E2-14: Use of palladium(II)-phosphine complex in organic synthesis

Sarath D Perera
(Open University, Nawala, Nugegoda)

There is an increasing interest in the use of transition metal complexes in organic synthesis. Palladium complexes are well known to catalyse carbon-carbon bond forming reactions, in particular, the Heck Olefination reaction (e.g. $ArX + CH_2 = CHR \rightarrow ArCH=CHR + HX$). Frequently, the catalyst is generated *in-situ* from $[Pd(OAc)_2]$ and a tertiary phosphine $L = PR_3$, and often 1 to 5 mol% catalyst is used giving maximum turnover number (TON) of only 100 to 20. In this communication, the synthesis and application of a new type of palladium(II) catalyst containing an anionic (P-N-O) ligand are described. $Z\text{-}PPh_2CH_2C(Bu^t)=NNHC(=O)Ph$ reacts with $[PdCl_2(NCPh)_2]$ to give the palladium(II) complex $[PdCl\{PPh_2CH_2C(Bu^t)=N\text{-}N=C(O)Ph\}]$ **(1)** containing two 5-membered chelate rings. Similarly, the analogous palladium(II) complex $[PdCl\{PPh_2CH_2C(C_6H_4OMe\text{-}4)=N\text{-}N=C(O)C_6H_4Me\text{-}4\}]$ **(2)** was prepared.

When a mixture of iodobenzene (10 mmol), styrene (12.5 mmol) and catalyst **(2)** ($4x10^{-4}$ mmol. $4x10^{-3}$ mol%) was heated with $^{n}Bu_3N$ (10mmol) and DMF at 95°C for 11d, a pale orange solution resulted, from which the product stilbene was isolated in 95% yield, i.e. a TON of 23750. Methyl acrylate and iodobenzene similarly gave methyl cinnamate in 74% and 91% yields with catalysts **(2)** and **(1)**, respectively. When N,N-dimethylacrylamide was reacting olefin with the catalyst (2) for 17h at 95°C the product N,N-dimethylcinnamide was isolated in 84% yield. The aryl bromides, 4-bromoacetophenone and 4-bromocyanobenzene, reached with styrene in the presence of catalyst **(2)** at 125°C to give substituted stilbenes in 95% and 94% yields.

It was found that the addition of free phosphine to the reaction mixture destroys the catalytic activity, probably, by blocking the coordinating sites of the palladium centre.