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1. Obituary

Eminent organic chemist and professor of Kyoto University, Hidemasa Takaya, died suddenly on the 15 October 1995, while he was attending a conference in Germany.

Dr. Takaya was born on 23 November 1940 in Kagawa prefecture, Japan. He studied organic chemistry at the Department of Industrial Chemistry, Faculty of Engineering of Kyoto University. After graduating in 1964, he continued his research in synthetic organic chemistry under the guidance of Professor Hitosi Nozaki. In 1968, he was given an assistant professorship at Nagoya University and, cooperating with Professor Ryoji Noyori, he began studying the application of organometallic complexes in synthetic chemistry. He was promoted to associate professor in 1969. In the same year, he obtained his doctorate from Kyoto University.

As soon as the Institute of Molecular Science was established, he was invited to assume an associate professorship in 1976. He returned to the Department of Industrial Chemistry of Kyoto University as full professor in 1988 (Division of Organic Chemistry of Natural Products), a position he occupied until his untimely death. He was dedicated to his research in the field of organic reaction and synthetic organic chemistry; contributing as many as 140 articles. As an educator, he has instructed many students.

Dr. Takaya's achievements can be grouped into three categories;

1.1. Catalytic asymmetric synthesis

He discovered the ability of chiral transition metal complexes as catalysts for homogeneous asymmetric synthesis and explored basic research on the development of chiral ligands. His results led to successful application to synthesis of optically active organic compounds in an industrial scale. The bidentate phosphine ligands that he developed, namely BINAP and BINAPHOS, have been used as versatile ligands of catalysts for asymmetric synthesis. He succeeded in almost perfect asymmetric synthesis of α -amino acid derivatives by using the Rh–BINAP catalyst. Using this catalyst, he studied the asymmetric isomerization of allylamines to enamines, whose result was applied to an industrial process for asymmetric synthesis of (-)-menthol from isoprene [1–3].

Subsequently he developed effective synthetic methods for (i) various chiral organic compounds by the Ru-BINAP-catalyzed asymmetric hydrogenation [4], (ii) optically active aldehydes by the Rh-BINAPHOS-catalyzed asymmetric hydroformylation [5], (iii) optically active polyketones by the Pd-BINAPHOS catalyzed alkene-CO-copolymerization [6] and so on. To these achievements, Professors Takaya and Noyori awarded the Fluka Prize in 1989.

1.2. Development of reactive intermediates and their application to organic synthesis

He revealed the unique property of 2-oxyallyl iron complexes generated by the reaction of iron carbonyl and α, α' -dibromoketones. Subsequent novel cycloaddition reactions led to the direct synthesis of odd-membered carbocycles [7,8]. This reaction sequence turned out to be an effective synthetic method for natural products such as tropons, tropan alkaloids, muscarine alkaloids, and terpenes [9,10]. For this achievement he was given the Chemical Society of Japan Award for Young Chemists in 1974.

1.3. Organic synthesis based on organometallic compounds

He investigated many fundamental aspects of organotransition metal complexes (variation of central metals, structure, properties and reactivity of ligands) and revealed the important role of metallacycles as intermediates in homogeneous catalytic organic transformations [11]. He also pioneered the development of organic reactions using main-group organometallics. The selective cycloaddition of organotin compounds serves as a novel synthetic method for yohinbane alkaloids [12].

Recently he studied molecular recognition based on the unique acidic property of the boron atom, and found that compounds containing two boron atoms could bind diamines in a specific manner to pave the way for development of molecular recognition tips [13].

Thus Dr. Takaya has made outstanding achievements in both research and education in his field over the past 27 years.We should not forget his contribution to work on chemistry outside Japan. He was one of the authors of the *Comprehensive Organic Synthesis* as well as an Editor of the *Journal of Molecular Catalysis*. He was highly noted for his insight into the structure and reactivity of organic compounds as well as organometallic complexes, which led to his pioneer studies regarding the innovative process in catalytic asymmetric synthesis. These achievements opened the way to numerous natural biologically active substances that we utilize today.



Dr. Hidemasa Takaya.

References

- R. Noyori, M. Ohta, Y. Hsiao, M. Kitamura, T. Ohta and H. Takaya, J. Am. Chem. Soc., 108 (1986) 7117.
- [2] T. Ohta, H. Takaya, M. Kitamura, K. Nagai and R. Noyori, J. Org. Chem., 52 (1987) 3174
- [3] R. Noyori, T. Ohkuma, M. Kitamura, H. Takaya, N. Sayo, H. Kumobayashi and S. Akutagawa, J. Am. Chem. Soc., 109 (1987) 5856.
- [4] T. Ohta, H. Takaya and R. Noyori, Tetrahedron Lett., (1990) 7189.
- [5] N. Sakai, S. Mano, K. Nozaki and H. Takaya, J. Am. Chem. Soc., 115 (1993) 7033.
- [6] K. Nozaki, N. Sato and H. Takaya, J. Am. Chem. Soc., 117 (1995) 9911.
- [7] R. Noyori, S. Makino and H. Takaya, J. Am. Chem. Soc., 93 (1971) 5894.
- [8] R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi and S. Tsutsumi, J. Am. Chem. Soc., 94 (1972) 7202.
- [9] R. Noyori, Y. Hayakawa, S. Makino and H. Takaya, J. Am. Chem. Soc., 95 (1973) 4103.
- [10] H. Takaya, Y. Hayakawa, S. Makino and R. Noyori, J. Am. Chem. Soc., 100 (1978) 1778.
- [11] A. Miyashita, M. Takahashi and H. Takaya, J. Am. Chem. Soc., 103 (1981) 6257.
- [12] R. Yamaguchi, T. Hamasaki, T. Sasaki, S. Kozima and H. Takaya, Synlett, (1991) 719.
- [13] K. Nozaki, M. Yoshida and H. Takaya, Angew. Chem., Int. Ed. Engl., 33 (1994) 2452.