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# Palladium-catalyzed reaction of arynes with a bis-π-allyl palladium complex. An efficient method for the synthesis of 1,2-diallylated derivatives of benzene

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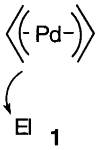
## Abstract

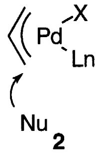
Palladium-catalyzed reaction of arynes with a bis-π-allyl palladium complex, an amphiphilic catalytic allylating agent, afforded 1,2-diallylated derivatives of benzene in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* palladium catalysts; arynes; bis-π-allyl palladium complex; diallyl benzene.

Transition-metal complexes have proved to be excellent mediators for multicomponent synthetic reactions. Among them, π-allyl palladium complexes are useful synthetic intermediates[1] since they can participate in reactions with a wide range of reaction partners to form C–C and C–hetero atom bonds in a highly stereo- and regioselective way. We previously found that bis-π-allyl palladium complex **1** reacts with electrophiles such as imines and aldehydes,[2] although it is well known that ordinary π-allyl palladium complexes **2** react with nucleophiles such as sodium malonate and certain enolates.[1] Furthermore, bis-π-allyl palladium complex reacts with activated olefins in an amphiphilic manner (**3**) forming diallylated products in high yields.[3]

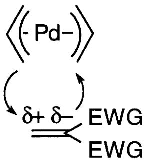


**1**



**2**

X = OAc, halides, OCOR etc.



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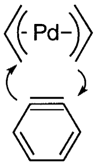

**4**

In a continuation of our interest in understanding the reactivity profile of bis-π-allyl palladium complexes, we undertook an investigation of the reaction of arynes with bis-π-allyl palladium complexes and the preliminary results of our investigation revealed that the triple bond of arynes reacts with bis-π-allyl palladium complexes in an amphiphilic fashion **4**.

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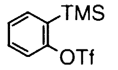
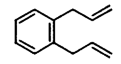
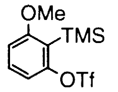
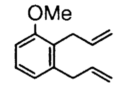
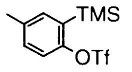
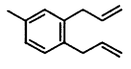
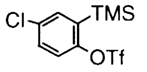
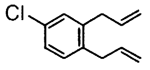
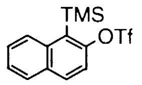
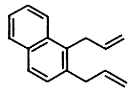
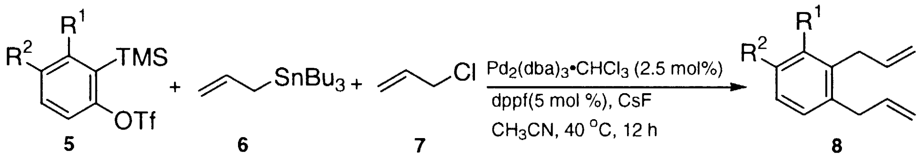
The results are illustrated in Table 1. The reaction of **5a** (0.4 mmol) with allyltributylstannane **6** (0.6 mmol) and allyl chloride **7** (0.6 mmol) in acetonitrile in the presence of 2.5 mol% $Pd_2(dba)_3 \cdot CHCl_3$–dppf catalyst at 40°C for 12 h afforded 1,2-diallyl benzene **8a** in 76% yield (entry 1).[4,5] The generation of benzyne from **5a** under the reaction conditions described above (CsF, $CH_3CN$, 40°C) was reported by Kobayashi et al.[6] and Guitian et al.[7,8]

Table 1
Palladium-catalyzed 1,2-diallylation of arynes with allyltributylstannane and allyl chloride

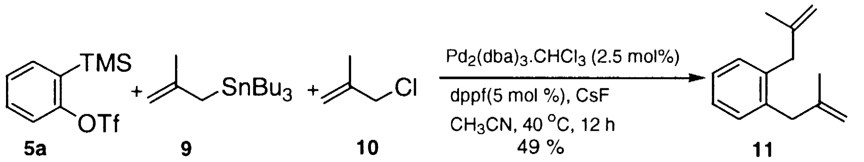
| entry | Aryne precursor **5** | | Product **8** ( % yield) [a, b] | |
|---|---|---|---|---|
| 1 |  | **5a** | **8a** (76) |  |
| 2 |  | **5b** | **8b**(81) |  |
| 3 |  | **5c** | **8c**(67) |  |
| 4 |  | **5d** | **8d**(40) |  |
| 5 |  | **5e** | **8e**(68) |  |

[a] Isolated yield based on the aryne precursor **5** [b] All compounds gave satisfactory spectroscopic and analytical data.



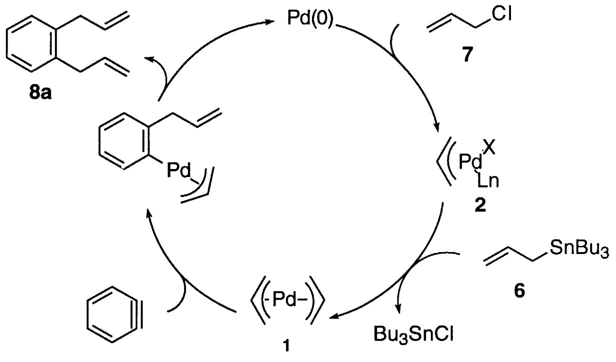
**5** **6** **7** **8**

Other substituted aryne precursors **5b**–**e** reacted similarly to give the corresponding diallylated products **8b**–**e** in high to fair yields (entries 2–5). The reaction of **5a** with methallyltributylstannane **9** and methallyl chloride **10** afforded 1,2-dimethallyl benzene **11** in 49% yield. When a combination of **6** and **10** or that of **9** and **7** was used instead of a combination of the same allylic moieties such as **9** and **10**, a mixture of benzene derivatives with totally random allylic–allylic addition was obtained.



**5a** **9** **10** **11**

The mechanism of the reaction appears to be similar to the one proposed for the diallylation of activated olefins[3] (Scheme 1). Insertion of Pd(0) to allyl chloride **7** would give the π-allyl palladium complex **2**, which would be converted to bis-π-allyl palladium **1** via the reaction with allyltributylstannane **6**. The addition of two allyl groups of **1** to the benzyne triple bond would give **8a** and Pd(0) species. It is known that benzyne undergoes palladium-catalyzed cyclotrimerization to give triphenylene,[7] cotrimerization with alkynes[8,9] to afford phenanthrene derivatives, and controlled insertion of **2** to benzyne and alkynes to afford phenanathrene and naphthalene derivatives, respectively.[10] We have found a new reaction of arynes with a bis-π-allyl palladium complex, leading to the formation of 1,2-diallylated benzene derivatives. The products are potentially amenable to some useful synthetic transformations; for example, upon treatment with an olefin metathesis reagent, **8** may give the corresponding carbocycles. Further extension of this new palladium-catalyzed reaction with other allyl systems is currently underway in our laboratory.



Scheme 1.

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4. Typical experimental procedure: Allyltributyl stannane **6** (0.186 mL, 0.6 mmol) and allyl chloride **7** (0.05 mL, 0.6 mmol) were added to a suspension of anhydrous CsF (0.122 g, 0.8 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%) and dppf (2.5 mol%) in $CH_3CN$ (2 mL) and the resulting mixture was stirred at room temperature for 10 min. The aryne precursor **5b** (0.098 mL, 0.4 mmol) was then added and the mixture was stirred at 40°C for 12 h. When the reaction was complete (monitored by TLC and GC), the reaction mixture was extracted with ether (2×20 mL) and washed successively with a saturated aqueous solution of KF, water and brine. The ether layer was then dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo. The residue obtained was subjected to column chromatography (silica gel, 1% ethyl acetate in hexane as eluent) to afford **8b** (0.061 g, 81%) as a colorless liquid.
5. Selected data for **8b**. IR (film): 3078, 3003, 2977, 2835, 1637, 1471, 1064 cm$^{-1}$. $^{1}$H NMR ($CDCl_3$): $\delta$ 7.14 (1H, Ar), 6.77 (2H, Ar), 5.92 (2H, m), 4.96 (4H, m), 3.80 (3H, S), 3.40 (4H, dd, $J$=6.3 Hz, 15.9 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 157.65, 139.63, 137.28, 136.72, 126.92, 121.95, 115.60, 114.37, 108.59, 55.63, 37.09, 29.91. HRMS calcd for $C_{13}H_{16}O$: 188.1200 (found: 188.1202). Anal. calcd for $C_{13}H_{16}O$: C, 82.92%; H, 8.57%. Found: C, 82.65%; H, 8.75%.
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