

American Chemical Society

National Awards Nomination Packet

ACS Award in Inorganic Chemistry:2018
for: Kin-ya Akiba

Received: 10/28/2015

Cycle Year: 2

"In recognition of lifelong outstanding contributions to the field of Main Group Element Chemistry through fundamental understanding, creative insight, and broadly useful applications."

NOMINATOR:

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- Have you discussed this award nomination with the nominee? Yes

NOMINEE:

Kin-ya Akiba
3-9-2-708 Azusawa
Itabashi KU
Tokyo, 174-0051
Japan

Tel: 8359152166
Email: ak-y@lapis.plala.or.jpXXX

ACS Current Member: Yes
Years of Service: 48
Date of birth: 01/01/1936
Present Position: Professor Emeritus, Hiroshima
University;Invited Researcher,
Waseda University
Industry: Academia

SAFETY PROTOCOLS:

- Does the nominee employ and require good safety protocols and practices in his/her laboratory? Yes

SUPPORTER 1

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October 28, 2015

Nomination for the ACS Award in Inorganic Chemistry

Kin-ya Akiba has made outstanding contributions to the science of the main-group elements. His ground-breaking discoveries extend from the fundamentals of structure, bonding and reactivity to development of reagents for synthesis. Professor Akiba's work has addressed compounds and reactivity central to both inorganic and organic chemistry. His work on electron-rich (hypervalent) bonding has addressed important issues among compounds of the main-group elements. Even carbon, often regarded as the hallmark of organic chemistry, has yielded to Professor Akiba's efforts to devise stable models of electron-rich bonding. Based upon the breadth, depth, and significance of these highly regarded achievements, Professor Akiba is herewith nominated for the ACS Inorganic Chemistry Award.

Professor Akiba's interests led him to begin his scientific career with studies in heterocyclic and heteroatom chemistry. His early work in these fields quickly enabled him to recognize the uniqueness and importance of electron-rich (hypervalent) bonding, a field that was not well understood at that time. A combination of expertise, keen insight, and exceptional experimental techniques allowed him to create an amazing variety of novel compounds at numerous main-group element centers that exemplified the concept and utility of hypervalent bonding. Over the course of his career, Professor Akiba's research grew to embrace many different elements and electronic structures. These endeavors culminated in a long-sought target, the creation of carbon-centered hypervalent compounds. In large part owing to the work of Professor Akiba, "hypervalency" has become an important and indeed staple concept in the chemistry of the main-group elements and has found its way into textbooks covering chemistry of the main-group elements. His achievements in these areas include:

- (Group 14 and 13), the first synthesis and structural characterization of pentacoordinated and hexacoordinated hypervalent carbon compounds;
- (Main Group Element heterocycle synthesis), the *Akiba reagent* has become a frequently cited and often employed reagent for the synthesis of tetrathiafulvene derivatives and analogs.
- (Group 16), (a) verification of bond switching equilibrium via hypervalent sulfur intermediates, (b) the first experimental evaluation of S—N hypervalent bond energy; (c) the first synthesis of homoleptic hexacoordinated tellurium compounds bearing carbon;
- (Group 15), (a) experimental evaluation of the edge-inversion mechanism using Sb(III) and Bi(III) compounds, (b) examination of selectivity of ligand exchange and ligand coupling of non-cyclic pentacoordinated Sb(V) compounds, (c) determination of apicophilicity, examination of pseudorotation, preparation of phosphoranes with chirality only on the phosphorus atom, and isolation and wide-ranging examination of a new class of "anti-apicophilic" phosphoranes (no other group had been able to prepare these thermodynamically less stable isomer analogs prior to the molecular designs emerging from Akiba's group), (d) synthesis of porphyrins bearing carbon-element bonds to phosphorus, arsenic, and antimony.

Professor Akiba's broad expertise in main group element chemistry is well-summarized in his highly cited book entitled "*Chemistry of Hypervalent Compounds*." This book is very well written and comprises not only Professor Akiba's seminal contributions to chemistry, but also highlights the contributions of other luminaries in the area. He has also published the authoritative textbook "Organo Main Group Chemistry" which is used by instructors in graduate special topic courses on the subject of main group element chemistry and also serves as useful resource for research and reference.

Beyond his activities in research and discovery Professor Akiba has been active in promoting international collaborations, and educational/research exchanges to facilitate the development of a new generation of scientists. When the ACS and the Pacific Rim Societies began the Pacificchem series of meetings, I was honored to be included with Professor Akiba, Professor J.C. Martin, and Professor Seppelt in organizing the first series of Main Group Element focused mini-symposia at Pacificchem. Later, during my association with DuPont, I continued these efforts together with Professor Akiba to nurture U.S.-Japanese cooperations in the area of unusual bonding and main group element chemistry. I was always inspired by Professor Akiba's tireless efforts to drive science for the public good and mentor next-generation scientists.

Professor Akiba's contributions and his preeminence as an international researcher, educator, and scientific leader is also reflected by the metrics his career boasts. His career status markers are commensurate with those of the recent ACS Inorganic Chemistry Award winners. He has a strong publication record with citations appearing from disparate disciplines. A useful reagent bears his name. He has been highly effective in support of science at both national and international levels. He is a member of professional societies in Asia, Europe, and the U.S. Career recognition for his science and service in Japan is extremely praiseworthy. He is a figure of truly international stature.

Sincerely,



Anthony J. Arduengo, III

Curriculum Vitae

Professor Dr. Kin-ya Akiba,

Professor Emeritus, Hiroshima University
Invited Researcher, Waseda University

Date of Birth: June 11, 1936 (Tokyo, Japan)

Address: 3-9-2-708 Azusawa,
Itabashi-ku, Tokyo 174-0051,
Japan

E-mail: akibaky5564@gmail.com; ak-y@lapis.plala.or.jp

Specialty: Organic Reaction Mechanism, Organic Main Group
Element Chemistry, Chemistry of Hypervalent Compounds

Education: 1955-1959 University of Tokyo (undergraduate)
1959-1964 University of Tokyo (Faculty of Science, Department of Chemistry, graduate course),
1964 Ph.D. University of Tokyo

Professional Career:

1964-1972 Assistant Professor, Faculty of Science, University of Tokyo
1969-1970 Post Doctoral Researcher, University of Florida (with Prof. W. R. Dolbier, Jr.)
1970-1971 Post Doctoral Researcher at Michigan State University (with Prof. H. Hart)
1972-1977 Lecturer, Faculty of Science, University of Tokyo
1978-1980 Associate Professor, Faculty of Science, University of Tokyo
1980-2000 Professor, Faculty of Science, Hiroshima University
1987-1989 Joint Research of Japan and The United States (with Prof. J. C. Martin, U. of Illinois; JSPS-NSF)
1990-1993 Chairman of Scientific Research on Priority Area of Organic Unusual Valence (Ministry of Education, Culture, Sports, Science, and Technology, Japan); organizing 69 Professors
1998-to date Active Member of New York Academy of Sciences
1998-1999 Vice President of Chemical Society of Japan
2000-2007 Adjunct Professor, Waseda University, Adjunct Professor, Toyo University
2003-2005 Adjunct Professor, The Open Air University of Japan
2007-to date Invited Researcher, Waseda University

Awards:

1985 The CSJ Award for Creative Work,
1996 Humboldt Research Award (A.v. H. Stiftung)
1997 The Chemical Society of Japan (CSJ) Award,
1998 Chugoku Cultural Award (Tyugoku News Paper Co.),
2000 Medal with Purple Ribbon (Prime Minister of Japan),
2004 *Wiedereinladung* by Humboldt Research Award (A.v. H. Stiftung)
2011 The Order of The Sacred Treasure, Gold Rays with Neck Ribbon (Emperor of Japan)

Membership:

Chemical Society of Japan;
The Society of Synthetic Organic Chemistry, Japan;
Kinki Chemical Society, Japan;
American Chemical Society (Emeritus Member);
New York Academy of Sciences;
The German Society of Chemists (GDCh)
Honorary Member of Humboldt-Society Japan (2015-present)



Publications: 269 Original Articles; 33 Review Articles; 23 Books and Book Chapters; 2 Book Translations

Research Interest and Outreach Activities:

Professor Akiba's interests are in the synthesis, bonding, and reactivity of main group-element compounds and lie at the interface of inorganic and organic chemistry. Activities focus on the chemistry of hypervalent bonding (3-center, 4-electron bond) and π -bonding at heavier main-group element centers. Accomplishments include (1) the reactions of nitrosoimines contained in main-group heterocycles, (2) the first bond formation, bond switching equilibration, and evaluation of bond energy of hypervalent N-S-N bonds, (3) pioneering studies of edge inversion processes of Sb(III) and Bi(III), (4) ligand exchange and ligand coupling reaction of Sb(V) compounds, (5) the first "anti-apicophilic" bicyclic phosphoranes and energy of pseudorotations of these phosphoranes, (6) the first P, As, and Sb porphyrins with carbon-element bonds, (7) the first completely characterized penta- and hexa- coordinate hypervalent carbon species, (8) hypervalent boron and tellurium compounds, (9) aza- and oxa-aromatic cations.

Professor Akiba founded in Japan "Young Chemist Association of Organic Reactions" in 1966 and he also organized and founded "Chemical Forum of University and Industry in Tyuhgoku- Shikoku District" in 1984. The district consists of nine prefectures such as Okayama, Hiroshima, Yamaguchi, Shimane, Tottori, Kagawa, Ehime, Tokushima, and Kohchi. Both the association and the forum are still active and thriving

Collaborators (last five years): Prof. Yohsuke Yamamoto (Hiroshima U.), Associate Prof. Satoshi Kojima (Hiroshima U.); Prof. Masaru Tada (Waseda U.), Prof. Hiromi Nakai (Waseda U.), Prof. Takanori Shibata (Waseda U.), Dr. Y. Yamauchi, Dr. Y. Kikuchi, Dr. T. Atsumi, Dr. Y. Ikabata, Dr. M. Okoshi, (Waseda U.); Prof. Tetsuji Taketugu (Hokkaido U.), Assistant Prof. Masato Kobayashi (Hokkaido U.); Prof. Karl. M. Kadish (U. Houston), Dr. D. Hashizume (RIKEN), Associate Prof. Shiro Matsukawa (Toho U.).

Undergraduate, Master Degree Students, Ph. D. Degree Students

At Tokyo U. (Prof. Akiba was Faculty member, 1964-1979): Undergraduate students (26 total), Master Degree Students (20 total), Ph. D. Students (6 total): Kazuhiro Tokunaga, Kohichi Yamada, Tohru Tsuchiya, Kiyofumi Ishikawa, Yoshio Ohara, Yohsuke Yamamoto (Supervisor was Prof. Naoki Inamoto, Prof. Akiba was Lecturer and Associate Prof. under Inamoto and lead and consulted experimental work with these students and wrote scientific papers with them and Inamoto; Japanese system, so called Koza).

At Hiroshima U.: (Prof. Akiba was Full Professor, 1980-2000): Undergraduate students (141 total), one year students from chemical company (9 total), Master Degree Students (87 total), Ph. D. Students (21 total): Takashi Kume, Ryukin Lee, Shou Chin, Satoshi Kojima, Kaori Ishimaru, Kazumasa Kajiyama, Wataru Satoh, Masaaki Nakamoto, Koichiro Toyota; Yoshihiko Ohyama (with Prof. K. Okuda), Keiji Okada (with Prof. K. Ohkata), Hiroshi Fujishima (worked at Tohoku U.), Tomoyuki Yano (with Prof. K. Ohkata), Kazuhiro Yamamoto (with Prof. Ohkata), Makoto Itagaki (with Prof. Y. Yamamoto), Syuji Masumoto (with Prof. M. Shibasaki), Ryukichi Takagi (with Prof. K. Ohkata), Koichiro Saruhashi (with Prof. T. Kawashima), Masataka Miysato (with Prof. Y. Yamamoto), Makoto Yamashita (with Prof. Y. Yamamoto), Shiro Matsukawa (with Prof. Y. Yamamoto).

*Candidates with the name of another professor in parentheses obtained their doctorates through a collaboration with the noted professor after K.-y. Akiba's retirement from Hiroshima University.

Kin-ya Akiba, Professor Emeritus, Hiroshima University
Selected Publications [citation numbers from Google Scholar]

- Chemistry of Hypervalent Compounds*, **1999**, ed. by K.-y. Akiba, pp414, Wiley-VCH. (Foreword by the late Nobel Prize Laureate Derek H. R. Barton) [229]
- Synthesis of 1,4-Dithiafulvenes and 1,4-Dithiafulvalenes by Carbonyl Olefination Using 2-Dimethoxyphosphinyl-1,3-benzodithiole* Kin-ya Akiba, Kiyofumi Ishikawa, Naoki Inamoto *Bul. Chem. Soc. Japan* **1978**, 51(9), 2674-2683. [118]
- Syntheses and Structures of Hypervalent Pentacoordinate Carbon and Boron Compounds Bearing an Anthracene Skeleton-Elucidation of Hypervalent Interaction Based on X-ray Analysis and DFT Calculation* M. Yamashita, Y. Yamamoto, K.-y. Akiba, D. Hashizume, F. Iwasaki, N. Takagi, and S. Nagase *J. Am. Chem. Soc.*, **2005**, 127, 4354-4371. [91]
- A Grignard-Type Addition of Allyl Unit to Aldehydes by Using Bismuth and Bismuth Salt* Makoto Wada, Hidenori Ohki, Kin-ya Akiba *Bul. Chem. Soc. Japan* **1990**, 63(6), 1738-1747. [83]
- Regioselective synthesis of 4-alkylpyridines via 1,4-dihydropyridine derivatives from pyridine* Kin-ya Akiba, Yuji Iseki, Makoto Wada *Tet. Lett.* **1982**, 23(4), 429-432. [72]
- Experimental Investigation on Edge Inversion at Trivalent Bismuth and Antimony: Great Acceleration by Intra- and Intermolecular Nucleophilic Coordination* Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, and K.-y. Akiba *J. Am. Chem. Soc.*, **1995**, 117, 3922-3932. [68]
- Metallic bismuth mediated allylation of aldehydes to homoallylic alcohols*, Makoto Wada, Kin-ya Akiba *Tet. Lett.* **1985**, 26(35), 4211-4212. [65]
- First Characterization of a 10-P-5 Spirophosphorane with an Apical Carbon-Equatorial Oxygen Ring. Kinetic Studies on Pseudorotation of Stereoisomers* S. Kojima, K. Kajiyama, M. Nakamoto, and K.-y. Akiba *J. Am. Chem. Soc.*, **1996**, 118, 12866-12867. [64]
- Regioselective synthesis of 4-(2-oxoalkyl) pyridines via 1, 4-dihydro-pyridine derivatives using silyl enol ethers and pyridinium salts* Kin-ya Akiba, Yoshihiro Nishihara, Makoto Wada *Tet. Lett.* **1983**, 24(47), 5269-5272 [60]
- Carbon—carbon bond formation with bismuth salt. A chemoselective Grignard-type addition of allyl unit to aldehyde* Makoto Wada, Hidenori Ohki, Kin-ya Akiba *Tet. Lett.* 1986, 27(39), 4771-4774. [58]
- First Experimental Evaluation of Hypervalent N-S-N Bond Energy from the Restricted Rotation of Pyrimidine Ring in 10-S-3 Sulfuranes* K.-y. Akiba, M. Ohsugi, H. Iwasaki, and K. Ohkata, *J. Am. Chem. Soc.*, **1988**, 110, 5576-5578. [48]
- Characteristic Reactions and Properties of C-Apical O-Equatorial (O-cis) Spirophosphoranes: Effect of the σ^*P-O Orbital in the Equatorial Plane and Isolation of a Hexacoordinate Oxaphosphetane as an Intermediate of the Wittig Type Reaction of 10-P-5 Phosphoranes* S. Matsukawa, S. Kojima, K. Kajiyama, M. Nakamoto, Y. Yamamoto, K.-y. Akiba, S. Y. Re, and S. Nagase *J. Am. Chem. Soc.*, **2002**, 124, 13154-13170. [45]
- Synthesis and Characterization of Stable Hypervalent Carbon Compounds (10-C-5) Bearing a 2,6-Bis(p-substituted phenyloxymethyl)benzene Ligand* K.-y. Akiba, Y. Moriyama, M. Mizozoe, H. Inohara, T. Nishii, Y. Yamamoto, M. Minoura, D. Hashizume, F. Iwasaki, N. Takagi, K. Ishimura, and S. Nagase *J. Am. Chem. Soc.*, **2005**, 127, 5893-5901. [43]
- Synthesis and Structure of Phosphorus(V) Octaethylporphyrins That Contain a σ -Bonded Element-Carbon Bond: Characterization of a Porphyrin Bearing R-P=O Bond and Relation of Ruffling of the Porphyrin Core with Electronegativity of the Axial Ligands* Y. Yamamoto, R. Nadano, M. Itagaki, and K.-y. Akiba, *J. Am. Chem. Soc.*, **1995**, 117, 8287-8288. [41]
- First Isolation and Characterization of an Anti-Apicophilic Spirophosphorane Bearing an Oxaphosphetane Ring: A Model for the Possible Reactive Intermediate in the Wittig Reaction* Satoshi Kojima, Masaya Sugino, Shiro Matsukawa, Masaaki Nakamoto, and Kin-ya Akiba *J. Am. Chem. Soc.*, **2002**, 124(26), 7674-7675. [41]
- First Example of an Isolable α -Sulfurane with an Apical Alkyl Group Effected by Transannular Bond Formation between The Amino and The Sulfonio Groups* K.-y. Akiba, K. Takee, K. Ohkata, and F. Iwasaki *J. Am. Chem. Soc.*, **1983**, 105, 6965-6966. [40]
- Synthesis and chemical behaviors of 12-substituted dibenz[c,f][1,5]azastibocine and dibenz[c,f][1,5]azabismocine derivatives: evidences of 10-Pn-4 type hypervalent interaction* Katsuo Ohkata, Shin Takemoto, Masako Ohnishi, Kin-ya Akiba *Tet. Lett.* **1989**, 30(36), 4841-4844. [40]
- Facile synthesis of 4-substituted pyridines using grignard reagents* Kin-ya Akiba, Yuji Iseki, Makoto Wada *Tet. Lett.* **1982**, 23(38), 3935-3936. [40]
- Characterization of Enantiomeric Pairs of Optically Active 10-P-5 Phosphoranes with Asymmetry Only at Phosphorus* S. Kojima, K. Kajiyama, K.-y. Akiba *Bull. Chem. Soc. Jpn.*, **1995**, 68, 1785-1797. [39]
- Synthesis and Structure of a Hexacoordinate Carbon Compound* T. Yamaguchi, Y. Yamamoto, D. Kinoshita, K.-y. Akiba, Y. Zhang, C. A.; Reed, D. Hashizume, F. Iwasaki *J. Am. Chem. Soc.* **2008**, 130, 6894-6895. [38]

October 26, 2015

Dear Selection Committee:

It is a pleasure to write in support of the nomination of Dr. Kin-ya Akiba for the ACS Award in Inorganic Chemistry. During the course of his academic career, largely at Hiroshima University, he contributed definitively and often uniquely to the field of Main Group Element Chemistry.

Early in his career, Dr. Akiba published a method for the general synthesis of benzodithiafulvenes, which over the years has become known as the Akiba reaction. At that time his research efforts encompassed both organic and inorganic reactivity, emphasizing the importance of the interactive behavior of elements of the main groups with organic entities. Then, in 1985 he became Professor at Hiroshima University and during the ensuing 20 years his research program was directed primarily at obtaining a fundamental understanding of the structure, bonding and reactivity of the main group elements, in particular with respect to understanding and exploiting the concept of hypervalency. This culminated in the publishing of his important book, *"Chemistry of Hypervalent Compounds"* in 1999, which had a huge impact on both the synthetic organic and inorganic communities.

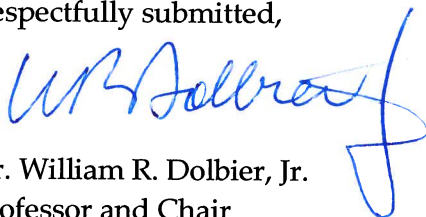
Always interested in heterocyclic compounds, his work emphasized organo-sulfur, phosphorous, bismuth and boron compounds. His highly creative, indeed ground-breaking work attracted world-wide attention, and led to his receiving the top two Chemical Society of Japan research awards, The CSJ Award for Creative Work in 1985 and the most selective CSJ Award "for significant contributions to the fundamentals and applications of chemistry" in 1997. His creative output did not diminish significantly when he retired from Hiroshima University. Some of his most highly recognized work came during his tenure as Adjunct Professor at Waseda University, which continues until today. This included his synthesis and characterization of stable hypervalent carbon compounds, reported in JACS articles in 2005 and 2008.

It is safe to say that the research and book-writing efforts of Professor Kin-ya Akiba have played a very significant role in bringing the field of main group element hypervalency to the functional attention of both the synthetic and theoretical community, to the extent that it has now become an essential component of one's understanding of the chemistry of the main group elements.

Dr. Akiba continues to make important contributions, not the least of which was the writing of his textbook on *"Organo Main Group Chemistry"*, which has not only been a resource for students moving into the field, but also for researchers, such as myself, for whom an understanding of the bonding and structure concepts outlined in this book contribute to the essential continual learning process of any active scientist.

Professor Akiba epitomizes the quintessential “teacher-scholar”, with his soft spoken, but highly articulate and creative contributions to both science and education that have continued through the approximately forty years of his independent scientific career. It is entirely appropriate for the American Chemical Society to recognize his lifetime achievement by bestowing upon him the ACS Award in Inorganic Chemistry.

Respectfully submitted,

A handwritten signature in blue ink, appearing to read "WR Dolbier", with a stylized flourish extending from the end.

Dr. William R. Dolbier, Jr.
Professor and Chair
Department of Chemistry



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October 28, 2015

I am pleased and honored to have this opportunity to provide support for the nomination of Professor Kin-ya Akiba for the ACS Award in Inorganic Chemistry. Because Professor Akiba's international accomplishments are covered in the other letters, I would like to primarily focus on Professor Akiba's stature in Japan.

Professor Akiba served as the Chairman of the *Priority Area of Scientific Research* on "Organic Unusual Valency" supported by the Japanese Ministry of Education, Culture, Sports, Science, and Technology (1990-1993), organizing 69 professors, active in main group chemistry. Such grants are approved only for high priority areas and in this case served to establish main group chemistry in Japan at its currently high level of international recognition. Professor Akiba also served as the Japanese organizer of the *Symposium on Bonding at Main Group Element Centers* in the International Chemical Congress of Pacific Basin Societies (Pacifichem 1989, 1995, 2000). The U.S.-Japan Cooperative Research supported by NSF and JSPS (1987-1989) on "Organic Compounds of Hypervalent Non-metals" was initiated by Professor Akiba in collaboration with the late Prof. J. C. Martin (Illinois and Vanderbilt). This Cooperative Research became an important stepping stone to Professor Akiba's prominent international activity.

Professor Akiba has presented plenary lectures at the International Conference of Heteroatom Chemistry (ICHAC, 1995, 2001), the International Symposium on the Organic Chemistry of Sulfur (ISOCS, 2004), the International Conference on the Chemistry of Selenium and Tellurium (ICCST, 2007), and the Annual Meeting of Poland (twice) and Korea in addition to a number of invited lectures. This international visibility has been contributed to Japan's strong reputation in the area of Main Group Element Chemistry.

Of course, Professor Akiba also contributed to the chemical community of Japan as a member of the editorial board of the *Journal of Synthetic Organic Chemistry*, Japan (1973-1975), *Bulletin of the Chemical Society of Japan* (1975-1977), and as a vice-President of the Chemical Society of Japan (1998-1999).

Professor Akiba's outstanding accomplishments in science have led to many domestic and international awards. He is the recipient of the Organic Division Award of the Chemical Society of Japan (1985), the Alexander von Humboldt Senior Research Award (1996; *Wiedereinladung* 2003), the Chemical Society of Japan Award (1997), and the Medal of the Prime Minister of the Japanese Government with Purple Ribbon (2000), the prestigious Order of the Sacred Treasure, Gold Rays with Neck ribbon (2011, by the Emperor of Japan).

Sincerely,

Yohsuke Yamamoto,
Professor of Chemistry
Graduate School of Science
Hiroshima University
Japan