A Palladium-catalysed Stannole Synthesis: Development and Mechanism

Jochen Krause, Christian Pluta, Klaus-R. Pörschke* and Richard Goddard

Max-Planck-Institut für Kohlenforschung, Postfach 10 13 53, D-4330 Mülheim a. d. Ruhr, Germany

A palladium-catalysed stannole synthesis is described and its mechanism elucidated by the synthesis of several conceivable intermediates, which have been fully characterized (NMR, X-ray structure analyses).

Stannylenes SnR_2 are known to react with cyclic alkynes to form stannacyclopropene and distannacyclobutene compounds.[1] However, SnR_2 [R = $CH(SiMe_3)_2$][2] and ethyne react above $-10\,°C$ to form a linear chain coupling product $(HC{\equiv}C)SnR_2(trans\text{-}CH{=}CH)SnR_2(CH{=}CH_2)$, while an uncatalysed [2 + 2 + 1] cycloaddition reaction with formation of the stannole $R_2Sn(C_4H_4)$ has been ruled out.[3] Metal-coordinated ethyne reacts differently. The nickel(0) complex $[(Pr^i_2PC_2H_4PPr^i_2)Ni(C_2H_2)]$ was found to react with $Sn[CH(SiMe_3)_2]_2$ below $-30\,°C$ to give the nickela(II)stanna(II)cyclobutene complex 1 (structure analogous to 5a). Above $-30\,°C$ 1 readily dissociates into the starting com-
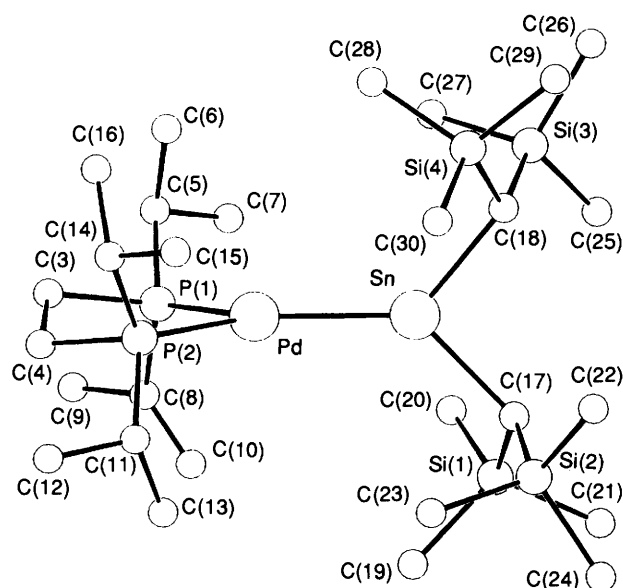
Fig. 1 Molecular structure of **4a**. Selected bond distances (Å) and angles (°): Pd–Sn 2.481(2), Pd–P(1) 2.285(4), Pd–P(2) 2.293(4), Sn–C(17) 2.21(2), Sn–C(18) 2.21(2), P(1)–Pd–P(2) 89.0(2), P(1)–Pd–Sn 133.9(1), P(2)–Pd–Sn 137.0(1), C(17)–Sn–C(18) 98.8(5), C(18)–Sn–Pd 129.9(4), C(17)–Sn–Pd 131.2(4), plane angle: P(1), P(2), Pd/C(17), C(18), Sn 86(1).

ponents which at 20 °C give another product.[4] Since the lability of **1** excludes a reaction of the four-membered ring with further ethyne above −30 °C, we have now synthesized pallada(II)stanna(II)cyclobutene complexes, found them to be more stable than **1**, and studied their reactions with ethyne.[5]

Reaction of the ethene palladium(0) complexes [(R′$_2$PC$_2$H$_4$PR′$_2$)Pd(C$_2$H$_4$)] (R′ = Pr^i **2a**, Bu^t **2b**) with ethyne results in displacement of ethene, and the ethyne derivatives [(R′$_2$PC$_2$H$_4$PR′$_2$)Pd(C$_2$H$_2$)] (R′ = Pr^i **3a**, Bu^t **3b**) are obtained in good yield.[6] The ethene complexes **2a,b** also react with SnR$_2$ (diethyl ether, 0 °C) to give red cubes of the new Pd^0–Sn^{II} adducts (R′$_2$PC$_2$H$_4$PR′$_2$)Pd=SnR$_2$ (R′ = Pr^i **4a**, Bu^t **4b**). Both the reactions of the complexes **3a,b** with SnR$_2$ (diethyl ether, −78/−30 °C) and of the complexes **4a,b** with ethyne (diethyl ether, >−100 °C) give the orange crystalline pallada(II)stanna(II)cyclobutene complexes **5a** (R′ = Pr^i) and **5b** (R′ = Bu^t), respectively, (all yields 60–90%). Formally, the former reaction represents an insertion of the stannylene into a Pd–C bond and the latter a [2 + 2] cycloaddition reaction (Scheme 1).

Complexes **4a** and **4b**† are thermally stable. The solution ¹H, ¹³C, and ³¹P NMR spectra at 27 °C are simple and are consistent with a symmetrical structure in which both phosphorus atoms are equivalent and coordinated together with the stannylene ligand at the palladium centre [$^2J_{119_{SnP}}$ 675 Hz

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(**4a**); 642 Hz (**4b**)]. A single crystal structure analysis of **4a**‡ (Fig. 1) reveals a short Pd–Sn bond indicative of a double bond [Pd–Sn 2.481(2) Å]. It is shorter than any of the Pd–Sn distances in the homoleptic, three-coordinate Pd complex [Pd{Sn(N(SiMe$_3$)$_2$)$_2$}$_3$] [2.533(1), 2.540(1), 2.517(1) Å].[7] The coordination plane of the Pd atom in **4a** lies almost exactly perpendicular to that of Sn [86(1)°], also in agreement with the formulation of a Pd=Sn double bond.§ Furthermore, the relatively small C(17)–Sn–C(18) angle of 98.8(5)° is less than that expected for either a trigonally or tetrahedrally coordinated Sn atom. It is also significantly smaller than the mean NSnN angles found in [Pd{Sn[N(SiMe$_3$)$_2$]$_2$}$_3$] [107(1)°][7] and suggests additional back donation from Pd to Sn in the SnR$_2$ plane.

The solid complexes **5a** and **5b**¶ are also thermally rather stable, and they are more stable than the nickel derivative **1** (decomp. 67 °C). When solutions of the complexes are kept at 27 °C for several days the ³¹P NMR signals of **5a,b** slowly disappear and the signals of **4a,b** appear. The four-membered rings of **5a,b**, therefore, decompose by cleavage of the ethyne ligand to form the Pd^0=Sn^{II} complexes **4a,b**, in contrast to the nickel derivative **1** (see above). Crystals of **5a** (Fig. 2) are isostructural‡ with the nickel complex **1** but there are significant differences in the geometries of the two molecules, particularly around the transition metals. The M–C and M–P distances are appreciably longer (0.12 Å) for Pd and reflect the change in metallic radius in going from Ni to Pd. Apart from the M–C distance, the geometry of the M–CH=CH–Sn unit is very similar in both **5a** and **1**, and the Pd–Sn distance is only 0.044(2) Å longer than the Ni–Sn distance. The C(17)–
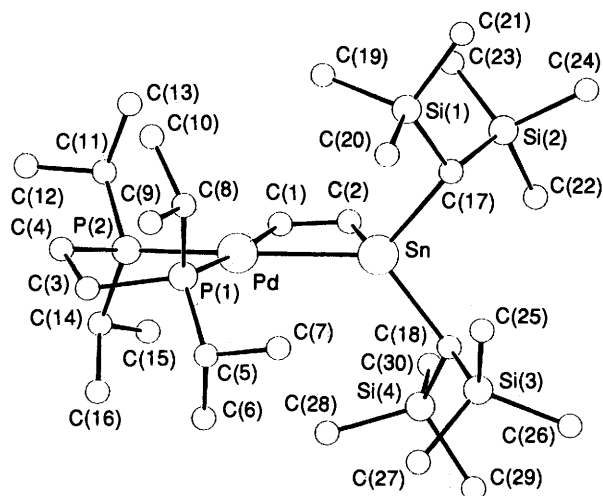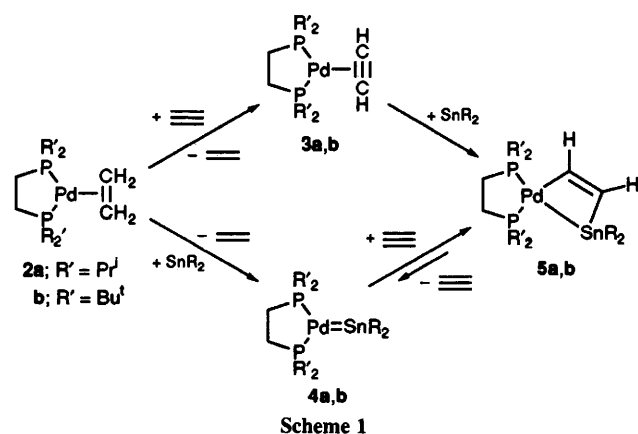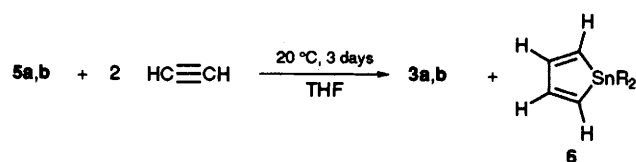

Fig. 2 Molecular structure of **5a**. Selected bond distances (Å) and angles (°): Pd–Sn 2.670(1), Pd–C(1) 2.051(3), Sn–C(2) 2.150(3), C(1)–C(2) 1.316(5), Pd–P(1) 2.341(1), Pd–P(2) 2.285(1), Sn–C(17) 2.233(3), Sn–C(18) 2.240(3), Sn–Pd–C(1) 67.9(1), Pd–C(1)–C(2) 119.3(3), C(1)–C(2)–Sn 98.8(2), C(2)–Sn–Pd 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 115.0(1), P(2)–Pd–Sn 158.5(1), C(17)–Sn–C(18) 103.0(1), plane angle: 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).
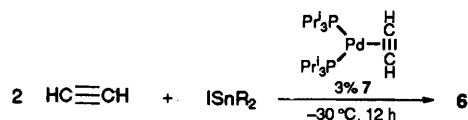

Scheme 1

Sn–C(18) angle at 103.0(1)° in **5a** is larger than in the corresponding Ni complex **1** [100.9(1)°] and both are larger than the equivalent C–Sn–C angle in **4a** [98.8(5)°].

When either **4a,b** or **5a,b** are exposed to additional ethyne at 20 °C, they slowly convert into the Pd⁰ ethyne complexes **3a,b** and a stoichiometric amount of the carbon unsubstituted stannole R₂Sn(C₄H₄) **6**‖ (Scheme 2). Repeated addition of an equimolar amount of SnR₂ to this mixture with formation of

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‖ **6**: Colourless solid; m.p. 39 °C; $C_{18}H_{42}Si_4Sn$ (489.6). MS [EI, 70 eV, 40 °C, m/z (%)] 490 (2, M⁺); IR (KBr) v/cm⁻¹ 3055, 3045, 3030, 3005 (=C–H), 1558, 1487 (C=C); ¹H NMR (400 MHz, [²H₈]THF) δ 7.10 (2H, –CH=), 6.70 (2H, SnCH=), 0.10 (36H, SiMe₃), –0.18 (2H, SnCH); ¹³C NMR (100.6 MHz, [²H₈]THF) δ 144.8 (2C, –CH=), 137.5 (2C, SnCH=), 6.32 (2C, SnCH), 0.00 (12C, SiMe₃).

Scheme 2

Scheme 3

5a,b and subsequent reaction with ethyne leads to recovery of **3a,b** and formation of an additional mole of **6**. Therefore, the synthesis of **6** from SnR₂ and ethyne is catalysed by **4a,b** and **5a,b**, but at this stage the process needs to be carried out discontinuously to avoid the immediate coupling of SnR₂ and ethyne to the linear chain product at 20 °C.

A continuous catalytic formation of **6** from SnR₂ and ethyne can, however, be accomplished by using [(Pr$^i_3$P)₂Pd(C₂H₂)] **7**** as the catalyst. Thermally labile **7**, containing two monodentate phosphane ligands, is more active than either of the (R′₂PC₂H₄PR′₂)Pd catalysts with a chelating diphosphane ligand and allows the reaction to be carried out at a temperature low enough to inhibit the competing uncatalysed reaction of SnR₂ and ethyne. When catalysed by 3% **7**, SnR₂ and C₂H₂ (2 equiv.) react at –30 °C (12 h) to form the stannole **6** in 87% yield (Scheme 3). The overall reaction thus represents a Pd catalysed [2 + 2 + 1] cycloaddition leading easily to a class of carbon unsubstituted stannoles that would otherwise only be accessible with difficulty.

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** **7**: Colourless cubes; $C_{20}H_{44}P_2Pd$ (452.9), IR (KBr) v/cm⁻¹ 3145 (≡C–H), 1650 (C≡C); ¹H NMR (200 MHz, [²H₈]THF, –80 °C) δ 6.21 (2H, C₂H₂), 2.15 (3H, PCH), 1.18 (36H, CH₃); ³¹P NMR (81 MHz, [²H₈]THF, –80 °C) δ 51.2.