in methanol and water, but insoluble in chlorobenzene, toluene, benzene, carbon tetrachloride, chloroform, *n*-hexane, *etc*.

The inherent viscosities were in the range 0.08-0.19. These values are superior to those of conjugated polymers from monopropargyl salt monomers such as propargyltriphenylphosphonium bromide[18] and propargylpyridinium bromide.[17] Also these values are similar with those of simple poly(2-ethynylpyridine).[16]

The ^{1}H-NMR spectrum of poly(EPPB) prepared by using PdCl$_2$ as the catalyst in DMSO showed broad peaks due to the conjugated double bonds and aromatic pyridyl protons at 6.0-9.2 ppm, and the methylene protons were observed in the range 2.5-3.2 ppm. The IR spectrum of poly(EPPB) did not show the acetylenic (C≡C) frequencies at 2129 and 2220 cm^{-1} and the acetylenic ≡C-H stretching frequencies at about 3300 cm^{-1}. Instead the carbon-carbon double bond stretching frequencies were observed at about 1620 cm^{-1} with the characteristic peaks of pyridyl moiety. The UV-visible spectrum of poly(EPPB) exhibit the characteristic broad absorption peak of 400-700 nm which originated from the $\pi \rightarrow \pi^*$ transition of the conjugated polyene, which had not been observed at the UV-visible spectrum of monomer. The values of elemental analysis for poly(EPPB) agreed well with the calculated values. Anal. calcd. for $(C_{10}H_8NBr)_n$: C, 54.08%, H, 3.64%, N, 6.31%, Br, 35.98%. Found: C, 53.21%, H, 3.55%, N, 6.30%, Br, 35.51%. These results suggest that poly(EPPB)s have a conjugated polyene backbone structure with cyclic recurring units fused with pyridinium ring.

In conclusion, an interesting conjugated polyelectrolyte was synthesized in a high yield via a cyclopolymeriztion of EPPB by the Pd, Pt, and Ru-based catalysts. A more detailed description of these and other studies on electrophysical properties of the poly(EPPB) will be discussed elsewhere.

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Dehydrogenative Dimerization of Phenylacetylene by Electrochemical Activation of Vaska's Complex

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The homogeneous catalytic transformation of organic substrates by transition-metal complexes is a very active research area[1] and generally involves the two distinctive steps, oxidation (addition of an organic substrate to a metal) and reduction (elimination of the substrate from metal) of the central metal ion.[2] There is also interest in using electrochemical techniques in conjunction with metal complex catalysts.[3] Electrochemical oxidation or reduction of metal complexes may produce reactive species which could be used to catalyze the organic reactions.

Reactions of terminal alkynes with transition metal complexes produce various kinds of oligomers.[4] There are few examples of the electrocatalytic oligomerization of alkynes in the presence of metal complexes. In this communication, we report the first example of the electrocatalytic dimerization of phenylacetylene using Vaska's complex, IrCl(CO)(PPh$_3$)$_2$ (Eq. 1). Vaska's complex does not show the catalytic activity for the dimerization unless it is activated by electro-

trochemical oxidation (see below).

$$PhC\equiv CH \xrightarrow[\text{DMF, 25 °C, +1.2 volt}]{Ir(CO)(Cl)(PPh_3)_2} PhC\equiv C-C\equiv CPh \quad (1)$$
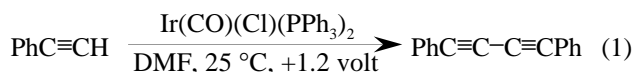
Electrochemical properties of 4 or 5-coordinate Ir(I) complexes had been investigated and the irreversible oxidation process was observed.[5] This process was interpreted as a 2 electron oxidation followed by rapid chemical reactions (EC$_{irrev}$. type reaction) possibly to produce 6-coordinate Ir(III) compounds or degraded products. This implies that the initially oxidized product is not stable and transforms to another compounds. A significant structural change upon electron transfer normally gives an irreversible shape of cyclic voltammogram.[6] Electrochemical studies for Vaska's complex has not been reported, and we present here that the complex undergoes irreversible electrochemical oxidation process similar to the other Ir(I) complexes.[5] Also, we paid attention to utilize this process since the unstable oxidized product might be a reactive metal species which can be used to activate organic compounds.

Cyclic voltammetric experiments show that IrCl(CO)-(PPh$_3$)$_2$ experiences an irreversible oxidation process at +0.6 V vs. Fc/Fc$^+$ in DMF at a gold disc electrode (Figure 1A). The reverse scan shows 2 or 3 peaks at $^-0.5 \sim {}^-2.0$ V region which might come from the products generated by following chemical reactions upon oxidation. The shape of cyclic voltammogram changes not much by increasing the scan rate up to 1 V/sec. The oxidation is a diffusion limited process since the peak current is linear to the square root of the scan rate. Phenylacetylene itself does not oxidize in the same potential region at gold electrode in the absence of IrCl(CO)-(PPh$_3$)$_2$ (Figure 1B). When phenylacetylene is added to the IrCl(CO)(PPh$_3$)$_2$ containing solution, one more irreversible oxidation peak around +1.1 V region is shown accompanying with the oxidation peak at +0.6 V (Figure 1C). As the amount of phenylacetylene increases, the peak current height at +1.1 V is increasing while the peak shape, height, and potential at +0.6 V are not significantly changed. Since the current at +1.1 V is responsible for the rate of phenylacetylene addition, these phenomena are typical for the addition reaction to the electrochemically oxidized complex. To investigate further, cyclic voltammograms were taken at various scan rates. The relative peak height of second peak at +1.1 V to the first peak at +0.6 V increases as decreasing the scan rate. It takes longer time for the oxidized product on the surface of the electrode to react with phenylacetylene at lower scan rate and more phenylacetylene adduct is generated near the surface of the electrode during the scan, which is responsible for the second peak at +1.1 V.

Controlled potential electrolyses were performed in H-type cell with large flag-type gold electrode to analyze the products after electrochemical oxidation. The electrolysis of Vaska's complex at +0.7 V in the presence of phenylacetylene (1 equivalent or more) consumes ~1.7 electrons per molecule. The electrolysis produced a mixture of uncharacterized metal complexes. No significant organic products were observed after the electrolysis at +0.7 V. The electrolysis at +1.2 V consumes ~2 electrons per phenylacetylene, which suggests that phenylacetylene is oxidized electrochemically in the pres-
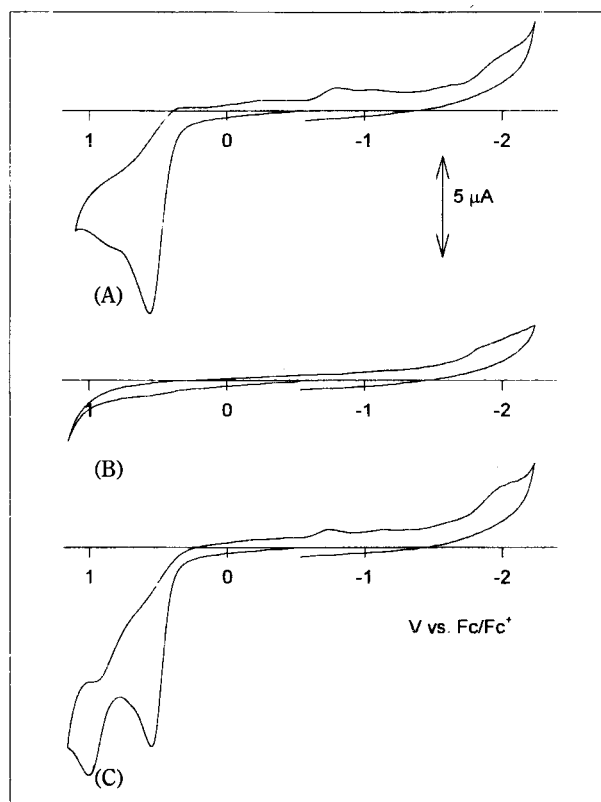

Figure 1. Cyclic voltammograms of (A) 2.0 mM of IrCl(CO) (PPh$_3$)$_2$, (B) 20 mM phenylacetylene, (C) 2.0 mM IrCl(CO)(PPh$_3$)$_2$ +20 mM phenylacetylene at gold electrode (area=0.02 cm^2) in DMF/ 0.1 M (CH$_3$)$_4$NPF$_6$ under Ar atmosphere. The reference electrode used was Ag/Ag$^+$ (0.01M) in DMF/0.1 M (CH$_3$)$_4$NPF$_6$. Fc/Fc$^+$ couple was +40 mV *vs.* the Ag/Ag$^+$ reference electrode in this system. All potentials were reported vs. Fc/Fc$^+$ couple. Scan rate is 50 mV/sec.

ence of Vaska's complex at this potential. The IR and ^{1}H-NMR spectral data for the metal products were similar to those electrolyzed at +0.7 V. Some organic products were observed after the electrolysis with excess phenylacetylene. The metal complexes were removed by the technique of the saturation and filtration, and the GC/MS and ^{1}H-NMR spectral data were taken for the organic products after being separated by column chromatography. The major product was found to be 1,4-diphenylbutadiyne (M.W.=202) which is the dehydrogenated head-to-head dimer of phenylacetylene. Small amounts of triphenylphosphine and triphenylphosphine oxide (Ph$_3$PO) were observed. This suggests that the iridium compound loses triphenylphosphine ligand to produce unknown complex(es) during the electrochemical reaction. (Uncoordinated triphenylphosphine is frequently oxidized to give Ph$_3$PO when it is handled in solution in air in the presence of metal complexes.) Other minor products were identified as styrene, benzaldehyde, acetophenone, and benzoic acid. It is not so surprising to observe styrene in the mixture of products since the dehydrogenative dimerization would give off hydrogen (most likely as H$_2$) one way or another. Then, the hydrogenation of phenylacetylene would occur to give styrene in the presence of iridium complexes. Acetophenone might be the product of the hydration of phenylacetylene, by

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