

Ei-ichi Negishi



Professor Ei-ichi Negishi, Nobel prize winner in Chemistry (2010), was born on 14 July 1935 in Changchun, China. He started his elementary education in Harbin. As his family moved to Japan finally after WWII, Negishi completed his junior high school (7th to 9th grades), high school (10th - 12th grades) and college years in Japan. In the University of Tokyo, while pursuing his bachelor degree, Negishi applied for prestigious Teijin scholarship. Negishi joined Teijin as part of the agreement of the scholarship and started working as research chemist in Teijin Iwakuni Research Laboratory. Using Teijin's company policy of promoting higher education of their employees, he applied for a Fulbright Smith-Mund All-Expense Scholarship and succeeded in winning this one-in-a-hundred competition. Negishi joined University of Pennsylvania as graduate student in 1960 and completed PhD degree in synthetic organic chemistry under the guidance of Prof. A. R. Day in 1963. In University of Pennsylvania, Negishi met Prof. Herbert Brown and later joined his laboratory as post-doctoral fellow in Purdue University. He was appointed Assistant Professor in Purdue in 1968. In 1972, Dr. Negishi moved to Syracuse University and rose to the rank of Professor in 1979. Prof. Herbert Brown won Nobel Prize in 1979 and in the same year Prof. Negishi returned back to Purdue. In 1999, Negishi became the first Herbert C. Brown distinguished professor of Chemistry at Purdue.

Prof. Negishi received many national and international awards during his illustrious academic career. Some of the important awards are Foreign Associate of the National Academy of Sciences (2014); Fellow of American Academy of Arts & Sciences (2011); Order of the Griffin (2011); Sagamore of the Wabash (2011); ACS Award for Creative Work in Synthetic Organic Chemistry (2010); The Order of Culture, Japan (2010); Invited Lectureship, 4th Mitsui International Catalysis Symposium (MICS-4), Kisarazu, Japan, (2009); Gold Medal of Charles University, Prague, Czech Republic (2007); Yamada-Koga Prize (2007); Sigma Xi Award, Purdue University (2003); Sir Edward Frankland Prize Lectureship (2000); Alexander von Humboldt Senior Researcher Award (1998-2000); American Chemical Society Award for Organometallic Chemistry (1998); Herbert N. McCoy Award (1998); Chemical Society of Japan Award (1997); A. R. Day Award (ACS Philadelphia Section award) (1996); Guggenheim Fellowship (1987); Harrison Fellowship at University of Pennsylvania (1962-63); Fulbright-Smith-Mund Fellowship (1960-61).

The Nobel Prize for Chemistry, 2010 was awarded to Prof. Negishi for his work on palladium-catalysed cross coupling in organic synthesis. The reaction has been named after him and known as 'Negishi coupling'. Negishi coupling has opened doors in many areas of science

and technology from the pharmaceutical industry to modern electronics. In nature, organic chemistry is utilized in myriad forms to generate biomolecules, metabolites and hormones etc. In majority of the cases, stable base of carbon is used. By using organic synthesis, researchers have been able to create new medicines from fungus (e.g. Penicillin) and new materials like plastics and light-emitting diodes (LED). These complex chemicals are difficult to create, mostly because; carbon is a stable chemical and relatively unreactive. Thus, early attempts to bind carbon atoms together worked for simple molecules but produced too many unwanted by-products when synthesizing more complex molecules.

Transition metal-catalyzed reactions of Grignard reagents (as arylmagnesium bromides) and organohalides in the presence of catalytic amounts of salts of cobalt, nickel and iron were reported by Kharasch in 1941 to give high yields of biaryls. However, this was via homocoupling of the Grignard reagent. Carbon-carbon bond formation via copper-catalyzed coupling between methylmagnesium bromide and methyl iodide was also reported by Gilman in 1952. These cross couplings with the aid of copper, iron, nickel acetylacetonate and nickel phosphine complexes were further studied in the 1960's and early 1970s. The highly reactive organometallic species, such as Grignard reagents, organolithium compounds, which had been employed in these early cross-coupling reactions do not tolerate certain functional groups and are associated with low chemoselectivity. Therefore, the use of these reagents in cross-coupling reactions was not optimal for synthetic applications. Negishi initiated a series of studies to explore more chemoselective organometallic species in the palladium-catalyzed couplings with organohalides. In his early and successful investigations, Negishi employed organozirconium or organoaluminium compounds as coupling partners. The positive results obtained from these studies stimulated him to try even less reactive organometallic species. The breakthrough came in 1977 when Negishi introduced organozinc compounds as the nucleophilic coupling partners in palladium-catalyzed cross coupling. The organozinc compounds gave superior yields compared to other organometallic compounds, and furthermore, they were very mild and highly selective. The use of organozinc compounds in the palladium-catalyzed cross-coupling reaction allowed a wide range of functional groups. This was in sharp contrast to previous methods employing a Grignard reagent or an organolithium compound as the nucleophilic coupling partner. The new coupling reaction became a very important method for making carbon-carbon single bonds. Negishi also noted in 1978 that an alkynylboron compound coupled with an organic halide in the presence of a palladium catalyst works well for certain coupling reactions, which was subsequently further developed by A. Suzuki and N. Miyaura. A large number of researchers worked on Negishi coupling from various angles such as J. F. Fauvarque, A. Jutand, P. Knochel. This has widened the scope of oligofunctional organozinc derivatives and thus enhanced the synthetic utility of the Negishi coupling.

Palladium is a rare silvery-white metal. Negishi showed that palladium can solve this problem of carbon-carbon coupling in a unique way. This metal can serve as an ideal catalyst

for introduction of carbon atoms and thus provided chemists endless opportunity for a precise and efficient 'breeding ground' for carbon reactions. Another big advantage is production of less waste by-products. Despite earlier related but different investigations by Heck and Mizoroki, Negishi is the one who introduced most widely applicable methods of cross-coupling. Negishi cross-coupled carbon-zinc compounds and organic halides (such as chloride, bromide and iodide) using palladium as the catalyst. He also utilized nickel as catalyst in some cases, but performance of palladium was far superior to that of nickel. In Negishi coupling, palladium is first oxidized, making it even more efficient. Negishi coupling is now used to produce a large number of medicines. Some of the examples are pain killer (naproxen) and one of the heavily used anti-cancer drug, taxol. This reaction is also used for fluorescent marking for DNA sequencing and in creating materials thin LED displays.

Negishi is married to his childhood sweetheart, Sumire who happens to be daughter of his Yamato Junior High School music class teacher, T. Suzuki. They have two daughters. Negishi lives in a house called, 'palladium', located near to Purdue University.

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