Palladium-catalysed borylsilylation of alkynes and borylsilylative carbocyclization of diynes and an enyne compound

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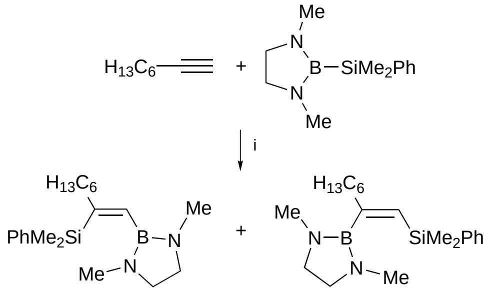
Addition reactions or addition–carbocyclization reactions of a borylsilane with alkynes, α,ω-diynes or an enyne compound proceed efficiently in the presence of palladium catalysts, $P(OCH_2)_3CEt$ being the ligand of choice.

Addition reactions of inter-heteroatom bonds such as Si–Si and Sn–Sn to unsaturated carbon bonds are extremely useful for one-step generation of two heteroatom–carbon bonds.[1] Similar chemistry starting with B–B bonds is also rapidly emerging.[2] An obvious extension is addition reactions of bonds comprising two different elements.[3] In a previous paper we disclosed palladium-catalysed addition of borylstannanes to alkynes (borylstannylation) leading to efficient synthesis of 1-boryl-2-stannyl alkenes.[4] α,ω-Diynes also react with borylstannanes, undergoing borylstannylative carbocyclization reactions to afford 1-borylmethylene-2-stannylmethylene cycloalkanes in high yields.[5a] 1,4-Addition of conjugated dienes also proceeds smoothly when $Pd(etpo)_2$ catalyst [etpo = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CEt$] is used.[5b] As regards corresponding borylsilylation, however, only unsuccessful results have been reported by Buynak and Geng.[6] While we were studying borylsilylation as a useful extension of the borylstannylation, Ito and co-workers briefly presented successful examples of addition reactions of a borylsilane (4,4,5,5-tetramethyl-2-dimethylphenylsilyl-2-bora-1,3-dioxapentane) to alkynes, mainly using the 1,1,3,3-tetramethylbutyl isocyanide–palladium diacetate catalyst system.[7] Their communication prompted us to report our own results.

A representative procedure for the reaction of alkynes was as follows. A mixture of $Pd_2(dba)_3$ (0.005 mmol; dba = dibenzylideneacetone) and etpo (0.02 mmol), *i.e.* $Pd_2(dba)_3$–etpo catalyst system in which P/Pd = 2, in C_6D_6 (0.2 ml) was heated at 80 °C for 5 min, while the colour of the solution was changing from red to green. 1,3-Dimethyl-2-dimethylphenylsilyl-2-bora-1,3-diazacyclopentane **1** (0.2 mmol), oct-1-yne (0.3 mmol) and 1,4-dioxane (20 μl; internal standard for NMR analysis) were added to the resulting solution and the mixture was heated at 80 °C in a sealed NMR tube. NMR and GC–MS analyses of the reaction mixture after 2 h indicated complete consumption of **1** and adduct **2a**† being formed in 92% yield (Scheme 1). Note that the regioselectivity was >99% and that only a trace of isomer **2b** was detected by NMR analysis. Isolation of the product was simple; evaporation of the reaction mixture, addition of hexane (2 ml) to the residue, filtration and distillation of the filtrate afforded nearly pure **2a** in 84% isolated yield, which exhibited satisfactory spectral and analytical data. Observation of an 8% NOE between the allylic protons and the vinylic proton suggested that selective *cis*-addition of the B–Si bond had taken place.

Unlike for the borylstannylation, Pd–PPh_3 complexes were not as efficient catalysts; the reaction of oct-1-yne with **1** did not proceed under the same conditions when either $Pd(PPh_3)_4$ or $PdCl_2(PPh_3)_2$ was used as the catalyst. The former did catalyse the reaction at higher temperatures, but the yields were still unsatisfactory, *e.g.* only 78% yield (**2a**/**2b** > 99 : 1) even after heating at 110 °C for 24 h. However the latter, which catalysed the borylstannylation at room temperature, was totally inactive even at 110 °C. We have reported that PMe_3 performs better than PPh_3 in the platinum-[8] or palladium-catalysed reactions[9] of unsaturated carbon compounds with disilanes or digermanes. The reaction of oct-1-yne with **1** was also better when catalysed by the $Pd_2(dba)_3$–4PMe_3 system (70% yield, 80 °C, 2 h) than by the $Pd_2(dba)_3$–4PPh_3 system (0% yield, 80 °C, 2 h *vs.* 18% yield, 110 °C, 7 h). However, as the foregoing typical experiment exemplifies, etpo is superior to the other phosphines as the ligand. In view of the decreasing trend of performance etpo > PMe_3 > PPh_3, the ligand effect in the borylsilylation is concluded to be similar to our previous observation made in the double silylation of acetylenes[9a,b] and quinones[9c] with disilanes and double germylation of acetylenes, dienes and alkenes.[9d]



2a **2b**

L = etpo 92% (**2a**:**2b** >99:1)

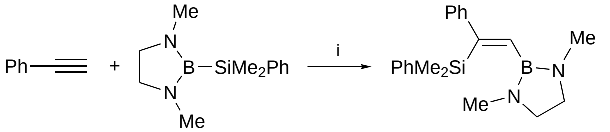
L = PMe_3 70% (**2a**:**2b** >99:1)

L = PPh_3 0%

Scheme 1 *Reagents and conditions*: i, $Pd_2(dba)_3$ (2.5 mol%), ligand (L/Pd = 2), C_6D_6, 80 °C, 2 h

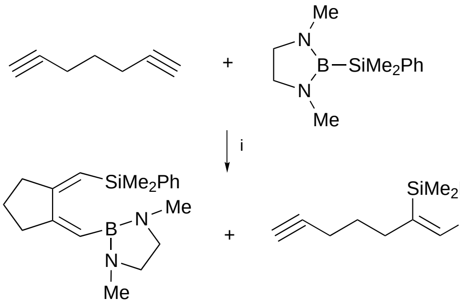
Phenylacetylene appeared to be slightly less reactive towards **1** than oct-1-yne, but the reaction did proceed smoothly at 110 °C in the presence of the $Pd_2(dba)_3$–4etpo catalyst system to give 97% yield of **3**† as the sole product in 2 h (Scheme 2). However, the reaction of dimethyl acetylenedicarboxylate resulted in a complicated mixture.

Borylsilylative carbocyclization of hepta-1,6-diyne (0.3 mmol) with **1** (0.2 mmol) was also catalysed smoothly by the $Pd_2(dba)_3$–4etpo system in C_6D_6 at 110 °C to afford **4** in 81% yield.† Configurations at the silylmethylidene and borylmethylidene moieties of **4** were confirmed by 19.3 and 18.2% NOEs between the vinylic and allylic protons. A byproduct **5** coming from simple addition of **1** to one of the two acetylenic bonds without carbocyclization was also formed in 18% yield (Scheme 3). The $Pd_2(dba)_3$–4PMe_3 system was as active, but less selective (84% total yield after 2 h at 110 °C, **4** : **5** = 30 : 70). The $Pd_2(dba)_3$–4PPh_3 system was less active and even less selective (88% total yield after 7 h at 110 °C, **4** : **5** = 26 : 74). $PdCl_2(PPh_3)_2$ was totally inactive at 110 °C.



3 97%

Scheme 2 *Reagents and conditions*: i, $Pd_2(dba)_3$ (2.5 mol%), etpo (etpo/Pd = 2), C_6D_6, 110 °C, 2 h



4 **5**

L = etpo, L/Pd = 2, 2 h, 98% (**4**:**5** = 81:19)

L = etpo, L/Pd = 1, 2 h, 97% (**4**:**5** = 87:13)

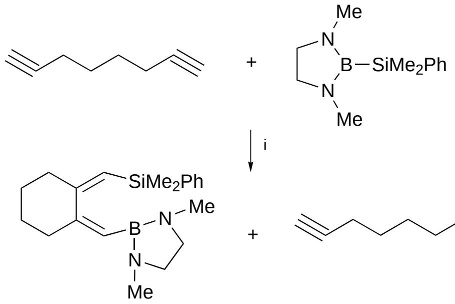
L = PMe_3, L/Pd = 2, 2 h, 84% (**4**:**5** = 30:70)

L = PPh_3, L/Pd = 2, 7 h, 98% (**4**:**5** = 26:74)

Scheme 3 *Reagents and conditons*: i, $Pd_2(dba)_3$ (2.5 mol%), ligand (L/Pd = 2 or 1), C_6D_6, 110 °C

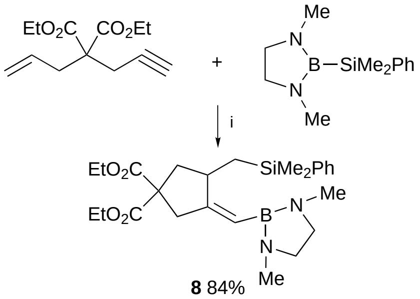
A decrease in the quantity of etpo relative to palladium is envisioned to be favourable to minimize the formation of byproduct **5** if simultaneous coordination of both acetylenic bonds to palladium is a prerequisite for the cyclization leading to **4**. Indeed, the reaction of hepta-1,6-diyne with **1** at etpo/Pd = 1 under otherwise identical conditions resulted in a slight increase in the selectivity for **4**; the **4**:**5** ratio was 87:13, obtained in a 97% combined yield. The reaction of octa-1,7-diyne with **1** was slightly less reactive and much less selective for the cyclization product **6**,† with **7** as the major product (Scheme 4). The selectivity was not appreciably improved even when etpo/Pd = 1, indicating the necessity for a new design of catalyst to circumvent the difficulty of coordination of both acetylenic bonds.

Finally an enyne compound, 4,4-bis(ethoxycarbonyl)hept-6-en-1-yne, also smoothly underwent similar cyclization with **1** to give **8**† in 84% yield (Scheme 5). The ^{1}H NMR spectrum of the reaction mixture displayed a weak singlet at δ 6.48, suggesting the formation of a small quantity (9%) of a byproduct, which might have come from plain addition of **1** to the triple bond.



6 17% **7** 62%

Scheme 4 *Reagents and conditions*: i, $Pd_2(dba)_3$ (2.5 mol%), etpo (etpo/Pd = 2), C_6D_6, 110 °C, 2 h



8 84%

Scheme 5 *Reagents and conditions*: i, $Pd_2(dba)_3$ (2.5 mol%), etpo (etpo/Pd = 2), C_6D_6, 110 °C, 2 h

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Footnotes

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† *Selected spectral and/or physical data* for the products ^{1}H NMR (C_6D_6), 270 MHz; *J*/Hz) for **2a**: bp 135–140 °C at 2.3 × 10^{-3} Torr; δ_H 0.43 (s, 6 H, $SiCH_3$), 0.86 [t, *J* 6.8, 3 H, $CH_2(CH_2)_4C\mathit{H}_3$], 1.14–1.53 [m, 8 H, $CH_2(C\mathit{H}_2)_4CH_3$], 2.28 [t, *J* 7.2, 2 H, $C\mathit{H}_2(CH_2)_4CH_3$], 2.51 (s, 6 H, NCH_3), 2.89 (s, 4 H, NCH_2), 6.36 (s, 1 H, =CH), 7.10–7.33 (m, 3 H, arom), 7.50–7.65 (m, 2 H, arom). For **3**: δ_H 0.40 (s, 6 H, $SiCH_3$), 2.49 (s, 6 H, NCH_3), 2.84 (s, 4 H, NCH_2), 6.56 (s, 1 H, =CH), 6.95–7.35 (m, 8 H, arom), 7.50–7.60 (m, 2 H, arom). For **4**: bp 128–132 °C at 2.8 × 10^{-3} Torr (mixture of **4** and **5**); δ_H 0.38 (s, 6 H, $SiCH_3$), 1.46–1.68 (m, 2 H), 2.31–2.41 (m, 4 H), 2.46 (s, 6 H, NCH_3), 2.83 (s, 4 H, NCH_2), 5.40 (s, 1 H, =CH), 5.62 (s, 1 H, =CH), 7.12–7.31 (m, 3 H, arom), 7.42–7.60 (m, 2 H, arom). For **6**: δ_H 0.40 and 0.43 (both s, 6 H, $SiCH_3$), 1.45–1.73 (m, 4 H), 2.20–2.40 (m, 4 H), 2.55 (s, 6 H, NCH_3), 2.83–2.97 (m, 4 H, NCH_2), 5.30 (s, 1 H, =CH), 5.47 (s, 1 H, =CH), 7.05–7.26 (m, 3 H, arom), 7.54–7.63 (m, 2 H, arom). For **8**: δ_H 0.24 (s, 3 H, $SiCH_3$), 0.26 (s, 3 H, $SiCH_3$), 0.82 (dd, *J* 11.9 and 14.6, 1 H, $SiCH_2$), 0.90 (t, *J* 7.1, 3 H, $OCH_2C\mathit{H}_3$), 0.91 (t, *J* 7.1, 3 H, $OCH_2C\mathit{H}_3$), 1.32 (dd, *J* 2.0 and 14.6, 1 H, $SiCH_2$), 1.80–1.93 (m, 1 H, CH_2), 2.50 (s, 6 H, NCH_3), 2.74–3.07 (m, 7 H, NCH_2, CH_2 and CH), 3.14 (d, *J* 17.5, 1 H, CH_2), 3.32 (d, *J* 17.5, 1 H, CH_2), 3.85–4.03 (m, 4 H, $OC\mathit{H}_2CH_3$), 5.43 (s, 1 H, =CBH), 7.13–7.27 (m, 3 H, arom), 7.45–7.53 (m, 2 H, arom).

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