

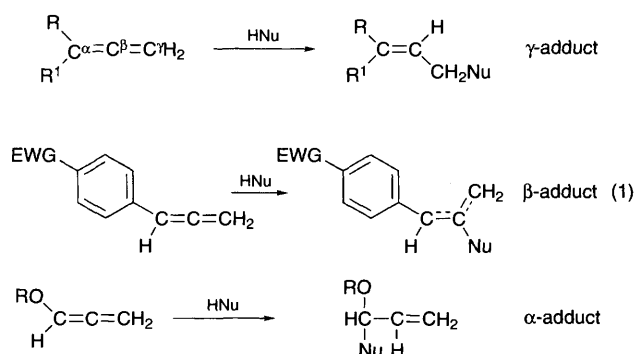
Palladium catalysed addition–substitution reaction of pronucleophiles with allenylstannanes and prop-2-ynylstannanes

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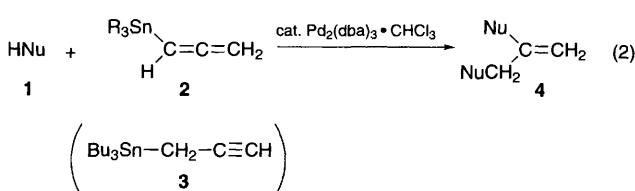
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The palladium catalysed reactions of pronucleophiles **1** with allenylstannanes **2** or prop-2-ynylstannanes **3** give the corresponding addition–substitution products **4** in reasonable to high yields; this double alkylation reaction most probably proceeds through an allenylstannane intermediate.

We reported recently that the addition of certain pronucleophiles (HNu) to allenes takes place in the presence of catalytic amounts of palladium complexes (hydrocarbonation reaction) [eqn. (1)]: monoalkyl substituted or di-substituted



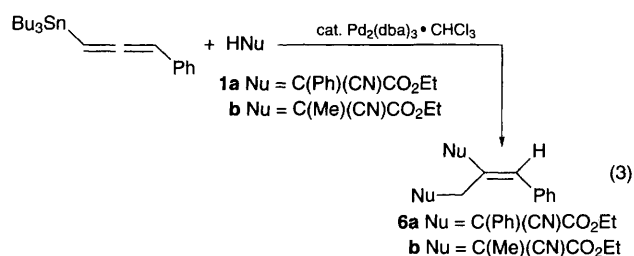
allenes give the γ -adducts.^{1a} arylallenes bearing an electron withdrawing *para*-substituent afford the β -adducts,^{1b} and alkoxy(aryloxy)allenes provide the α -addition products.^{1c} We now report that the addition of pronucleophiles **1** to allenylstannanes **2** (and prop-2-ynylstannane **3**) in the presence of catalytic amounts of Pd₂(dba)₃·CHCl₃ affords the addition–substitution products **4** in reasonable to high yields [eqn. (2)].



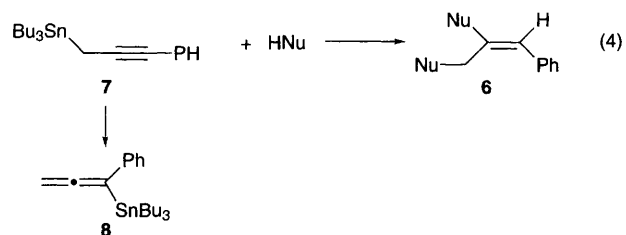
The results are summarized in Table 1. The reaction of ethyl phenylcyanoacetate **1a** (2.2 equiv.) with allenylstannanes **2** (1 equiv.) proceeded smoothly in THF in the presence of 10 mol% Pd₂(dba)₃·CHCl₃ and 52 mol% 1,4-bis(diphenylphosphino)butane to give **4a** in high to good yields (entries 1–3). Without the palladium catalyst, no reaction took place. The use of tributylstannylallene produced higher yield than that of triphenyl and trimethylstannylallenes (entries 1 vs. 2 and 3). The use of other ligands, such as DPPE, DPPF and PPh₃, gave lower yields. Similarly, the reaction of ethyl methylcyanoacetate **1b** with tributylstannylallene gave **4b** in high yield (entry 4) although the reaction with triphenylstannylallene afforded **4b** in only 35% yield (entry 5). The reaction of methylmalononitrile **1c** with stannylallenes produced **4c** in

good yields (entries 6 and 7). The masked formylcyanide² **1d** reacted with tributylstannylallene under the same reaction conditions as above to give **4d** in 35% yield (entry 8). It should be noted that such a highly functionalized pronucleophile undergoes the alkylation reaction. Very interestingly, the reaction of **1a** with prop-2-ynyl(tributyl)stannane **3** produced **4a** (entry 9). Accordingly, the same product was obtained both from allenyl and from prop-2-ynyl stannanes, suggesting that the starting prop-2-ynylstannane undergoes isomerization to allenylstannane under the palladium catalyst. However, treatment of prop-2-ynyltributylstannane with catalytic amounts of Pd₂(dba)₃·CHCl₃ in THF gave allenyltributylstannane.

We also examined the reaction of substituted allenyl and prop-2-ynyl(tributyl)stannanes. The reaction of 3-phenyl(tributylstannyl)allene **5** with pronucleophiles gave the corresponding double alkylation products **6** in good yields [eqn. (3)]:



6a was obtained from **1a** in 50% yield and **6b** in 55% yield from **1b**. The *E*-geometry of **6** was confirmed by NOE experiments. The reaction of 3-phenylprop-2-ynyl(tributyl)stannane **7** with pronucleophiles also produced **6** in good yield [eqn.(4)]: **6a** was



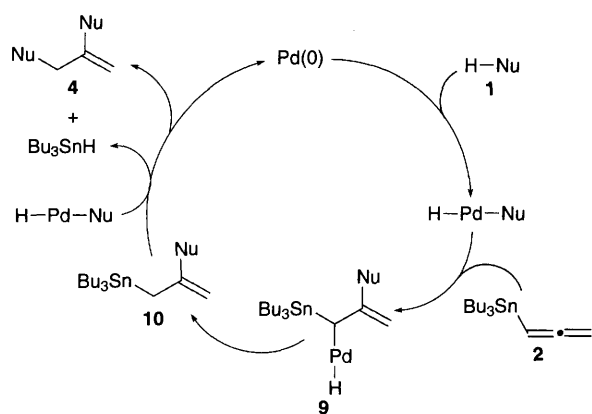
obtained in 50% yield from **1a** and **6c** in 70% yield from **1c**. Treatment of **7** in the presence of catalytic amounts of Pd₂(dba)₃·CHCl₃ gave the isomerized allenylstannane **8** in essentially quantitative yield. Therefore, the reaction of **7** would proceed through the allenylstannane **8**.

A possible mechanism for the double alkylation reaction is shown in Scheme 1. Oxidative insertion of Pd(0) into H–Nu followed by carbopalladation to the central β -carbon of stannylallenes would give the palladium(II) intermediate **9**. The β -attack of NuPd_n species is reasonable since a positive charge at the β -position of alkenylstannanes would be stabilized by the tributylstannyl group.³ Reductive elimination of Pd(0) from **9** would give allenylstannane **10**. Since it is known that the palladium catalysed reaction of allenylstannanes with pronucleo-

Table 1 Pd-catalysed addition–substitution reaction of pronucleophiles with allenylstannanes and prop-2-ynylstannanes^a

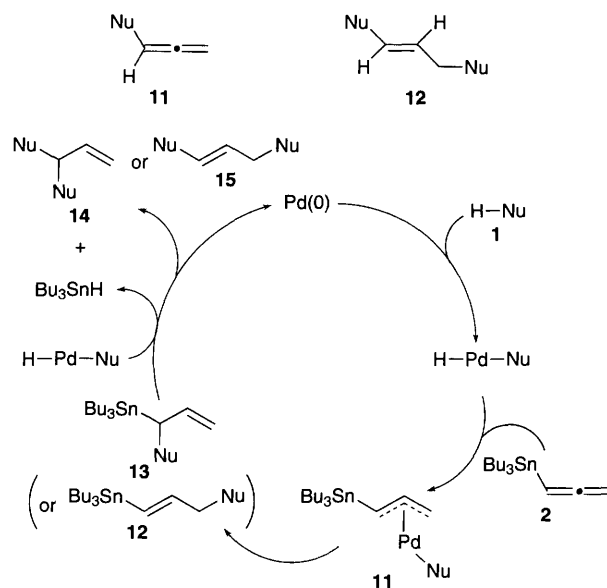
Entry	1	Stannane	Product	Isolated yield (%)
1	HC(Ph)(CN)CO ₂ Et 1a	2 (R=Bu)	 4a	90
2	1a	2 (R=Ph)	4a	72
3	1a	2 (R=Me)	4a	70
4	HC(Me)(CN)CO ₂ Et 1b	2 (R=Bu)	 4b	90
5	1b	2 (R=Ph)	4b	35
6	HC(Me)(CN) ₂ 1c	2 (R=Bu)	 4c	64
7	1c	2 (R=Ph)	4c	59
8	HC(CN) ₂ OCH ₂ OMe 1d	2 (R=Bu)	 4d	35
9	1a	3 (R=Bu)	4a	53

^a A mixture of **1** (1.1 mmol), **2** (0.5 mmol) (or **3**), Pd₂(dba)₃·CHCl₃ (10 mol%, 52 mg), DPPB (52 mol%, 112 mg) and THF (2 ml) was refluxed for 48 h under an Ar atmosphere. The crude reaction mixture was filtered through a celite pad, the solvent was evaporated and the product purified by column chromatography using cyclohexane–ethyl acetate (20:1) as an eluent.



Scheme 1 Carbopalladation–transmetalation

philes (HNu) affords the corresponding allylation product (allylNu),⁴ **10** would react further with pronucleophiles to give the double alkylation products **4** and Pd(0). One may consider a possibility that the palladium catalysed reaction of **1** with **2** will



Scheme 2 Hydropalladation–transmetalation

give the direct substitution product **11** for some reason, and this allene will react with **1** in an ordinary manner^{1a} to give **4**. However, we confirmed that monoalkylallenes afford the γ -adduct **12**,^{1a} and the β -adduct such as **4** is given only in the case of arylallenes bearing *para*-EWG group.^{1b}

If hydropalladation of **2**, instead of carbopalladation, was involved, a π -allylpalladium intermediate **11** would be produced (Scheme 2).⁵ Reductive elimination from **11** would give either the alkenylstannane **12** or allylstannane **13**. It was confirmed that no further reaction of alkenylstannanes took place under the reaction conditions. The reaction of **13** with pronucleophiles would produce either **14** or **15**, which are totally different from **4**. Consequently, the hydropalladation mechanism seems to be not involved in the double alkylation reaction.[†]

Footnote

[†] A referee pointed out that the decomposition of **11** does not have to give either **12** or **13**. For example, Nu may attack the β -position of π -allyl unit to give a cyclopropylstannane, which may react further with HNu–Pd cat. to afford **4**. Accordingly, the hydropalladation mechanism can not be excluded completely.

References

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