Highly efficient palladium catalyst system for addition of trihydrosilanes to acetylenes and its application to thermally stable polycarbosilane synthesis

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Regio- and stereo-selective mono-, di- and tri-alkenylation of trihydrosilanes with monoynes proceeded smoothly with a Pd–PCy₃ catalyst, while the reaction of phenylsilane with 1,4-diethynylbenzene provided a thermally stable and blue light emissive polycarbosilane.
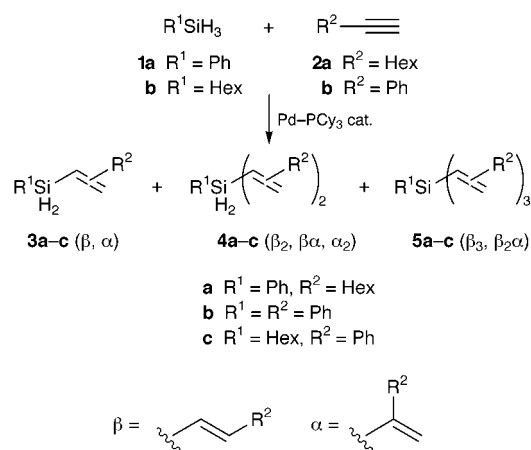
Transition metal-catalysed hydrosilylation is a versatile reaction affording useful organosilicon derivatives.[1] Addition of trihydrosilanes to acetylenes is expected to give C=C and/or Si–H bond-containing alkenylsilanes utilisable as new synthetic reagents, monomers for silicon polymers *etc.*[2] However, in our hands conventional Pt catalysts such as Speier's (H_2PtCl_6) and Karstedt's ($Pt_2(dvs)_3$, dvs = [(H_2C=CH)Me_2Si]$_2$O) systems have proved to be inefficient (*vide infra*).[3,4] Through a survey of group 10 metal complexes we have found that a Pd–PCy₃ system is highly active for the reaction. In addition, the catalysis affords the first successful example of polymerisation of a trihydrosilane with diynes providing polycarbosilanes with unique thermal and optical properties.[5]

Thus, when a mixture of phenylsilane (**1a**, 0.20 mmol) and oct-1-yne (**2a**, 1 equiv.) in benzene-d_6 (0.05 ml) was treated with a benzene-d_6 (0.10 ml) solution of Pd₂(dba)₃ (1 mol% Pd) and PCy₃ (P/Pd = 2) at room temperature for 15 min, (*E*)-2- and 1-hexylvinylsilane [**3a**(β) and **3a**(α), respectively] were formed with high linear selectivity (β : α = 94 : 6) and in good combined yields (80%) (≥98% conversion of **2a**; Scheme 1, Table 1, run 1).† The formation of the *Z* isomer of **3a**(β) and diphenylsilane (a redistribution byproduct from **1a**) was negligible according to NMR analysis. A small amount of dialkenylsilane **4a** (9%) was also formed with recovery of **1a** (8%). In contrast, previously reported RhCl(PPh₃)₃[3] was not effective under the present conditions [yield of **3a** = 29% (β : α = 73 : 27)]. Conventional H_2PtCl_6 and $Pt_2(dvs)_3$ catalysts also resulted in much lower yields [3% (β : α = 5 : 1) and 14% (81 : 19), respectively]. In the cases of RhCl(PPh₃)₃[3] and $Pt_2(dvs)_3$, unfavorable diphenylsilane formation (10 and 20%, respectively) was also observed. The Pd–PCy₃ system was very active, and only 0.01 mol% Pd effectively converted ≥98% of **2a** after heating at 60 °C for 3 h (run 2). Di- and tri-alkenylation took place cleanly by controlling the charged amount of **2a**; using 2 or 3 equiv. of **2a** respectively provided **4a** or **5a**, each in >90% yield (runs 3 and 4). These reactions proceeded regioselectively, yielding **4a**(β₂) and **5a**(β₃) with linear alkenyl moieties as the major products.

Besides **2a**, phenylacetylene (**2b**, 1 equiv.) also readily reacted with **1a** to give the corresponding mono- and di-alkenylsilane (**3b**, 75%; **4b**, 13%) with predominant formation of the linear regioisomers (run 5). Aromatic acetylene **2b** was much more reactive than **2a**, and even 0.01 mol% Pd catalyst completed the reaction after 3 h at room temperature (run 6). Dialkenylsilane **4b** was obtained in a high yield (83%) by using 2 equiv. of **2b** (run 7). Likewise, hexylsilane (**1b**) underwent smooth mono- and di-alkenylation with **2b** (runs 8 and 9).

Instead of Pd₂(dba)₃–PCy₃, PdCl₂(PCy₃)₂ could be used as well, although the reaction was slower; the yields of **3b** and **4b** in the reaction of **1a** and **2b** were respectively 20 and ≤2 (room temp., 15 min) and 75 and 12% (40 °C, 2 h). Other Pd–trialkylphosphine catalysts were also active, albeit in lower efficiency; the yields of **3b** and **4b** (40 °C, 2 h) were 63 and 5


Scheme 1

Table 1 Pd-catalysed hydrosilylation of trihydrosilanes **1** with acetylenes **2**[a]

Run	1	2 (2/1)	Conditions	3 (β : α)	4 (β₂ : βα : α₂)	5 (β₃ : β₂α)
1	**1a**	**2a** (1)	r.t., 15 min	80 (94 : 6)	9 (9 : 1 : 0)	0
2[c]	**1a**	**2a** (1)	60 °C, 3 h	81 (93 : 7)	9 (9 : 1 : 0)	0
3	**1a**	**2a** (2)	40 °C, 6 h	4 (9 : 1)	92 (87 : 14 : 0)	≤2
4	**1a**	**2a** (3)	40 °C, 6 h	0	4 (9 : 1 : 0)	92 (86 : 14)
5	**1a**	**2b** (1)	r.t., 15 min	75 (79 : 21)	13 (7 : 3 : 0)	0
6[c]	**1a**	**2b** (1)	r.t., 3 h	77 (77 : 23)	12 (7 : 3 : 0)	0
7	**1a**	**2b** (2)	r.t., 15 min	8 (7 : 3)	83 (63 : 32 : 5)	≤2
8	**1b**	**2b** (1)	r.t., 15 min	63 (74 : 26)	17 (2 : 1 : 0)	0
9	**1b**	**2b** (2)	r.t., 5 h	4 (7 : 3)	86 (60 : 35 : 5)	≤2

[a] **1** (0.20 mmol), **2** (0.20–0.60 mmol), Pd₂(dba)₃–PCy₃ (dba = dibenzylideneacetone, Cy = cyclohexyl, P/Pd = 2) (0.002 mmol Pd), C₆D₆ (0.15 ml). [b] Based on **1** (estimated by NMR and/or GC). [c] 0.00002 mmol Pd.

a R³ = –(CH₂)₅–
b R³ = 1,4-phenylene

Scheme 2
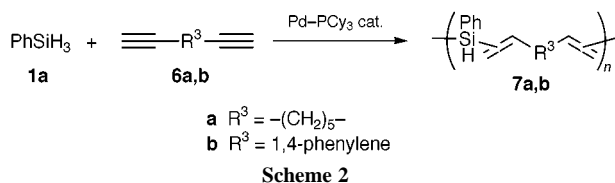
[PdCl₂(PBuⁱ₃)₂], 47 and 5 [PdCl₂(PEt₃)₂] and 34 and 5% [PdCl₂(PBu₃)₂]. Accordingly, the Pd⁰–PCy₃ system is the best catalyst among the Pd complexes examined.

Since acetylenes **2** (2 equiv.) react with **1a** cleanly, C=C–SiH–C=C linkage-containing polycarbosilanes can be readily prepared. Thus, treatment of a mixture of **1a** (0.20 mmol) and nona-1,8-diyne (**6a**, 1 equiv.) with the Pd–PCy₃ catalyst (0.1 mol% Pd) in benzene-d_6 (0.15 ml) at 40 °C for 4 h gave a new polymer (**7a**) with one Si–H bond being intact nearly quantitatively (by ¹H NMR, Scheme 2).‡ The molecular weight M_w (M_w/M_n) was estimated by GPC (polystyrene standards) to be 29 000 (3.1). The vinylic moieties in the C=C–SiH–C=C linkages were assigned by ¹H NMR to be VL × 2 (VL = vinylene) and VL + VD (VD = vinylidene) in the ratio of 88:12. Similarly, the use of 1,4-diethynylbenzene (**6b**) (0.1 mol% Pd cat., 40 °C, 1 h) yielded **7b** with phenylene rings (≥95% NMR yield; M_w = 49 000, M_w/M_n = 4.8; VL × 2 : VL + VD : VD × 2 = 63:33:4 for the vinylic moieties).

Polymers **7** have reactive C=C and Si–H bonds, and cross-linking between them easily proceeds to form thermally stable polymeric materials. Thus, heating a cast film of **7b** on a glass plate at 100 °C for 2 h under vacuum formed a hard film that was nearly insoluble in toluene, CHCl₃ and THF. The mp was > 300 °C and thermogravimetric analysis revealed considerably high T_{d_1} and T_{d_5} values (1 and 5% weight loss temperatures, 444 and 504 °C, respectively, under N₂) and a good char yield (78% at 980 °C). This suggests that **7b** is utilisable for manufacturing heat-resistant materials and/or SiC ceramics. In addition, **7b** has interesting light-emitting properties; a film of **7b** exhibited intense blue emission on irradiation with a UV lamp, and a THF solution of **7b** [λ_{max} in UV: 308 nm (ε = 2.2 × 10⁴)] showed photoluminescence with λ_{max} = 445 and 466 nm (excitation at 393 nm).[6]

To summarize, the Pd–PCy₃ catalyst is demonstrated to be highly efficient for hydrosilylation of acetylenes with trihydrosilanes and applicable to the synthesis of polycarbosilanes, which are promising as new functional materials. Extension of the substrates and application of the resulting polycarbosilanes are under way.

Notes and references

† All the major alkenylsilanes **3–5** were purified by preparative TLC (or GPC) and identified by their NMR, (HR)MS and/or IR spectra; for the ¹H NMR data [δ_H(C₆D₆, 300 MHz)] of the characteristic SiH signals of **3** and **4**, **3a**(β): 4.78 (d, J 3.1); **3a**(α): 4.75 (s); **4a**(β₂): 5.05 (t, J 2.9); **4a**(βα): 5.01 (d, J 3.4); **3b**(β): 4.88 (d, J 3.2); **3b**(α): 4.98 (s); **4b**(β₂): 5.33 (t, J 2.9); **4b**(βα): 5.44 (d, J 3.0); **4b**(α₂): 5.60 (s); **3c**(β): 4.29 (q, J 3.5); **3c**(α): 4.40 (t, J 3.7); **4c**(β₂): 4.74 (quint, J 3.3); **4c**(βα): 4.84 (q, J 3.5); **4c**(α₂): 4.93 (t, J 3.8). Relatively large J values (18–19 Hz) between the vinylene protons for **3–5** suggest E stereochemistry.

‡ In separate 0.50 mmol scale reactions in benzene preparative GPC gave purified **7a** (M_w = 20 000, M_w/M_n = 3.0, 88% yield) and **7b** (M_w = 23 000, M_w/M_n = 3.7, 80%), which were fully characterised by NMR, IR and microanalysis. *Selected data* for **7a**: δ_H(C₆D₆, 300 MHz) 1.0–1.6 [br m, =CC(CH₂)₃], 1.9–2.4 (br m, =CCH₂), 5.06 [d, J ~ 3, (VL)(VD)SiH], 5.12 [br t-like, (VL)₂SiH], 5.66 (d, J ~ 2, SiC=CHᵃHᵇ), 5.8–6.0 (br m, SiCH= and SiC=CHᵃHᵇ), 6.35 (br dt, J 18.5 and 6.1, SiCH=CH), 7.1–7.4 and 7.6–7.9 (each br m, C₆H₅); v_{max}(film)/cm⁻¹ 2142 (Si-H). For **7b**: δ_H(C₆D₆) 5.3–5.4 [br m, (VL)₂SiH], 5.4–5.5 [br m, (VL)(VD)SiH], 5.6–5.7 [br m, (VD)₂SiH], 5.7–5.9 and 6.1–6.3 (each br m, SiC=CH₂), 6.5–6.8 (br m, SiCH=), 7.0–7.9 (br m, SiCH=CH, C₆H₅ and C₆H₄); v_{max}(film)/cm⁻¹ 2126 (Si-H).

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