

A Palladium-catalysed Stannole Synthesis: Development and Mechanism

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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 [$\text{R} = \text{CH}(\text{SiMe}_3)_2$]² and ethyne react above -10°C to form a linear chain coupling product $(\text{HC}\equiv\text{C})\text{SnR}_2(\text{trans-CH=CH})\text{SnR}_2(\text{CH=CH}_2)$, while an uncatalysed [2 + 2 + 1] cycloaddition reaction with formation of

the stannole $\text{R}_2\text{Sn}(\text{C}_4\text{H}_4)$ has been ruled out.³ Metal-coordinated ethyne reacts differently. The nickel(0) complex $[(\text{Pr}^i_2\text{PC}_2\text{H}_4\text{PPr}^i_2)\text{Ni}(\text{C}_2\text{H}_2)]$ was found to react with $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ 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-

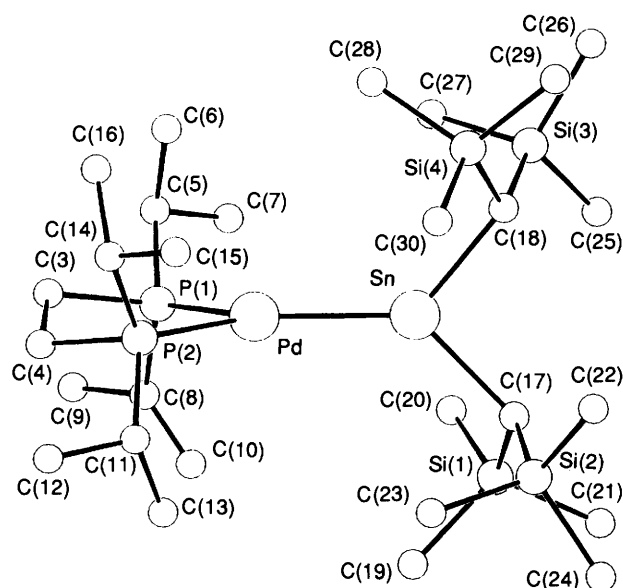


Fig. 1 Molecular structure of **4a**. Selected bond distances (Å) and angles (°): Pd–Sn 2.481(2), Pd–P(1) 2.285(4), Pd–P(2) 2.293(4), Sn–C(17) 2.21(2), Sn–C(18) 2.21(2), P(1)–Pd–P(2) 89.0(2), P(1)–Pd–Sn 133.9(1), P(2)–Pd–Sn 137.0(1), C(17)–Sn–C(18) 98.8(5), C(18)–Sn–Pd 129.9(4), C(17)–Sn–Pd 131.2(4), 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'²PC₂H₄PR'²)Pd(C₂H₄)] (R' = Prⁱ **2a**, Bu^t **2b**) with ethyne results in displacement of ethene, and the ethyne derivatives [(R'²PC₂H₄PR'²)Pd(C₂H₂)] (R' = Prⁱ **3a**, Bu^t **3b**) are obtained in good yield.⁶ The ethene complexes **2a,b** also react with SnR₂ (diethyl ether, 0 °C) to give red cubes of the new Pd⁰–Sn^{II} adducts (R'²PC₂H₄PR'²)Pd=SnR₂ (R' = Prⁱ **4a**, Bu^t **4b**). Both the reactions of the complexes **3a,b** with SnR₂ (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' = Prⁱ) 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_{119SnP} 675 Hz

[†] *Spectroscopic data for 4a*: Dark-red crystals; m.p. 171 °C. MS [EI, 70 eV, 120 °C, *m/z* (%)] 806 (1.5, M⁺), 368 (8, [(dippe)Pd]⁺); ¹H NMR (200 MHz, [²H₈]THF) δ 1.99 (m, 4H, PCH), 1.67 (m, 4H, PCH₂), 1.13, 1.07 (each dd, 12H, diastereotopic CH₃), d'ppe; 0.87 (s, 2H, SnCH), –0.01 (s, 36H, SiMe₃), SnR₂; ¹³C NMR (100.6 MHz, [²H₈]THF) δ 26.6 (4C, PCH), 22.7 (2C, PCH₂), 20.5, 19.4 (each 4C, diastereotopic CH₃), dippe; 40.8 (2C, SnCH), 4.6 (12C, SiMe₃), SnR₂; ³¹P NMR (81 MHz, [²H₈]THF) δ 65.3 [²J_{119SnP} 675 Hz]. [d'ppe = di(isopropylphosphino)ethane].

4b: Red cubes; m.p. 214 °C; C₃₂H₇₈P₂PdSi₄Sn (862.4). MS [EI, 70 eV, 150 °C, *m/z* (%)] 862 (2, M⁺), 424 (15, [(d'bpe)Pd]⁺); ¹H NMR (200 MHz, [²H₈]THF) δ 1.84 (m, 4H, PCH₂), 1.25 (d, 36H, CH₃), d'bpe; 0.92 (s, 2H, SnCH), 0.18 (s, 36H, SiMe₃), SnR₂; ³¹P NMR (81 MHz, [²H₈]THF) δ 88.5 [²J_{119SnP} 642 Hz]. [d'bpe = di(*tert*-butylphosphino)ethane].

(**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(SiMe₃)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(SiMe₃)₂]₂}₃] [107(1)°]⁷ and suggests additional back donation from Pd to Sn in the SnR₂ 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 Pd⁰–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)–

[‡] *Crystal data for 4a*: C₂₈H₇₀P₂PdSi₄Sn, *M* = 806.3, monoclinic, space group *P2₁/n*, *a* = 10.007(2), *b* = 32.036(5), *c* = 13.203(1) Å, β = 91.98(1)°, *V* = 4230.0 Å³, *T* = 293 K, *D_c* = 1.27 g cm^{–3}, *Z* = 4, μ(Cu–Kα) = 102.76 cm^{–1}, spherical absorption correction, 9265 measured reflections (±*h*, +*k*, +*l*), 8704 independent and 3602 observed reflections [*I* > 2σ(*I*)], 325 refined parameters, *R* = 0.065, *R_w* = 0.081, final difference Fourier ρ = 2.14 eÅ^{–3} near the Pd atom.

5a: C₃₀H₇₂P₂PdSi₄Sn, *M* = 832.3, monoclinic, space group *P2₁/n*, *a* = 12.424(1), *b* = 22.647(2), *c* = 15.601(1) Å, β = 104.05(1)°, *V* = 4258.3 Å³, *T* = 293 K, *D_c* = 1.30 g cm^{–3}, *Z* = 4, μ(Mo–Kα) = 12.07 cm^{–1}, 10317 measured reflections (±*h*, +*k*, +*l*), 9703 independent and 7979 observed reflections [*I* > 2σ(*I*)], 343 refined parameters, *R* = 0.035, *R_w* = 0.041, final difference Fourier ρ = 0.63 eÅ^{–3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Various well known MO calculations of d¹⁰ metal complexes indicate that the back-bonding orbitals lie in the coordination plane of the transition metal which also contains the Sn accepting orbital. Therefore, the Pd and Sn coordination planes are perpendicular to each other.

¶ *Spectroscopic data for 5a*: Yellow–orange crystals; m.p. 157 °C. IR (KBr) ν/cm^{–1} 1470 (C=C); MS [70 eV, 120 °C, *m/z* (%)] 806 (1.5, [M–C₂H₂]⁺); ¹H NMR (400 MHz, [²H₈]THF) δ 8.37 (ddd, 1H, ³J 9.4 Hz, PdCH=), 7.60 (ddd, 1H, SnCH=); 2.35, 2.20 (each m, 2H, PCH and P'CH), 1.80, 1.80 (each m, 2H, PCH₂ and P'CH₂), 1.24, 1.21, 1.17, 1.15 (each m, 6H, CH₃), d'ppe; 0.14, 0.16 (each s, 18H, diastereotopic SiMe₃), –0.25 (s, 2H, SnCH), SnR₂; ¹³C NMR (100.6 MHz, [²H₈]THF) δ 177.2 (1C, PdCH=), 158.7 (1C, SnCH=); 26.3, 25.6 (each 1C, PCH and P'CH), 21.6, 21.4 (each 1C, PCH₂ and P'CH₂), 21.5, 19.8, 18.6, 18.6 (each 2C, CH₃), dippe; 5.0, 4.9 (each 6C, diastereotopic SiMe₃), 2.48 (2C, SnCH), SnR₂; ³¹P NMR (162 MHz, [²H₈]THF) δ 75.6 [²J_{119SnP} 2441 Hz], 67.7 [²J_{SnP} 100 Hz], *J*_{PP} 12.7 Hz.

5b: Orange microcrystals; 20 °C (slow decomp.); C₃₄H₈₀P₂PdSi₄Sn (888.4). IR (KBr) ν/cm^{–1} 1475 (C=C); ¹H NMR (400 MHz, [²H₈]THF, –30 °C) δ 8.22 (m, 1H, PdCH=), 8.18 (m, 1H, SnCH=); 2.00, 1.90 (each m, 2H, PCH₂ and P'CH₂), 1.35, 1.34 (each d, 18H, CH₃), d'bpe; 0.16, 0.15 (each s, 18H, SiMe₃), –0.14 (s, 2H, SnCH), SnR₂; ³¹P NMR (81 MHz, [²H₈]THF, –30 °C) δ 85.7 [²J_{119/117SnP} 82.6 Hz], 82.1 [²J_{119SnP} 2478 Hz], *J*_{PP} 4.3 Hz.

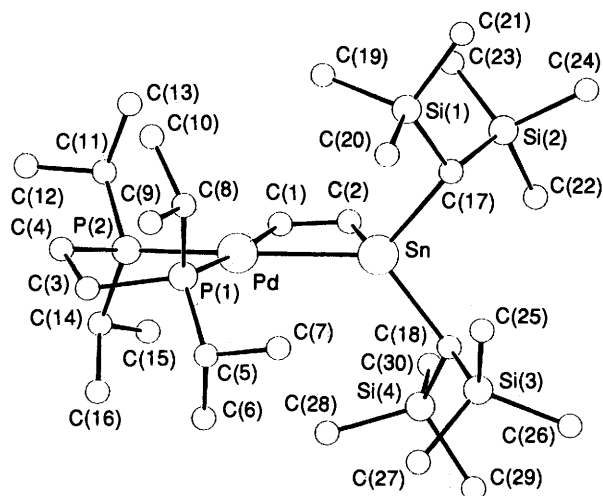
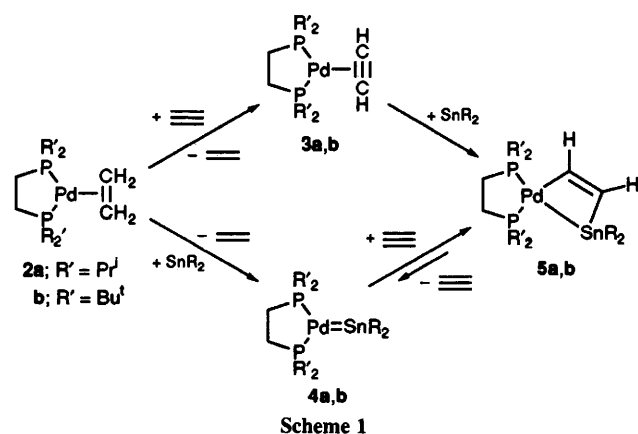
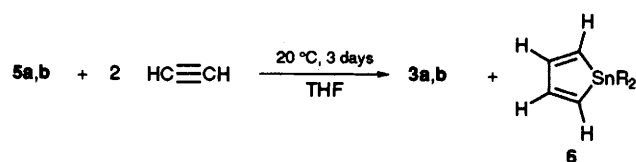


Fig. 2 Molecular structure of **5a**. Selected bond distances (Å) and angles (°): Pd–Sn 2.670(1), Pd–C(1) 2.051(3), Sn–C(2) 2.150(3), C(1)–C(2) 1.316(5), Pd–P(1) 2.341(1), Pd–P(2) 2.285(1), Sn–C(17) 2.233(3), Sn–C(18) 2.240(3), Sn–Pd–C(1) 67.9(1), Pd–C(1)–C(2) 119.3(3), C(1)–C(2)–Sn 98.8(2), C(2)–Sn–Pd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

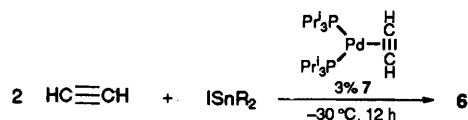


Sn–C(18) angle at 103.0(1)° in **5a** is larger than in the corresponding Ni complex **1** [100.9(1)°] and both are larger than the equivalent C–Sn–C angle in **4a** [98.8(5)°].

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



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 [(Prⁱ₃P)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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** **6**: Colourless solid; m.p. 39 °C; C₁₈H₄₂Si₄Sn (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).

** **7**: Colourless cubes; C₂₀H₄₄P₂Pd (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.