_2$. For the *$[(R'_2PC_2H_4PR'_2)Pd]$*-catalyzed system, the starting Pd(0)−ethene complexes $(R'_2PC_2H_4PR'_2)Pd(C_2H_4)$ (R′ = ^{i}Pr (**3**), ^{t}Bu (**4**)) react both with ethyne to give the Pd(0)−ethyne derivatives $(R'_2PC_2H_4PR'_2)Pd(C_2H_2)$ (R′ = ^{i}Pr (**5**), ^{t}Bu (**6**)) and with SnR_2 to yield the Pd(0)−Sn(II) adducts $(R'_2PC_2H_4PR'_2)Pd{=}SnR_2$ (R′ = ^{i}Pr (**7**), ^{t}Bu (**8**)). The Pd−Sn bond [2.481(2) Å] of **7** is very short, indicative of partial multiple bonding. Subsequent reactions of the Pd(0)−ethyne complexes **5** and **6** with SnR_2 or of the Pd(0)−Sn(II) complexes **7** and **8** with ethyne afford the 1,2-palladastannete complexes $(R'_2PC_2H_4PR'_2)Pd(CH{=}CH)SnR_2$ (*Pd−Sn*) (R′ = ^{i}Pr (**10**), ^{t}Bu (**11**)). The derivative with R′ = Me (**9**) has also been synthesized. In **10** a Pd−Sn single bond [2.670(1) Å] is present. Complexes **10** and **11** (as well as **7** and **8** but not **9**) react slowly with additional ethyne at 20 °C to reform the Pd(0)−ethyne complexes **5** and **6** with concomitant generation of the stannole $(C_4H_4)SnR_2$ (**2a**). Likely intermediates of this reaction are the Pd(0)−η^2-stannole complexes $(R'_2PC_2H_4PR'_2)Pd(\eta^2\text{-}C_4H_4SnR_2)$ (R′ = ^{i}Pr (**12**), ^{t}Bu (**13**)), which have been synthesized independently. The stannole ligand in **12**, **13** is easily displaced by ethyne to yield **5** or **6** or by SnR_2 to yield **7** or **8**. Thus, the isolated complexes **5**−**8** and **10**−**13** are conceivable intermediates of the catalytic stannole formation, and from their stoichiometric reactions the catalysis cycle can be assembled. For the *$[(R'_3P)_2Pd]$*-catalyzed system, the corresponding intermediates $(Me_3P)_2Pd(C_2H_2)$ (**15**), $(^iPr_3P)_2Pd(C_2H_2)$ (**17**), $(Me_3P)_2Pd{=}SnR_2$ (**18**), $(^iPr_3P)_2Pd{=}SnR_2$ (**20**), and $(Me_3P)_2Pd(CH{=}CH)SnR_2$ (*Pd−Sn*) (**19**) have been isolated or detected by NMR, and $(^iPr_3P)_2Pd(CH{=}CH)SnR_2$ (*Pd−Sn*) (**21**) is postulated as an intermediate. The $[(Me_3P)_2Pd]$ system (stannole formation above 0 °C) is catalytically more active than any of the $[(R'_2PC_2H_4PR'_2)Pd]$ systems (slow stannole formation for R′ = ^{t}Bu at 20 °C). Most active is the $[(^iPr_3P)_2Pd]$ system, allowing a catalytic synthesis of the stannole **2a** from SnR_2 and ethyne at −30 °C [1% of **17**; yield **2a**: 87%; TON (turnover number): 87]. By carrying out the catalysis in pentane at 20 °C (0.04% of **17**), the TON is increased to 1074 but the yield of **2a** is diminished to 43% due to uncatalyzed thermal side reactions.

There has been a long-standing interest in uncatalyzed and metal-catalyzed reactions of (partly in situ generated) silylenes,[1a] germylenes,[1b] and stannylenes[1b] with alkynes. Primary cyclic addition products are silirenes,[2a] germirenes,[2b] and stannirenes,[2c] which exhibit a decreasing stability in the given order.[3] Their formation is supported when strained and sterically demanding cyclic alkynes like 3,3,6,6-tetramethyl-1-thiacycloheptyne are employed.[4] For example, the Lappert tin(II) dialkyl SnR_2 [R = $CH(SiMe_3)_2$],[5] which is dimeric in the solid state but monomeric in solution, reacts with this alkyne to yield the corresponding stannirene[2c] while it reacts with cyclooctyne to give a distannacyclobutene derivative.[6] In addition, we have shown that SnR_2 reacts with ethyne in THF above −10 °C to yield $(HC{\equiv}C)SnR_2(\mu\text{-}trans\text{-}CH{=}CH)SnR_2(CH{=}CH_2)$ as the main product (Scheme 1). The compound is presumably formed by an initial oxidative addition of an ethyne C−H bond to the tin(II) atom and subsequent hydrostannylation steps.[7a] In pentane (20 °C) the formation of this compound is retarded but other products arise.[7b] An uncatalyzed (2 + 2 + 1) cycloaddition reaction of SnR_2 and two C_2H_2 with formation of the stannole $(C_4H_4)SnR_2$ (**2a**) does not occur in either solvent.

A quite different picture arises when transition metals are present.[8] For example, according to Ando et al., $Ge_3(mes)_6$ (mes = mesityl) dissociates in toluene at 80 °C into $[Ge(mes)_2]$ and

---

[†] NMR spectra.

[‡] X-ray structure determinations.

[§] Preliminary experiments.

[||] IR and Raman spectra.

[⊥] Abbreviations: d^{i}ppe, bis(diisopropylphosphino)ethane, $^iPr_2PC_2H_4P^iPr_2$; d^{t}bpe, bis(di-*tert*-butylphosphino)ethane, $^tBu_2PC_2H_4P^tBu_2$; dmpe, bis(dimethylphosphino)ethane, $Me_2PC_2H_4PMe_2$; tmeda, *N,N,N′,N′*-tetramethylethylenediamine, $Me_2NC_2H_4NMe_2$.

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) (a) Gaspar, P. P.; Holten, D.; Konieczny, S.; Corey, J. Y. *Acc. Chem. Res.* **1987**, *20*, 329 and references cited therein. (b) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.

(2) (a) Hirotsu, K.; Higuchi, T.; Ishikawa, M.; Sugisawa, H.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, 726. (b) Egorov, M. P.; Kolesnikov, S. P.; Struchkov, Yu. T.; Antipin, M. Yu.; Sereda, S. V.; Nefedov, O. M. *Isv. Akad. Nauk, Ser. Khim.* **1985**, 959; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1985**, 878. See also: Ando, W.; Ohgaki, H.; Kabe, Y. *Angew. Chem.* **1994**, *106*, 723; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 659. (c) Sita, L. R.; Bickerstaff, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 5208; *Phosphorus Sulfur* **1989**, *41*, 31.

(3) MO calculations: Boatz, J. A.; Gordon, M. S.; Sita, L. R. *J. Phys. Chem.* **1990**, *94*, 5488 and references cited therein.

(4) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189. Krebs, A.; Berndt, J. *Tetrahedron Lett.* **1983**, *24*, 4083.

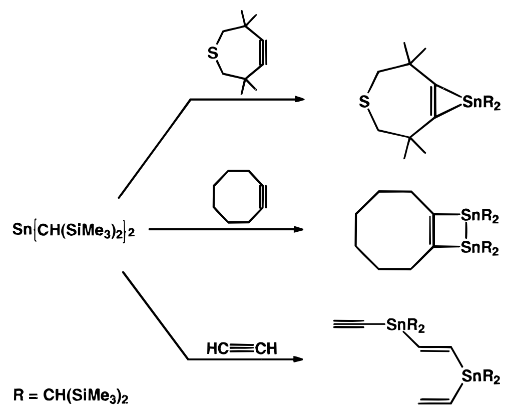
(5) (a) Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 317. Davidson, D. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Thorne, A. J.; Fjeldberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387.

(6) Sita, L. R.; Kinoshita, I.; Lee, S. P. *Organometallics* **1990**, *9*, 1644.

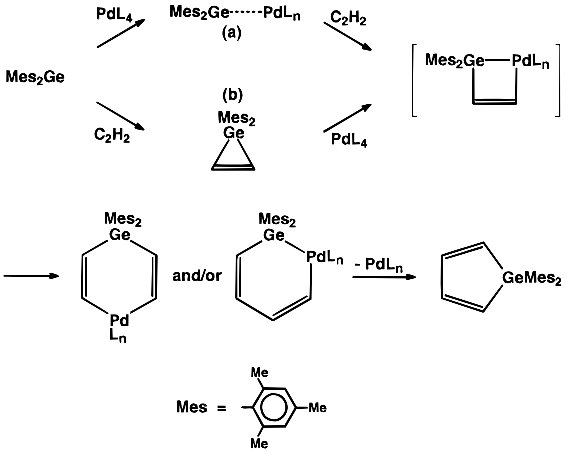
(7) (a) Pluta, C.; Pörschke, K.-R. *J. Organomet. Chem.* **1993**, *453*, C11. (b) The reaction of $Sn\{CH(SiMe_3)_2\}_2$ and ethyne in pentane (20 °C) affords mainly $(C_2H_2)_n[Sn\{CH(SiMe_3)_2\}_2]_{2n}$ (>95%) as a colorless insoluble polymer of unknown structure. The solution contains several other components of which $(HC{\equiv}C)(H_2C{=}CH)Sn\{CH(SiMe_3)_2\}_2$, isomeric to **2a**, has been separated by preparative GC. For spectroscopic data, see Experimental Section.

0002-7863/96/1518-0804$12.00/0

Scheme 1



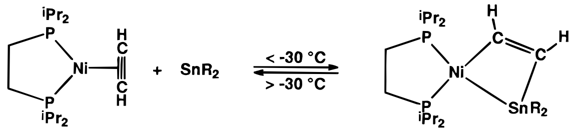
Scheme 2



[(mes)$_2$Ge=Ge(mes)$_2$], which in the presence of ethyne and 10% Pd(PPh$_3$)$_4$ are converted into the corresponding germole (C$_4$H$_4$)-Ge(mes)$_2$ and 1,4-digermacyclohexa-2,5-diene.[9a] For the germole formation it has been suggested that a 1,2-palladagermete [1,2-pallada(II)germa(II)cyclobutene] intermediate is produced via two alternative routes (a and b) and that this intermediate reacts further with ethyne to yield the germole, with recovery of Pd(0) (Scheme 2). Evidence for the 1,2-palladagermete intermediate, which is crucial for the mechanism, was not obtained.[9a]

Similarly, Neumann and co-workers observed that Pd(PPh$_3$)$_4$ catalyzes the reaction of in situ generated GeMe$_2$ (72 °C, 4h) with alkynes to give germoles as main products. For the mechanism, they also postulated a 1,2-palladagermete intermediate, and as another possible route for its formation, they considered that prior to the reaction with GeMe$_2$ the alkyne might be activated by coordination to palladium(0). Their report concluded by stating a "surprising catalytic activity of Pd".[9b] Common features of both studies[9] are that (a) the reacting germylene has to be generated from a precursor compound, (b) the effective palladium(0) catalyst needs to be developed from Pd(PPh$_3$)$_4$ as precursor complex, (c) the reaction temperatures are rather high, and (d) no intermediates could be isolated or detected.

Our own studies on this matter commenced with the finding that the Ni(0)−ethyne complex (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_2$)[10] reacts with the Lappert stannylene SnR$_2$ below −30 °C to yield the 1,2-nickelastannete complex (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(CH=CH)-SnR$_2$ (*Ni*−*Sn*) (**1**) as the kinetically controlled product (eq 1).[11,12]



1

(1)

Formally, the reaction implies an insertion of SnR$_2$ into a nickelacyclopropene Ni−C bond. According to an X-ray structure analysis, the 1,2-nickelastannete ring is planar, the Ni−Sn bond (2.626(1) Å) being distinctly longer than the sum of the covalent radii of Ni and Sn (2.56 Å). The bonding situation has been described as an inner complex in which a stannate(II) anion is coordinated to a nickel(II) cation. Although **1** is quite stable as a solid (mp 67 °C dec), in solution above −30 °C, it readily dissociates into the starting components by cleaving the ring Ni−Sn and Sn−C bonds. Complex **1** does not react further with ethyne (−30 °C). At 20 °C, (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Ni(C$_2$H$_2$) and SnR$_2$ react irreversibly by insertion of SnR$_2$ into an ethyne ligand C−H bond.[11]

With the 1,2-nickelastannete **1** we had an isolated compound at hand which was quite similar to the 1,2-palladagermete postulated before. However, the lability of **1** in solution excluded a further investigation of its reactivity above −30 °C. It appeared to us that the palladium analogue of **1**, i.e., a 1,2-palladastannete, might be more stable due to the larger palladium atom. We thought that if this ring were preserved in solution at temperatures higher than −30 °C it might undergo ring insertion reactions with unsaturated substrates. Since we had also synthesized the first Pd(0)−ethyne complexes at that time,[13] reactions analogous to eq 1 were easily carried out.

Here we report our results of a detailed investigation of low-temperature reactions (−100 to 20 °C) within the system comprising Pd/SnR$_2$/C$_2$H$_2$ (a) which led to the development and mechanistic exploration of a Pd-catalyzed synthesis of *C*-unsubstituted stannoles (C$_4$H$_4$)SnR$_2$ (**2a,c**). Part of this work[14a,15]

---

[8] For pioneering studies in this area, see: (a) Liu, C.; Cheng, C. *J. Am. Chem. Soc.* **1975**, *97*, 6746. (b) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1977**, 352. Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. Ishikawa, M.; Sugisawa, H.; Kumada, M.; Higuchi, T.; Matsui, K.; Hirotsu, K. *Organometallics* **1982**, *1*, 1473. Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1984**, *3*, 1930; **1985**, *4*, 2040. Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417. Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050. (c) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (d) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* **1977**, *135*, C37. Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57.

[9] (a) Tsumuraya, T.; Ando, W. *Organometallics* **1990**, *9*, 869. (b) Billeb, G.; Brauer, H.; Neumann, W. P.; Weisbeck, M. *Organometallics* **1992**, *11*, 2069.

[10] Pörschke, K.-R. *Angew. Chem.* **1987**, *99*, 1321; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1288.

[11] Pluta, C.; Pörschke, K.-R.; Ortmann, I.; Krüger, C. *Chem. Ber.* **1992**, *125*, 103.

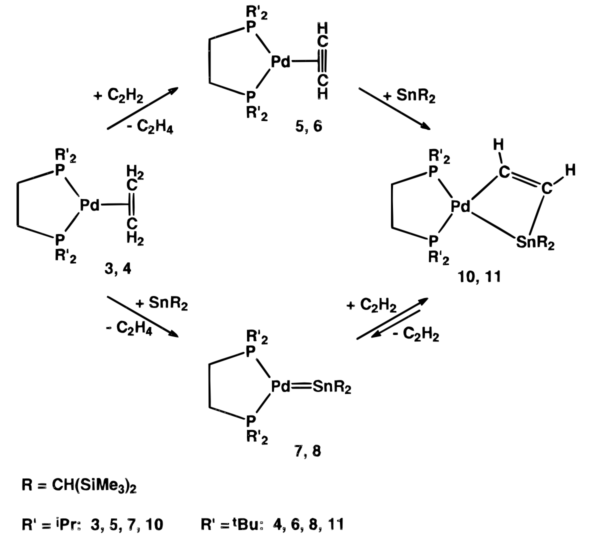
[12] The partially deuterated derivative of **1**, (d^{i}ppe)Ni(CD=CD)SnR$_2$ (*Ni*−*Sn*) (**1a**), shows for the 1,2-nickelastannete moiety a C(D)=C(D) absorption band ν 1430 cm^{-1} (additional intense C−D absorption bands are observed at 2208, 2155, and 2120 cm^{-1}). From a comparision of the IR spectra of **1** and its deuterated derivative **1a**, it follows that the 1,2-nickelastannete C(H)=C(H) stretching band in **1** can be expected at about 1460 cm^{-1}, but it is obscured by a strong absorption of the phosphane ligand. A previously observed absorption (1605 cm^{-1}), which we have ascribed[11] to this vibration, is probably due to the ethyne complex (d^{i}ppe)Ni(C$_2$H$_2$) (ν C≡C 1598 cm^{-1})[10] as an impurity.

[13] Krause, J.; Bonrath, W.; Pörschke, K.-R. *Organometallics* **1992**, *11*, 1158.

[14] (a) Krause, J. Dissertation, Universität Düsseldorf, 1993. Goddard, R. Unpublished results. (b) Krause, J.; Pörschke, K.-R. 5th International Conference on the Chemistry of the Pt Group Metals, St. Andrews, Scotland, 1993; Abstract 199.

[15] Haack, K.-J. Dissertation, Universität Düsseldorf, 1994. Goddard, R. Unpublished results.

Scheme 3



has already been communicated.[16] In addition, we have studied the systems Pt/SnR_2/C_2H_2 (b) and Pd/GeR_2/C_2H_2 (c), which will be reported on later.[15]

Results

For the Pd/SnR_2/C_2H_2 system, a series of stoichiometric reactions have been observed which can be easily combined to afford a catalytic stannole synthesis. Of central relevance to the system is the formation and reactivity of a 1,2-palladastannete complex. The subject is best covered by describing first the stoichiometric reactions of $(R'_2PC_2H_4PR'_2)Pd$ and $(R'_3P)_2$-Pd complexes (part I), followed by the catalysis and its optimization (part II) and supplementary results (part III). Finally, certain aspects of the catalysis cycle are discussed.

I. Palladium Coordination Compounds

$(R'_2PC_2H_4PR'_2)Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (R′ = ^iPr (7), ^tBu (8)). The ethene ligands in $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_4)$ (**3**) and $(^tBu_2PC_2H_4P^tBu_2)Pd(C_2H_4)$ (**4**) are readily displaced by ethyne at −78/−30 °C to yield the corresponding Pd(0)−ethyne complexes $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2H_2)$ (**5**) and $(^tBu_2PC_2H_4P^tBu_2)$-$Pd(C_2H_2)$ (**6**) (Scheme 3).[13] In addition, the ethene ligands are just as readily displaced by stannylenes. Thus, when pentane solutions of **3** and **4** are combined with the magenta ethereal solution of SnR_2 at 0 °C, the color turns red and at −30/−78 °C large dark red cubes of the Pd(0)−stannylene complexes **7** (90%) and **8** (84%), respectively, separate (Scheme 3). Complexes **7** (mp 171 °C) and **8** (mp 214 °C) are thermally stable and are very soluble in ether or hydrocarbons. In the EI mass spectra (70 eV; 120−150 °C), the molecular ions of **7** (806) and **8** (862) are detected which fragment with stepwise destruction of the stannylene ligand to form the ions $[(d^ippe)Pd]^+$ and $[(d^tbpe)Pd]^+$, respectively. Complexes **7** and **8** represent adducts of stannylene with $(R'_2PC_2H_4PR'_2)Pd(0)$ fragments in which both metal atoms are trigonal-planar (*TP*-3) coordinated.

NMR Spectra of 7 and 8. According to the ^1H, ^{13}C, and ^{31}P NMR spectra, **7** and **8** have C_{2v} symmetry. The spectra seem to be independent of the solvent (THF-d_8, $C_6D_5CD_3$) and the temperature (−100, 27 °C), unlike the spectra of a related complex $(C_2H_4)_2Ni{=}SnR_2$.[17] In **7**, the isopropyl Me groups are diastereotopic but the stannylene ligand $SiMe_3$ groups are enantiotopic. The ^1H NMR spectrum of **8** displays two signals each for the phosphane and stannylene ligands. In the ^{31}P NMR spectra the singlets are attended by satellites due to coupling with ^{117}Sn and ^{119}Sn. In **7** the coupling $^2J(^{119}SnP)$ = 675 Hz has a value similar to that for the corresponding Ni complex but markedly smaller than that for the Pt derivative (Table 1). No information is obtained from the NMR spectra on the relative orientation of the Pd(0) and Sn(II) coordination planes. Regarding a possible rotation about the Pd=Sn bond, it is assumed that the energy barrier is low and that the rotation is essentially unhindered in solution, similar as in Fischer-type carbene complexes.[18]

Table 1. ^{31}P NMR Data of Trigonal-Planar (phosphane)M(0)=Sn(II) Complexes (M = Ni, Pd, Pt)[a]

	δ(P)	^2J(SnP) (Hz)
$(^iPr_2PC_2H_4P^iPr_2)Ni{=}Sn\{CH(SiMe_3)_2\}_2$ (**1**)[15]	76.9	677
$(^iPr_2PC_2H_4P^iPr_2)Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (**7**)	65.3	675
$(^iPr_2PC_2H_4P^iPr_2)Pt{=}Sn\{CH(SiMe_3)_2\}_2$[15]	97.0	1093
$(^tBu_2PC_2H_4P^tBu_2)Ni{=}Sn\{CH(SiMe_3)_2\}_2$[15]	101.1	637
$(^tBu_2PC_2H_4P^tBu_2)Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (**8**)	88.5	642
$(Me_3P)_2Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (**18**)	−23.4	716
$(^iPr_3P)_2Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (**20**)[b]	58.7	570
$(^iPr_3P)_2Pt{=}Sn\{CH(SiMe_3)_2\}_2$[15]	82.6	891
$(^iPr_2PC_2H_4P^iPr_2)Pd{=}Sn\{N(SiMe_3)_2\}_2$ (**22**)	66.6	725
$(^iPr_3P)_2Pd{=}Sn\{N(SiMe_3)_2\}_2$ (**25**)[c]	56.4	651

[a] Solvent THF-d_8. Temperature 27 °C unless otherwise indicated. [b] −80 °C. [c] −30 °C.

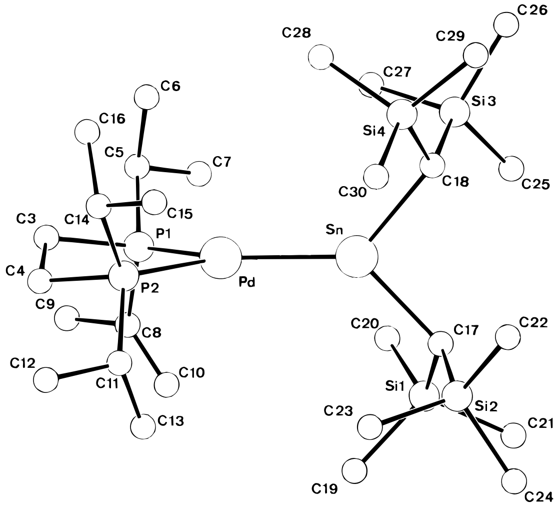


Figure 1. Molecular structure of **7**. Selected bond distances (Å) and angles (deg): Pd−Sn [2.481(2)], Pd−P(1) [2.285(4)], Pd−P(2) [2.293(4)], Sn−C(17) [2.21(2)], Sn−C(18) [2.21(2)], P(1)−Pd−P(2) [89.0(2)], P(1)−Pd−Sn [133.9(1)], P(2)−Pd−Sn [137.9(1)], C(17)−Sn−C(18) [98.8(5)], C(18)−Sn−Pd [129.9(4)], C(17)−Sn−Pd [131.2(4)], P(1),P(2),Pd/C(17),C(18),Sn [86(1)].

Molecular Structure of 7. The single-crystal molecular structure of **7**[16] is depicted in Figure 1. The compound exhibits a very short Pd−Sn bond [2.481(2) Å], see below. The coordination plane of the Sn atom is perpendicular [86(1)°] to that of Pd. Hence the Sn accepting orbital lies in the transition metal coordination plane which contains, according to various MO calculations,[19] the d^{10} metal back-bonding orbitals. Thus, the Pd(0)−Sn(II) bond can best be rationalized by a Pd(0) $\leftarrow$ Sn(II) donor bond and substantial Pd(0) $\rightarrow$ Sn(II) back-donation, resulting in the formulation of a Pd=Sn bond as a canonical form. The angle C(17)−Sn−C(18) [98.8(5)°] is relatively small. It is less than in Sn_2R_4 [109.2(2)°][5b] and $(C_2H_4)_2Ni{=}SnR_2$

---

(16) Krause, J.; Pluta, C.; Pörschke, K.-R.; Goddard, R. *J. Chem. Soc., Chem. Commun.* **1993**, 1254.

(17) Pluta, C.; Pörschke, K.-R.; Mynott, R.; Betz, P.; Krüger, C. *Chem. Ber.* **1991**, *124*, 1321.

(18) For a compilation of literature relevant to this issue, see: Guerchais, V.; Lapinte, C.; Thépot, J.-Y. *Organometallics* **1988**, *7*, 604.

(19) (a) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656. (b) Schaefer, H. F., III *J. Mol. Struct.* **1981**, *76*, 117.

[103.3(1)°][17] and similar to the angles in $(CO)_5Cr{=}SnR_2$ [98°][20] and monomeric SnR_2 [97(2)°];[21] for the cited metal stannylene complexes (partial) π character of the M−Sn bonds has been invoked. The Pd−P (2.29 Å, av) and Sn−C (2.21 Å, av) bond distances in **7** are as expected.

Pd(0,II)−Sn(II) Bond Lengths. An assessment of the Pd−Sn bond distances in **7** and **10** is based on a comparison with known structural data of both metals. According to Pauling, the Pd(0) single-bond radius is 1.28 Å and the Pd(II/IV) covalent radius 1.31 Å.[22a] From $Pd_2(\mu\text{-}chx_2PC_2H_4Pchx_2)_2$ (chx = cyclohexyl), which contains a $d^{10}-d^{10}$ interaction, a Pd(0) bond radius of 1.38 Å can be inferred, which is the same as for palladium metal.[22b] Pd(I)−Pd(I) dimers exhibit a Pd(I) single-bond radius of 1.26−1.35.[22c] From the Pd−C distance in *trans*-$(Et_3P)_2Pd(Me)OC(O)OH$ (2.05 Å)[22d] or $(tmeda)PdMe_2$ (2.03 Å),[22e] considering $r(C) = 0.77$ Å, the covalent radius of Pd(II) is deduced to be 1.27 Å. For Sn(IV) the covalent radius (Sn−C single bond) is assumed to be 1.40 Å.[22a] The Sn(III,II) metal radius in $Ph_3Sn-SnPh_3$[22f] and $(SnPh_2)_6$[22g] was found to be about 1.39 Å. From $Sn_2\{CH(SiMe_3)_2\}_4$ [Sn−Sn (2.77 Å), Sn−C (2.22 Å)],[5] the Sn(II) radius for metal−Sn(II) bonds of 1.39 Å and the Sn(II) covalent radius of 1.45 Å can be inferred. Particularly for palladium the data document a broad range of the atomic radii. Nevertheless, estimates of "expected" Pd(0,II)−Sn(II) bond lengths of 2.65−2.70 Å seem reasonable.

Up to now, the X-ray structures of about 10 compounds containing Pd−Sn bonds have been reported and the Pd−Sn bonds in these compounds are in the range of 2.47−2.72 Å. For example, the homoleptic Pd(0)−Sn(II) complex $Pd[Sn\{N(SiMe_3)_2\}_2]_3$, which is closely related to complex **7**, exhibits Pd−Sn bonds of 2.51−2.54 Å.[22h] Similar Pd−Sn distances have been found in the Pd(II)−Sn(II) complexes $(Ph_3P)Pd(C_3H_5)SnCl_3$,[22i] $(2\text{-}Me\text{-}C_3H_4)Pd(PhCH{=}CH_2)(SnCl_3)$,[22k] and $(2\text{-}Me\text{-}C_3H_4)Pd(CO)(SnCl_3)$[22l] and also in the Pd(I)−Sn(II) complex $ClPd(\mu\text{-}Ph_2PCH_2PPh_2)_2Pd(SnCl_3)$ (2.56 Å).[22m] In the palladate(II) stannate(II) dianion $[Cl_3Pd-SnCl_3]^{2-}$ (2.47 Å) the Pd−Sn bond is exceedingly short.[22n] In all these complexes, Sn is in the formal oxidation state +II and the Pd−Sn(II) bond distance is apparently independent of the oxidation state of palladium (0, +I, +II). Long Pd−Sn bonds (2.62−2.72 Å) have so far only been found in compounds in which Sn bridges two Pd atoms.[22o,p]

Thus, the experimental Pd−Sn bonds are generally found to be shorter than expected from the atomic radii of the metals. We attribute this fact to a rather favorable overlap of the palladium and tin orbitals. A similar conclusion has recently been drawn for a Zr(II)−SnR_2 bond.[23]

$(R'_2PC_2H_4PR'_2)Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ *(Pd−Sn)* (R′ = Me (9), ^{i}Pr (10), ^{t}Bu (11)). When the colorless ethereal solution of the Pd(0)−ethyne complex **5** and the magenta solution of SnR_2 are mixed at −30 °C, orange crystals of the 1,2-palladastannete complex **10** separate in 94% yield. The reaction proceeds virtually instantaneously at −30 °C and is also fast at −100 to −78 °C. Correspondingly, the pentane suspension of **6** reacts with SnR_2 at −78 °C to produce the orange precipitate of **11** in 74% yield (Scheme 3). By reacting the deuterated ethyne complex $(^iPr_2PC_2H_4P^iPr_2)Pd(C_2D_2)$ (**5a**) with SnR_2, the ring deuterated derivative $(^iPr_2PC_2H_4P^iPr_2)Pd(CD{=}CD)SnR_2$ (*Pd−Sn*) (**10a**) can be synthesized.

The 1,2-palladastannete complexes **10** and **11** are also obtained by treating the Pd(0)−stannylene complexes **7** and **8** with ethyne. When the red ethereal or pentane solutions of **7** and **8** are exposed to ethyne at −78 °C, the color lightens immediately and soon after complexes **10** (93%) and **11** (60%) precipitate (Scheme 3). It is important that the syntheses are carried out at low temperatures (**10**, −30 °C or below; **11**, −78 °C) and that **11** quickly precipitates from the solution (pentane) to avoid the ring degradation reaction which is described below. The solid ^{i}Pr-substituted derivative **10** (mp 157 °C dec) is stable at 20 °C for a long period, whereas the ^{t}Bu-substituted derivative **11** (mp 91 °C dec) decomposes at 20 °C in the course of several days. Thus, the ^{t}Bu-substituted derivative is thermally less stable than the ^{i}Pr-substituted derivative, but both Pd complexes **10** and **11** are markedly more stable than the analogous ^{i}Pr-substituted Ni complex **1**.

The Me-substituted 1,2-palladastannete derivative **9** (orange cubes; mp 96 °C dec) is obtained by reacting **11** with $Me_2PC_2H_4PMe_2$ at 0 °C (1 h) under exchange of the $^tBu_2PC_2H_4P^tBu_2$ ligand (or by exchange of the PMe_3 ligands in **19** by dmpe; see below). As a solid and in solution complex **9** is temporarily stable at 20 °C. It does not react further with ethyne (20 °C).

In principle the formation of the 1,2-palladastannete complexes **10** and **11** from the Pd(0)−stannylene complexes **7** and **8** and ethyne represents an equilibrium. For a solution (THF-d_8, 20 °C) of ^{i}Pr-substituted, ring deuterated **10a** and C_2H_2, an exchange of the ring C_2D_2 moiety for C_2H_2 is observed within 1 h (^{1}H NMR) to afford **10** and free C_2D_2. This exchange is thought to proceed by ring degradation of **10a** to generate the Pd(0)−stannylene complex **7** as an intermediate, followed by a recombination of **7** with C_2H_2. Furthermore, when a solution of **10** (THF-d_8 or $C_6D_{11}CD_3$) is kept at 20 °C for several days, in addition to the AB spin system of **10**, the singlet of **7** arises in the ^{31}P NMR spectrum. The process, which is slow for **10**, can better be followed for the ^{t}Bu-substituted derivative **11**. Thus, when a solution of **11** is warmed from −30 to 20 °C, a new ^{31}P singlet arises for the Pd(0)$=SnR_2$ complex **8** (major component) in addition to the ^{31}P AB spin system of **11** (minor component). In the ^{1}H NMR spectrum the signal of ethyne is found. After several days at 20 °C, **11** is no longer detected but new signals of the Pd(0)−ethyne complex **6** (^{1}H and ^{31}P NMR) and the stannole $(C_4H_4)SnR_2$ (**2a**) (^{1}H NMR) are observed. The reaction is best explained by a partial and reversible ring degradation of **11** into **8** and ethyne in the first step (eq 2a). Unchanged **11** reacts subsequently with eliminated ethyne to form **6** and **2a** (eq 2b; cp. eq 5). This second reaction step is irreversible, and concomitant depletion of ethyne in the

---

(20) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

(21) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

(22) (a) Pauling, L. *Die Natur der Chemischen Bindung*, 3rd ed.; VCH: Weinheim, Germany, 1976. (b) Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842. (c) Barnard, C. F. J.; Russell, M. J. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 5, p 1103 f and references therein. (d) Crutchley, R. J.; Powell, J.; Faggiani, R.; Lock, C. J. L. *Inorg. Chim. Acta* **1977**, *24*, L15. (e) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. (f) Preut, H.; Haupt, H.-J.; Huber, F. *Z. Anorg. Allg. Chem.* **1973**, *396*, 81. (g) Olson, D. H.; Rundle, R. E. *Inorg. Chem.* **1963**, *2*, 1310. (h) Hitchcock, P. B.; Lappert, M. F.; Misra, M. C. *J. Chem. Soc., Chem. Commun.* **1985**, 863. (i) Mason, R.; Whimp, P. O. *J. Chem. Soc. A* **1969**, 2709. (k) Musco, A.; Pontellini, R.; Grassi, M.; Sironi, A.; Rüegger, H. Ammann, C.; Pregosin, P. S. *Organometallics* **1988**, *7*, 2130. (l) Grassi, M.; Meille, St. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1989**, 615. (m) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, 193. (n) Yurchenko, E. N.; Khodashova, T. S.; Porai-Koshits, M. A.; Nikolaev, V. P. *Koord. Khim.* **1980**, *6*, 1290. (o) Bashilov, V. V.; Sokolov, V. I.; Slovokhotov, Yu. L.; Struchkov, Yu. T.; Mednikov, E. G.; Eremenko, N. K. *J. Organomet. Chem.* **1987**, *327*, 285. (p) Bashilov, V. V.; Sokolov, V. I.; Slovokhotov, Yu. L.; Struchkov, Yu. T.; Mednikov, E. G.; Eremenko, N. K. *Dokl. Akad. Nauk USSR* **1987**, *292*, 863.

(23) Piers, W. E.; Whittal, R. M.; Ferguson, G.; Gallagher, J. F.; Froese, R. D. J.; Stronks, H. J.; Krygsman, P. H. *Organometallics* **1992**, *11*, 4015.

reaction solution shifts the preceeding equilibrium to the right. The overall reaction corresponds to eq 2c.

$$2\,\mathbf{11} \rightleftharpoons 2\,\mathbf{8} + 2\,C_2H_2 \qquad (2a)$$

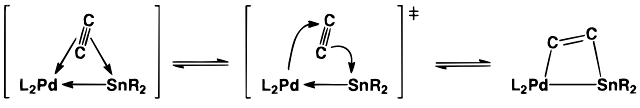
$$\mathbf{11} + 2\,C_2H_2 \rightarrow \mathbf{6} + \mathbf{2a} \qquad (2b)$$

$$3\,\mathbf{11} \rightarrow 2\,\mathbf{8} + \mathbf{6} + \mathbf{2a} \qquad (2c)$$

A similar degradation of the 1,2-palladastannetes is observed in the EI mass spectra (70 eV) of **10** and **11**. Instead of the molecular ions of **10** and **11**, the molecular ions of the Pd(0)═SnR$_2$ complexes **7** (806) and **8** (862) are observed due to a *loss of ethyne*. The selective ring cleavage is less facile for **9**, which decomposes differently under similar conditions.

The equilibrium degradation of the 1,2-palladastannetes **10** and **11** is to be distinguished from that of the 1,2-nickelastannete **1**, although both processes imply a reduction of the transition metal to afford Pd(0) and Ni(0) complexes, respectively. The degradation of the 1,2-nickelastannete ring of **1** proceeds exclusively by *breaking the Ni−Sn bond*, eliminating SnR$_2$, and forming an Ni(0)−ethyne complex (see Introduction). In contrast, the degradation of the 1,2-palladastannetes **10** and **11** involves the elimination of ethyne to form a Pd(0)−stannylene complex, thus *by preserving the Pd−Sn bond and increasing its bond order formally to 2, thereby even reinforcing it.*

Mechanistic Considerations. The synthetic routes to the 1,2-palladastannetes depicted in Scheme 3 appear macroscopically to be quite different. The upper route can be considered as an insertion of the stannylene into a Pd−C bond of a palladacyclopropene moiety while the lower route formally represents a [2 + 2] cycloaddition of ethyne to a Pd═Sn bond. Taking into account that the reactions proceed equally extraordinarily facile, it is tempting to suggest that the reactions involve a common intermediate and transition state. Such a possible intermediate is seen in an adduct[24] of the three components Pd(0), SnR$_2$, and C$_2$H$_2$ in which ethyne perpendicularly bridges a Pd−Sn bond (**A**). The single interactions of this moiety [Pd(0)−SnR$_2$, Pd(0)−alkyne, SnR$_2$−alkyne] have all been verified in two-component compounds which are described above. The combined interactions may result in the formation of this quasi-tetrahedral PdSnC$_2$ moiety. Although there are numerous complexes of homo- and heterodinuclear μ-alkyne complexes,[25] a novel aspect of structure **A** is that the alkyne bridges a transition and a main group metal. The intermediate **A** may further stabilize itself by a rotation of the ethyne ligand in a position parallel to the Pd−Sn bond,[26] thereby forming the 1,2-palladastannete.



A

IR Spectra. The ═C−H and C═C stretching absorption bands of the 1,2-palladastannete ethenediyl moiety of **9**−**11** are largely obscured by phosphane or SiMe$_3$ bands. The C═C stretching bands could be assigned unequivocally by comparison of the spectrum of **10** with that of the derivative **10a**, deuterated at the ring positions. The C═C stretching bands of **10** (1469 cm^{-1}) and **10a** (1438 cm^{-1}) appear at slightly higher wavenumbers than for the corresponding Ni derivatives **1** (1460 cm^{-1}) and **1a** (1430 cm^{-1}).[12] Three intense C−D stretching bands of the Pd complex **10a** (2205, 2153, and 2118 cm^{-1}) nearly coincide with those of the Ni complex **1a**.[12]

^{1}H, ^{13}C, and ^{31}P NMR Spectra. The solution ^{1}H, ^{13}C, and ^{31}P NMR spectra (THF-d_8) of **9**, **10** (27 °C), and **11** (−30 °C) are very complex due to the inequivalence of the phosphorus atoms and the presence of the additional spin-active nuclei ^{119}Sn, ^{117}Sn, and ^{29}Si. The most significant NMR data of the 1,2-palladastannetes **9**−**11** and further derivatives (**19** and **23**, to be discussed below), together with the data of the 1,2-nickelastannete **1**[11] and the 1,2-platinastannete **26**[27] are compiled in Table 2. The spectra of **10** are described here in detail. They provide the reference for the NMR characterization of the other 1,2-palladastannetes.

For the ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$ ligand of **10** the inequivalent phosphorus atoms give rise to an AX spin system with a small coupling J(PP) = 12.1 Hz. The P atom [δ(P) 75.6] which exhibits the large coupling $^{2}J(^{119}$SnP) = 2440 Hz is assumed to be positioned *trans* to the Sn atom, and the P atom [δ(P) 67.7] which exhibits the much smaller coupling ^{2}J(SnP) = 105 Hz is assumed to be coordinated *cis* to tin.[28] In the ^{1}H and ^{13}C NMR spectra the different "sides" of the ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$ ligand give rise to two sets of signals, namely two signals for PCH$_2$ and P′CH$_2$ [δ(H) 1.80, 1.80; δ(C) 21.6, 21.4], two signals for PCH and P′CH [δ(H) 2.35, 2.20; δ(C) 26.3, 25.6], and four signals for the diastereotopic methyl groups of ^{i}Pr$_2$P and ^{i}Pr$_2$P′. The CH(SiMe$_3$)$_2$ substituents of the Sn atom are equivalent and give rise to one ^{1}H and ^{13}C signal each for enantiotopic SnCH groups [δ(H) −0.25, δ(C) 2.48; ^{1}J(SnC) = 90 Hz] and two signals for diastereotopic SiMe$_3$ groups [δ(H) 0.14, 0.16; δ(C) 5.0, 4.9]. Very small couplings ^{1}J(SnC) < 100 Hz have been encountered before[29a] and appear to be typical for Sn−CH(SiMe$_3$)$_2$ groups.[29] The spectral features indicate that a mirror plane passes through the phosphorus atoms and the 1,2-palladastannete ring atoms.

Of special interest are the ^{1}H and ^{13}C signals of the 1,2-palladastannete SnCH═ and PdCH═ groups. The olefinic protons display multiplets [δ(H) 8.37, 7.60] which are the A and B parts of an ABXY spectrum due to the coupling with the neighboring olefinic proton and two inequivalent P atoms. The signals further exhibit satellites due to coupling(s) with tin. The coupling ^{3}J(HH) = 9.4 Hz is consistent with the vicinal *cis* position of the ring protons. The couplings J(PH) and J(SnH) are unfortunately not informative enough for an immediate signal assignment. With regard to the olefinic C atoms, one signal [δ(C) 158.9] exhibits two distinct different phosphorus couplings [$^{2}J(\mathrm{PC})_{trans}$ = 126 Hz; $^{2}J(\mathrm{PC})_{cis}$ = 1 Hz] and is therefore, in accordance with numerous local reference data assigned to the PdCH═ group. Thus the second olefinic signal [δ(C) 176.7] is caused by the SnCH═ group. The couplings J(SnC) for both signals are surprisingly similar, i.e., ^{1}J(SnC) is much smaller and ^{2}J(SnC) much larger than expected. On the basis of the assignment of the ^{13}C resonances, the proton

---

[24] For the adduct of a Fischer-type carbene complex with an alkyne function, see: (a) Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem.* **1992**, *104*, 1257; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236. (b) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064.

[25] For heterodinuclear μ-alkyne complexes, see: Jensen, S. D.; Robinson, B. H.; Simpson, J. *Organometallics* **1986**, *5*, 1690 and references cited therein.

[26] We are aware that this suggestion is in contradiction to MO calculations carried out on homodinuclear μ-alkyne complexes.[26a] For a heterodinuclear μ-alkyne complex, however, see note added in proof on p 3865 of ref 26a. (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

[27] (d^{i}ppe)Pt(CH═CH)Sn{CH(SiMe$_3$)$_2$}$_2$ (*Pt*−*Sn*) (**26**), the platinum derivative of **1** and **10**, has been fully characterized.[15]

[28] Ostoja Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Helv. Chim. Acta* **1982**, *65*, 785.

[29] (a) Pluta, C.; Pörschke, K.-R.; Gabor, B.; Mynott, R. *Chem. Ber.* **1994**, 127, 489. (b) Wrackmeyer, B.; Horchler, K.; Zhou, H. *Spectrochim. Acta, Part A* **1990**, *46*, 809. (c) Westerhausen, M.; Hildenbrand, T. *J. Organomet. Chem.* **1991**, *411*, 1.

Table 2. Selected ^{1}H, ^{13}C, and ^{31}P NMR Data of the Metallastannete Complexes **1** (M = Ni), **9**, **10**, **11**, **19**, **23** (M = Pd), and **26** (M = Pt)[a]

	δ(H)		δ(C)		δ(P)	
	SnCH═	MCH═	SnCH═	MCH═	$P_{trans\text{ to Sn}}$	$P_{cis\text{ to Sn}}$
1[d]	8.14	7.08	178.5	157.8	83.5	73.3
	^3J(HH) 10.4	^3J(HH) 10.4	^1J(CH) 136	^1J(CH) 128		
	^4J(PH) 24.6, 7.1	^3J(PH) 24.5, 20.3	^3J(PC) 10.9, ...	^2J(PC) 80, 21.0	^2J(PP) 10.4	^2J(PP) 10.4
					^2J(^{119}SnP) 1694	^2J(SnP) 306
9[b]	8.28	7.51	176.9	156.6	30.9	13.6
	^3J(HH) 9.6	^3J(HH) 9.6	^1J(CH) 140	^1J(CH) 135		
	^4J(PH) 33, 6	^3J(PH) 29, 27	^3J(PC) 12.4, ...	^2J(PC) 135, 3.8	^2J(PP) 14.6	^2J(PP) 14.6
	^2J(SnH) 40	^3J(SnH) 27	^1J(SnC) 105	^2J(SnC) 122	^2J(^{119}SnP) 2501	^2J(SnP) 89
10[b]	8.37	7.60	176.7	158.9	75.6	67.7
	^3J(HH) 9.4	^3J(HH) 9.4				
	^4J(PH) 30.8, 6.2	^3J(PH) 26.8, 25.8	^3J(PC) 12.0, 1.5	^2J(PC) 126, 1.0	^2J(PP) 12.1	^2J(PP) 12.1
	^2J(SnH) 48.0	^3J(SnH) 27.6	^1J(SnC) 104	^2J(SnC) 108	^2J(^{119}SnP) 2440	^2J(SnP) 105
11[c]	8.22	8.18	174.6	155.9	82.1	85.7
	^3J(HH) 9.4	^3J(HH) 9.4				
			^3J(PC) 9.0, 2.0	^2J(PC) 121, 5.6	^2J(PP) 4.3	^2J(PP) 4.3
					^2J(^{119}SnP) 2478	^2J(SnP) 83
19[d]	8.01	6.97	173.8	163.2	−12.2	−23.9
	^3J(HH) 9.8	^3J(HH) 9.8	^1J(CH) 140	^1J(CH) 135		
	^4J(PH) 31, 6.4	^3J(PH) 30, 30	^3J(PC) 11.8, ...	^2J(PC) 136, 9.0	^2J(PP) 28	^2J(PP) 28
	^2J(SnH) 45	^3J(SnH) 22	^1J(SnC) 120	^2J(SnC) 102	^2J(^{119}SnP) 2443	^2J(SnP) 148
23[d]	9.38	7.58	204.0	170.1	84.6	71.3
	^3J(HH) 10.6	^3J(HH) 10.6	^1J(CH) 138	^1J(CH) 135		
	^4J(PH) 29.5, 6.6	^3J(PH) 20.9, 19.7	^3J(PC) 6.5, 2.5	^2J(PC) 125, 4.5	^2J(PP) 10.3	^2J(PP) 10.3
	^2J(SnH) 41	^3J(SnH) 61	^1J(SnC) 86	^2J(SnC) 176	^2J(^{119}SnP) 3311	^2J(SnP) 96
26[b]	9.83	8.36	181.1	154.3	78.6	76.9
	^3J(HH) 10.2	^3J(HH) 10.2	^1J(CH) 132	^1J(CH) 136		
	^4J(PH) 26.9, 2.4	^3J(PH) 19.2, 15.2	^3J(PC) 11.4, 4.8	^2J(PC) 112, 5.7	^2J(PP) 5.9	^2J(PP) 5.9
					^2J(^{119}SnP) 2232	^2J(SnP) 82
	^3J(PtH) 189	^2J(PtH) 76			^1J(PtP) 2193	^1J(PtP) 1676

[a] Solvent THF-d_8. Coupling constants in Hz. [b] Temperature 27 °C. [c] Temperature −30 °C. [d] Temperature −80 °C.

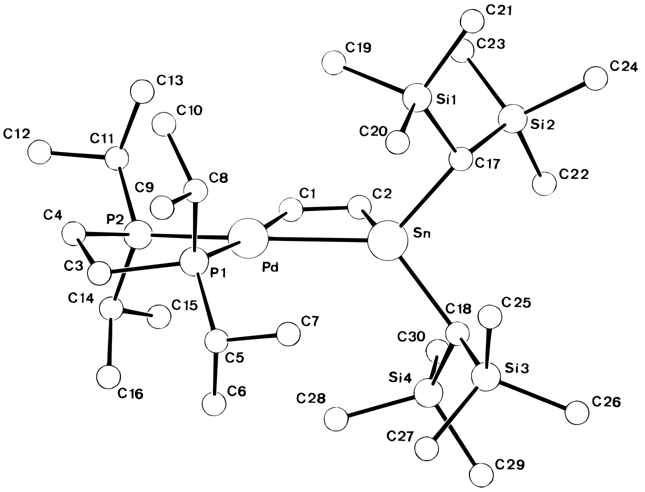


Figure 2. Molecular structure of **10**. Selected bond distances (Å) and angles (deg): Pd−Sn [2.670(1)], Pd−C(1) [2.051(3)], Sn−C(2) [2.150(3)], C(1)−C(2) [1.316(5)], Pd−P(1) [2.341(1)], Pd−P(2) [2.285(1)], Sn−C(17) [2.233(3)], Sn−C(18) [2.240(3)], Sn−Pd−C(1) [67.9(1)], Pd−C(1)−C(2) [119.3(3)], C(1)−C(2)−Sn [98.8(2)], C(2)−Sn−Pd [74.0(1)], P(1)−Pd−P(2) [86.2(1)], P(2)−Pd−C(1) [91.2(1)], P(1)−Pd−C(1) [174.8(1)], P(1)−Pd−Sn [113.0(1)], P(2)−Pd−Sn [158.5(1)], C(17)−Sn−C(18) [105.0(1)], P(1),Pd,P(2)/Pd,C(1),C(2),Sn [7(1)], Pd,C(1),C(2),Sn/Sn,C(17),C(18) [89(1)].

resonances have been assigned by means of ^{13}C,^{1}H correlated NMR spectroscopy.

Structures. The molecular structure of **10** (Figure 2) was determined by a single crystal X-ray structure analysis.[16] In **10** a distorted square-planar (*SP*-4) coordinated Pd(II) ion and a distorted tetrahedrally (*T*-4) substituted Sn(II) ion are part of the central 1,2-palladastannete ring. The Pd atom is coordinated by the chelating diphosphane, the Sn atom, and an ethenediyl C atom. The Sn atom is bound to Pd and the second ethenediyl C atom, and it further bears two CH(SiMe$_3$)$_2$ substituents. The 1,2-palladastannete ring is planar, and its dihedral angle to the P,P,Pd plane is 7°. Complex **10** is isostructural with the Ni complex **1**,[11] and it is worthwhile comparing details of both structures.

The distances P(1)−Pd [2.341(1) Å], P(2)−Pd [2.285(1) Å], and Pd−C(1) [2.051(3) Å] are appreciably longer (0.12 Å) than the corresponding data for **1** and reflect the change in metallic radius in going from Ni to Pd. However, the Pd−Sn distance of 2.670(1) Å is only 0.044(2) Å longer than the Ni−Sn distance and is compatible with a Pd−Sn single bond. The distance C(1)−C(2) [1.316(5) Å] (same as for **1**) agrees well with a C═C bond, and the distance Sn−C(2) [2.150(3)] [**1**: 2.133(4) Å] reflects sp^2 hybridization of the C atom as compared with Sn−C(17) [2.233(3) Å] and Sn−C(18) [2.240(3) Å]; the latter are longer than in Sn$_2${CH(SiMe$_3$)$_2$}$_4$ (2.22 Å) or in the Pd(0)═SnR$_2$ complex **7** (2.21 Å).

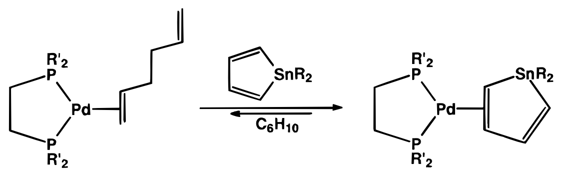
The angles inside the 1,2-pallada- (**10**) and 1,2-nickelastannete rings (**1**) are practically identical. In **10**, the angle Pd−C(1)−C(2) [119.3(3)°] is as expected for sp^2 C whereas C(1)−C(2)−Sn [98.8(2)°] is much smaller. Furthermore, the angles C(1)−Pd−Sn [67.9(1)°] and C(2)−Sn−Pd [74.0(1)°] differ much from the expected values for *SP*-4 Pd(II) (90°) or *T*-4 Sn (109°). The angle C(17)−Sn−C(18) at 103.0(1)° is larger than in **1** [100.9(1)°], and both are larger than the analogous angle in the Pd(0)═SnR$_2$ complex **7** [98.8(5)°].

We conclude from the structural data of **10** that the 1,2-palladastannete ring is as strained as has been proposed for the 1,2-nickelastannete ring in **1**. However, while the Ni−Sn bond is long and weak, the Pd−Sn bond of similar length is strong. In analogy to **1**, the Pd−Sn bond in **10** can be formally described as an inner complex of a stannate(II) anion coordinated to a Pd(II) cation. An alternatively invoked Pd(I)−Sn(III) bond appears to be less likely because of the resulting large difference in the oxidation states.

(R′$_2$PC$_2$H$_4$PR′$_2$)Pd[η^2-C$_4$H$_4$Sn{CH(SiMe$_3$)$_2$}$_2$] (R′ = ^{i}Pr (12), ^{t}Bu (13)). As will be shown in part II the reaction of the

1,2-palladastannetes **10** and **11** with ethyne results in a Pd-catalyzed synthesis of the stannole $(C_4H_4)SnR_2$ (**2a**). With regard to the mechanism of this catalysis it was of interest to know whether and how Pd(0) interacts with **2a**. The Pd(0)$=SnR_2$ complexes **7** and **8** do not react, and the Pd(0)−ethene complexes **3** and **4** react only very reluctantly with **2a**. We therefore started with the precursor complexes of **3** and **4**. Upon warming from −50 to −30 °C the Pd(II) compounds $(R'_2PC_2H_4PR'_2)Pd(\eta^1\text{-}C_3H_5)_2$ ($R' = {}^iPr, {}^tBu$) yield the more reactive Pd(0)−1,5-hexadiene complexes $(R'_2PC_2H_4PR'_2)Pd(\eta^2\text{-}C_6H_{10})$.[13] These can be reacted further either as isolated complexes or in situ.

When $({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^2\text{-}C_6H_{10})$ suspended in pentane is treated with solid **2a** in 20% excess at −30/20 °C, a yellow solution is formed. Upon cooling to −78 °C, yellow crystals of the pure Pd(0)−stannole complex **12** separate in 72% yield. When a concentrated ethereal solution of $({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^2\text{-}C_6H_{10})$ is reacted with the 2-fold molar amount of **2a** and the solvent is evaporated (including some 1,5-hexadiene), the Pd(0)−stannole complex **13** is obtained only as a 70:30 mixture with unreacted starting complex, together with the excess of **2a**. The isolation of complexes **12** and **13** is impeded by their extreme solubility in the usual solvents. The syntheses (eq 3) basically represent slow equilibria in which the coordination of stannole is competed by the coordination of 1,5-hexadiene. The formation of the complexes is counteracted by the bulk of the substituents R′ at phosphorus. Thus, the reaction equilibria are shifted to the right only if an excess of **2a** is employed, and for $R' = {}^tBu$, the formation of **13** is still incomplete under these conditions. It can be deduced from the ligand exchange studies that the strength of coordination of the stannole to Pd(0) is intermediate between that of 1,5-hexadiene (slightly weaker) and ethene (discernibly stronger).

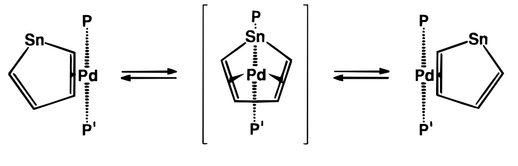


(3)

12, 13

NMR Spectra and Structure. In the ^1H NMR spectrum (200 MHz, 27 °C), complex **12** exhibits two signals of the olefinic stannole protons at δ 6.10 [$=C_\beta H-$] and 4.32 [$=C_\alpha(H)Sn$] which are moderately shifted upfield as compared to those of uncoordinated **2a** [δ(H) 7.10, 6.70]. The signals represent the *time average* of coordinated and uncoordinated C(H)=C(H) groups [calculated proton shifts for the coordinated group: δ(H) 5.10, 1.94; cp. C_2H_4 ligand in **3**: δ(H) 2.30]. Correspondingly, other signals are also degenerate. The $CH(SiMe_3)_2$ substituents at Sn are inequivalent (directed toward or away from Pd) and give rise to two singlets for SnCH protons and two singlets for $SiMe_3$ groups. The $SiMe_3$ groups of each $CH(SiMe_3)_2$ substituent are equivalent. Both "sides" of the ${}^iPr_2PC_2H_4P{}^iPr_2$ ligand are presumed to be different (cp. ^{31}P NMR), but the signals for PCH_2 and $P'CH_2$ [δ(H) 1.64] as well as PCH and P′CH [δ(H) 2.04] and the diastereotopic CH_3 groups of two kinds of ^iPr substituents [δ(H) 1.11; four signals expected for the dynamic structure] are not resolved. At −80 °C, the ^1H NMR spectrum (400 MHz) is essentially unchanged but the signals have lost their fine structure. In the ^{31}P NMR spectrum of **12** (27 °C), an AB spin system is observed for two chemically different ^{31}P nuclei [δ 61.4, 59.0; $J(PP) = 36.5$ Hz] with slightly different couplings to Sn [$J(SnP) = 16.5$ and 19.2 Hz].

The NMR spectra can be rationalized by a *TP*-3 coordination of the Pd atom in the ground state structure of complex **12**. The stannole ligand is π-bound to the $({}^iPr_2PC_2H_4P{}^iPr_2)Pd(0)$ fragment by *one* of the two C=C bonds which oscillate in their coordination to the Pd atom. The ^{31}P NMR shifts are characteristic for 16-e $({}^iPr_2PC_2H_4P{}^iPr_2)$Pd(0)−alkene complexes [**3**: δ(P) 62.7], and the ^{31}P AB system is due to the unsymmetric substitution of the stannole C=C bonds, excluding a rotation of the coordinated C=C bond about the bond axis to Pd(0).[13] The spectroscopic properties of **12** (equivalent C=C bonds but inequivalent phosphorus atoms) are analogous to those of $(R'_2PC_2H_4PR'_2)Pd(\eta^2\text{-butadiene})$ complexes.[30] Thus, a similar exchange mechanism can be assumed, particularly as the stannole shows a *s-cis*-butadiene-type structural element. As depicted in eq 4, the C=C bonds of the stannole ligand exchange their coordination to the Pd atom via *a transient tetrahedral coordination* of the Pd atom. The internal bond exchange process is fast even at −80 °C, i.e., the activation energy is small. The complex is expected to be chiral in the nondynamic ground state structure for which the limiting low-temperature ^1H NMR spectrum has not been observed. The fluxionality invokes an apparent mirror plane, passing through the coordination plane of the *TP*-3 Pd(0) center. Similar NMR spectra are observed for **13**.



(4)

Reaction with Ethyne or SnR₂. Since the strength of coordination of the η^2-stannole ligand to Pd(0) is comparable with that of the η^2-1,5-hexadiene ligand, the Pd(0)−stannole complexes **12** and **13** correspond in their reactivity to the complexes $(R'_2PC_2H_4PR'_2)Pd(\eta^2\text{-}C_6H_{10})$.[13] For example, the exchange of the stannole ligand in **12** and **13** with uncoordinated **2a** is slow at 27 °C on the ^1H and ^{31}P NMR time scales as is the exchange of coordinated and free 1,5-hexadiene. In contrast to this slow exchange, both types of complexes react extraordinary easily with ethyne or SnR_2.

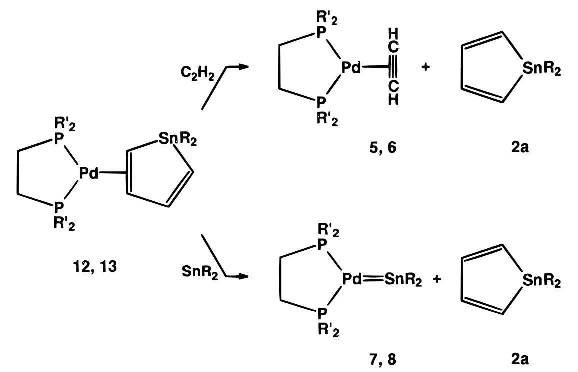
When a solution of the Pd(0)−stannole complex **12** in THF-d_8 is exposed to ethyne at −78 °C, the ^{31}P AB signals of **12** disappear immediately and the singlet of the Pd(0)−ethyne complex **5** [δ(P) 69.5] is observed. The ^1H NMR spectrum exhibits the signals of **5** and uncoordinated stannole **2a**. An analogous reaction is observed for **13** (as part of a mixture, see above) and ethyne to yield **6** and **2a**. Furthermore, when a solution of **12** and **13** in THF-d_8 is reacted with the equimolar amount of SnR_2 at −78 °C, the signals of the Pd(0)−stannylene complexes **7** and **8** and those of **2a** arise. Thus, the Pd(0)−η^2-stannole complexes **12** and **13** react with both ethyne and SnR_2 under exceedingly mild conditions by displacing the stannole ligand and affording the corresponding Pd(0)−ethyne (**5**, **6**) or Pd(0)−stannylene (**7**, **8**) complexes (Scheme 4).

$(Me_3P)_2Pd=Sn\{CH(SiMe_3)_2\}_2$ (18), $(Me_3P)_2Pd(CH=CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (19), and $({}^iPr_3P)_2Pd=Sn\{CH(SiMe_3)_2\}_2$ (20). In the course of this study we tried to complement the group of bidentate phosphane $[(R'_2PC_2H_4PR'_2)Pd]$ complexes ($R' = Me, {}^iPr, {}^tBu$) by $[(R'_3P)_2Pd]$

---

[30] (a) Benn, R.; Jolly, P. W.; Joswig, T.; Mynott, R.; Schick, K.-P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 680. (b) Topalović, I. Dissertation, Universität Siegen, 1990. (c) Benn, R.; Betz, P.; Goddard, R.; Jolly, P. W.; Kokel, N.; Krüger, C.; Topalović, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1991**, *46*, 1395.

Scheme 4



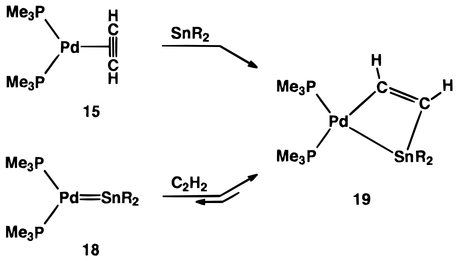
derivatives (R′ = Me, ^{i}Pr) comprising two monodentate phosphane ligands. The latter complexes lack the chelate effect and as a result are markedly less stable. Starting complexes were the Pd(0) compounds $(Me_3P)_2Pd(C_2H_4)$ (**14**),[31] $(Me_3P)_2Pd(C_2H_2)$ (**15**),[32] $(^iPr_3P)_2Pd$,[33] $(^iPr_3P)_2Pd(C_2H_4)$ (**16**),[34] and $(^iPr_3P)_2Pd(C_2H_2)$ (**17**)[35] for which experimental details[14] will be published separately.

When ethereal solutions of colorless **14** and magenta SnR_2 (equimolar amounts) are combined at −78 °C, the reaction solution immediatedly turns dark red, indicating the presence of the *TP*-3 Pd(0)−stannylene complex **18**. In the ^{31}P NMR spectrum (THF-d_8) **18** displays a singlet with typical $^{119/117}$Sn spin−spin coupling satellites (Table 1). Complex **18** is extremely soluble in diethyl ether or pentane at low temperatures and has not been isolated.

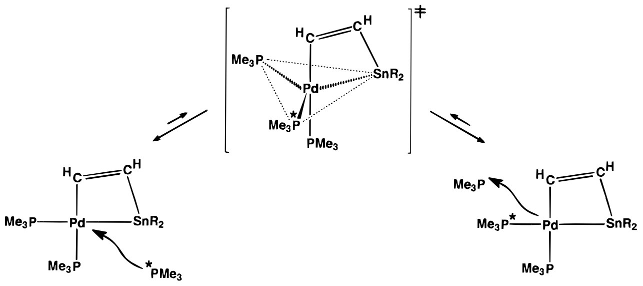
Upon exposure to ethyne at −78 °C the dark red diethyl ether solution of **18** immediately changes color to orange. In the course of several days orange-yellow crystals of the 1,2-palladastannete complex **19** separate in 86% yield. By the same route the ring deuterated derivative $(Me_3P)_2Pd(CD{=}CD)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (**19a**) has been synthesized. Complex **19** is just as readily formed from the Pd(0)−ethyne complex **15** and SnR_2 (Scheme 5). The complex is quite stable as a solid (mp 70 °C dec) and in solution (at 27 °C for longer than 1 h; see below). The IR spectra of **19** and **19a** correspond to those of **9**−**11**.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra (THF-d_8) of complex **19**, recorded at −80 °C, exhibit the signals typical of a 1,2-palladastannete (Table 2). The PdCH═ and SnCH═ ring

Scheme 5



Scheme 6



proton and carbon resonances are sharp and display spin−spin couplings to two phosphorus atoms as well as satellites due to couplings with $^{119/117}$Sn. The ^{31}P AX spin system is attributed to neighboring phosphorus atoms [^2J(PP) = 28 Hz] which are positioned *trans* to Sn [δ −12.2; $^2J(^{119}SnP)$ = 2443 Hz] or *cis* to Sn [δ −23.9; ^2J(SnP) = 148 Hz] at the *SP*-4 Pd(II) center. The spectra are temperature dependent and change significantly at about 0 °C. At 27 °C the signal of P *trans* to Sn is broad and deprived of the Sn coupling satellites while the signal of P *cis* to Sn becomes a sharp singlet with Sn couplings maintained. The PdCH═ and SnCH═ proton signals are somewhat broadened, and for PdCH═ the smaller coupling to P and for SnCH═ one of the numerically identical couplings to P is lost. For the PdCH═ and SnCH═ carbon signals the smaller couplings to P are lost while the larger couplings to P as well as the couplings ^1J(CH) and $^{1,2}J$(SnC) remain unchanged.

The ambient-temperature NMR spectra can be explained by a ligand exchange process at the *SP*-4 Pd(II) center involving the *PMe_3 ligand trans to Sn* which exchanges with traces of uncoordinated PMe_3 present as an impurity. These might be due to commencement of thermal decomposition of **19**. When more PMe_3 is added the rate of the exchange increases, i.e., the coalesced spectra are observed at lower temperatures. The corresponding exchange of the *PMe_3 ligand trans to sp^2 C* is much slower and not detected by NMR. The general lability of this ligand is shown by the fact that **19** reacts with 1 equiv of a bidentate phosphane $R'_2PC_2H_4PR'_2$ (R′ = Me, ^{i}Pr, ^{t}Bu) at −78 °C by exchange of both PMe_3 ligands to give **9**−**11**. However, it has not been possible to trap one of the PMe_3 ligands in **19** by adding BEt_3 (1 equiv) at −30 °C.[36] Apparently, both PMe_3 ligands in **19** are tightly bound and do not dissociate. The exchange of the PMe_3 ligand *trans* to Sn by additional PMe_3 does not reflect an inherently weak coordination but is the result of a kinetic effect.

Without a doubt the ligand exchange proceeds by an associative mechanism (Scheme 6).[37] Formally, incoming PMe_3 is coordinated at an apical position of a coordinatively unsatur-

---

[31] $(Me_3P)_2Pd(C_2H_4)$ (**14**): Yellow crystals: >−10 °C dec; very soluble in pentane and other solvents even at low temperature; reversible partial dissociation in solution into $[(Me_3P)_2Pd]$ and ethene above −30 °C (NMR). Anal. Calcd for $C_8H_{22}P_2Pd$ (286.6): C, 33.52; H, 7.74; P, 21.61; Pd, 37.13. Found: C, 33.64; H, 7.78; P, 21.49; Pd, 37.18. ^{1}H NMR (200 MHz, THF-d_8, −80 °C): δ 2.14 (d, 4H, C_2H_4), 1.28 (m, 18H, PMe_3). ^{31}P NMR (81 MHz, THF-d_8, −80 °C): δ −24.8.

[32] $(Me_3P)_2Pd(C_2H_2)$ (**15**): Light yellow cubes from the reaction of **14** with ethyne: >−20 °C dec. Anal. Calcd for $C_8H_{20}P_2Pd$ (284.6): C, 33.76; H, 7.08; P, 21.77; Pd, 37.39. Found: C, 33.70; H, 7.14; P, 21.84; Pd, 37.28. ^{1}H NMR (200 MHz, THF-d_8, −80 °C): δ 6.26 (m, 2H, C_2H_2), 1.33 (m, 18H, PMe_3). ^{31}P NMR (81 MHz, THF-d_8, −80 °C): δ −22.8.

[33] Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1975**, *12*, 187. Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673.

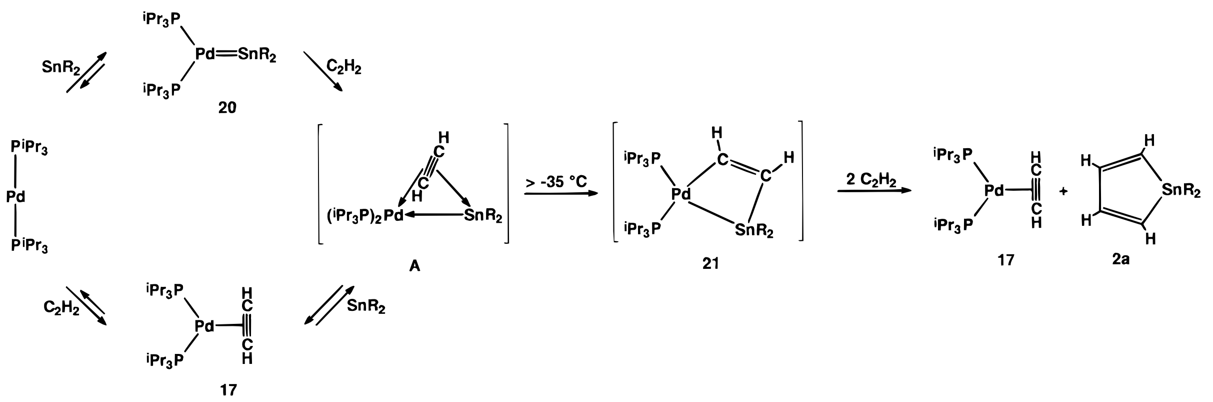
[34] $(^iPr_3P)_2Pd(C_2H_4)$ (**16**): Colorless crystals from solutions of $(^iPr_3P)_2Pd$[33] saturated with ethene at −30/−78 °C; dissociates reversibly in solution. Anal. Calcd for $C_{20}H_{46}P_2Pd$ (455.0): C, 52.80; H, 10.19; P, 13.62; Pd, 23.39. Found: C, 52.94; H, 10.15; P, 13.65; Pd, 23.29. ^{1}H NMR (200 MHz, THF-d_8, −80 °C): δ 2.32 (s, 4H, C_2H_4), 2.11 (m, 6H, PCH), 1.19 (m, 36H, CH_3). ^{31}P NMR (81 MHz, THF-d_8, −80 °C): δ 48.7.

[35] $(^iPr_3P)_2Pd(C_2H_2)$ (**17**): Colorless crystals from the reaction of $(^iPr_3P)_2Pd$ or **16** with ethyne; stable up to 0 °C; reversible dissociation in solution into $(^iPr_3P)_2Pd$ and ethyne. Anal. Calcd for $C_{20}H_{44}P_2Pd$ (452.9): C, 53.04; H, 9.79; P, 13.68; Pd, 23.50. Found: C, 53.10; H, 9.73; P, 13.65; Pd, 23.41. ^{1}H NMR (200 MHz, THF-d_8, −80 °C): δ 6.21 (m, 2H, C_2H_2), 2.15 (m, 6H, PCH), 1.18 (dd, 36H, CH_3). ^{31}P NMR (81 MHz, THF-d_8, −80 °C): δ 51.2.

[36] For adducts $(R_3P)BR'_3$, see: (a) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101. (b) Apel, J.; Grobe, J. *Z. Anorg. Allg. Chem.* **1979**, *53*, 28. (c) Reference 29a.

[37] Peloso, A. *Coord. Chem. Rev.* **1973**, *10*, 123.

Scheme 7



ated (16-e) *SP*-4 Pd(II) center of **19**. A trigonal-bipyramidal (*TB*-5) "activated complex"[38a,b] **19**·PMe_3[38c] results, in which the sp^2 C atom occupies an axial and the Sn atom an equatorial position. This arrangement is supported by the "apicophilicity"[39] of the more electronegative substituent (sp^2 C) and the expectation that the substituent with the shorter (stronger) bond to Pd is in the axial position (cp. **10**: Pd−C (2.05 Å)) and the substituent with the longer (weaker) bond is in the equatorial position (cp. **10**: Pd−Sn (2.67 Å)). The remaining three positions are occupied by PMe_3 ligands, of which the PMe_3 ligand at the second axial position is more strongly bound than the two equivalent equatorial PMe_3 ligands. By dissociation of one of the equatorial PMe_3 ligands the starting *SP*-4 complex is reformed. An exchange of the PMe_3 ligand *trans* to sp^2 C by uncoordinated PMe_3 probably requires the isomeric, high-energy *TB*-5 "activated complex" in which the sp^2 C atom and the Sn atom have interchanged positions.

It therefore appears that the 1,2-palladastannete ring strongly distinguishes between both PMe_3 ligands through the geometry of the *TB*-5 "activated complex". Similar ligand exchange reactions have been observed by Carmona et al. for a nickelabenzocyclopentene complex.[40] However, the effect of differentiation of the PMe_3 ligands is much more pronounced for the 1,2-palladastannete **19**, which is presumably due to the smaller ring size (four-membered ring *vs* five-membered ring), the larger difference in the substituent electronegativities [C(sp^2) (2.75), Sn (1.8) *vs* C(sp^2) (2.75), C(sp^3) (2.5)] and the larger covalent radius of the special equatorial substituent (Sn (1.40 Å) *vs* C (0.77 Å)).

When a colorless ethereal solution of $(^iPr_3P)_2Pd$ or the ethene adduct **16** is combined with the stoichiometric amount of magenta SnR_2 at −78 °C, a dark red solution of the pure Pd(0)−stannylene complex **20** is formed immediately. Complex **20** is exceedingly soluble in diethyl ether or pentane, even at low temperature, and has not been isolated. According to the NMR spectra (Table 1) **20** is undissociated at low temperature but dissociates partially when warmed to 27 °C (loss of the $^{119/117}Sn,^{31}P$ spin−spin couplings).

When ethyne is added to the ethereal solution of **20** at −78 °C, the red color changes to magenta within a few minutes and a solution of the Pd(0)−ethyne complex **17** (^{31}P NMR: δ 51.2) and free stannylene is obtained (Scheme 7). The stannylene/ethyne displacement reaction at the $(^iPr_3P)_2Pd$ fragment presumably proceeds by an associative mechanism implying a type **A** intermediate, but a dissociative mechanism via $(^iPr_3P)_2Pd$ as an intermediate cannot be excluded. No further reaction between **17** and SnR_2 to produce the corresponding 1,2-palladastannete complex **21** is observed between −78 and −35 °C (for higher temperatures, see part II).

II. Palladium Catalysis

The $Pd/SnR_2/C_2H_2$ system becomes much more complex when SnR_2 and/or C_2H_2 are present in excess and when the temperature is raised above −30 °C. It will be shown that the 1,2-palladastannetes play the key role in the catalytic formation of $(C_4H_4)SnR_2$ (**2a**). The thermal degradation of **10** and **11** in solution, yielding small amounts of the stannole **2a** (eq 2c), already indicates a facile formation of **2a**.

A *stoichiometric synthesis* of **2a** can be developed as follows: when a solution of the 1,2-palladastannete **11** ($^tBu_2PC_2H_4P^tBu_2$ derivative) in THF at 20 °C is exposed to ethyne and the reaction is monitored by ^{31}P NMR, the signals of **11** (δ 85.7, 82.1) slowly disappear and the singlet of the Pd(0)−ethyne complex **6** (δ 91.3) arises. In the ^1H NMR spectrum (THF-d_8) new signals of **6** and of the stannole **2a** are observed. The reaction is complete after about 1 day. When the solvent is evaporated, a mixture of the palladium complex **6** and the tin compound **2a** is left as the only products, which can be separated by pentane extraction of **2a** (75% isolated yield). The $^iPr_2PC_2H_4P^iPr_2$ complex **10** reacts with ethyne in the same way as **11** but much more slowly. After 1 week, the ^1H NMR spectrum of the reaction solution still shows the signals of the starting 1,2-palladastannete **10** as the major component (85%) but also additional signals of the ethyne complex **5** and of the stannole **2a** as products. Therefore, the 1,2-palladastannetes **10** and **11**

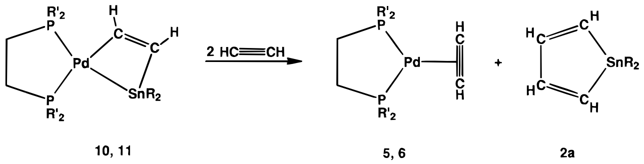
---

[38] (a) Cardwell, H. M. E. *Chem. Ind. (London)* **1955**, 422. (b) The term activated complex in the narrow sense refers to the configuration of reactants and products at the transition state in the reaction profile (ref 39a, p 545 f). By using this term in quotation marks we do not strictly distinguish between a transition state or a close by intermediate. (c) We *assume* that **19**·PMe_3 represents a transition state. This assumption is supported by the following results: When **19** is dissolved in neat PMe_3 at −78 °C no adduct can be isolated. After addition of some THF-d_8 the ^{31}P NMR spectrum displays the signals expected for a mixture of **19** and PMe_3. Similarly, in $\{(MeC(CH_2PMe_2)_3\}Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (**27**), only two of the three phosphorus atoms of the tripodal ligand $MeC(CH_2PMe_2)_3$ are coordinated at *SP*-4 Pd(II). **27**: mp 87 °C dec. IR (KBr): 1460, 1045, 500 cm^{-1} (−CH=CH−). MS (80 °C): *m/e* 796 ($[M - C_2H_2]^+$, 1). ^{31}P NMR (161 MHz, −80 °C): δ −9.7 (broad) ($^2J(SnP_{trans})$ = 2333 Hz), −25.2 ($^2J(SnP_{cis})$ not resolved), −63.1 (broad). The broad signals result from a slow exchange between the P atom *trans* to Sn and the uncoordinated P atom. Anal. Calcd for $C_{27}H_{67}P_3PdSi_4Sn$ (822.2): C, 39.44; H, 8.21; P, 11.30; Pd, 12.94; Si, 13.66; Sn, 14.44. Found: C, 39.31; H, 8.29; P, 11.18; Pd, 12.85; Si, 13.54; Sn, 14.35.

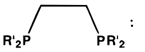
[39] (a) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; p 277. (b) Hollemann-Wiberg. *Lehrbuch der Anorganischen Chemie*, 101st ed.; de Gruyter: Berlin, 1995; p 754.

[40] (a) Carmona, E.; Gutiérrez-Puebla, E.; Martin, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruíz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883. (b) Carmona, E.; Paneque, M.; Poveda, M. L.; Gutiérrez-Puebla, E.; Monge, A. *Polyhedron* **1989**, *8*, 1069. (c) Cámpora, J.; Llebaría, A.; Moretó, J. M.; Poveda, M. L.; Carmona, E. *Organometallics* **1993**, *12*, 4032. (d) Cámpora, J.; Gutiérrez, E.; Monge, A.; Palma, P.; Poveda, M. L.; Ruíz, C.; Carmona, E. *Organometallics* **1994**, *13*, 1728.

react with the *2-fold* molar amount of ethyne to afford the ethyne complexes **5** and **6**, respectively, and the stannole **2a** (eq 5).



(5)

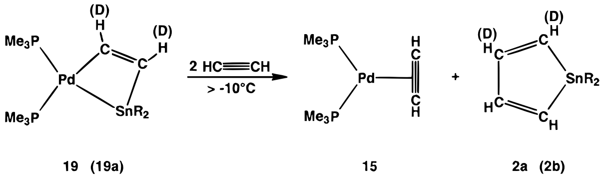


: $^iPr_2PC_2H_4P^iPr_2$, $^tBu_2PC_2H_4P^tBu_2$

For a *two-step catalytic synthesis* of **2a**, the solutions obtained from the reaction of the 1,2-palladastannetes **10** and **11** with ethyne (eq 5) are treated repeatedly with an equimolar amount of SnR_2 and, subsequently, with ethyne in excess. When SnR_2 is added in THF or pentane at 20 °C to the product mixture of the Pd(0)−ethyne complex **6** and **2a**, **6** is immediately converted into the 1,2-palladastannete **11**. This intermediate reacts with ethyne slowly but completely (>1 day, as monitored by ^1H and ^{31}P NMR) with recovery of **6** and formation of an additional 1 equiv of **2a** (yield 75%, as referred to total Sn). Repeating the procedure leads to a further catalysis cycle. It is necessary that a catalysis cycle has finished completely before the next portion of SnR_2 is added to assure that added SnR_2 quickly reacts with **6** to give **11**. If an excess of SnR_2 is present in solution at 20 °C, it will for the most part react uncatalyzed with ethyne to give various thermal products (see Introduction). Stannole **2a** is the catalytically exclusively formed tin product. By adding SnR_2 to the reaction solution of **10** and ethyne (containing a mixture of **5** and **2a**, together with unreacted **10**), the catalysis principally proceeds as well but is slower and thermal byproducts cannot be avoided. The catalysis is also initiated by the Pd(0)−stannylene complexes **7** and **8** and, self-evidently, by the 1,2-palladastannetes **10** and **11** and the Pd(0)−stannole complexes **12** and **13**. Thus, with *(R'$_2$PC$_2$H$_4$PR'$_2$)Pd catalysts* (R' = ^{i}Pr, ^{t}Bu) at 20 °C, (a) the catalysis can be carried out batchwise and (b) each catalysis cycle is very slow, even in the case of the R' = ^{t}Bu derived catalysts (**6**, **8**, **11**, and **13**).

In order to speed up the catalysis and to run it continuously it was necessary to increase the activity of the catalyst. A more active catalyst will restrain the problem of the thermal side reactions if the catalysis (a) is fast enough at ambient temperature to compete with the side reactions or (b) can be carried out at a lower temperature than −10 °C to surpress these. We therefore turned our attention to *(R'$_3$P)$_2$Pd catalysts* (R' = Me, ^{i}Pr).

When the yellow THF-d_8 solution of the PMe_3-modified 1,2-palladastannete **19** is saturated with ethyne and warmed from −30 to 0 °C, the solution decolorizes within about 3 h and in a stoichiometric reaction (eq 6), equimolar amounts of the Pd(0)−ethyne complex **15** and the stannole **2a** are formed (^1H and ^{31}P NMR). The reaction of **19** proceeds at a lower temperature (0 °C) and is markedly faster (3 h) relative to that of **10** (20 °C, >7 days) or **11** (20 °C, 1 day). In particular, the reaction is now fast enough to cope with the ring degradation reaction of the 1,2-palladastannetes (cp. **10a** and Scheme 3). When the ring deuterated derivative **19a** is reacted with a 10-fold excess of C_2H_2 at −10 °C for 2.5 h, only a partial reaction according to eq 6 takes place. In the NMR spectra (^1H and ^{31}P), besides the signals of **19a** and C_2H_2, those of non-deuterated **19**, of the Pd(0)−ethyne complex **15**, and of partially deuterated stannole $(C_4D_2H_2)Sn\{CH(SiMe_3)_2\}_2$ (**2b**) (Table 3) are observed. The products **19**, **15**, and **2b** are formed in about equal amounts, and detectable amounts of non-deuterated stannole **2a** are formed only after about 11 h reaction time. This experiment shows that (a) an expected ring degradation reaction of **19a** takes place which is the reverse of the synthesis reaction (lower part of Scheme 5) and by which a C_2D_2/C_2H_2 exchange occurs, i.e., the synthesis reaction represents an equilibrium (as for **10** and **11**) and (b) in the concurrent stannole formation one of the C_2H_2/C_2D_2 components of **2a** (**2b**) originates from the 1,2-palladastannete **19** (**19a**) and the other one from added ethyne, i.e., *the 1,2-palladastannete is a prerequisite for the stannole formation*.



(6)

It is furthermore to be noted that the reaction of **19** according to eq 6 is almost completely inhibited by relatively small amounts of added PMe_3 (0.5−1 equiv). This observation will become clear later.

In order to attempt a one-step catalysis on the basis of a $[(Me_3P)_2Pd]$ catalyst, a pentane solution of any of the $(Me_3P)_2$-Pd complexes **14**, **15**, **18**, or **19** is reacted at 0 °C with an excess of SnR_2 (Sn:Pd = 12:1) and the mixture is kept saturated with ethyne. A total conversion of SnR_2 takes place within less than 4 h. While about 25% of SnR_2 is converted into insoluble $(C_2H_2)_n(SnR_2)_{2n}$, the solution contains a mixture of roughly equal amounts of thermally formed $(HC{\equiv}C)SnR_2(\mu\text{-}trans\text{-}(CH{=}CH)\text{-}SnR_2(CH{=}CH_2)$ and $(HC{\equiv}C)(H_2C{=}CH)SnR_2$[7] as well as catalytically formed stannole **2a** (^1H and ^{13}C NMR). Thus, **2a** is in fact formed in a slow continuous catalytic reaction but the thermal byproducts are not sufficiently retarded. Lowering the temperature below 0 °C further inhibits the side reactions but also slows down the catalysis.

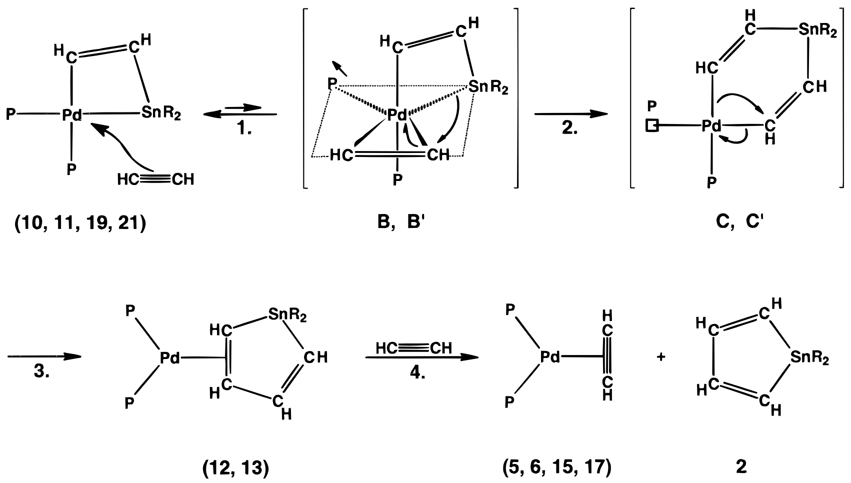
It has not been possible to isolate nor to detect spectroscopically between −78 and −35 °C the $^iPr_3P$ modified 1,2-palladastannete **21** (part I). When the magenta colored 1:1 mixture of $(^iPr_3P)_2Pd(C_2H_2)$ (**17**) and SnR_2—obtained from the reaction of $(^iPr_3P)_2Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (**20**) and excess ethyne—is warmed to −30 °C, the color changes to orange-yellow within a few minutes. In the NMR spectra (^1H, ^{31}P) of this solution, the ^1H signals of **2a** instead of those of SnR_2 are observed while the signals of **17** are unchanged. Thus, SnR_2 and ethyne have been completely and rapidly transformed into the stannole **2a** in a synthesis catalyzed by **17**. After evaporation of the solvent under vacuum (−50 °C) a dark-red oil remains which consists mainly of $(^iPr_3P)_2Pd$ and the stannole **2a** (**17** is converted into $(^iPr_3P)_2Pd$ under vacuum). In view of the stoichiometric reactions of the 1,2-palladastannetes **10**, **11**, **19**, and **19a** with ethyne (eqs 5 and 6), it can be anticipated that the stannole formation catalyzed by **17** proceeds via the 1,2-palladastannete *intermediate* **21** (Scheme 7). Intermediate **21** is higher in energy as compared with the isolable 1,2-palladastannetes **10**, **11**, and **19**. It is apparently not formed below −35 °C, but once it is formed (−30 °C) in the presence of ethyne, it immediately reacts further to give **17** and **2a**.[41] So far this reaction shows that the stannole **2a** may be formed below −10 °C and furthermore it sheds light on the fate of the catalyst.

A *one-step low-temperature catalysis* (−30 °C) to convert larger amounts of SnR_2 into **2a** proceeds as follows. A magenta suspension of SnR_2 in a small volume of THF or pentane, kept

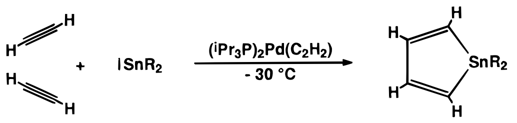
---

[41] When a mixture (1:1) of $(^iPr_3P)_2Pd(C_2H_2)$ (**17**) and SnR_2 is warmed to −30 °C without additional ethyne equal amounts of $(^iPr_3P)_2Pd{=}Sn\{CH\text{-}(SiMe_3)_2\}_2$ (**20**), $(^iPr_3P)_2Pd$ and **2a** are formed. Thus, SnR_2 reacts with coordinated ethyne to give **2a** to the extent that one of the components (ethyne) is consumed.

Scheme 8



saturated with ethyne at −30 °C, is mixed with a catalytic amount (1%) of any of the $[(^{i}Pr_3P)_2Pd(0)]$ complexes $(^{i}Pr_3P)_2$-Pd, **16**, **17**, or **20**. Upon stirring, all SnR_2 dissolves within 2 h and the reaction mixture changes the color to red-violet due to the formation of some polyacetylene. After a few simple separation steps, the analytically pure, crystalline stannole **2a** is obtained in 87% yield, corresponding to a turnover number (TON) of 87. If less catalyst is employed, the TON increases but the full consumption of SnR_2 takes more time. Thereby, the side reactions consume a larger share of SnR_2, lowering the yield of **2a**. Thus, when 0.1% $[(^{i}Pr_3P)_2Pd(0)]$ is employed as catalyst, the reaction takes 6 h and **2a** is isolated in 66% yield, corresponding to TON = 660.



(7)

If still smaller amounts of catalyst (<0.1% Pd) are used at −30 °C, the reaction time and the amount of byproducts increase further, thereby reducing the yield of **2a**. In this case an increase in temperature will speed up both the catalysis and the side reactions but also shorten the reaction time. For the side reactions, the effect of an increase in temperature is more or less cancelled out by the decrease in the reaction time. Thus, in a *one-step high-temperature catalysis* (20 °C, pentane) with 0.04% $[(^{i}Pr_3P)_2Pd(0)]$ as catalyst the reaction of SnR_2 with ethyne affords, within 15 min, stannole **2a** in 43% yield (TON = 1075).

The Mechanism of the Stannole Formation. The reaction of the 1,2-palladastannetes **10**, **11**, **19,** and the nonisolated derivative **21** with the 2-fold molar amount of ethyne involves the *conversion of three C_2H_2 moieties* to yield selectively the corresponding Pd(0)−ethyne complexes (**5**, **6**, **15**, and **17**) and the stannole **2a**. Most likely this reaction proceeds by a stepwise mechanism (Scheme 8) which is derived in the following.

The reaction is believed to be initiated by a ring enlargement of the four-membered ring of **10**, **11**, **19**, and **21** by insertion of ethyne. It first needs to be clarified *where* the insertion occurs for which three routes are conceivable. Insertion of an ethyne molecule into the Pd−Sn bond (a) causes the cleavage of this bond and leads to a 1-pallada(II)−4-stanna(IV)-2,5-cyclohexadiene intermediate **C** (for **B**, see below), whereas insertion of ethyne into either the Pd−C or Sn−C bond (b, c) with preservation of the Pd−Sn bond would lead to a 1-pallada(II)-2-stanna(II)-3,5-cyclohexadiene intermediate. Although routes b and c cannot be strictly excluded, we strongly favor route a because of the following arguments:

(i) Insertion of alkynes into metal−SnR_3 bonds (e.g., for Al, Cu, Si, Sn, and Zn; *cis*-addition) is a well-known process,[42] whereas insertions of alkynes into Pd−*vinyl*-C bonds are rare[43] and insertions of alkynes into Sn−*vinyl*-C bonds are apparently not known.

(ii) The ultimate specifity of the stannole formation suggests that an essential functional element is abolished in the course of the reaction. If an insertion of the ethyne occurred into either the Pd−*vinyl*-C or Sn−*vinyl*-C bond of **10**, **11**, **19**, and **21**, the reactive site would be retained. In this case one might expect that a further insertion would occur and that, besides the stannole, to some extent also larger rings (e.g., a stannepine) would be formed. There are, however, no Pd-mediated byproducts observed. Since the ring enlargement step obviously proceeds only once, it seems reasonable that it proceeds by an insertion of ethyne into the Pd−Sn bond which is thereby cleaved.

(iii) In the suggested intermediate **C** the Pd atom contains two vinyl substituents. Such a compound is expected to be very labile and to undergo an oxidative coupling of the vinyl substituents at low temperature, concomitant with a reduction Pd(II) → Pd(0).[44]

(iv) A related 1-platina(II)-4-sila(IV)-2,5-cyclohexadiene derivative has recently been synthesized by an in situ reaction of $[(Et_3P)_2Pt{=}SiMe_2]$ with PhC≡CH and characterized by X-ray crystallography. When heated to 120 °C the Pt(II) derivative eliminates the corresponding silole.[45]

It is now explained *how* the insertion of ethyne into the 1,2-palladastannete Pd−Sn bond proceeds (steps 1 and 2). It seems reasonable that the insertion step is initiated by coordination of an ethyne molecule at an apical coordination site of the *SP*-4 Pd(II) center (16e) to afford an “activated complex” [38a,b] (step

---

[42] (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 21−23. (b) Harrison, P. G. *Chemistry of Tin*; Blackie: Glasgow, U.K., 1989; pp 159−160.

[43] (a) Tohda, Y.; Sonogashira, K.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1975**, 54. (b) Mann, B. E.; Bailey, P. M.; Maitlis, P. M. *J. Am. Chem. Soc.* **1975**, *97*, 1275. (c) Kelly, E. A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1977**, 289. (d) Clark, H. C.; Milne, C. R. C.; Wong, C. S. *J. Organomet. Chem.* **1977**, *136*, 265.

[44] (a) Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174. (b) Negishi, E.; Takahashi, T.; Akiyoshi, K. *J. Organomet. Chem.* **1987**, *334*, 181. (c) Brown, J. M.; Cooley, N. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1345. (d) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989**, *8*, 180. (e) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431.

[45] Yamashita, H.; Tanaka, M.; Goto, M. *Organometallics* **1992**, *11*, 3227.

1). For this adduct the coordination geometry of Pd(II) is square pyramidal (*SPY*-5) or trigonal bipyramidal (*TB*-5) if ethyne is considered to occupy a single coordination site. The *TB*-5 1,2-palladastannete ethyne "activated complex" corresponds to the already discussed PMe_3 "activated complex" **19**·PMe_3. However, in order to obtain information on the preferred orientation of the η^2-ethyne ligand in the "activated complex", it is worthwhile to assume that ethyne occupies *two* adjacent coordination sites, invoking a palladacyclopropene-type structural element. In this case the geometry is changed from *SPY*-5/*TB*-5 to octahedral (*OC*-6), formally implying Pd(IV) (**B**). The *TB*-5 and *OC*-6 models are limiting structural descriptions for the intermediate. If the more electronegative sp^2 C atom of the 1,2-palladastannete moiety is located in an "axial" position and the Sn(II) atom in an "equatorial" position, the phosphorus atom which is fixed *trans* to sp^2 C (as is expected from the PMe_3 exchange reaction of **19**, Scheme 6) is likewise located in an axial position. Thus, on the basis of the *OC*-6 model, the ethyne ligand is coordinated at two adjacent equatorial coordination sites while the remaining equatorial site is left for the second phosphorus atom. In this arrangement the ethyne ligand is coplanar with the Pd−Sn bond and is thus perfectly orientated for an "insertion" into this bond. Organo-Pd(IV) compounds as isolated complexes or intermediates in organic reactions are now evidenced by numerous examples.[46] Moreover, complexes (2,9-Me_2-1,10-phenanthroline)(alkene)Pd(Cl)Me, for which the structure has also been discussed in the sense of a *TB*-5−*OC*-6 dualism, are good models for **B**.[47]

In the subsequent reaction step 2, the ethyne ligand of the "activated complex" **B** "inserts" into the Pd−Sn bond, causing the ring enlargement to afford formally the *SP*-4 Pd(II) intermediate **C**. Macroscopically step 2 is classified as an oxidative coupling of the Sn and ethenyl substituents. However, in detail, the course of action is rather complicated. At first the "equatorial" phosphane ligand of **B** leaves the coordination sphere to lower the coordination number of formal Pd(IV) (forming an additional intermediate **B′**). Subsequently the stannate(II) ligand nucleophilicly displaces the Pd(IV) center from the ethenyl C atom which is adjacent to Sn in the "equatorial" plane. Sn(II) is thereby oxidized to Sn(IV) and Pd(IV) is reduced to Pd(II). Thus, a 3-fold coordinated intermediate (**C′**) is generated which upon recoordination of the phosphane ligand forms the *SP*-4 Pd(II) intermediate **C**. The suggested sequence in step 2 is in full agreement with the mechanism of reductive eliminations from Pd(IV) complexes.[48] For example, it has been demonstrated by Canty et al. that ethane elimination from (bipy)Pd(I)Me_3 is preceded by dissociation of iodide and is inhibited by addition of KI.[48b] As mentioned above the ethyne insertion reaction of the 1,2-palladastannete **19** (eq 6) is indeed inhibited by added PMe_3. We assume that step 2 (overall) is rate determining for the stannole formation when starting from isolable 1,2-palladastannetes (**10**, **11**, and **19**).

In a third reaction step, intermediate **C** (or more likely its 3-fold coordinated equivalent **C′**)[49] undergoes an oxidative coupling of the *cis*-vinyl substituents concomitant with a reduction Pd(II) → Pd(0). From reference reactions it can be expected that this step proceeds very easily,[44] i.e., it is not rate determining for the overall reaction. Several mechanisms can be envisaged of which the following appears to be the most likely. One vinyl ligand attacks the other nucleophilicly and displaces the Pd atom from it. Thereby, the stannole is formed and Pd(II) is reduced to Pd(0). At this stage, the stannole stays as a ligand in the coordination sphere of *TP*-3 Pd(0) and Pd(0)−stannole complexes like **12** and **13** are formed as further intermediates. There is some controversy on the question whether[49a,c] or not[50] reductive elimination reactions from Pd(II) are induced by coordination of a π ligand. For **C** (**C′**) we discard an induction of the vinyl coupling step by ethyne coordination to the *SP*-4 Pd(II) center, which would lead directly to the Pd(0)−ethyne complex as the final product. We consider the *cis*-divinyl Pd(II) intermediate **C** to be quite similar to *cis*-bis(σ-allyl) Pd(II) complexes, $(R'_2PC_2H_4PR'_2)Pd(\eta^1\text{-}C_3H_5)_2$, for which the thermally induced (−30 °C) oxidative C−C coupling of the allyl substituents affords a Pd(0)-η^2-1,5-hexadiene complex as the primary product. This allyl coupling reaction is unaffected by the presence of ethyne, and in an in situ synthesis the corresponding Pd(0)−ethyne complex is formed by displacing 1,5-hexadiene from the Pd(0)−η^2-1,5-hexadiene intermediate.[13]

In the ultimate reaction step the *TP*-3 Pd(0)−stannole intermediate (e.g., **12** or **13**) reacts with ethyne by displacement of the stannole ligand to yield the final Pd(0)−ethyne complex (**5**, **6**, **15**, or **17**). As shown for the isolated Pd(0)−stannole complexes **12** and **13**, the stannole displacement by ethyne (or stannylene) proceeds extremely easily and is certainly not rate determining for the overall reaction.

Hence, in the formation of the stannole according to Scheme 8, one ethyne molecule incorporated into the stannole was part of a 1,2-palladastannete (**10**, **11**, **19**, or **21**) and the second ethyne molecule is taken from the solution. The third ethyne molecule serves to recover the Pd(0)−ethyne complexes (**5**, **6**, **15**, and **17**) which in turn may act as starting complexes for the synthesis of the 1,2-palladastannetes.

The ethyne insertion and its inhibition by added PMe_3 is related to other insertion reactions at Ni(II) or Pd(II) which have been studied, among others, by Bergman,[51] Norton,[52] and Carmona.[40] These authors conclude from the phosphane inhibition that one of the phosphane ligands at the *SP*-4 Ni(II) or Pd(II) center is labile and is displaced by an alkene or alkyne. It is suggested that the insertion of the π ligand into a corresponding Ni−C or Pd−C bond proceeds from this *SP*-4 intermediate. The authors maintain that the mechanism is supported by MO calculations.[53] Applying this mechanism to the reaction of 1,2-palladastannetes with ethyne implies that, after phosphane dissociation, an *SP*-4 intermediate is formed in which the ethyne ligand is coordinated *trans* to the Pd−Sn

---

[46] (a) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83. (b) Canty, A. J. *Platinum Metals Rev.* **1993**, *37*, 2. (c) Asselt, R. van; Rijnberg, E.; Elsevier, C. J. *Organometallics* **1994**, *13*, 706.

[47] Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitagliano, A. *Organometallics* **1990**, *9*, 1269.

[48] (a) For a pioneering study concerning Pt(IV) complexes, see: Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. *J. Chem. Soc., Dalton Trans.* **1974**, 2457. (b) Byers, P. K.; Canty, A. J.; Crespo, M.; Puddephatt, R. J.; Scott, J. D. *Organometallics* **1988**, *7*, 1363. Dücker-Benfer, C.; van Eldik, R.; Canty, A. J. *Organometallics* **1994**, *13*, 2412.

[49] (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933. (b) Moravskiy, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4182. (c) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (d) Ozawa, F.; Kurihara, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 399. (e) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2, p 625.

[50] (a) Sustmann, R.; Lau, J. *Chem. Ber.* **1986**, *119*, 2531. (b) Sustmann, R.; Lau, J.; Zipp, M. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 356.

[51] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.

[52] Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 5505.

[53] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. This EH-MO study concludes that "... insertion from a five-coordinate complex requires some rearrangement and unexpected distortion from preferred equilibrium geometries which add up to a *modestly* large energy barrier. If a ligand is lost to form a four-coordinate complex, then there remains a requirement of a *trans* to *cis* (ethylene and hydride) rearrangement, but the insertion barrier becomes appreciably smaller". This statement should not be generalized to the effect that an insertion reaction at Pd(II) necessarily implies an *SP*-4 intermediate.

bond. We discard a mechanism involving such an intermediate for the following reasons:

(i) Phosphanes are strongly bound at the *SP*-4 Pd(II) center, as has also been demonstrated by the failure to trap one of the PMe_3 ligands in **19** by BEt_3. The displacement of a predominantly electron-donating phosphane ligand, albeit feasible for other donors, appears to be unfavorable for a predominantly electron-accepting alkyne ligand.

(ii) An insertion reaction of the ethyne ligand into the *trans* Pd−Sn bond of a *SP*-4 Pd(II) intermediate requires a preceding *trans* → *cis* isomerization. Such isomerizations imply a rather high activation energy and are usually slow at ambient temperature.[49a,c,54,55]

The problem of *trans* coordination of the alkyne can, however, be avoided if one assumes that the coordination sphere of the Pd atom expands from *SP*-4 to five-coordinate [Pd(II)] or six-coordinate [Pd(IV)] as shown above.[56]

III. Additional Results

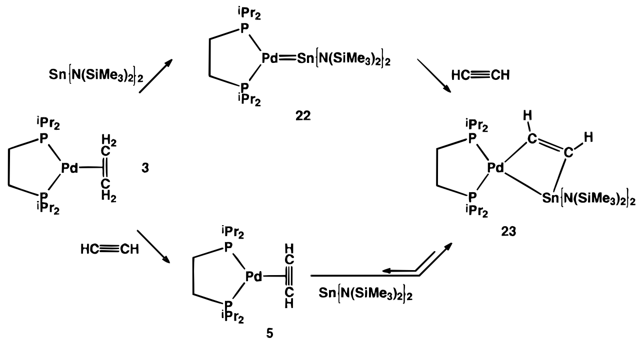
From the results presented above a clear picture of the Pd-catalyzed formation of stannole **2a** emerges. In addition, supplementary studies were undertaken to determine (a) whether the catalysis can be generalized to synthesize stannoles from stannylenes SnR_2 other than $Sn\{CH(SiMe_3)_2\}_2$, (b) whether stannoles are also formed from inorganic Sn(II) compounds like $SnCl_2$ or $Sn\{N(SiMe_3)_2\}_2$, and (c) what the properties of the stannoles produced are.

So far, it has been possible to extend the catalysis to the conversion of Kira's stannylene $Sn\{C(SiMe_3)_2CH_2\}_2$[57] and ethyne into the stannole $(C_4H_4)Sn\{C(SiMe_3)_2CH_2\}_2$ (**2c**). Under conditions similar to those for **2a** and by applying **17** as a catalyst (3%; THF; −30 °C), colorless crystals of **2c** are obtained in 87% yield. It is most probable that the formation of **2c** proceeds by the same mechanism as for **2a**, and hence, no attempts were made to characterize intermediates of this process. A detailed description of the properties of both **2a** and **2c** is given below.

Further experiments have shown that the colorless Pd(0)−ethene complex **3** reacts with $Sn(\eta^5\text{-}C_5H_5)_2$ and $SnCl_2$ (THF, −30 °C) to afford red solutions. However, products could neither be isolated nor identified spectroscopically. After addition of ethyne no corresponding stannole is formed (NMR). We still have to determine how aryl-substituted stannylenes like $Sn(C_6H_2\text{-}2,4,6\text{-}{}^iPr_3)_2$ (generated in situ),[58a] $Sn(C_6H_2\text{-}2,4,6\text{-}{}^tBu_3)_2$,[58b] or $Sn\{C_6H_2\text{-}2,4,6\text{-}(CF_3)_3\}_2$[58c] react in the system Pd/SnR_2/C_2H_2.

The Pd(0)/Sn{N(SiMe$_3$)$_2$}$_2$/C$_2$H$_2$ System. Intense but futile efforts were undertaken to develop a stannole synthesis from $Sn\{N(SiMe_3)_2\}_2$[59] and ethyne. When colorless **3** is reacted with orange $Sn\{N(SiMe_3)_2\}_2$, the ethene ligand is displaced and the red crystalline Pd(0)−tin(II) amide complex $({}^iPr_2PC_2H_4P^iPr_2)Pd{=}Sn\{N(SiMe_3)_2\}_2$ (**22**) is obtained in 89% yield (Scheme 9).

Scheme 9



Like the Pd(0)=SnR_2 complexes **7** and **8**, complex **22** is thermally stable (mp 97 °C). In the EI-MS spectrum at 130 °C the molecular ion is observed (808, 1%). The solution ^{31}P NMR signal (27 °C; Table 1) exhibits sharply resolved ^{119}Sn coupling satellites which indicate an undissociated Pd=Sn bond. Complex **22** reacts with ethyne in pentane at −50 °C to give the 1,2-palladastannete complex $({}^iPr_2PC_2H_4P^iPr_2)Pd(CH{=}CH)Sn\{N(SiMe_3)_2\}_2$ (*Pd−Sn*) (**23**) as a yellow precipitate in 89% yield. Furthermore, **23** is obtained by reaction of the Pd(0)−ethyne complex **5** and $Sn\{N(SiMe_3)_2\}_2$ (pentane, −78/−60 °C; yield 69%). In the low-temperature ^1H, ^{13}C, and ^{31}P NMR spectra (THF-d_8; −80 to −30 °C), complex **23** displays the typical (sharp) resonances of a 1,2-palladastannete (Table 2).

The 1,2-palladastannete **23** is thermally labile and decomposes as a solid and in solution above 0 °C, forming numerous components of which the Pd(0)−ethyne complex **5** has been identified by NMR. Presumably, **23** degrades thermally and irreversibly into **5** and $Sn\{N(SiMe_3)_2\}_2$, from which secondary products develop. The thermal ring degradation of **23** is distinct from the dissociation of the 1,2-palladastannetes **10**, **11**, and **19** into Pd(0)−stannylene complexes and ethyne (Schemes 3 and 5). It rather resembles the dissociation of the (catalytically inactive) 1,2-nickelastannete **1** (eq 1). Correspondingly, no reaction proceeds between **23** and ethyne (−30/0 °C).

As for **5**, the Pd(0)−ethyne complex **6** reacts with $Sn\{N(SiMe_3)_2\}_2$ at −78 °C to yield an orange precipitate of the presumed 1,2-palladastannete complex $({}^tBu_2PC_2H_4P^tBu_2)Pd(CH{=}CH)Sn\{N(SiMe_3)_2\}_2$ (*Pd−Sn*) (**24**). Complex **24** is even less stable than **23** and decomposes in solution above −60 °C, giving rise to intense signals of the Pd−ethyne complex **6**. Furthermore, **17** reacts with $Sn\{N(SiMe_3)_2\}_2$ by displacement of ethyne to give dark red cubes of $({}^iPr_3P)_2Pd{=}Sn\{N(SiMe_3)_2\}_2$ (**25**) in 79% yield. Complex **25** is also formed when an excess of $Sn\{N(SiMe_3)_2\}_2$ is added and in the presence of an excess of ethyne (below −10 °C). When such a solution is warmed to −10 °C an undefined polymeric material precipitates.

These experiments show that $Sn\{N(SiMe_3)_2\}_2$ and ethyne do not undergo a Pd-mediated reaction to afford the stannole "$(C_4H_4)Sn\{N(SiMe_3)_2\}_2$".[60] This is explained by the fact that the corresponding 1,2-palladastannetes, which are conceived as being the key intermediates for a prospective stannole synthesis, are either not formed or suffer a thermal ring degradation with cleavage of the Pd−Sn bond (**23** and **24**) rather than tolerate a ring enlargement reaction with ethyne. It follows from the above that the Pd-catalyzed stannole synthesis is so far confined to the use of stannylenes SnR_2 with R as an organic substituent and that it has not been feasible to extend it to inorganic Sn(II) compounds.

---

[54] Redfield, D. A.; Nelson, J. H.; Henry, R. A.; Moore, D. W.; Jonassen, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 6298.

[55] Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

[56] For the insertion of alkynes into Pd−Si bonds, an *SPY*-5 Pd(II) [*OC*-6 Pd(IV)] intermediate has been suggested before: Watanabe, H.; Kobayashi, M.; Higuchi, K.; Nagai, Y. *J. Organomet. Chem.* **1980**, *186*, 51. For recent publications on related subjects, see: Sakaki, S.; Ogawa, M.; Musashi, Y.; Arai, T. *J. Am. Chem. Soc.* **1994**, *116*, 7258. Hada, M.; Tanaka, Y.; Ito, M.; Murakami, M.; Amii, H.; Ito, Y.; Nakatsuji, H. *J. Am. Chem. Soc.* **1994**, *116*, 8754.

[57] Kira, M.; Yauchibara, R.; Hirano, R.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 7785.

[58] (a) Masamune, S.; Sita, L. R. *J. Am. Chem. Soc.* **1985**, *107*, 6390. (b) Weidenbruch, M.; Schlaefke, J.; Schäfer, A.; Peters, K.; von Schnering, H. G.; Marsmann, H. *Angew. Chem.* **1994**, *106*, 1938; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1846. (c) Grützmacher, H.; Pritzkow, H.; Edelmann, F. T. *Organometallics* **1991**, *10*, 23.

[59] Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

[60] For the reaction of $Sn\{N(SiMe_3)_2\}_2$ with MeOOCC≡CCOOMe, see: Hitchcock, P. B.; Jasmin, H. A.; Lappert, M. F.; Leung, W.-P.; Rai, A. K.; Taylor, R. E. *Polyhedron* **1991**, *10*, 1203.

Table 3. ^1H and ^{13}C NMR Stannole Ring Data of **2a**−**c** (THF-d_8) and $(C_4H_4)Sn^nBu_2$ ($CDCl_3$)[a]

	δ(H)		δ(C)	
	SnCH=CH$_\beta$	SnCH$_\alpha$=CH	SnCH=CβH	SnC$_\alpha$H=CH
$(C_4H_4)Sn^nBu_2$[62b]	7.16 $^3J(^{119}SnH)$ 147 (?)	6.50 $^2J(^{119}SnH)$ 157	145.6	131.6
2a	7.10 $^3J(HH)$ 11 $^3J(^{119}SnH)$ 160	6.70 $^3J(HH)$ 11 $^2J(^{119}SnH)$ 157	144.8 $^1J(CH)$ 157 $^2J(^{119}SnC)$ 71.6	137.5 $^1J(CH)$ 165 $^1J(^{119}SnC)$ 420
2b	7.10 $^3J(HH)$ 10.1	6.70 $^3J(HH)$ 10.1		
2c	7.12 $^3J(^{119}SnH)$ 161	6.52 $^2J(^{119}SnH)$ 163	143.5 $^1J(CH)$ 157 $^2J(^{119}SnC)$ 71.0	133.9 $^1J(CH)$ 162 $^1J(^{119}SnC)$ 378

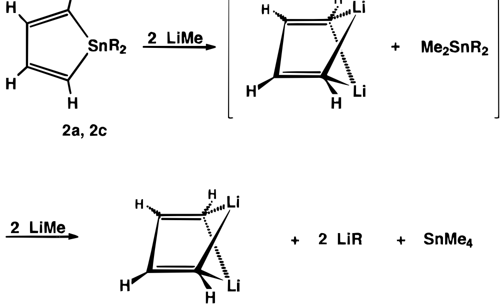
[a] Coupling constants in Hz.

Stannoles 2a,c. The stannoles **2a**,**c** belong to the general class of heteroles (heterocyclopenta-2,4-dienes), for which innumerable members are known. The *C*-unsubstituted parent compounds are partly easily accessible for group 15 and 16 elements (pyrrole, furane, thiophene); for other elements, only the *C*-substituted derivatives have been prepared so far. As stated by Dubac et al., "*the synthesis of C-unsubstituted group 14 metalloles has been one of the most interesting challenges, pursued by a number of research groups between 1960 and 1980.*"[61] Indeed, several *C*-unsubstituted siloles and germoles and only one *C*-unsubstituted stannole $[(C_4H_4)Sn^nBu_2]$[62] have been synthesized. The latter was obtained (1988) in 28% yield from $^nBu_2SnCl_2$ and (*Z,Z*)−dilithio-μ-1,3-butadiene-1,4-diyl ($Li_2C_4H_4$), which was hitherto only accessible by a laborious procedure. This is in contrast to the facile catalytic synthesis of stannoles **2a**,**c** from the corresponding stannylenes and ethyne.

Both **2a** (mp 39 °C) and **2c** (mp 116 °C) form colorless microcrystals which are extremely soluble in the usual organic solvents. In the mass spectra of $(C_4H_4)SnR_2$ (EI, 70 eV; **2a**: 40 °C; **2c**: 80 °C), the molecular ions are observed (**2a**: m/e = 490, 2%; **2c**: m/e 516, 4%) which fragment by cleavage of the substituents R. Whereas for **2a** the ion $[(C_4H_4)SnCH(SiMe_3)_2]^+$ (331) stabilizes by disrupture of the stannole moiety (formally expelling $SnMe_2$), the stannole ring stays intact for **2c** ($[C_4H_4Sn]^+$, m/e = 172, 4%). In the IR and Raman spectra several bands appear in the range of 3062−3004 cm^{-1} and at about 1560, 1490, and 1090 cm^{-1} for the −CH=CH−CH=CH− skeleton.

The ^1H and ^{13}C NMR data of the stannole ring protons and carbon atoms of **2a**−**c** and $(C_4H_4)Sn^nBu_2$[62] are listed in Table 3. The stannole C atoms give rise to two signals at about δ 144 for SnCH=CH$_\beta$ and about δ 135 for SnCH$_\alpha$=CH. The assignment of the carbon resonances is unequivocal due to the coupling constants $^1J(^{119}SnC) \gg {}^2J(^{119}SnC)$. On the basis of this, the proton resonance have been assigned by means of $^{13}C,^1H$ correlated NMR spectroscopy. The ring protons show the signals of an AA′BB′ spin system at δ 7.1 for SnCH=CH$_\beta$ and at about δ 6.6 for SnCH$_\alpha$ (**2b**: broadened AB type signals). The vicinal coupling constant $^3J(HH) \sim 10$ Hz (**2b**) corresponds to the *cis* position of the protons. The couplings $^3J(^{119}SnH)$ and $^2J(^{119}SnH)$ of the ring protons are of similar value (about 160 Hz). By comparison, the NMR data of **2a,c** also allow an assignment of the stannole ring resonance data mentioned for $(C_4H_4)Sn^nBu_2$.[62] These assignments confirm the general observation that the α-CH protons and carbon atoms of Si, Ge, and Sn metalloles are more shielded than the β-CH protons and carbon atoms.[61]

The most interesting feature of stannoles results from the presence of Sn−C(sp^2) bonds which are known to be cleavable by electrophilic or nucleophilic reagents.[63] The reactivity toward nucleophiles is exemplified by the classical synthesis of vinyllithium from tetravinyltin and phenyllithium.[64] Therefore, we were interested to test the reactivity of the stannoles **2a,c** with alkyllithium compounds. When an initially colorless mixture of the stannole **2a** and of $(MeLi)_4(tmeda)_2$[65] in THF is stirred at 20 °C, a very intense dark blue solution is obtained. The ^1H and ^{13}C NMR spectra of this solution (THF-d_8) show low-field resonances for $(THF\text{-}d_8)_xLi_2C_4H_4$ (see below), a singlet at high field with the corresponding couplings for $SnMe_4$, and signals for $LiCH(SiMe_3)_2$ and uncoordinated tmeda. Thus, all carbon substituents of the stannole Sn atom are replaced by methyl groups and a mixture of the solvated lithium reagents $Li_2C_4H_4 + 2LiCH(SiMe_3)_2$ is formed (eq 8). As shown by NMR the formation of this mixture is quantitative with only a minute amount of another component (possibly an oligomer of $Li_2C_4H_4$). When one-half the stoichiometric amount of $(MeLi)_4(tmeda)_2$ is used, a mixture of products, presumably $Me_2Sn\{CH(SiMe_3)_2\}_2$, $Me_3SnCH(SiMe_3)_2$ and $SnMe_4$ (among others), is formed besides small amounts of $Li_2C_4H_4$. It has further been substantiated that $Me_2Sn\{CH(SiMe_3)_2\}_2$, which was obtained from Me_2SnCl_2 and $2LiCH(SiMe_3)_2$, reacts easily with $(MeLi)_4(tmeda)_2$ in diethyl ether to afford a colorless solution of $SnMe_4$ and $2LiCH(SiMe_3)_2$. Therefore, the reaction of the stannole **2a** with LiMe is best explained by assuming that $Me_2Sn\{CH(SiMe_3)_2\}_2$ as a possible primary product readily reacts further with LiMe so that a total of 4 equiv of LiMe is necessary for a quantitative conversion of the stannole into $Li_2C_4H_4$. The stannole **2c** reacts in a similar way as does **2a**.



(8)

So far we have not been able to isolate $(THF)_xLi_2C_4H_4$ or a donor derivative thereof. According to the NMR data the product is identical to (*Z,Z*)-dilithio-μ-1,3-butadiene-1,4-diyl described by Ashe.[62] Thus, whereas Ashe used $Li_2C_4H_4$ to synthesize a *C*-unsubstituted stannole in low yield, we converted the catalytically accessible stannoles **2a,c** quantitatively into this reagent.

---

(61) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215.

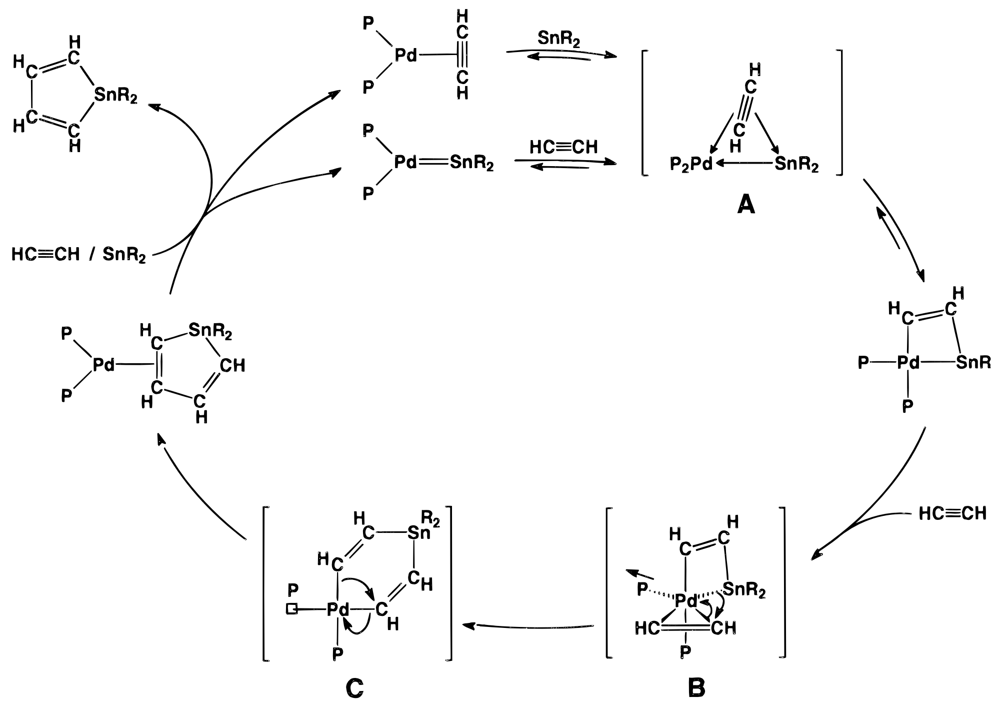
(62) (a) Ashe, A. J., III; Drone, F. J. *Organometallics* **1985**, *4*, 1478. (b) Ashe, A. J., III; Mahmoud, S. *Organometallics* **1988**, *7*, 1878. (c) Ashe, A. J., III; Kampf, J. W.; Savla, P. M. *Organometallics* **1993**, *12*, 3350.

(63) (a) Reference 42a, pp 149−164. (b) Reference 42b, pp 169−182.

(64) Seyferth, D.; Weiner, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 3583.

(65) Köster, H.; Thoennes, D.; Weiss, E. *J. Organomet. Chem.* **1978**, *160*, 1.

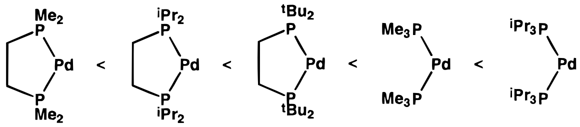
Scheme 10



Discussion of the Catalysis Cycle. We have presented a palladium-catalyzed (2 + 2 + 1) cycloaddition reaction of ethyne and the stannylenes Sn{CH(SiMe$_3$)$_2$}$_2$ and Sn{C(SiMe$_3$)$_2$-CH$_2$}$_2$ to yield the *C*-unsubstituted stannoles **2a,c**. From the stoichiometric reactions described in parts I and II the catalysis loop depicted in Scheme 10 has been assembled. When chelating phosphanes R′$_2$PC$_2$H$_4$PR′$_2$ (R′ = ^{i}Pr, ^{t}Bu) or PMe$_3$ are coordinated at the Pd center, the catalysis is slow and the individual (stoichiometric) steps of the cycle are best studied. For ^{i}Pr$_3$P, the catalysis is fast, so it is more difficult to characterize potential intermediates. There appears, however, no doubt that the "slow" and the "fast" catalysis as well as the catalysis at "low temperature" (−30 °C) or "high temperature" (20 °C) follow the same mechanism. Noteworthy, examples of four of the seven intermediates proposed for the catalysis cycle have been isolated and characterized by X-ray structure determinations and/or high-resolution NMR. It is also emphasized that with the exception of the rate-determining step ([(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd] catalyst: 20 °C; [(^{i}Pr$_3$P)$_2$Pd]: −30 °C) the other individual steps of the catalysis may proceed under exceedingly mild reaction conditions (−100 to −78 °C). In this section further aspects relevant to the catalysis are considered.

A. As has been pointed out (part I) the three components Pd(0), SnR$_2$, and C$_2$H$_2$ are presumed to form an initial labile adduct **A**. Excluding a triple collision reaction it is reasonable to assume a stepwise association in the ways that in equilibrium reactions (a) a preformed Pd(0)−C$_2$H$_2$ complex combines with SnR$_2$, (b) a Pd(0)═SnR$_2$ complex with C$_2$H$_2$, or (c) a stannirene (C$_2$H$_2$)SnR$_2$ with Pd(0). Although the individual routes a−c may differ in their contribution to the formation of **A**,[66] they cannot be separated from each other. Once intermediate **A** is formed on a route it either may fall apart back into the starting components or into "ligand exchange" products or may convert into the corresponding 1,2-palladastannete.

B. We consider the 1,2-palladastannete complexes to be the *key intermediates* in the catalysis. The catalysis is accelerated by an activation of the 1,2-palladastannete intermediate by appropriate ligands. The activation of the palladium catalyst by phosphane ligation follows the series in eq 9. The activity


(9)

is least for a bidentate, strongly chelating phosphane R′$_2$PC$_2$H$_4$-PR′$_2$ with small substituents R′ and it increases with the size of R′ (Me < ^{i}Pr < ^{t}Bu). The activity further increases by changing to monodentate phosphanes PR′$_3$ with a similar dependence on R′ (Me < ^{i}Pr). The increase in activity is paralleled by a decrease in thermal stability of the (solid) 1,2-palladastannetes (**10**, mp 157 °C; **11**, 91 °C dec; **19**, 70 °C dec).

The intrinsic ability of 1,2-palladastannetes to undergo either ring cleavage reactions by ethyne elimination to afford Pd═SnR$_2$ complexes (Schemes 3 and 5) or ring enlargement reactions by ethyne insertion to give rise via intermediate **B** to a 1-pallada(II)-4-stanna(IV)-2,5-cyclohexadiene intermediate **C** is explained by the ring strain inherent in the four-membered ring, as evidenced, for example, by the structural data of **10**. In both types of reaction the four-membered ring is destroyed. However, as long as the steric requirements of the phosphane ligands at the Pd center are small (i.e., chelating phosphanes with small substituents), the 1,2-palladastannete reactivitiy is still low. As the bulk of the phosphane ligand becomes larger (enlarging the substituents at phosphorus or turning to two monodentate ligands), additional steric strain is imposed, thereby further "activating" the four-membered ring. There is likely a mutual destabilization of the 1,2-palladastannete ring and the phosphane coordination at the Pd center. As shown by the reaction of ring deuterated **19a** with C$_2$H$_2$ to yield the semi-deuterated stannole **2b**, when the 1,2-palladastannete is "activated" by PMe$_3$ ligation, the ethyne insertion reaction becomes as facile as the ethyne elimination (ring degradation) reaction.

C. The rate-determining step of the catalysis depends on the stabilizing effect of the phosphane ligation (Figure 3). In the case of isolated 1,2-palladastannetes **I** (**10**, **11**, and **19**), the consecutive reaction with ethyne is rate determining. The

---

[66] Apparently, the mechanism of Scheme 10 is quite general for the catalytic systems Pd(0)/alkyne/ER$_2$ (E = Si, Ge, Sn), leading to the formation of siloles, germoles, and stannoles. When E changes from Sn via Ge to Si routes a and b become less and route c becomes more significant for the formation of intermediate **A**.

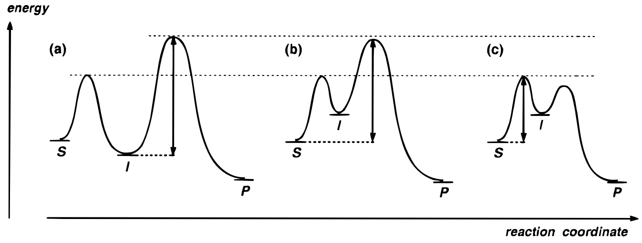


Figure 3. Schematic reaction profiles for the formation of (intermediary) 1,2-palladastannetes **I** from starting components ***S*** and the conversion of **I** into products **P** upon reaction with ethyne. Effect of the increasing steric bulk of phosphane ligation on the profile is shown: (a) reactions involving isolable 1,2-palladastannetes **I** (**10**, **11**, and **19**); (b) reaction involving nonisolable **I** (**21**) and an energetically slightly lowered transition state for **I** → **P**; (c) reaction involving nonisolable **I** (**21**) and an energetically significantly lowered transition state for **I** → **P**. The double arrow indicates the activation energy for the overall reaction.

activation energy for this step is highest as the 1,2-palladastannetes are relatively strongly stabilized by the phosphanes (Figure 3a). A less stabilizing phosphane coordination will raise the 1,2-palladastannete in energy. If **I** is richer in energy than the starting components, it cannot be isolated anymore as is the case for **21** in the $[({}^iPr_3P)_2Pd]$-based catalysis. In addition, the energy of the transition state of the following reaction step will be lowered if, for example, a phosphane ligand needs to dissociate in the course of this step. If the combined effects are just moderate the insertion reaction of **I** with ethyne is still rate determining (Figure 3b) while a larger reduction of the activation energy of this step will cause the formation of **I** to become rate determining (Figure 3c).

D. The stannole formation is catalyzed neither by nickel nor by platinum. What property of palladium makes it suitable for a catalyst? To answer this question the known 1,2-nickela-, 1,2-pallada-, and 1,2-platinastannete complexes can be compared in their properties. Of this series the 1,2-nickelastannete **1**[11] is thermally *least stable* and in solution at −30 °C or above completely and instantaneously dissociates by cleaving the Ni−Sn bond, forming the corresponding Ni(0)−ethyne complex and uncoordinated SnR_2. In contrast, the 1,2-platinastannete derivative **26**[27] is thermally *most stable* and neither dissociates nor reacts further with ethyne (20 °C). Thus, while the 1,2-nickela- and 1,2-platinastannete complexes are either too unstable (exhibiting an undesired reactivity) or too stable (unreactive) for a subsequent ring enlargement reaction with ethyne, the 1,2-palladastannete complexes **10**, **11**, and **19** exhibit an intermediate thermal stability, paired with a marked reactivity. The stability and oppositely directed reactivity sequence

$$\mathrm{Ni} < \mathrm{Pd} < \mathrm{Pt} \qquad (10)$$

for 1,2-metallastannete complexes, substituted $R = CH(SiMe_3)_2$ at Sn, reflects an increasing strength of the metal−Sn bonds in the four-membered ring.

In summary, for palladium, there is a delicate balance between stability and reactivity of the 1,2-palladastannete rings. Thus, in the system $Pd/SnR_2/C_2H_2$ with suitable substituents R, the 1,2-palladastannete intermediates may be "fine-tuned" in stability and reactivity by the choice of phosphanes. Currently the most active key intermediate for the Pd-catalyzed stannole synthesis is the ${}^iPr_3P$-modified nonisolable 1,2-palladastannete **21**.

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by standard Schlenk techniques. $({}^iPr_2PC_2H_4P{}^iPr_2)Pd(\eta^1\text{-}C_3H_5)_2$,[13] $({}^tBu_2PC_2H_4P{}^tBu_2)Pd(\eta^2\text{-}C_6H_{10})$,[13] $(R'_2PC_2H_4PR'_2)Pd(C_2H_4)$ ($R' = {}^iPr$ (**3**), ${}^tBu$ (**4**)),[13] $(R'_2PC_2H_4PR'_2)Pd(C_2H_2)$ ($R' = {}^iPr$ (**5**), ${}^tBu$ (**6**)),[13] $Sn\{CH(SiMe_3)_2\}_2$,[5a] $Sn\{C(SiMe_3)_2CH_2\}_2$,[57] $Sn\{N(SiMe_3)_2\}_2$,[59] and $(LiMe)_4(tmeda)_2$[65] were prepared by published procedures. Microanalyses were performed by the Mikroanalytisches Labor Dornis und Kolbe, Mülheim a. d. Ruhr, Germany. ^1H NMR spectra (δ relative to internal TMS) were measured at 200, 300, and 400 MHz, ^{13}C NMR spectra (δ relative to internal TMS) at 50.3, 75.5, and 100.6 MHz, and ^{31}P NMR spectra (δ relative to external 85% aqueous H_3PO_4) at 81 and 162 MHz on Bruker AM-200, WM-300, and WH-400 instruments. For all NMR spectra, solutions of the compounds in THF-d_8 were used. EI mass spectra were recorded at 70 eV on a Finnigan MAT 95, IR spectra on a Nicolet 7199 FT-IR, and Raman spectra on a Coderg T 800 instrument.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (7). A light yellow pentane solution (10 mL) of **3** (397 mg, 1.0 mmol) is added to a magenta ethereal solution (20 mL) of $Sn\{CH(SiMe_3)_2\}_2$ (438 mg, 1.0 mmol) at 0 °C. Immediately the mixture turns orange red, and at −30/−78 °C, large dark red crystals separate. The product is freed from the mother liquor by means of a capillary tube, washed twice with cold pentane, and dried under vacuum at 20 °C: yield 726 mg (90%); mp 171 °C. IR (KBr): no band characteristic of a Pd=Sn bond assignable. MS (120 °C): *m/e* 806 (M^+, 1.5), 647 ($[M - CH(SiMe_3)_2]^+$, 1.5), 368 ($[(d^ippe)Pd]^+$, 8). ^1H NMR (200 MHz, 27 °C): δ 1.99 (m, 4H, PCH), 1.67 (m, 4H, PCH_2), 1.13, 1.07 (each dd, 12H, diastereotopic CH_3), d^ippe; 0.87 (s, 2H, SnCH), −0.01 (s, 36H, $SiMe_3$), SnR_2. ^{13}C NMR (100.6 MHz, 27 °C): δ 26.6 (4C, PCH), 22.7 (2C, PCH_2), 20.5, 19.4 (each 4C, diasterotopic CH_3), d^ippe; 40.8 (2C, SnCH), 4.6 (12C, $SiMe_3$), SnR_2. ^{31}P NMR (81 MHz): see Table 1. Anal. Calcd for $C_{28}H_{70}P_2PdSi_4Sn$ (806.3): C, 41.71; H, 8.75; P, 7.68; Pd, 13.20; Si, 13.93; Sn, 14.72. Found: C, 41.91; H, 8.82; P, 7.61; Pd, 13.34; Si, 13.81; Sn, 14.61.

$({}^tBu_2PC_2H_4P{}^tBu_2)Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (8). The colorless pentane solution (10 mL) of **4** (453 mg, 1.0 mmol) is combined with the magenta ethereal solution (20 mL) of $Sn\{CH(SiMe_3)_2\}_2$ (438 mg, 1.0 mmol) at 0 °C. When the orange red mixture is cooled to −30/−78 °C, red cubes slowly crystallize (24 h). Isolation as for **7**: yield 725 mg (84%); mp 214 °C. IR (KBr): no band characteristic of a Pd=Sn bond assignable. MS (150 °C): *m/e* 862 (M^+, 2), 703 ($[M - CH(SiMe_3)_2]^+$, 1.5), 424 ($[(d^tbpe)Pd]^+$, 15). ^1H NMR (200 MHz, 27 °C): δ 1.84 (m, 4H, PCH_2), 1.25 (d, 36H, CH_3), d^tbpe; 0.92 (s, 2H, SnCH), 0.18 (s, 36H, $SiMe_3$), SnR_2. ^{31}P NMR (81 MHz): see Table 1. Anal. Calcd for $C_{32}H_{78}P_2PdSi_4Sn$ (862.4): C, 44.57; H, 9.12; P, 7.18; Pd, 12.34; Si, 13.03; Sn, 13.77. Found: C, 44.68; H, 9.02; P, 7.03; Pd, 12.18; Si, 13.15; Sn, 13.85.

$(Me_2PC_2H_4PMe_2)Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (9). To an orange ethereal solution (10 mL) of **19** (722 mg, 1.0 mmol) is added 0.17 mL (1 mmol) $Me_2PC_2H_4PMe_2$ at −30 °C. After the solution is stirred for 5 min, the solvent is exchanged for pentane (−30 °C) and the mixture is filtered (−30 °C). Cooling the orange-red solution to −78 °C (2 d) affords orange cubes. Isolation as described for **10**: yield 583 mg (81%); mp 96 °C dec. IR (KBr): 1456, 1038, 508 cm^{-1} (−CH=CH−). MS (80 °C; considerable decomposition): *m/e* 694 ($[M - C_2H_2]^+$, 1). ^1H NMR (400 MHz, 27 °C) (for SnCH= and PdCH=, see Table 2): δ 1.76, 1.67 (each m, 2H, PCH_2 and $P'CH_2$), 1.46, 1.44 (each d, 6H, PMe_2 and $P'Me_2$), dmpe; 0.14, 0.12 (each s, 18H, diastereotopic $SiMe_3$), −0.37 (s, 2H, SnCH), SnR_2. ^{13}C NMR (100.6 MHz, 27 °C) (for SnCH= and PdCH=, see Table 2): δ 30.9, 26.8 (each 1C, PCH_2 and $P'CH_2$), 15.7, 13.1 (each 2C, PMe_2 and $P'Me_2$), dmpe; 4.8, 4.6 (each 6C, diastereotopic $SiMe_3$), 2.13 (2C, $^3J(PC) = 21$ Hz, $^1J(SnC) = 76$ Hz, SnCH), SnR_2. ^{31}P NMR (162 MHz, 27 °C): see Table 2. Anal. Calcd for $C_{22}H_{56}P_2PdSi_4Sn$ (720.1): C, 36.69; H, 7.84; P, 8.60; Pd, 14.78; Si, 15.60; Sn, 16.49. Found: C, 36.71; H, 7.90; P, 8.48; Pd, 14.71; Si, 15.74; Sn, 16.39.

$({}^iPr_2PC_2H_4P{}^iPr_2)Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (10). (a) Combination of a colorless ethereal solution (10 mL) of **5** (395 mg, 1.0 mmol) and a magenta ethereal solution (20 mL) of $Sn\{CH(SiMe_3)_2\}_2$ (438 mg, 1.0 mmol) at −30 °C affords an orange-red reaction mixture, from which orange-yellow crystals precipitate. After the crystallization is completed at −78 °C, the product is separated from the mother liquor, washed twice with cold pentane, and dried under vacuum at −30 °C: yield 783 mg (94%).

(b) The red ethereal solution (10 mL) of **7** (806 mg, 1.0 mmol) is exposed to ethyne gas (about 50 mL, 2 mmol) at −78 °C. The color turns to light orange, and a microcrystalline yellow precipitate is obtained. After filtration the product is isolated as described above: yield 774 mg (93%); mp 157 °C. IR (KBr): 1470, 1056, 509 cm^{-1} (−CH=CH−). Raman (excitation at 6471 Å) 1473 cm^{-1} (ν C=C). MS (120 °C): *m/e* 806 ([M − C_2H_2]$^+$, 1.5); the spectrum is identical to that of **7**. ^{1}H NMR (400 MHz, 27 °C) (for SnCH= and PdCH=, see Table 2): δ 2.35, 2.20 (each m, 2H, PCH and P′CH), 1.80, 1.80 (each m, 2H, PCH_2 and $P'CH_2$), 1.24, 1.21, 1.17, 1.15 (each m, 6H, CH_3, CH_3', CH_3'', CH_3'''), d^{i}ppe; 0.14, 0.16 (each s, 18H, diastereotopic $SiMe_3$), −0.25 (s, 2H, SnCH), SnR_2. ^{13}C NMR (100.6 MHz, 27 °C) (for SnCH= and PdCH=, see Table 2): δ 26.3 (1C, ^1J(PC) = 14.3 Hz, PCH), 25.6 (1C, ^1J(P′C) = 16.2 Hz, P′CH), 21.6 (1C, ^1J(PC) = 28.6 Hz, ^2J(P′C) = 17.2 Hz, PCH_2), 21.4 (1C, ^1J(P′C) = 21.0 Hz, ^2J(PC) = 17.2 Hz, $P'CH_2$), 21.5, 19.8, 18.6, 18.6 (each 2C, CH_3), d^{i}ppe; 5.0, 4.9 (each 6C, diastereotopic $SiMe_3$), 2.48 (2C, ^3J(PC) = 20.3 Hz, ^1J(SnC) = 90 Hz, SnCH), SnR_2. ^{31}P NMR (162 MHz): see Table 2. Anal. Calcd for $C_{30}H_{72}P_2PdSi_4Sn$ (832.3): C, 43.29; H, 8.72; P, 7.44; Pd, 12.79; Si, 13.50; Sn, 14.26. Found: C, 43.42; H, 8.79; P, 7.56; Pd, 12.66; Si, 13.64; Sn, 14.13.

$(^iPr_2PC_2H_4P^iPr_2)Pd(CD{=}CD)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (10a). Synthesis analogous to that of **10** but starting with (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)-Pd(C_2D_2) (**5a**). IR (KBr): 2210, 2159, 2124, 1440, 526 cm^{-1} (−CD=CD−).

$(^tBu_2PC_2H_4P^tBu_2)Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (11). (a) The magenta pentane solution (15 mL) of Sn{CH($SiMe_3$)$_2$}$_2$ (438 mg, 1.0 mmol) is added to the colorless suspension of **6** (451 mg, 1.0 mmol) in pentane (10 mL) at −78 °C. The reaction mixture immediately turns orange-red, and a microcrystalline precipitate is obtained which is kept at −78 °C for complete crystallization. After filtration at −78 °C, the orange solid is washed twice with cold pentane and dried at −78 °C under high vacuum: yield 658 mg (74%).

(b) When the red solution of **8** (862 mg, 1.0 mmol) in pentane (10 mL) is exposed to ethyne gas (about 50 mL, 2 mmol) at −78 °C, the color changes to light orange and a microcrystalline precipitate forms. Isolation of the product as described in a: yield 533 mg (60%); mp 91 °C; the complex decomposes as a solid slowly at 20 °C and in solution >−30 °C. IR (KBr): 1465, 1049, 513 cm^{-1} (−CH=CH−). ^{1}H NMR (400 MHz, −30 °C) (for SnCH= and PdCH=, see Table 2): δ 2.00 (m, 2H, PCH_2), 1.90 (m, 2H, $P'CH_2$), 1.35, 1.34 (each d, 18H, CH_3, CH_3'), d^{t}bpe; 0.16, 0.15 (each s, 18H, diastereotopic $SiMe_3$), −0.14 (s, 2H, SnCH), SnR_2. ^{13}C NMR (100.6 MHz, −30 °C) (for SnCH= and PdCH=, see Table 2): δ 37.2 (1C, ^1J(PC) = 6.0 Hz, $PCMe_3$), 35.4 (1C, ^1J(P′C) = 7.2 Hz, $P'CMe_3$), 31.5 (6C, ^2J(PC) = 6.6 Hz, CH_3), 30.6 (6C, ^2J(P′C) = 5.0 Hz, CH_3), 24.2 (1C, ^1J(PC) = 16.0 Hz, ^2J(P′C) = 11.4 Hz, PCH_2), 23.8 (1C, ^1J(P′C) = 18.6 Hz, ^2J(P′C) = 13.4 Hz, $P'CH_2$), d^{t}bpe; 5.3, 5.0 (each 6C, diastereotopic $SiMe_3$), 2.3 (2C, ^3J(PC) = 19.6 Hz, SnCH), SnR_2. ^{31}P NMR (81 MHz): see Table 2. Anal. Calcd for $C_{34}H_{80}P_2PdSi_4Sn$ (888.4): C, 45.97; H, 9.08; P, 6.97; Pd, 11.98; Si, 12.65; Sn, 13.36. Found: C, 45.86; H, 9.18; P, 6.84; Pd, 12.10; Si, 12.45; Sn, 13.52.

$(^iPr_2PC_2H_4P^iPr_2)Pd[\eta^2\text{-}C_4H_4Sn\{CH(SiMe_3)_2\}_2]$ (12). To a suspension of (^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(η^1-C_3H_5)$_2$ (451 mg, 1.0 mmol) in pentane (2 mL) is added a pentane solution (1 mL) of **2a** (587 mg, 1.2 mmol) at −30 °C. When the mixture is warmed to 20 °C a yellow solution is formed. Upon cooling the mixture to −78 °C for 2 d, yellow crystals are obtained which are freed of the mother liquor, washed with cold pentane, and dried under vacuum at −30 °C: yield 620 mg (72%). IR (KBr): 3048, 2999, 1518, 1348, 1188, 972 cm^{-1} (−CH=CH−CH=CH−). ^{1}H NMR (400 MHz, 27 °C): δ 6.10 (m, 2H, ^3J(SnH) = 142 Hz, =CH−), 4.32 (m, 2H, ^2J(SnH) = 122 Hz, SnCH=), C_4H_4Sn; 2.04 (m, 4H, PCH and P′CH), 1.64 (m, 4H, PCH_2 and $P'CH_2$), 1.18, 1.14, 1.07, 1.03 (each m, 6H, four types of CH_3), d^{i}ppe; 0.18, 0.12 (each s, 18H, $SiMe_3$ and $SiMe_3'$), −0.12, −0.20 (each s, ^{1}H, SnCH and SnCH′), SnR_2. ^{31}P NMR (81 MHz, 27 °C): δ 61.4 (td, J(^{119}SnP) = 16.5 Hz), 59.0 (td, J(^{119}SnP) = 19.2 Hz, J(PP) = 36.5 Hz). Anal. Calcd for $C_{32}H_{74}P_2PdSi_4Sn$ (858.4): C, 44.78; H, 8.69; P, 7.22; Pd, 12.40; Si, 13.09; Sn, 13.83. Found: C, 44.92; H, 8.76; P, 7.10; Pd, 12.51; Si, 12.88; Sn, 13.71.

$(^tBu_2PC_2H_4P^tBu_2)Pd[\eta^2\text{-}C_4H_4Sn\{CH(SiMe_3)_2\}_2]$ (13). When a colorless solution of (^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(η^2-C_6H_{10}) (102 mg, 0.25 mmol) in diethyl ether (3 mL) is combined with an ethereal solution (1 mL) of **2a** (245 mg, 0.5 mmol) at 20 °C, the mixture turns yellow. Since no product separates at −78 °C the solvent is evaporated under vacuum. The ^{31}P NMR spectrum (81 MHz, 27 °C) shows an AB spin system at δ 83.5, 82.1 (J(PP) = 45.8 Hz) which is ascribed to **13** (72%) but also the signal of the starting complex (δ 81.4, 28%).

$(Me_3P)_2Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (18). Spectroscopic Evidence. Combination of a colorless ethereal solution (5 mL) of **14** (287 mg, 1.0 mmol) and a magenta ethereal solution (5 mL) of SnR_2 (438 mg, 1.0 mmol) at −78 °C immediately affords a dark red solution of **18** to which some THF-d_8 is added. Part of the solution is transferred into an NMR tube at −78 °C. ^{31}P NMR (81 MHz): see Table 1.

$(Me_3P)_2Pd(CH{=}CH)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (19). To the dark red solution of **18** (1.0 mmol) in diethyl ether (5 mL) is added ethyne gas (100 mL) at −78 °C, whereupon the color changes to orange. Within about 10 d orange-yellow crystals separate which are isolated as described for **10**: yield 615 mg (86%); mp 70 °C (dec). IR (KBr, −70 °C): 1460, 1042, 512 cm^{-1} (−CH=CH−). ^{1}H NMR (400 MHz, −80 °C) (for SnCH= and PdCH=, see Table 2): δ 1.43, 1.42 (each d, 9H, PMe_3 and PMe_3'); 0.16, 0.13 (each s, 18H, diastereotopic $SiMe_3$), −0.23 (broad, 2H, SnCH), SnR_2. The broad signal at δ −0.23 is explained by a restricted rotation of the substituents R about the Sn−C bonds. The signal is sharp at −50 °C. ^{13}C NMR (75.5 MHz, −80 °C) (for SnCH= and PdCH=, see Table 2): δ 15.6 (3C, ^1J(PC) = 18.5 Hz, ^3J(PC) = 1.6 Hz, PMe_3 *trans* to Sn), 20.0 (3C, ^1J(PC) = 20.7 Hz, ^3J(PC) = 5.2 Hz, PMe_3 *cis* to Sn); 0.3 (2C, SnCH), 4.6, 4.4 (each 6C, $SiMe_3$), SnR_2. ^{31}P NMR (162 MHz): see Table 2. Anal. Calcd for $C_{22}H_{58}P_2PdSi_4Sn$ (722.1): C, 36.59; H, 8.10; P, 8.58; Pd, 14.74; Si, 15.56; Sn, 16.44. Found: C, 36.51; H, 8.18; P, 8.48; Pd, 14.59; Si, 15.75; Sn, 16.28.

$(Me_3P)_2Pd(CD{=}CD)Sn\{CH(SiMe_3)_2\}_2$ (*Pd−Sn*) (19a). Synthesis as for **19**, but using C_2D_2. IR (KBr): 2198, 2153, 2121, 1432, 526 cm^{-1} (−CD=CD−).

$(^iPr_3P)_2Pd{=}Sn\{CH(SiMe_3)_2\}_2$ (20). Spectroscopic Evidence and Reaction with Ethyne at −78 °C. Combination of a colorless ethereal solution (5 mL) of **16** (455 mg, 1.0 mmol) and a magenta ethereal solution (5 mL) of SnR_2 (438 mg, 1.0 mmol) at −78 °C immediately affords a dark red solution of **20**. THF-d_8 (1 mL) is added. ^{31}P NMR (−80 °C, 81 MHz): see Table 1. When the solution of **20** is exposed to ethyne (100 mL) at −78 °C, the color changes to yellow within about 5 min and **17** is formed. ^{31}P NMR (−80 °C, 81 MHz): δ 51.2.

$(^iPr_2PC_2H_4P^iPr_2)Pd{=}Sn\{N(SiMe_3)_2\}_2$ (22). A light yellow pentane solution (10 mL) of **3** (397 mg, 1.0 mmol) is added to an orange pentane solution (10 mL) of Sn{N($SiMe_3$)$_2$}$_2$ (439 mg, 1.0 mmol) at 0 °C. Immediately the mixture turns orange red, and at −30 °C, large red crystals separate. The product is freed from the mother liquor by means of a capillary tube, washed once with cold pentane, and dried under vacuum at 20 °C: yield 720 mg (89%); mp 97 °C. MS (130 °C): *m/e* 808 (M$^+$, 1), 648 ([M − N($SiMe_3$)$_2$]$^+$, 1), 368 ([(d^{i}ppe)Pd]$^+$, 25). ^{1}H NMR (200 MHz, 27 °C): δ 2.04 (m, 4H, PCH), 1.73 (m, 4H, PCH_2), 1.14, 1.07 (each dd, 12H, diastereotopic CH_3), d^{i}ppe; 0.26 (s, 36H, $SiMe_3$), Sn{N($SiMe_3$)$_2$}$_2$. ^{13}C NMR (50.3 MHz, 27 °C): δ 26.5 (4C, PCH), 23.0 (2C, PCH_2), 20.7, 19.4 (each 4C, diastereotopic CH_3), d^{i}ppe; 6.5 (12C, $SiMe_3$), Sn{N($SiMe_3$)$_2$}$_2$. ^{31}P NMR (81 MHz): see Table 1. Anal. Calcd for $C_{26}H_{68}N_2P_2PdSi_4Sn$ (808.3): C, 38.64; H, 8.48; N, 3.47; P, 7.66; Pd, 13.17; Si, 13.90; Sn, 14.69. Found: C, 38.39; H, 8.33; N, 3.44; P, 7.80; Pd, 13.29; Si, 14.00; Sn, 14.56.

$(^iPr_2PC_2H_4P^iPr_2)Pd(CH{=}CH)Sn\{N(SiMe_3)_2\}_2$ (*Pd−Sn*) (23). (a) Combination of a colorless ethereal solution (10 mL) of **5** (395 mg, 1.0 mmol) and an orange ethereal solution (10 mL) of Sn{N($SiMe_3$)$_2$}$_2$ (439 mg, 1.0 mmol) at −60 °C affords a yellow reaction mixture from which yellow crystals precipitate. After the crystallization is completed at −78 °C, the product is separated from the mother liquor, washed twice with cold pentane, and dried under vacuum at −60 °C: yield 575 mg (69%); the compound decomposes as a solid slowly at 0 °C, in solution >−30 °C. (b) The red solution of **22** (808 mg, 1.0 mmol) in pentane (10 mL) is exposed to ethyne gas (about 50 mL, 2 mmol) at −50 °C. The color immediately turns to light orange, and a microcrystalline yellow precipitate is obtained. After filtration the product is isolated as described above: yield 742 mg (89%). IR (KBr, −50 °C): δ 1443, 1051, 506 cm^{-1} (−HC=CH−). ^{1}H NMR (400 MHz, −80 °C) (for SnCH= and PdCH=, see Table 2): δ 2.42, 2.24 (each m, 2H, PCH and P′CH), 1.99, 1.87 (each m, 2H, PCH_2 and $P'CH_2$), 1.22−1.14 (24H, four nonresolved CH_3 signals), d^{i}ppe; 0.20 (s, 36H, $SiMe_3$), Sn{N($SiMe_3$)$_2$}$_2$. ^{13}C NMR (75.5 MHz, −80 °C) (for SnCH= and PdCH=, see Table 2): δ 26.8, 25.9 (each 2C, PCH and P′CH), 21.4, 20.9 (each 1C, PCH$_2$ and P′CH$_2$), 21.2, 19.5, 18.5, 18.3 (each 2C, CH$_3$), d^{i}ppe; 6.9 (12C, SiMe$_3$), Sn{N(SiMe$_3$)$_2$}$_2$. ^{31}P NMR (162 MHz): see Table 2. Anal. Calcd for $C_{28}H_{70}N_2P_2PdSi_4Sn$ (834.3): C, 40.31; H, 8.46; N, 3.36; P, 7.43; Pd, 12.76; Si, 13.47; Sn, 14.23. Found: C, 40.10; H, 8.31; N, 3.40; P, 7.44; Pd, 12.58; Si, 13.39; Sn, 14.14.

(^{i}Pr$_3$P)$_2$Pd═Sn{N(SiMe$_3$)$_2$}$_2$ (25). Combining a colorless solution of **16** (454 mg, 1.0 mmol) in pentane (5 mL) with an orange solution of Sn{N(SiMe$_3$)$_2$}$_2$ (440 mg, 1 mmol) in pentane (5 mL) at 20 °C immediately affords a dark red solution. Upon cooling the mixture to −78 °C, dark red cubes crystallize. Isolation as described for **7**: yield 684 mg (79%); mp 85 °C. ^{1}H NMR (400 MHz, −30 °C): δ 2.10 (m, 6H, PCH), 1.25 (m, 18H, CH$_3$), ^{i}Pr$_3$P; 0.22 (s, 36H, SiMe$_3$), Sn{N(SiMe$_3$)$_2$}$_2$. ^{31}P NMR (161 MHz): see Table 1. ^{31}P NMR (81 MHz, 27 °C): δ 57.0 (broad). Anal. Calcd for $C_{30}H_{78}N_2P_2PdSi_4Sn$ (866.4): C, 41.59; H, 9.07; N, 3.23; P, 7.15; Pd, 12.28; Si, 12.97; Sn, 13.70. Found: C, 41.48; H, 9.18; N, 3.28; P, 7.12; Pd, 12.42; Si, 12.88; Sn, 13.60.

(C$_4$H$_4$)Sn{CH(SiMe$_3$)$_2$}$_2$ (2a). (a) Stoichiometric Synthesis in THF. An orange-red solution of **11** (888 mg, 1.0 mmol) in THF (20 mL) is exposed to ethyne gas (100 mL, 4 mmol; excess) at −30 °C. The reaction mixture is warmed to 20 °C, and in the course of 1 d, a complete conversion of **11** [δ(P) 85.7, 82.1] into **6** [δ(P) 91.3] proceeds as monitored by ^{31}P NMR spectroscopy. From the red solution the volatile components are evaporated under vacuum at 20 °C. The remaining solid is dissolved/suspended in pentane (2−3 mL), and the solution is purified by passing over a Florisil column [10 cm; pentane (100 mL) as eluent]. After reduction of the volume under vacuum to about 5 mL, an equal volume of acetone is added. At −30 °C colorless microcrystals are obtained: yield 367 mg (75%); mp 39 °C.

(b) Two-Step Catalytic Synthesis in THF at 20 °C. To the reaction mixture of a, after quantitative formation of **6**, are added Sn{CH(SiMe$_3$)$_2$}$_2$ (437 mg, 1.0 mmol) and ethyne gas (100 mL, 4 mmol) at −30 °C. The mixture is warmed to 20 °C and treated again as described for a: yield 715 mg (73%, with reference to total Sn). Additional synthesis cycles may be carried out in the same way.

(c) One-Step Catalytic Synthesis in THF at −30 °C. To a red suspension of Sn{CH(SiMe$_3$)$_2$}$_2$ (2.62 g, 6.0 mmol) and **17** (45 mg, 0.1 mmol) in THF (25 mL) is added ethyne gas (400 mL, 16 mmol) in excess at −78 °C. Upon stirring the mixture at −30 °C for 12 h, the color intensifies because of polyacetylene formation. After evaporation of the solvent under vacuum (20 °C) the residue is purified as described for a: yield 2.55 g (87%).

(d) One-Step Catalytic Synthesis in Pentane at 20 °C. To a red suspension of Sn{CH(SiMe$_3$)$_2$}$_2$ (4.38 g, 10.0 mmol) and **17** (2 mg, 0.004 mmol) in pentane (70 mL) is added ethyne gas in excess (700 mL, 31 mmol) at 20 °C. Upon stirring for 1 h the color of the mixture changes to orange. After evaporation of the solvent the remaining oil is purified as described for a: yield 2.104 g (43%); 1074 catalytic cycles. IR (KBr): 3054, 3041, 3030, 3004, 1557, 1487, 1089 cm^{-1} (−CH═CH−CH═CH−). Raman (excitation at 5145 Å): 3044, 3007 cm^{-1} (ν ═C−H), 1488 cm^{-1} (ν C═C). MS (40 °C): *m/e* 490 (M$^+$, 2), 475 ([M − CH$_3$]$^+$, 4), 331 ([M − CH(SiMe$_3$)$_2$]$^+$, 71). ^{1}H NMR (400 MHz, 27 °C) (for C$_4$H$_4$Sn see Table 3): δ 0.10 (s, 36H, SiMe$_3$), −0.18 (s, 2H, ^2J(^{119}SnH) = 88.3 Hz, SnCH), SnR$_2$. ^{13}C NMR (100.6 MHz, 27 °C) (for C$_4$H$_4$Sn see Table 3): δ 6.32 (2C, ^1J(CH) = 109 Hz, ^1J(^{119}SnC) = 156 Hz, SnCH), 3.50 (12C, ^1J(CH) = 119 Hz, ^3J(SnC) = 17.3 Hz, SiMe$_3$), SnR$_2$. Anal. Calcd for $C_{18}H_{42}Si_4Sn$ (489.6): C, 44.16; H, 8.65; Si, 22.95; Sn, 24.25. Found: C, 43.96; H, 8.82; Si, 22.95; Sn, 24.07.

(C$_4$H$_4$)Sn{C(SiMe$_3$)$_2$CH$_2$}$_2$ (2c). One-Step Catalytic Synthesis. Reaction and workup procedure as for **2a**, protocol c, with Sn{C(SiMe$_3$)$_2$CH$_2$}$_2$ (2.78 g, 6.0 mmol), **17** (96 mg, 0.2 mmol), and ethyne gas (400 mL, 16 mmol). Colorless crystals: yield 2.69 g (87%); mp 116 °C. IR (KBr): 3062, 3004, 1563, 1492, 1090 cm^{-1} (−CH═CH−CH═CH−). MS (80 °C): *m/e* 516 (M$^+$, 4), 344 ([M − C$_4$H$_4$Sn]$^+$, 4), 172 ([C$_4$H$_4$Sn]$^+$, 4). ^{1}H NMR (400 MHz, 27 °C) (for C$_4$H$_4$Sn see Table 3): δ 2.21 (4H, ^3J(^{119}SnH) = 69 Hz, −C$_2$H$_4$−), 0.12 (36H, SiMe$_3$), Sn{C(SiMe$_2$)$_2$CH$_2$}$_2$. ^{13}C NMR (50.3 MHz, 27 °C) (for C$_4$H$_4$Sn see Table 3): δ 35.5 (2C, −C$_2$H$_4$−), 16.0 (2C, SnC), 3.4 (12C, SiMe$_3$), Sn{C(SiMe$_3$)$_2$CH$_2$}$_2$. Anal. Calcd for $C_{20}H_{44}Si_4Sn$ (515.6): C, 46.59; H, 8.60; Si, 21.79; Sn, 23.02. Found: C, 46.45; H, 8.84; Si, 21.63; Sn, 22.92.

(*Z*,*Z*)-Dilithio-*μ*-1,3-butadiene-1,4-diyl. (a) From (C$_4$H$_4$)Sn{CH(SiMe$_3$)$_2$}$_2$ (2a). A colorless solution of **2a** (489.5 mg, 1.0 mmol) in THF-d_8 (2 mL) is added to solid (MeLi)$_4$(tmeda)$_2$ (320.3 mg, 1.0 mmol) at −78 °C. When stirred and warmed to room temperature the slurry dissolves to give a pale blue solution which changes to dark blue within another 30 min. Part of the solution is transferred into an NMR tube and characterized by ^{1}H and ^{13}C NMR. ^{1}H NMR (300 MHz, 29 °C): δ 8.03 (m, 2H), 6.67 (m, 2H), Li$_2$C$_4$H$_4$.[62] The spectrum also shows the signals of uncoordinated tmeda [δ 2.32 (8H), 2.16 (24H)], SnMe$_4$ [δ 0.06 (12H, ^2J(^{119}SnH) = 54 Hz)], and LiCH(SiMe$_3$)$_2$ [δ −0.15 (36H), −2.23 (2H)]. ^{13}C NMR (75.5 MHz, 29 °C): δ 175.4 (broad, 2C, ^1J(CH) = 104 Hz, LiCH═), 150.8 (2C, ^1J(CH) = 140 Hz, ═CH−), Li$_2$C$_4$H$_4$.[62] Further components: tmeda [δ 58.6 (4C), 46.2 (8C)], SnMe$_4$ [δ −9.4 (4C), ^1J(CH) = 127 Hz, ^1J(^{119}SnC) = 337 Hz], LiCH(SiMe$_3$)$_2$ [δ 6.6 (12C, ^1J(CH) = 115.5 Hz, ^1J(SiC) = 45.7 Hz), 0.8 (2C, ^1J(CH) = 100 Hz, ^1J(SiC) = 55 Hz)]. When the reaction is carried out in diethyl ether a deep red solution is obtained. The ^{1}H NMR spectrum of the Et$_2$O-d_{10} solution is practically identical to that of the THF-d_8 solution.

(b) From (C$_4$H$_4$)Sn{C(SiMe$_3$)$_2$CH$_2$}$_2$ (2c). Synthesis as from **2a**, but employing **2c** (515.6 mg, 1.0 mmol). ^{1}H NMR (200 MHz, 27 °C): spectrum as for a, but instead of the signals of LiCH(SiMe$_3$)$_2$, the signals of {LiC(SiMe$_3$)$_2$CH$_2$}$_2$ [δ 1.96 (4H), −0.16 (36H)] are observed.

Me$_2$Sn{CH(SiMe$_3$)$_2$}$_2$. To a diethyl ether (10 mL) solution of Me$_2$SnCl$_2$ (220 mg, 1.0 mmol) is added an ethereal solution (0.2 M, 10 mL) of LiCH(SiMe$_3$)$_2$ (2.0 mmol) at 20 °C. After stirring for 10 min, the solvent is evaporated, the residue extracted with pentane (5 mL), which is also evaporated, and finally the product is crystallized from acetone at −30 °C. Colorless crystals: yield 420 mg (90%); mp 44 °C. MS (30 °C): *m/e* 453 ([M − CH$_3$]$^+$, 6), 309 ([M − CH(SiMe$_3$)$_2$]$^+$, 56), 129 ([Me$_3$Si$_2$C$_2$H$_4$]$^+$, 100). ^{1}H NMR (200 MHz, 27 °C): δ 0.32 (s, 6H, ^2J(^{119}SnH) = 50 Hz, Me$_2$Sn), 0.12 (s, 36H, SiMe$_3$), −0.42 (s, 2H, SnCH). ^{13}C NMR (50.3 MHz, 27 °C): δ 3.9 (12C, SiMe$_3$), 1.9 (2C, Me$_2$Sn), −1.9 (2C, SnCH). Anal. Calcd for $C_{16}H_{44}Si_4Sn$ (467.6): C, 41.10; H, 9.48; Si, 24.03; Sn, 25.39. Found: C, 40.97; H, 9.72; Si, 24.02; Sn, 25.26.

(C$_2$H$_2$)$_n$[Sn{CH(SiMe$_3$)$_2$}$_2$]$_{2n}$. To a stirred magenta solution of Sn{CH(SiMe$_3$)$_2$}$_2$ (437 mg, 1.0 mmol) in pentane (20 mL) is added ethyne in excess (20 °C). Within 10 min, the color changes to bright pink and a colorless precipitate is formed which is separated by filtration, washed with pentane and acetone, and dried under vacuum: yield 428 mg (95%); mp 177 °C dec. IR (KBr): 1140 cm^{-1}. Anal. Calcd for {C$_{15}$H$_{39}$Si$_4$Sn}$_{2n}$ (450.5): C, 39.99; H, 8.73; Si, 24.94; Sn, 26.35. Found: C, 39.88; C, 8.73; Si, 24.95; Sn, 26.39. The insoluble compound is thought to be an oligomer, formed by hydrostannylation reactions of HR$_2$SnC≡CSnR$_2$H moieties.

(HC≡C)(H$_2$C═CH)Sn{CH(SiMe$_3$)$_2$}$_2$. The compound was separated from the mother liquor of (C$_2$H$_2$)$_n$[Sn{CH(SiMe$_3$)$_2$}$_2$]$_{2n}$ by means of preparative GC. $C_{18}H_{42}Si_4Sn$ (489.6). ^{1}H NMR (400 MHz, 27 °C): δ 6.64 (dd, 1H, ^3J(HH$_Z$) = 20 Hz, ^3J(HH$_E$) = 13.2 Hz, ^2J(^{119}SnH) = 147 Hz, ═CHSn), 6.30 (dd, 1H, ^2J(H$_E$H$_Z$ = 3.2 Hz, ^3J(^{119}SnH) = 201 Hz, ═CHH$_E$), 6.22 (dd, 1H, ^3J(^{119}SnH) = 125 Hz, ═CH$_Z$H), 2.72 (s, 1H, ^3J(SnH) = 31 Hz, ≡CH), 0.22, 0.14 (each s, 18H, diastereotopic SiMe$_3$), −0.29 (s, 2H, ^2J(^{119}SnH) = 92 Hz, SnCH). ^{13}C NMR (100.6 MHz, 27 °C): δ 141.4 (1C, ^1J(^{119}SnC) = 528 Hz, SnCH═), 135.6 (1C, H$_2$C═), 101.7 (1C, ^2J(SnC) = 79 Hz, ≡CH), 91.6 (1C, ^1J(^{119}SnC) = 421 Hz, SnC≡), 5.0 (2C, ^1J(^{119}SnC) = 227 Hz, SnCH), 3.6, 3.5 (each 6C, diastereotopic SiMe$_3$).

Acknowledgment. We would like to thank the Volkswagen-Stiftung and the Fonds der Chemischen Industrie for financial support.

JA952495B