COVER FEATURE

Professor Ei-ichi Negishi *

Recipient of the RSC Sir Edward Frankland Prize Lectureship for 2000

Career

Ei-ichi Negishi grew up in Japan and received his baccalaureate degree in 1958 from the University of Tokyo. He first worked as a research chemist at a Japanese chemical company, Teijin, Ltd. He went to the USA as a Fulbright scholar in 1960 and earned a PhD in organic chemistry in 1963 from the University of Pennsylvania. Negishi resumed his post at Teijin, but returned to the United States in 1966 for post-doctoral work in organoborane chemistry in Professor Brown's laboratories at Purdue University. After holding a series of academic positions at Purdue and Syracuse, Negishi became a chemistry professor at Purdue in 1979. In 1999 he became the inaugural Herbert C. Brown Distinguished Professor. Negishi's research has earned him numerous awards and honors:

Fulbright–Smith–Mund All Expense Scholarship, 1960–63
J. S. Guggenheim Memorial Foundation Fellowship, 1987
A. R. Day Award, 1996
The Chemical Society of Japan Award, 1997
The American Chemical Society Organometallic Chemistry Award, 1998
Herbert N. McCoy Award, Purdue University, 1998
Alexander von Humboldt Award, Germany, 1998–2001
Herbert C. Brown Distinguished Professor, Purdue University, 1999

* Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393, USA.

He has given lectures throughout the world and has published about 300 scientific papers, several patents, and a few dozen essays. Negishi is among the most extensively cited synthetic organic chemists. For example, he is one of the ten most frequently cited chemists in both *Comprehensive Organic Synthesis*, 1991, Vols. 1–9, Pergamon, and *Comprehensive Organic Functional Group Transformations*, 1995, Vols. 1–7, Pergamon.

Research

In 1966 Ei-ichi Negishi began devoting himself to research on organometallic chemistry when he came to Purdue as a post-doctoral associate in Professor H. C. Brown's research group and participated in Brown's systematic exploration of organoboron chemistry.

At Syracuse University, Negishi began his career by exploring organotransition metal chemistry for organic synthesis. With the recognition that various reactions of 24 d-block transition metals for the formation of carbon–carbon and other types of bonds can be classified into just a few fundamentally discrete patterns, *i.e.*, (1) reductive elimination, (2) carbometallation and related addition reactions, (3) migratory insertion, and (4) nucleophilic and electrophilic attack on ligands, he initially focused his attention on reductive elimination, and developed the nickel-catalyzed cross-coupling reaction of organoaluminiums, analogous to the Kumada–Corriu reaction of Grignard reagents. This led to the discovery of the corresponding palladium-catalyzed organoaluminium reaction in 1976. This represents one of the earliest examples of the Pd-catalyzed cross coupling along with those reported by Murahashi, Ishikawa, Fauvarque and others. This also demonstrated, for the first time, the feasibility of the hydrometallation–Pd-catalyzed cross-coupling tandem process. Negishi's subsequent systematic exploration led to findings on palladium-catalyzed cross-coupling reactions of organometals containing aluminium, zinc, and zirconium, commonly known as the Negishi coupling, as well as the earliest, or one of the earliest, reports on the use of boron and tin in Pd-catalyzed cross-coupling, thus etablishing one of the most straightforward and versatile methods for the construction of organic compounds,[1,2] before a number of his followers, notably J. K. Stille and A. Suzuki, began developing the related methods that bear their names.

While Negishi's efforts regarding Pd- or Ni-catalyzed cross-coupling were still ongoing, he began publishing in 1978 in his second major area of research—carbometallation of alkynes and alkenes. The following five represent his major contributions to this area.

(1) Zirconium-catalyzed carboalumination of alkynes known as the Negishi carboalumination (since 1978).[3]

(2) Zirconium-catalyzed enantioselective carboalumination of alkenes (since 1995).[4,5]

(3) Zirconium-promoted cyclization reactions of alkenes and alkynes in particular those with the Negishi reagent (since 1985).[6,7]

(4) Palladium-catalyzed cyclic cascade carbopalladation (since 1988).[8,9]

(5) Palladium-catalyzed cyclic acylpalladation (since 1983).[8,9]

DOI: 10.1039/b009326m

In the Zr-catalyzed carboalumination and related reactions, a potentially general and synthetically important principle of activation of electrophiles by electrophiles through dimeric association (two are better than one),[10] has emerged. This concept has not only promoted the discovery and development of catalytic bimetallic reactions but also helped delineate the mechanisms of zirconium- and titanium-catalyzed processes. Negishi's contributions in the area of carbometallation are easily as important as those on reductive elimination, and their widespread applications by others, as in the case of palladium-catalyzed cross coupling, appear to be imminent.

More recently, Negishi and his research group have discovered and developed novel migratory insertion reactions of organozirconium and other organometallic species other than the widely known carbonylation. This is one area of research Negishi hopes to pursue extensively in the future.

References

1 E. Negishi, *Pure Appl. Chem.*, 1981, **53**, 2333.
2 E. Negishi and F. Liu, in *Cross Coupling Reactions*, ed. P. J. Stang and F. Diederich, VCH, Weinheim, 1998, ch. 1, p. 1.
3 E. Negishi, *Pure Appl. Chem.*, 1981, **53**, 2333.
4 E. Negishi and D. Y. Kondakov, *Chem. Soc. Rev.*, 1996, **26**, 417.
5 E. Negishi, in *Catalytic Asymmetric Synthesis II*, ed. I. Ojima, J. Wiley & Sons, Inc., New York, 2000, ch. 4, p. 165.
6 E. Negishi and T. Takahashi, *Acc. Chem. Res.*, 1994, **27**, 124.
7 E. Negishi and J. L. Montchamp, in *Metallocenes*, ed. R. L. Halterman and A. Togni, VCH, Weinheim, 1998, ch. 5, p. 241.
8 E. Negishi, *Pure Appl. Chem.*, 1992, **74**, 323.
9 E. Negishi, C. Coperet, S. Y. Liou, F. Liu and S. Ma, *Chem. Rev.*, 1996, **96**, 365.
10 E. Negishi, *Chem. Eur. J.*, 1999, **5**, 411.