trace amount of water in the solvent, DMF, which will be studied in detail. Hydration of terminal alkynes has been known to be catalyzed to produce ketones in the presence of related iridium complexes.[7] The formation of both benzaldehyde and benzoic acid could also result from the reaction of phenylacetylene with water, *i.e.*, the cleavage of the C−C triple bond of phenylacetylene by water since it has been known that transition metal complexes catalyze the hydration of alkynes to carbonyl compounds with one less carbon atom.[8] Oligomers higher than the dimer were not observed. Further investigation is currently being performed.

In conclusion, the electrochemical activation of Vaska's complex can catalyze the dimerization reaction of phenylacetylene. It seems that the dimerization is oxidative process of phenylacetylene catalyzed by the electrochemically oxidized product of Vaska's complex. We are currently investigating the mechanism by detailed analysis of the products and characterization of the intermediate species by fast voltammetric techniques using ultramicroelectrode and rotaing ring-disk electrode technique. Various kinds of acetylenes and different types of 4-coordinate Ir(I) complexes are currently being used to compare with the results in this paper.

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Pd(0)-Catalyzed Coupling Reaction of Allyl *N*,*N*-Ditosylimide and Allyl *N*-Tosylamides as New Substrates for the Formation of π-Allylpalladium Complexes

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The addition of nucleophiles to π-allylpalladium complexes is one of the most powerful methods for allylic functionalization.[2] A very wide range of allylic substrates such as allylic halides, esters, carbonates, carbamates, phosphates, sulfones, and selenides have generally been the preferred substrates, with a few other special allylic systems, vinyl epoxides and oxetanes also having been used.[2a] In general, however, allylic nitrogen functionality does not prove to be as useful as a leaving group in this process. Several research groups have reported that allyltrialkylammonium salts and allylic nitro compounds are substrates for this process.[3] Some of examples of this process using allylic *N*,*N*-disulfonimides or *N*-sulfonamides have been reported.[4]

Here we wish to generalize the Pd(0)-catalyzed coupling

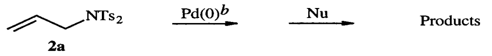
1

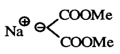
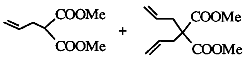
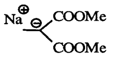
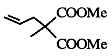
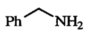
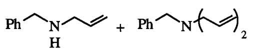
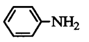
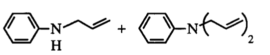
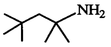
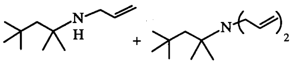
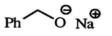
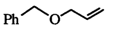
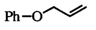
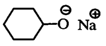
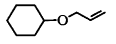
2a; X = Ts (quant.)
2b; X = Piv (69%)
2c; X = Ac (71%)

Scheme 1. *Reagents and conditions*: for **2a**: NaH, THF, 0 °C, 20 min then, TsCl, THF, rt, 1.5 h; for **2b**: a) TsCl, CH_2Cl_2, rt, 1 h b) NaH, DMF, pivaloyl chloride, 6 h; for **2c**: a) TsCl, CH_2Cl_2, rt, 1 h b) NaH, THF, AcCl, 1 h.

reaction using allyl *N,N*-ditosylimide (**2a**) and *N*-tosylamides (**2b**, **2c**) which are readily prepared from allylamine (**1**). Allyl *N,N*-ditosylimide (**2a**), allyl *N*-pivaloyl-*N*-tosylimide (**2b**), and allyl *N*-acetyl-*N*-tosylimide (**2c**) have been prepared as shown in Scheme 1 and used as substrates for this process.

Table 1. Pd(0)-catalyzed coupling reaction of allyl *N,N*-ditosylimide (**2a**).[a]



Entry	Nucleophile	Reaction condition	Products & yield (%)[c]
1		23°C, 10 min	 (63) (17)
2		23°C, 10 min	 (85)
3		-10°C → 23°C, 10 min	 (42) (44)
4		-10°C → 23°C, 10 min	 (79) (13)
5		23°C,1 h	 (57) (13)
6		23°C, 2.5 h	 (83)
7	$Ph{-}\overset{\ominus}{O}\,Na^{\oplus}$	23°C, 10 min	 (75)
8		23°C, 2 h	 (31)

[a]Blank test: without Pd(0) catalyst the reaction did not proceed. [b]Pd(0) catalyst was prepared in situ from $Pd(OAc)_2$ with trisopropyl phosphite and *n*-BuLi. [c]All yields are isolated ones.

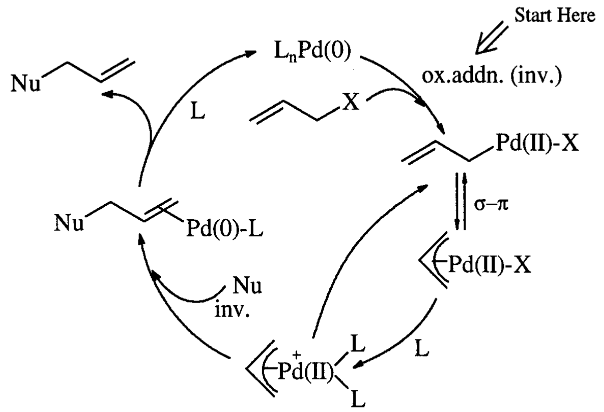


Figure 1. The general reaction mechanism of the Pd(0)-catalyzed reaction of allylic compounds.

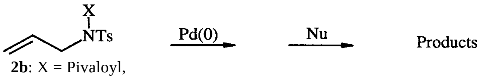
The results of the Pd(0)-catalyzed coupling reaction of allyl *N,N*-ditosylimide (**2a**) are shown in Table 1. Sodium dimethylmalonate (entry 1) and primary amines (entries 3-5) afforded the monoallylated and diallylated products. The ratio of these products seems to be mainly depended on steric factor of nucleophiles. Upon monoallylation at the nucleophile, it became a better nucleophile and the diallylation can be also proceeded (entries 1, 3-5). Upon the more sterically congested nucleophile by the allylation, however, the less diallylated product was produced (entries 3-5). In addition, the reaction with free alcohols did not work at all. However, the reaction proceeded when free alcohols were converted to the corresponding alcohol anions (entries 6-8). The general reaction mechanism of this process is given in Figure 1.[5] Palladium (0) attacks the opposite site of the leaving group to give the inversion of stereochemistry in the oxidative addition stage. Then, the nucleophile attacks the opposite site of the palladium metal to provide another inversion of stereochemistry in the π-allylpalladium complex. Thus, the reaction product having retention of stereochemistry is eventually obtained. Comparing this route, the results of entries 6 and 8 imply that aliphatic alkoxy nucleophiles would be attached to the palladium metal in the reaction, so the yield of the reaction can be explained by the steric reason. It has been known that the presence of a main group organometallic compound (most commonly a tin reagent) causes transmetallation of π-allylpalladium complex and the following reductive elimination of π-allyl-σ-alkylpalladium(II) complex results in the coupling product with the overall inversion of stereochemistry.[5] We are currently examining the Pd(0)-catalyzed coupling reaction route of stereoisomeric allylic nitrogen compounds with alcohol anions.

The results of the Pd(0)-catalyzed coupling reaction of allyl *N*-pivaloyl-*N*-tosylimide (**2b**) and allyl *N*-acetyl-*N*-tosylimide (**2c**) are given in Table 2. Similar to allyl *N,N*-ditosylimide (**2a**), sodium dimethylmalonate (entries 1, 4) and benzylamine (entries 2, 5) afforded the monoallylated and diallylated products. In the case of benzylamine, it gave *N*-allyl tosylamide as well, which is obtained by the nucleophile attack on the carbonyl carbon of acyl amide (entries 2, 5). With benzyl alcohol sodium salt, the coupling reaction did not proceed at all, and only an ester was obtained as a product (entries 3, 6). Allyl *N*-acyl-*N*-tosylimides (**2b**, **2c**) are prone to have weaker reactivities than allyl *N,N*-ditosylimide (**2a**).

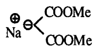
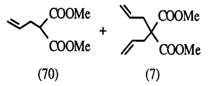
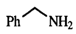
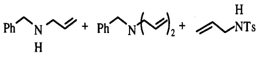
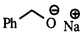
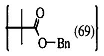
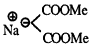
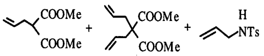
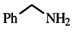
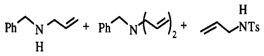
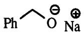
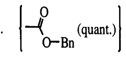
From the above results, we have demonstrated that allyl *N,N*-ditosylimide (**2a**) and *N*-acyl-*N*-tosylimides (**2b**, **2c**) can serve as new substrates in the preparation of π-allyl palladium complexes. Further studies in the area of nitrogen leaving groups for the utilization toward carbocyclic nucleoside synthesis are currently underway.

Acknowledgment. This work was supported by a school grant from Hanyang University.

Table 2. Pb(0)-catalyzed coupling reaction of allyl *N*-acyl-*N*-tosylimide (**2b**, **2c**)



2b: X = Pivaloyl,
2c: X = Acetyl

Entry	X	Nucleophile	Reaction condition	Products & yield (%)[a]
1	Pivaloyl		20°C, 3.5 h	 (70) (7)
2	Pivaloyl		20°C, 4 h	 (39) (14) (13)
3	Pivaloyl		20°C, 10 min	No rxn. 
4	Pivaloyl		20°C, 11 h	 (45) (2) (37)
5	Pivaloyl		20°C, 11 h	 (31) (14) (49)
6	Pivaloyl		20°C, 10 min	No rxn. 

[a]All yields are isolated ones.

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Formation of Self-assembled Zirconium *N,N'*-Bis (benzyl phosphonic acid)-3,4,9,10-perylene(dicarboximide) Multilayer Films on Silicon Substrate

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Self-assembled mono- and multilayer formed on solid substrates have generated considerable interest because of the potential of controlling the molecular architecture and chemical and physical properties of layered assemblies on surfaces such as electron transfer, nonlinear optics, photocatalysis, molecular recognition. Researchers have utilized the transition metal phosphonates multilayer films on surfaces to study a system in which interlayer distance and orientation of the organic components are crucial. The metal phosphonate films provide an attractive means of constructing thermally and sovolytically stable films of controlled thickness, which consist of spatially well-defined molecular components[1-4]. In this communication, we report on the preparation of multilayer of zirconium *N,N'*-bis(benzyl phosphonic acid)-3,4,9,10-perylene(dicarboximide)(Zr-BPPI) based on the sequential adsorption of metal ion and bisphosphonic acid and on the characterization of the mutilayer structure using UV-visible absorption measurement, ellipsometry, and cyclic voltammetry. The perylenedicarboximide derivatives have been well known as photoconducting materials in xerography[5-7] and as photoinduced electron transporting materials. The photoconductivity of the BPPI comes from the strong π-π interactions between fused aromatic ring structures. One of the goals of our research is to incorporate photoactive BPPI molecules into multilayer assemblies, in order to prepare thin films which undergo efficient photoinduced chage separation and directional conductivity.

In the multilayer structure of Zr-BPPI presented here the adjacent perylene chromophore in each layer can be stacked each other perpendicularly to the substrate as shown sche-